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(54) **PLATINUM(II) COMPLEXES FOR OLED APPLICATIONS**

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(52) **U.S. Cl.**
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546/256

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(57) **ABSTRACT**

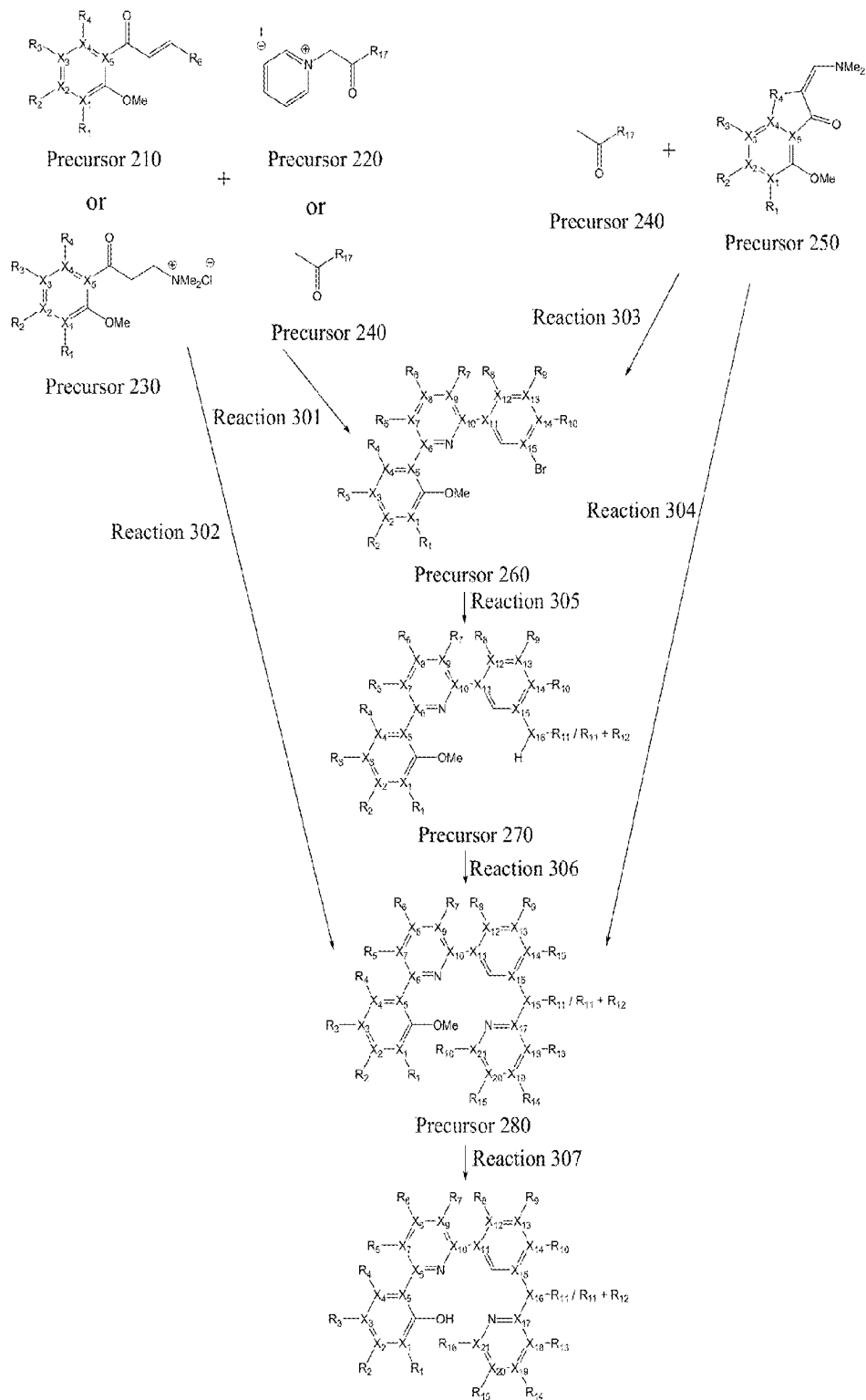
(21) Appl. No.: **13/861,119**

The current invention relates to novel platinum(II) based organometallic materials. These materials show high emission quantum efficiencies and low self-quenching constant. Also provided are high efficiency, green to orange emitting organic light-emitting diode (OLED) that are fabricated using platinum(II) based organometallic materials as the light-emitting material. The organometallic materials of the invention are soluble in common solvents; therefore, solution process methods such as spin coating and printing can be used for device fabrication. The devices fabricated from these materials show low efficiency roll-off.

(22) Filed: **Apr. 11, 2013**

Related U.S. Application Data

(60) Provisional application No. 61/623,339, filed on Apr. 12, 2012.



Structure II

FIG. 1

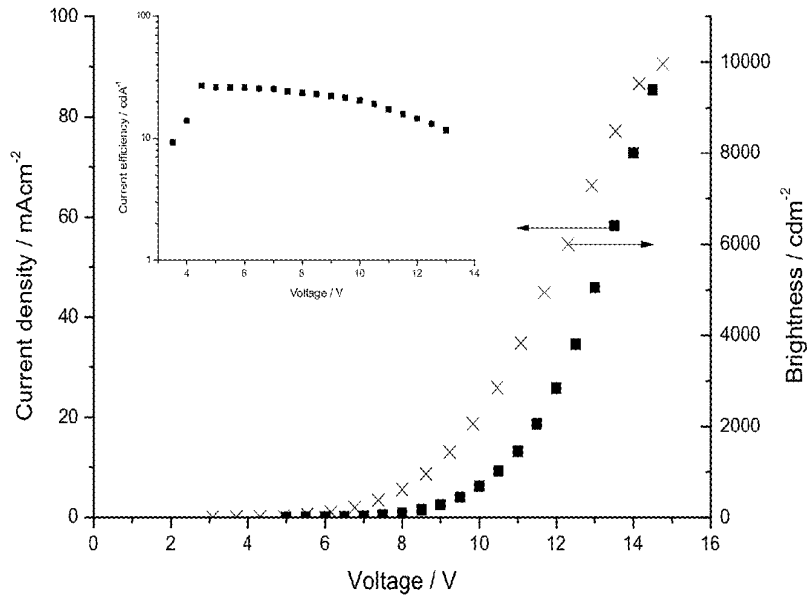


FIG. 2

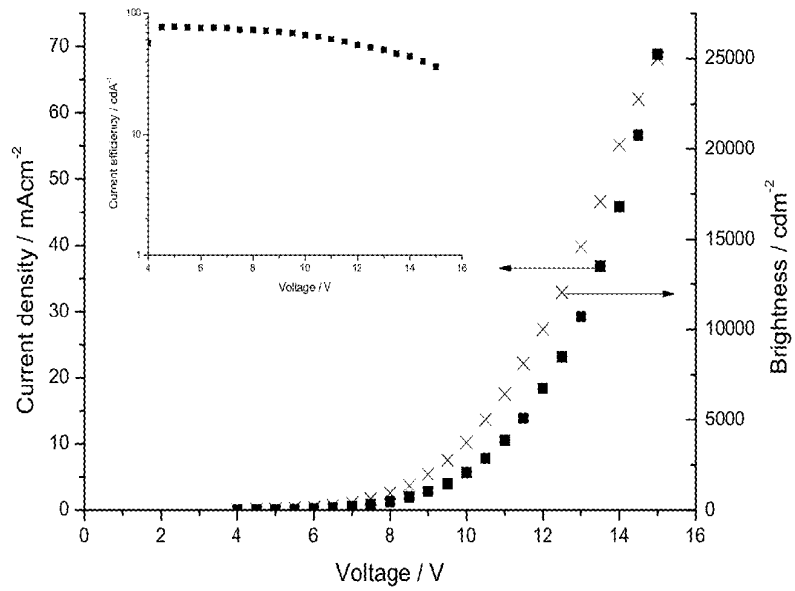


FIG. 3

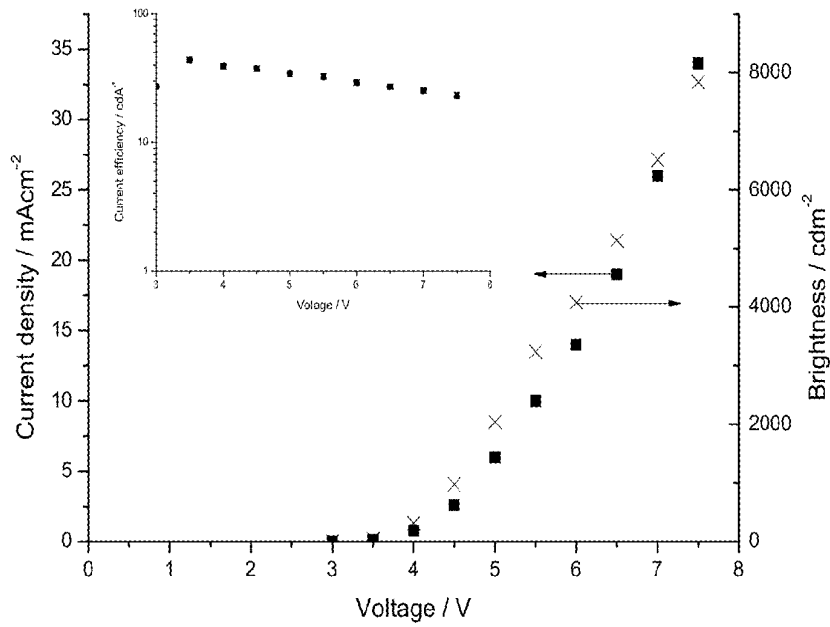


FIG. 4.

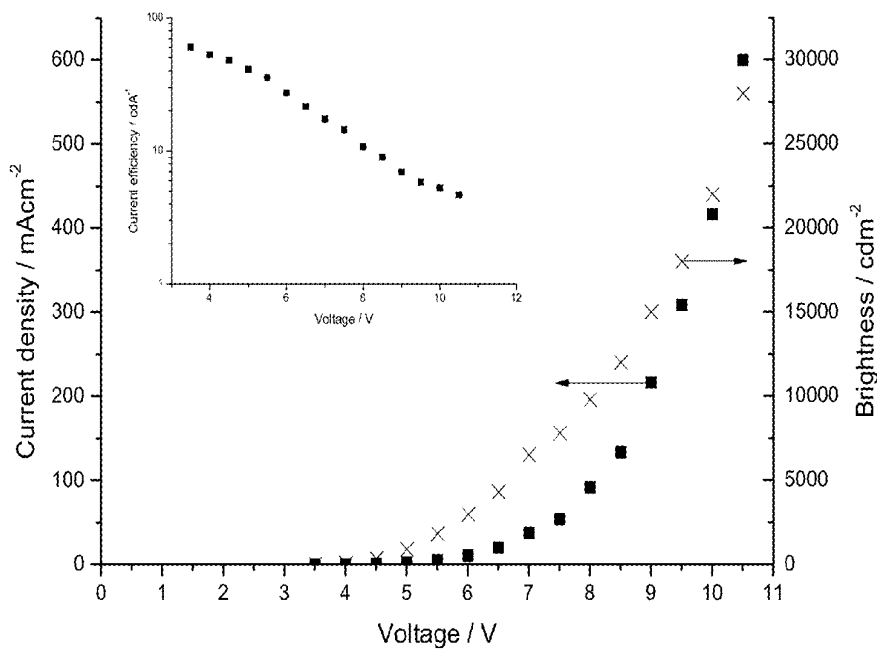


FIG. 5

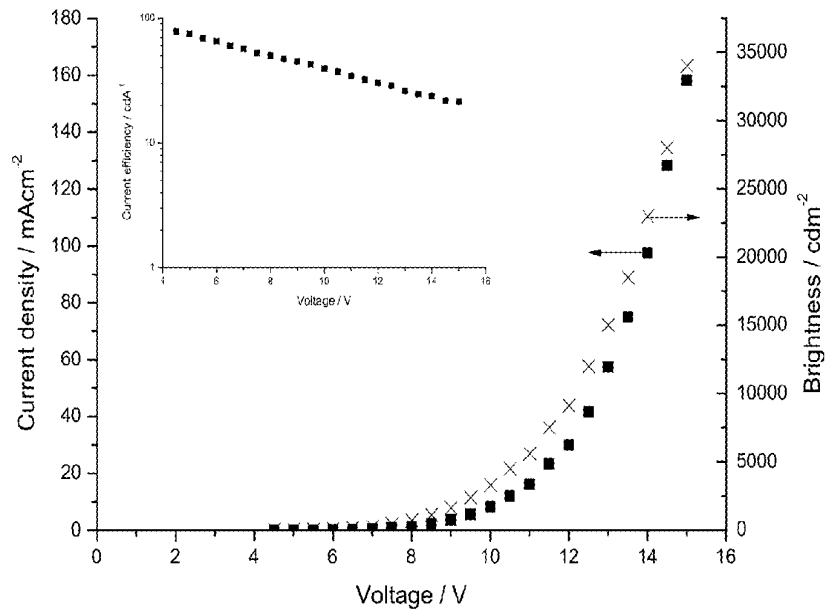


FIG. 6

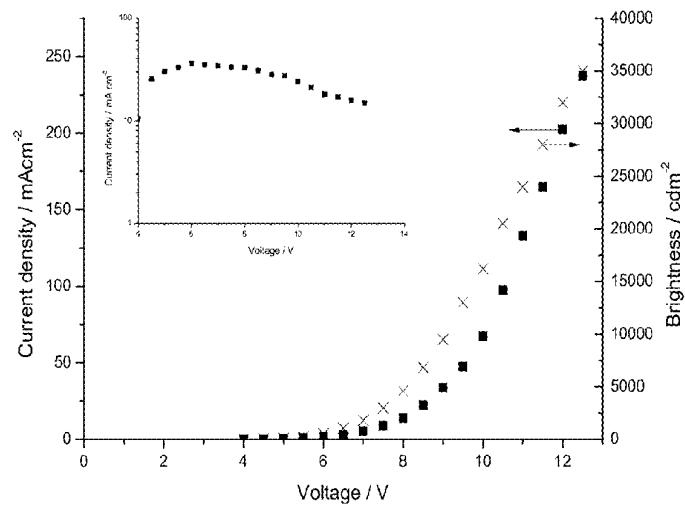


FIG. 7

PLATINUM(II) COMPLEXES FOR OLED APPLICATIONS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The subject application claims the benefit of U.S. Provisional Application Ser. No. 61/623,339, filed Apr. 12, 2012, which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] The present invention relates to a class platinum(II) complexes, their preparation methods, and their applications in organic light-emitting diodes (OLED).

BACKGROUND

[0003] As organic light-emitting diodes (OLEDs) are recognized as the next-generation display and lighting technology, OLED related technologies are rapidly developing. Organic-based emitting material is one of the most important core technologies in OLED; therefore, much effort has been devoted to this area. Since triplet emitters could fully utilize all excitons generated in the device, they are the focus in the field of emissive material development.

[0004] The idea of using phosphorescent materials in OLED was independently introduced by Baldo et al., Ma, and Che et al. in 1998. The world's first phosphorescent OLED (P-OLED) was fabricated using phosphorescent platinum(II) complex [Pt(OEP)] (OEP=octaethylporphin) (Nature 1998, 395, 151-154) and osmium(II) complex [Os(CN)₂(PPh₃)(X)] (X=4,4'-diphenyl-2,2'-bipyridine) (Synth. Met. 1998, 94, 245-248) as emitting materials respectively. High efficiency P-OLEDs have continuously been fabricated from new phosphorescent materials and are useful in various mobile electronics devices such as cellphones.

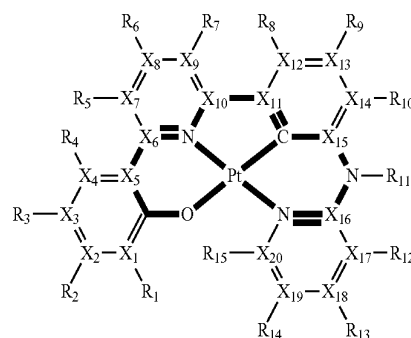
[0005] Although the phosphorescent materials that are currently used in the OLED industry have high emissive quantum efficiency (more than 60%), improved phosphorescent materials are needed. As a result, continuous attempts have been made in the development of new materials, especially blue-emitting materials.

[0006] In addition, most P-OLEDs suffer from high roll-off. In the cases of platinum containing materials, more than 90% roll-off is observed in 1,000 cd/m² (Applied Physics Letter 92, 163305 (2008), Chemical Communications 2005, 1408-1410, Chemical Communications 2004, 1484-1485, Applied Physics Letter 91, 063508 (2007), Chemistry A European Journal 2010, 16, 233-247). This problem of high efficiency roll-off is due to triplet-triplet annihilation and/or excimer formation. To solve this problem, previous researchers added bulky groups such as tert-butyl groups in the emissive molecules; nevertheless, the P-OLEDs fabricated from these materials still have more than 50% roll-off (Applied Physics Letter 91, 063508 (2007), Advanced Material 2007, 19, 3599-3603).

BRIEF SUMMARY

[0007] This present invention relates to novel platinum(II)-based materials having the chemical structure of Structure I. Also provided are methods of preparing the platinum(II)-based materials, and their applications in organic light-emitting diode (OLED).

[0008] In one embodiment, the platinum(II)-based compounds of Structure I are shown as follows:



Structure I

[0009] wherein R₁-R₁₅ 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;

[0010] wherein each pair of adjacent R groups of R₁-R₁₅ can be independently two separated groups (or atoms) or one group (or atom), and form 5-8 member ring(s) with 2 or 4 X groups; and

[0011] wherein X₁-X₂₀ are independently boron, carbon, nitrogen, oxygen, silicon, germanium, phosphorous, sulphur or selenium.

[0012] In one embodiment, the platinum(II) center is surrounded by the ligands featuring with a 6-5-6 fused member ring system (the bolded line in structure I).

[0013] In one embodiment, R₁₁ is aryl or substituted aryl group, and R₁₀ can be one of the carbon atoms on R₁₁, thereby forming a 6-5-6 fused ring system with the adjacent aryl ring.

[0014] The present invention also provides devices fabricated from the platinum(II)-based compounds of Structure I. Advantageously, the devices of the invention exhibit high efficiency and low roll-off.

BRIEF DESCRIPTION OF DRAWING

[0015] FIG. 1 shows one embodiment of the synthetic scheme of the platinum(II)-based organometallic compounds of Structure I. In an exemplified embodiment, the compound of Structure I is prepared using a ligand of Structure II. For the Precursors 210 to 280 and the compound of Structure II, R₁-R₁₅ 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; and X₁-X₂₀ are independently boron, carbon, nitrogen, oxygen, silicon, germanium, phosphorous, sulphur or selenium. In certain embodiments, each pair of adjacent R groups of R₁-R₁₅ can be independently two separated groups (or atoms) or one group (or atom), and form 5-8 member ring(s) with 2 or 4 X groups.

[0016] FIG. 2 shows the current density-voltage-brightness (J-B-V) relationship and efficiency-voltage curves of OLED 1.

[0017] FIG. 3 shows the current density-voltage-brightness (J-B-V) relationship and efficiency-voltage curves of OLED 2.

[0018] FIG. 4 shows the current density-voltage-brightness (J-B-V) relationship and efficiency-voltage curves of OLED 3.

[0019] FIG. 5 shows the current density-voltage-brightness (J-B-V) relationship and efficiency-voltage curves of OLED 4.

[0020] FIG. 6 shows the current density-voltage-brightness (J-B-V) relationship and efficiency-voltage curves of OLED 5.

[0021] FIG. 7 shows the current density-voltage-brightness (J-B-V) relationship and efficiency-voltage curves of OLED 6.

DETAILED DESCRIPTION

Definitions

[0022] To facilitate the understanding of the subject matter disclosed herein, a number of terms, abbreviations or other shorthand as used herein are defined below. Any term, abbreviation or shorthand not defined is understood to have the ordinary meaning used by a skilled artisan contemporaneous with the submission of this application.

[0023] "Amino" refers to a primary, secondary, or tertiary amine which may be optionally substituted. Specifically included are secondary or tertiary amine nitrogen atoms which are members of a heterocyclic ring. Also specifically included, for example, are secondary or tertiary amino groups substituted by an acyl moiety. Some non-limiting examples of an amino group include —NR'R" wherein each of R' and R" is independently H, alkyl, aryl, aralkyl, alkaryl, cycloalkyl, acyl, heteroalkyl, heteroaryl or heterocycyl.

[0024] "Alkyl" refers to a fully saturated acyclic monovalent radical containing carbon and hydrogen, and which may be branched or a straight chain. Examples of alkyl groups include, but are not limited to, methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, n-heptyl, n-hexyl, n-octyl, and n-decyl.

[0025] "Alkylamino" means a radical —NHR or —NR_2 where each R is independently an alkyl group. Representative examples of alkylamino groups include, but are not limited to, methylamino, (1-methylethyl)amino, methylamino, dimethylamino, methylethylamino, and di(1-methylethyl)amino.

[0026] The term "hydroxyalkyl" means an alkyl radical as defined herein, substituted with one or more, preferably one, two or three hydroxy groups. Representative examples of hydroxyalkyl include, but are not limited to, hydroxymethyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 1-(hydroxymethyl)-2-methylpropyl, 2-hydroxybutyl, 3-hydroxybutyl, 4-hydroxybutyl, 2,3-dihydroxypropyl, 2-hydroxy-1-hydroxymethylethyl, 2,3-dihydroxybutyl, 3,4-dihydroxybutyl and 2-(hydroxymethyl)-3-hydroxy-propyl, preferably 2-hydroxyethyl, 2,3-dihydroxypropyl, and 1-(hydroxymethyl)-2-hydroxyethyl.

[0027] The term "alkoxy," as used herein, refers the radical —OR_x . Exemplary alkoxy groups include, but are not limited to, methoxy, ethoxy, and propoxy.

[0028] "Aromatic" or "aromatic group" refers to aryl or heteroaryl.

[0029] "Aryl" refers to optionally substituted carbocyclic aromatic groups. In some embodiments, the aryl group includes phenyl, biphenyl, naphthyl, substituted phenyl, sub-

stituted biphenyl or substituted naphthyl. In other embodiments, the aryl group is phenyl or substituted phenyl.

[0030] "Aralkyl" refers to an alkyl group which is substituted with an aryl group. Some non-limiting examples of aralkyl include benzyl and phenethyl.

[0031] "Acyl" refers to a monovalent group of the formula —C(=O)H , —C(=O)-alkyl , —C(=O)-aryl , —C(=O)-aralkyl , or —C(=O)-alkaryl .

[0032] "Halogen" refers to fluorine, chlorine, bromine and iodine.

[0033] "Styryl" refers to a univalent radical $\text{C}_6\text{H}_5\text{—CH=CH—}$ derived from styrene.

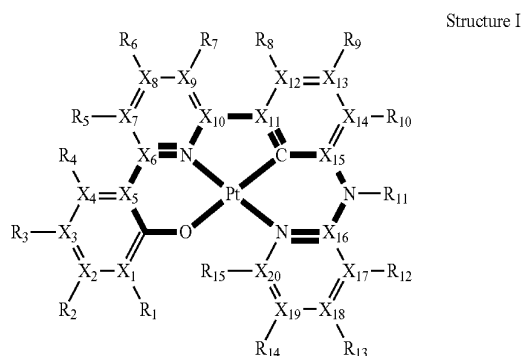
[0034] "Substituted" as used herein to describe a compound or chemical moiety refers to that at least one hydrogen atom of that compound or chemical moiety is replaced with a second chemical moiety. Non-limiting examples of substituents are those found in the exemplary compounds and embodiments disclosed herein, as well as halogen; alkyl; heteroalkyl; alkenyl; alkynyl; aryl; heteroaryl; hydroxy; alkoxy; amino; nitro; thiol; thioether; imine; cyano; amido; phosphonato; phosphine; carboxyl; thiocarbonyl; sulfonyl; sulfonamide; ketone; aldehyde; ester; oxo; haloalkyl (e.g., trifluoromethyl); carbocyclic cycloalkyl, which can be monocyclic or fused or non-fused polycyclic (e.g., cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl) or a heterocycloalkyl, which can be monocyclic or fused or non-fused polycyclic (e.g., pyrrolidinyl, piperidinyl, piperazinyl, morpholinyl or thiazinyl); carbocyclic or heterocyclic, monocyclic or fused or non-fused polycyclic aryl (e.g., phenyl, naphthyl, pyrrolyl, indolyl, furanyl, thiophenyl, imidazolyl, oxazolyl, isoxazolyl, thiazolyl, triazolyl, tetrazolyl, pyrazolyl, pyridinyl, quinolinyl, isoquinolinyl, acridinyl, pyrazinyl, pyridazinyl, pyrimidinyl, benzimidazolyl, benzothiophenyl or benzofuran-yl); amino (primary, secondary or tertiary); o-lower alkyl; o-aryl, aryl; aryl-lower alkyl; $\text{—CO}_2\text{CH}_3$; —CONH_2 ; $\text{—OCH}_2\text{CONH}_2$; —NH_2 ; $\text{—SO}_2\text{NH}_2$; —OCHF_2 ; —CF_3 ; —OCF_3 ; —NH(alkyl) ; —N(alkyl)_2 ; —NH(aryl) ; —N(alkyl)(aryl) ; —N(aryl)_2 ; —CHO ; —CO(alkyl) ; —CO(aryl) ; $\text{—CO}_2(\text{alkyl})$; and $\text{—CO}_2(\text{aryl})$; and such moieties can also be optionally substituted by a fused-ring structure or bridge, for example $\text{—OCH}_2\text{O—}$. These substituents can optionally be further substituted with a substituent selected from such groups. All chemical groups disclosed herein can be substituted, unless it is specified otherwise. For example, "substituted" alkyl, alkenyl, alkynyl, aryl, hydrocarbyl or heterocyclo moieties described herein are moieties which are substituted with a hydrocarbyl moiety, a substituted hydrocarbyl moiety, a heteroatom, or a heterocyclo. Further, substituents may include moieties in which a carbon atom is substituted with a heteroatom such as nitrogen, oxygen, silicon, phosphorus, boron, sulfur, or a halogen atom. These substituents may include halogen, heterocyclo, alkoxy, alkenoxy, alkynoxy, aryloxy, hydroxy, protected hydroxy, keto, acyl, acyloxy, nitro, amino, amido, cyano, thiol, ketals, acetals, esters and ethers.

Light-Emitting Platinum(II)-Based Organometallic Complex

[0035] In one aspect, the present invention provides platinum(II)-based organometallic compounds. In one embodiment, an organometallic complex represented by Structure I, also referred herein as cyclometallated complexes, is provided. The platinum center in Structure I is in +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 featuring with 6-5-6 fused membered rings 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 (O⁻N⁺C^{*}N ligand; i.e., 4 connecting covalent bonds (either single or double) between O⁻N, 3 connecting covalent bonds (either single or double) between N⁺C, 4 connecting covalent bonds (either single or double) between C^{*}N). The metal-oxygen bond is a bond between deprotonated phenol or substituted phenol and platinum, the nitrogen donors are from pyridine and/or isoquinoline groups, and the metal-carbon bond is formed by benzene or substituted benzene and platinum.

[0036] In one embodiment, the platinum(II)-based organometallic compounds have the chemical structure of Structure I



Structure I

[0037] wherein R₁-R₁₅ 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, aryloxy carbonyl, phenoxy carbonyl, or an alkoxy carbonyl group;

[0038] wherein each pair of adjacent R groups of R₁-R₁₅ can be independently two separated groups (or atoms) or one group (or atom), and form 5-8 member ring(s) with 2 or 4 X groups; and

[0039] wherein X₁-X₂₀ are independently boron, carbon, nitrogen, oxygen, silicon, germanium, phosphorous, sulphur or selenium.

[0040] In one embodiment, the platinum(II) center is surrounded by the ligands featuring with a 6-5-6 fused membered ring system (the bolded line in structure I).

[0041] In one embodiment, R₁₁ is aryl or substituted aryl group, and R₁₀ can be one of the carbon atoms on R₁₁ thereby forming a 6-5-6 fused ring system with the adjacent aryl ring.

[0042] In one embodiment, each R₁-R₁₅ 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 4 to 20 carbon atoms, an unsubstituted aryl containing from 6 to 20 carbon atoms, a substituted aryl containing from 6 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

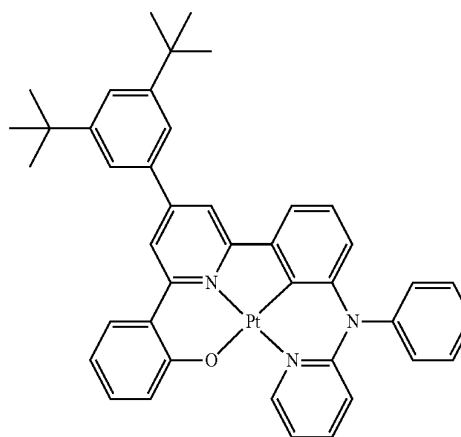
atoms, thiol, styryl, aminocarbonyl containing from 1 to 20 carbon atoms, carbamoyl containing from 1 to 20 carbon atoms, aryloxy carbonyl containing from 1 to 20 carbon atoms, phenoxy carbonyl containing from 1 to 20 carbon atoms, or an alkoxy carbonyl group containing from 1 to 20 carbon atoms.

[0043] In another embodiment, the total number of carbon atoms provided by the R₁-R₁₅ groups is from 1 to 40.

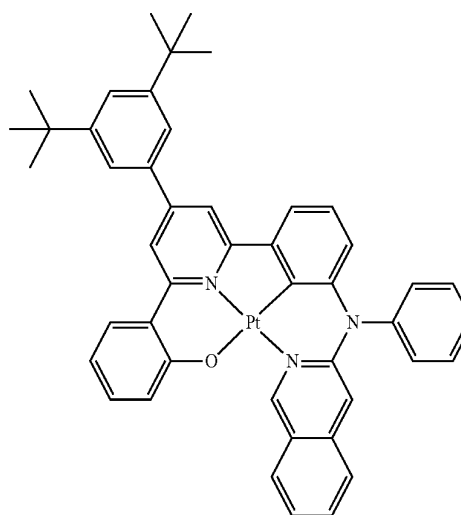
[0044] In another embodiment, the total number of carbon atoms provided by the R₁-R₁₅ groups is from 2 to 30.

[0045] Certain specific, non-limiting examples of the organometallic complexes with Structure I are shown as follows:

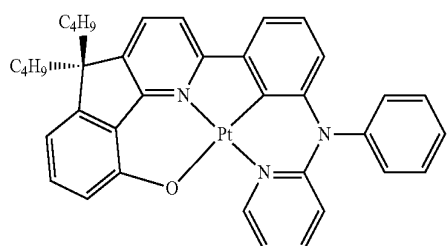
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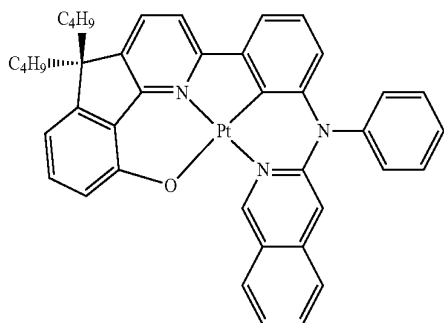
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Complex 103

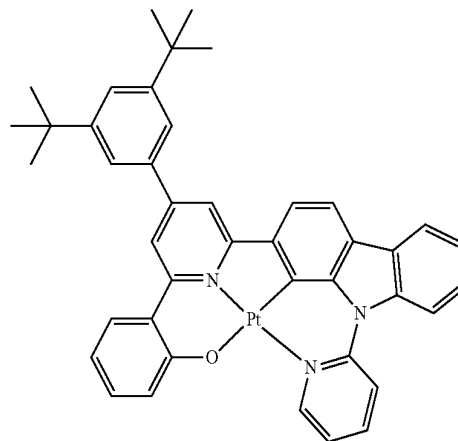


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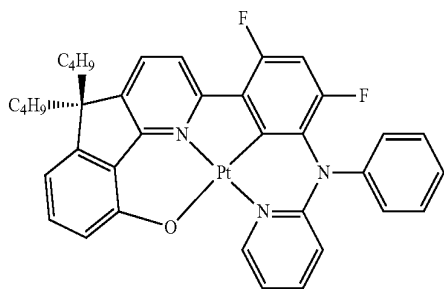
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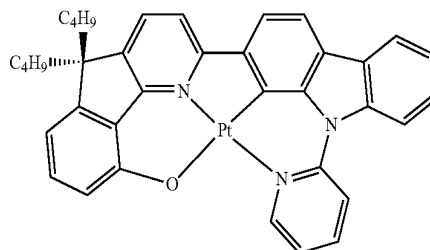


Complex 108

Complex 5

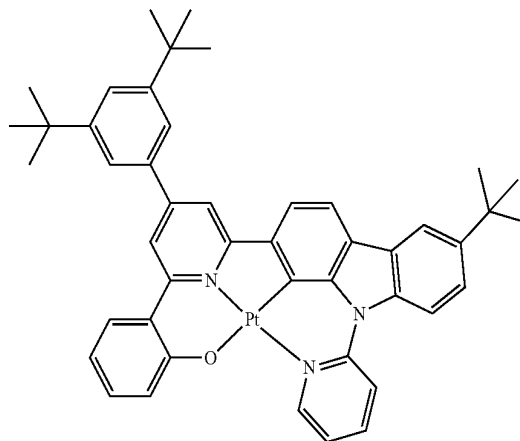
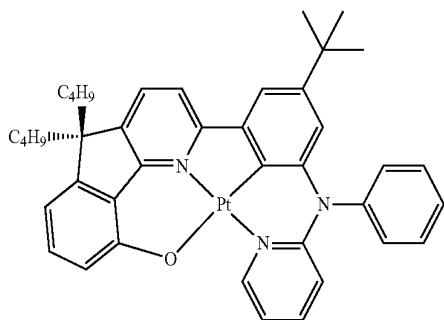


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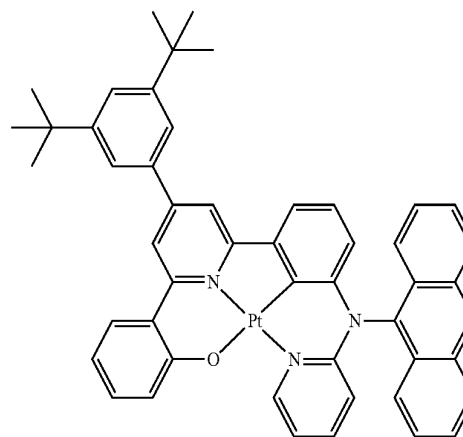
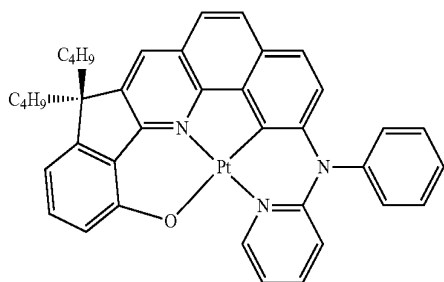
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Complex 6



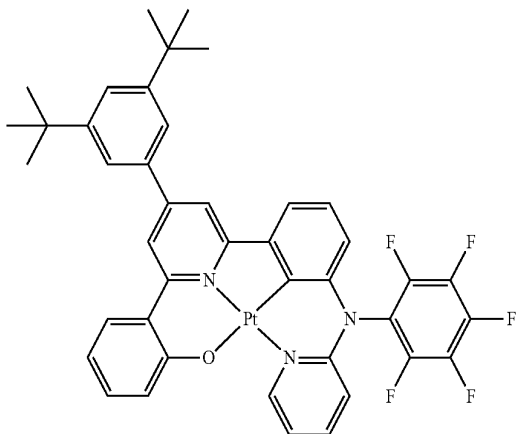
Complex 111

Complex 7



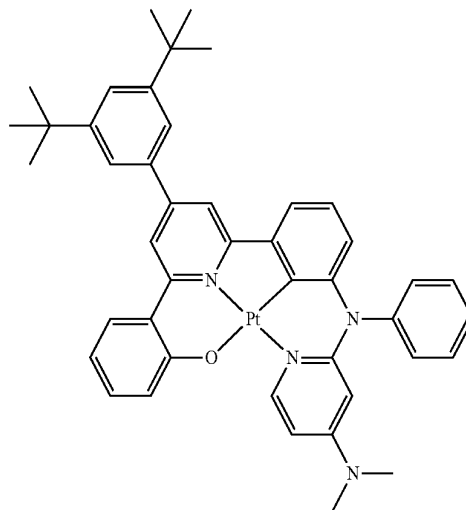
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Complex 112

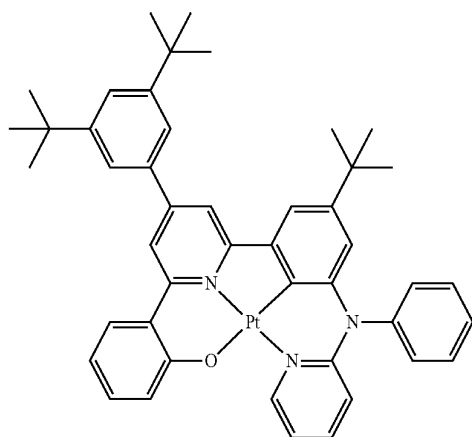


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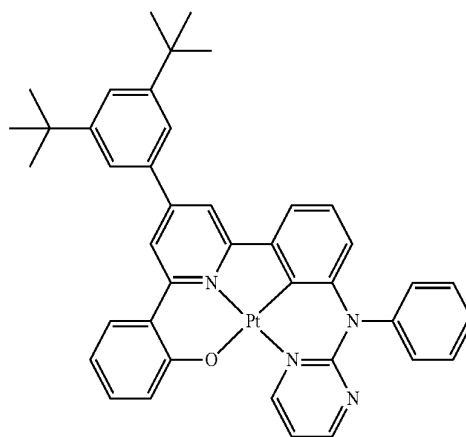
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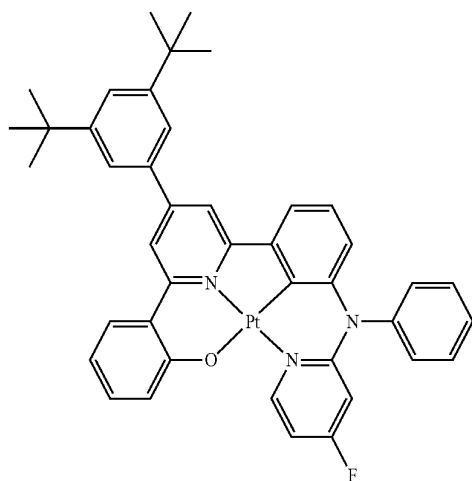
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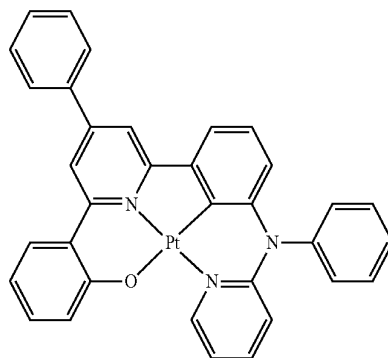
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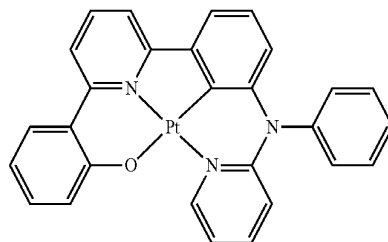
Complex 114



Complex 117

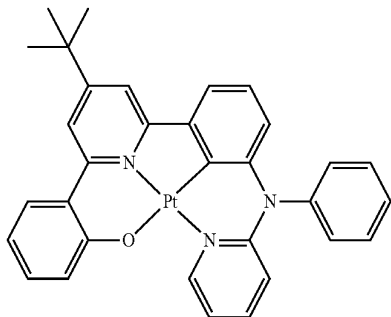


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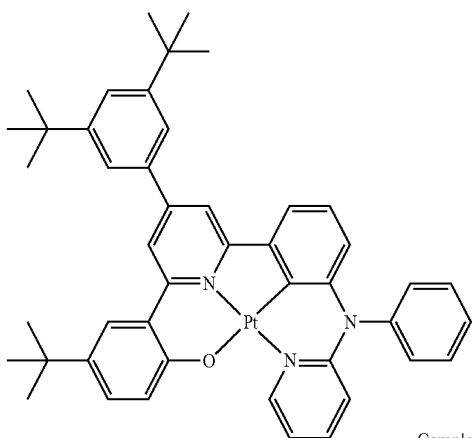


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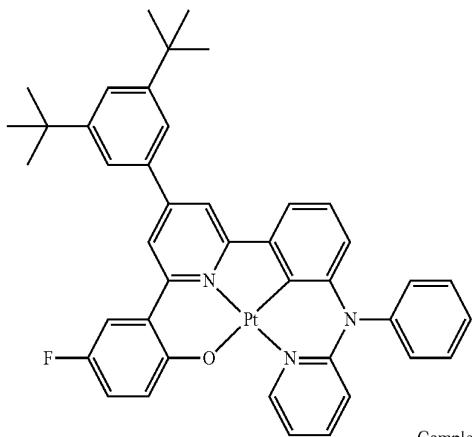
Complex 119



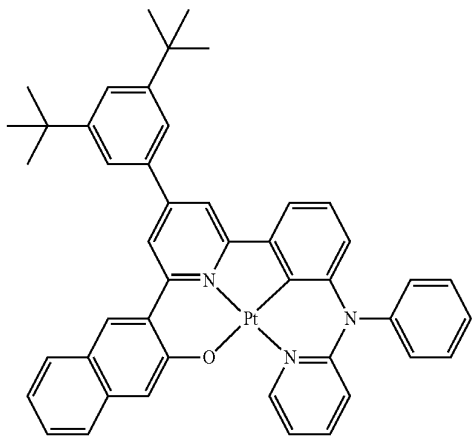
Complex 120



Complex 121

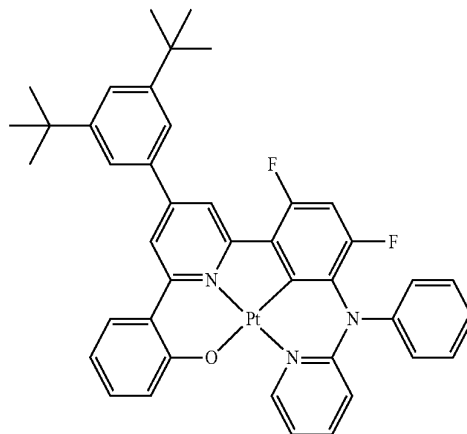


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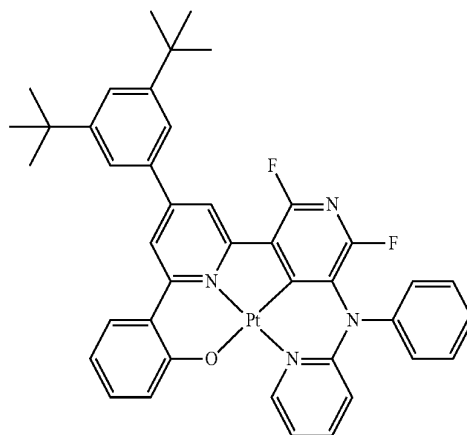


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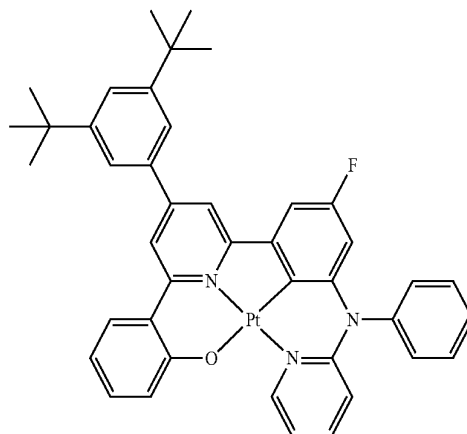
Complex 123



Complex 124

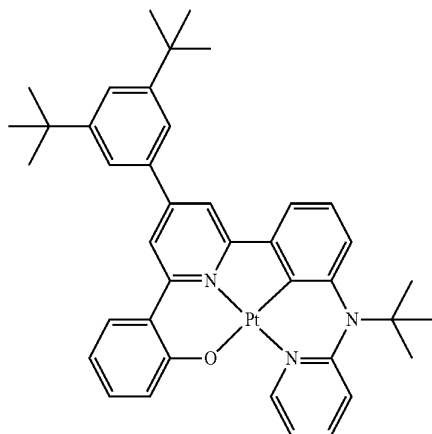


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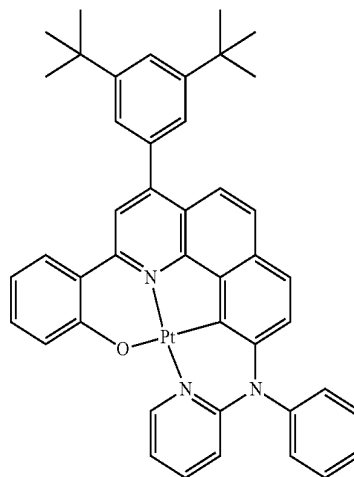
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Complex 126



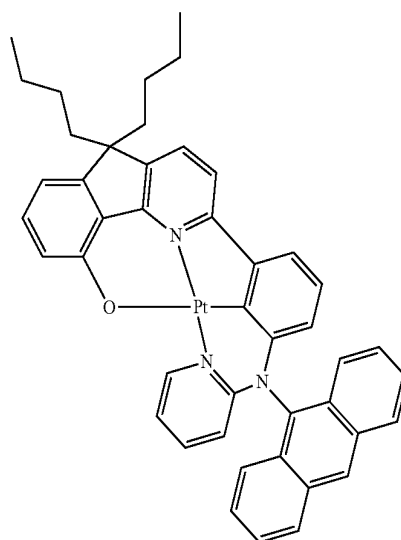
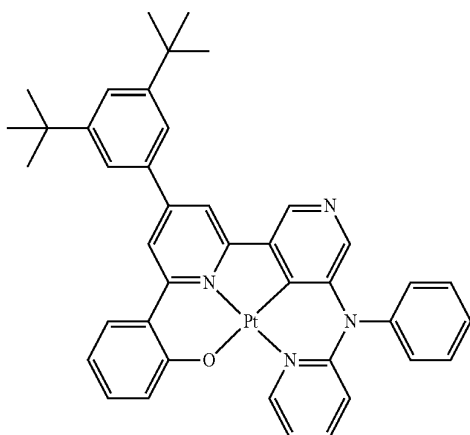
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Complex 129



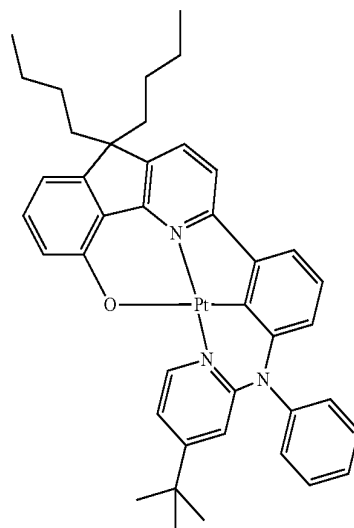
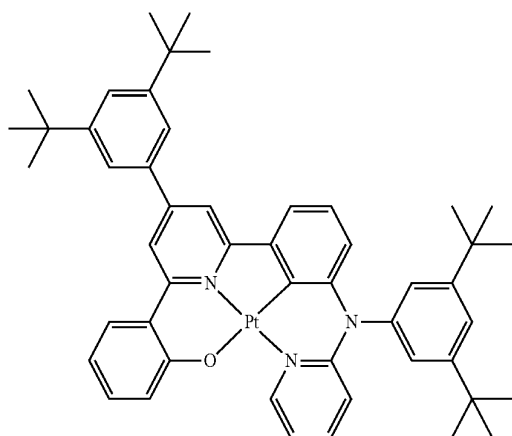
Complex 130

Complex 127



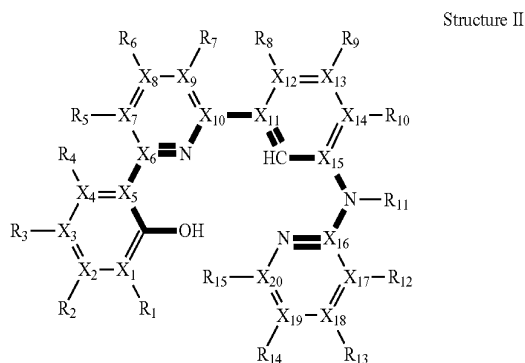
Complex 131

Complex 128



Preparation of Platinum(II)-Based Organometallic Complex

[0046] In one embodiment, the organometallic complex with the chemical structure of Structure I can be prepared from a tetradentate ligand with a chemical structure of Structure II:



[0047] wherein R_1 - R_{15} 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, aryloxy carbonyl, phenoxycarbonyl, or an alkoxy carbonyl group;

[0048] wherein each pair of adjacent R groups of R_1 - R_{15} can be independently two separated groups (or atoms) or one group (or atom), and form 5-8 member ring(s) with 2 or 4 X groups; and

[0049] wherein X_1 - X_{20} are independently boron, carbon, nitrogen, oxygen, silicon, germanium, phosphorous, sulphur or selenium.

[0050] In one embodiment, R_{11} is aryl or substituted aryl group, and R_{10} can be one of the carbon atoms on R_{11} , thereby forming a 6-5-6 fused ring system with the adjacent aryl ring.

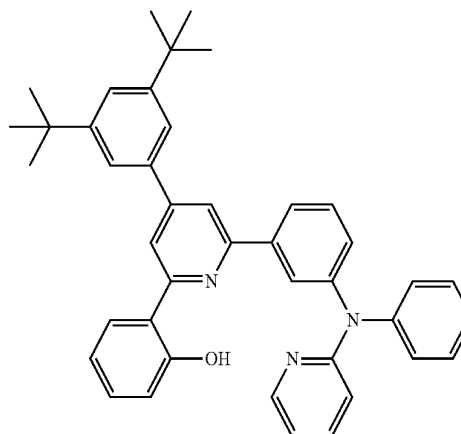
[0051] In one embodiment, each R_1 - R_{15} is independently hydrogen, halogen (such as fluorine, chlorine bromine, and iodine), hydroxyl, an unsubstituted alkyl containing from 1 to 10 carbon atoms, a substituted alkyl containing from 1 to 20 carbon atoms, cycloalkyl containing from 4 to 20 carbon atoms, an unsubstituted aryl containing from 6 to 20 carbon atoms, a substituted aryl containing from 6 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, aryloxy carbonyl containing from 1 to 20 carbon atoms, phenoxycarbonyl containing from 1 to 20 carbon atoms, or an alkoxy carbonyl group containing from 1 to 20 carbon atoms.

[0052] In another embodiment, the total number of carbon atoms provided by the R_1 - R_{15} groups is from 1 to 40.

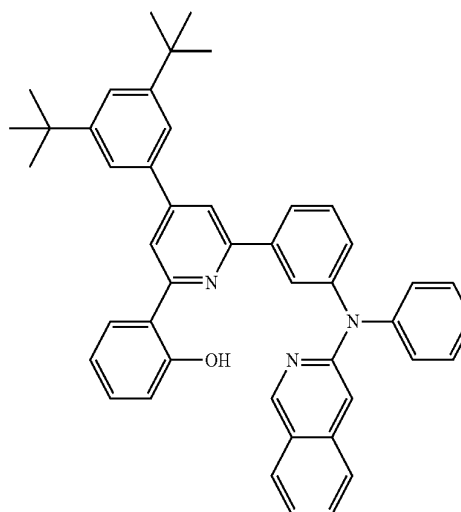
[0053] In another embodiment, the total number of carbon atoms provided by the R_1 - R_{15} groups is from 2 to 30.

[0054] Certain specific non-limiting examples of the tetradentate ligand with Structure II are shown below:

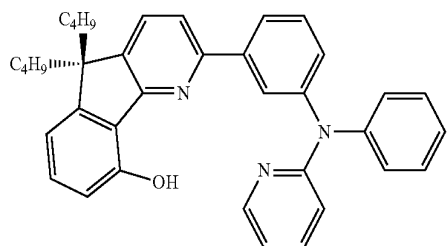
Ligand 401



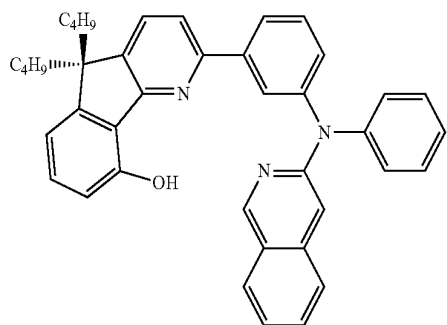
Ligand 402



Ligand 403

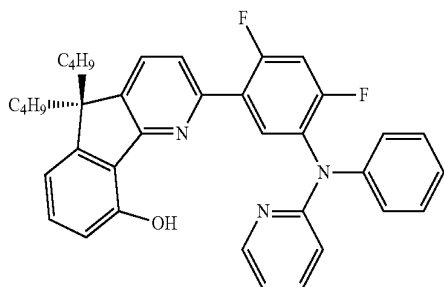


Ligand 404



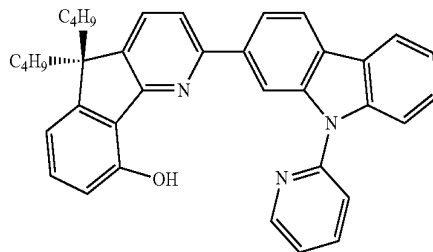
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Ligand 405



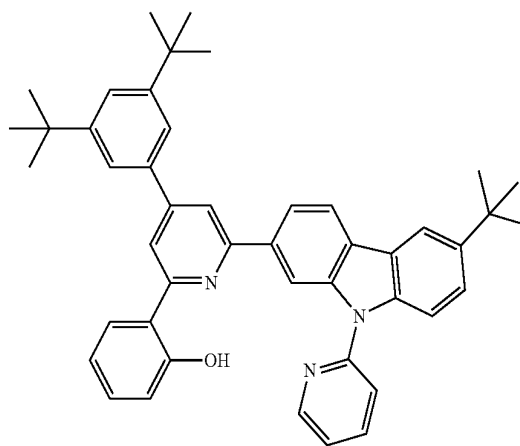
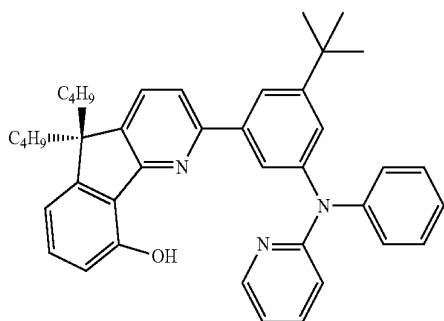
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Ligand 409



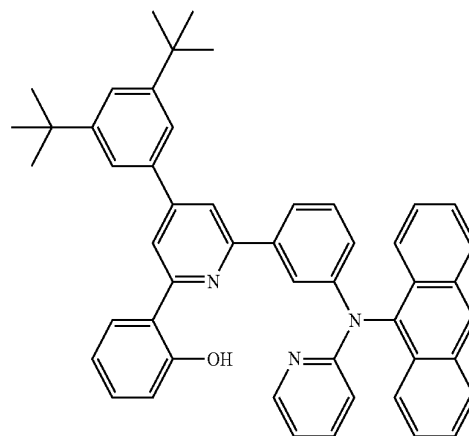
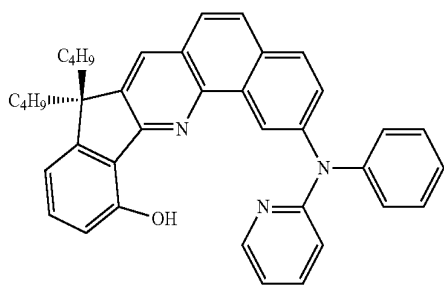
Ligand 410

Ligand 406



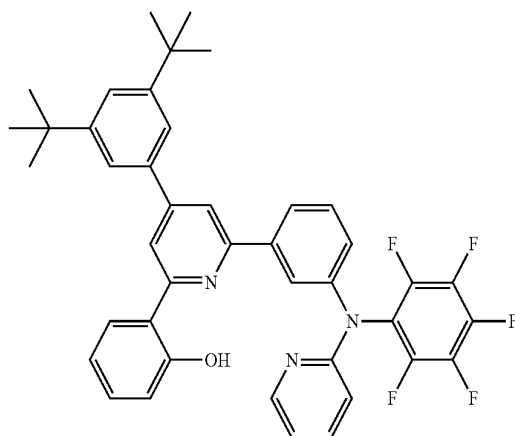
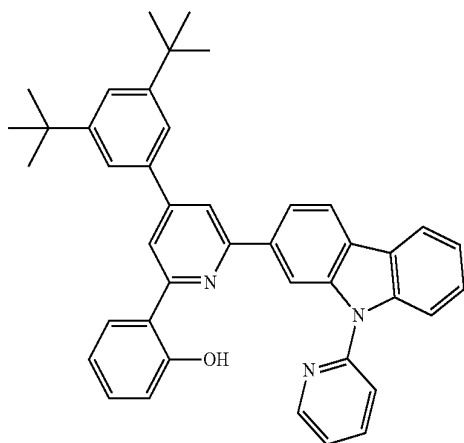
Ligand 411

Ligand 407



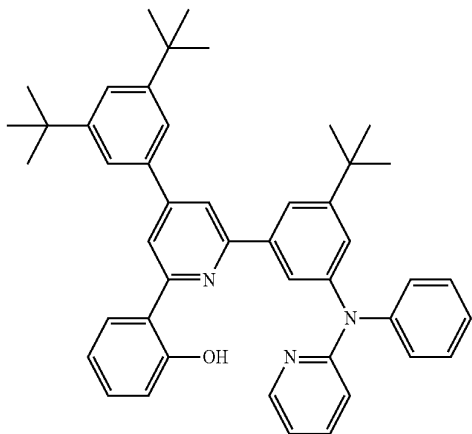
Ligand 412

Ligand 408



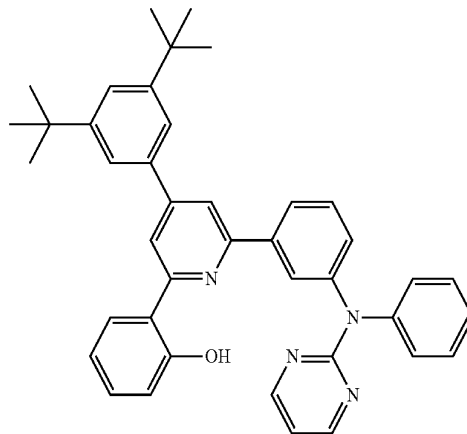
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Ligand 413

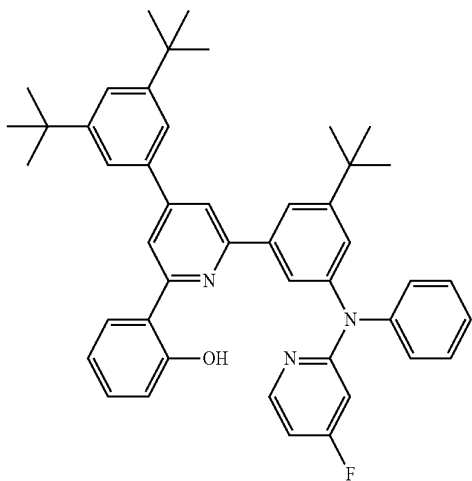


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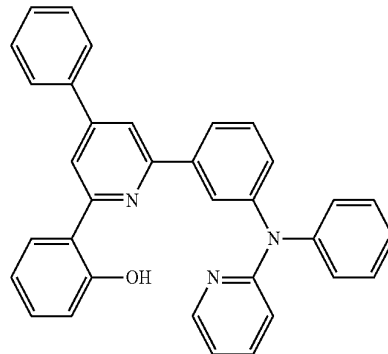
Ligand 416



Ligand 414

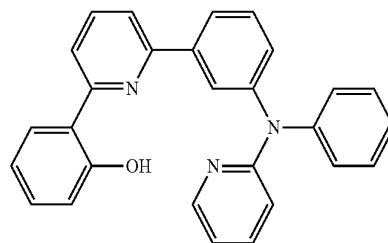
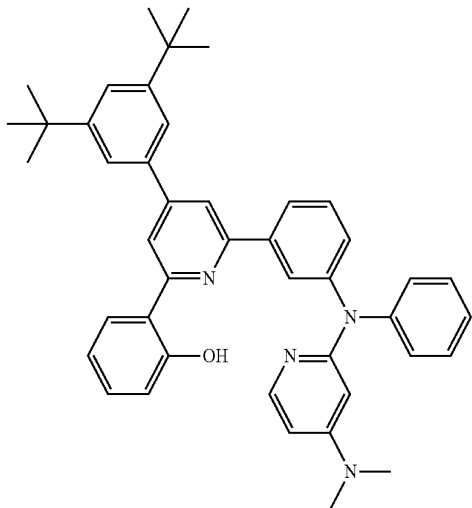


Ligand 417

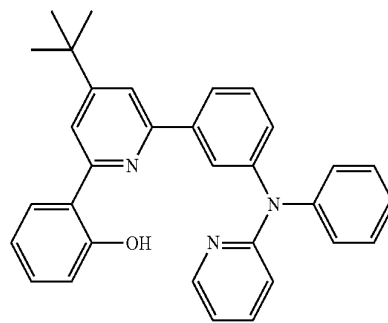


Ligand 418

Ligand 415

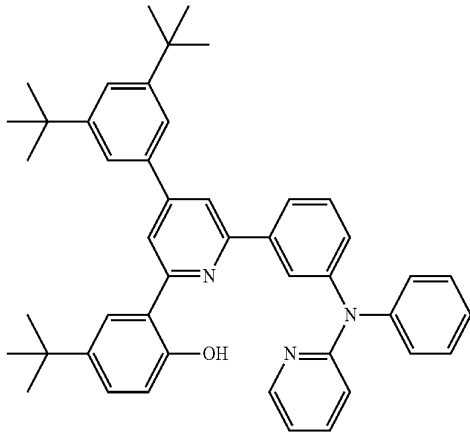


Ligand 419



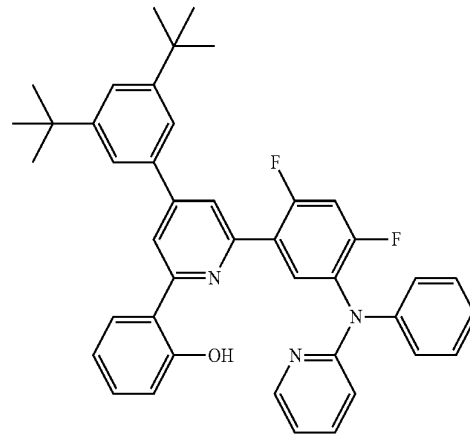
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Ligand 420

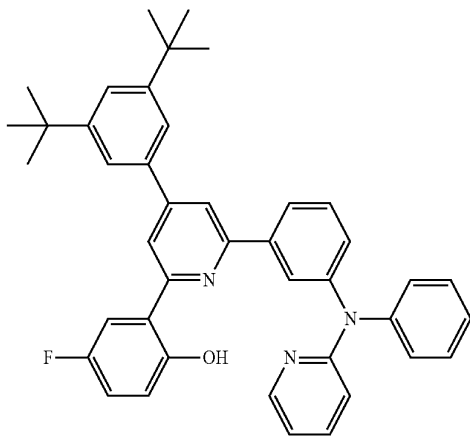


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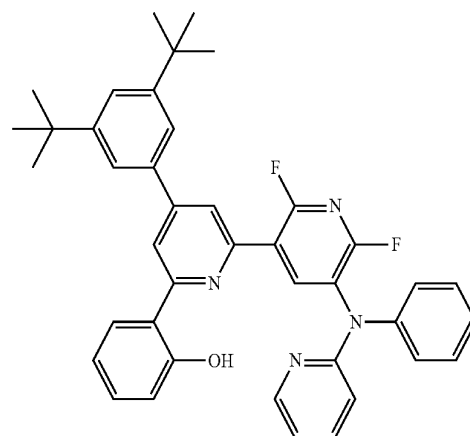
Ligand 423



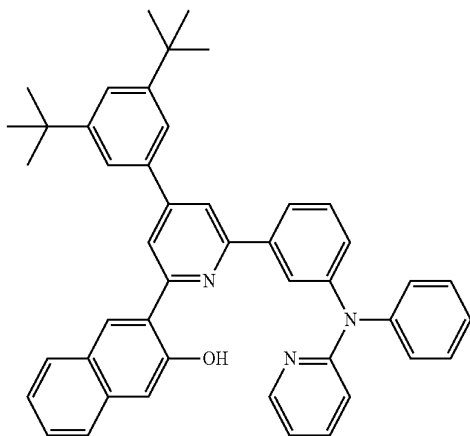
Ligand 421



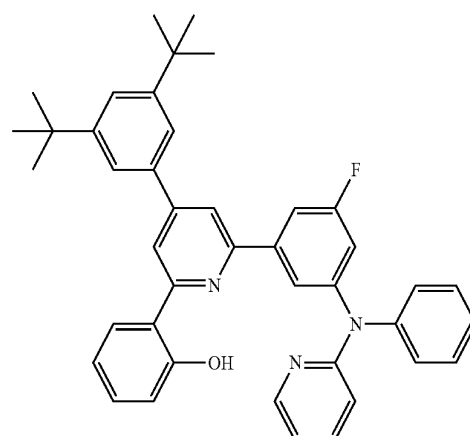
Ligand 424



Ligand 422

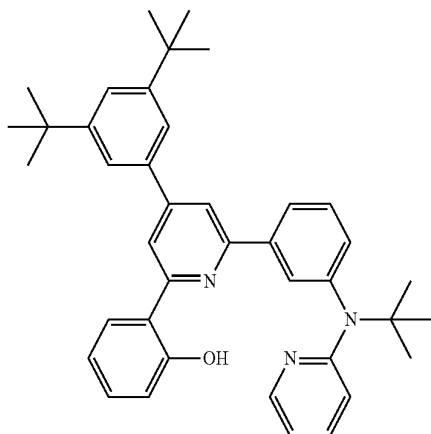


Ligand 425



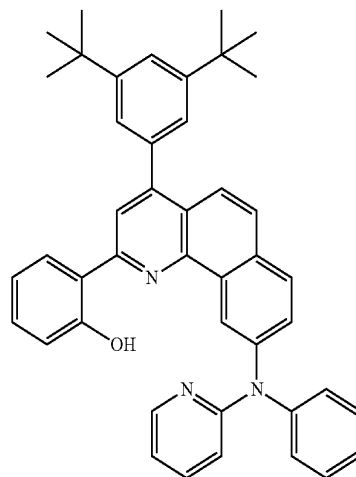
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Ligand 426



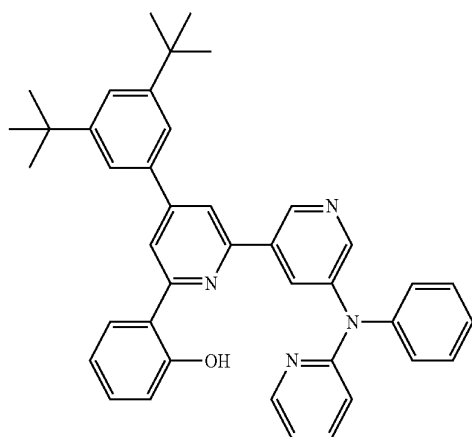
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Ligand 429

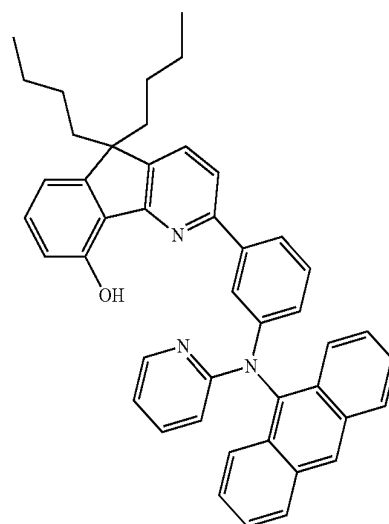
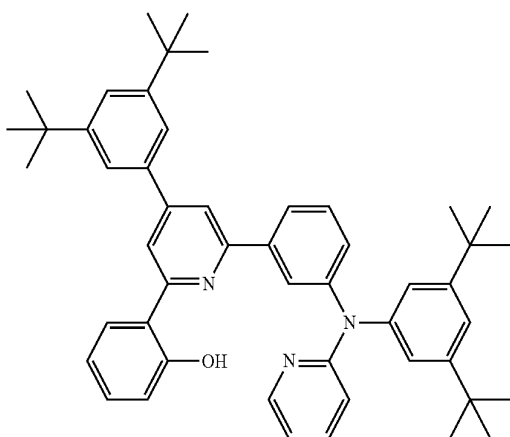


Ligand 430

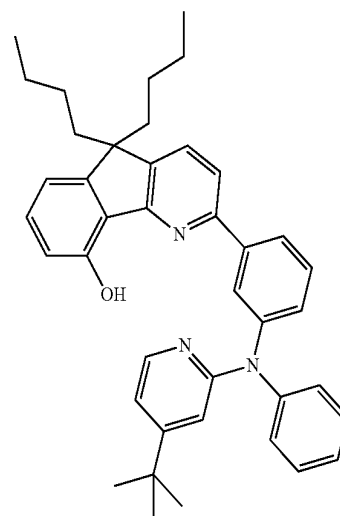
Ligand 427



Ligand 428



Ligand 431



[0055] In one embodiment, the tetradentate ligands with Structure II can be prepared by a series of reactions depicted in FIG. 1.

[0056] According to FIG. 1, Precursor 210 reacts with Precursor 220 or Precursor 230 reacts with Precursor 240, through Reaction 301 to form Precursor 260 or through Reaction 302 to form Precursor 280, depending on the chemical structure of the Precursor 210-Precursor 240. If Precursor 260 is produced, it is transformed to Precursor 270 through Reaction 305 and then transformed to Precursor 280 through Reaction 306. Finally, Precursor 208 is transformed to a ligand with a chemical structure of Structure II by Reaction 307. Precursor 260 and Precursor 280 can also be produced by reacting Precursor 240 with Precursor 250 through Reaction 303 or Reaction 304. All reactions **301-307** can be a single step or multi-step reaction.

[0057] In one embodiment, Reaction 301 comprises reacting Precursor 210 and Precursor 220 or Precursor 230 and Precursor 240. In one embodiment, Reaction 301 is performed in the presence of excess ammonium acetate and a solvent under a reflux condition. Suitable solvents for Reaction 301 include, but are not limited to, methanol. In one embodiment, Reaction 305 comprises a palladium coupling reaction using bis[2-(diphenylphosphine)phenyl]ether (DPE-phos) as a ligand, tris(dibenzylideneacetone)dipalladium(0) as the catalyst, potassium tert-butoxide as the base and toluene as the solvent, under an inert nitrogen environment at 80° C.

[0058] In one embodiment, Reaction 306 is the same as Reaction 305.

[0059] In one embodiment, Reaction 307 comprises reacting pyridine hydrogen chloride with Precursor 280.

[0060] In one embodiment, Reaction 307 comprises reacting carbon tetrabromide with Precursor 280.

[0061] In another embodiment, the present invention provides a method of preparing the organometallic complex with chemical structure of Structure I, comprising reacting a ligand with chemical structure of Structure II with a platinum (II) salt in the presence of solvent(s). Other chemicals such as based will be added if they are needed in the reaction. In one embodiment, the platinum(II) salt is potassium tetrachloroplatinate. In another embodiment, the solvents are glacial acetic acid and chloroform.

Industrial Applications of Platinum(II) Based Organometallic Complexes

[0062] The platinum(II) based organometallic complexes having the chemical structure of Structure I show strong emission with high solution quantum yield.

[0063] As the platinum(II) based organometallic complexes of Structure I have a rigid structure which reduces the non-radioactive decay, the emission quantum efficiency of these complexes are high. Therefore, high efficiency organic light emitting diode (OLED) can be fabricated by using these complexes as emitting material.

[0064] In one embodiment, the OLED fabricated using the organometallic complex of Structure I shows a high efficiency of greater than 70 cd/A. In another embodiment, the OLED fabricated using the organometallic complex of Structure I shows a high efficiency of greater than 40 cd/A, including, but not limited to, greater than 45 cd/A, 50 cd/A, 55 cd/A, 60 cd/A, 65 cd/A, 70 cd/A, 75 cd/A, 80 cd/A, or 85 cd/A.

[0065] In one embodiment, the organometallic complexes with the chemical structure of Structure I have a $X_{15}-N-X_{16}-R_{11}$ substructure which makes the complexes non-planar; as a result, the self-quenching effect of these complexes are low. In one embodiment, the self-quenching constant for

the complexes of Structure I are in the order of 10^7 or lower, including, but not limited to, lower than in the order of 7×10^6 , 5×10^6 , 3×10^6 , 10^6 , 7×10^5 , 5×10^5 , 3×10^5 , or 10^5 .

[0066] The effect of triplet-triplet annihilation in the devices is suppressed. As a result, the efficiency roll-off in the devices fabricated by using these complexes as emitting materials are low.

[0067] In one embodiment, the efficiency roll-off of the device at 1000 cd/A is less than 7%. In another embodiment, the efficiency roll-off of the device at 1000 cd/A is less than 20%, or any percentages lower than 20%, including, but not limited to, lower than 17%, 15%, 13%, 10%, 7%, 5%, or 3%.

[0068] Furthermore, due to the low self-quenching, higher doping concentration can be used to increase the device efficiency while the CIE can be kept as the excimer emission is avoided, or is substantially avoided.

[0069] In one embodiment, a device shows no, or almost no, excimer emission with 10% doping concentration.

[0070] As the complexes show emission from green to orange region, green to orange OLED can be fabricated by using the organometallic complex of Structure I as the single emitter. In an embodiment, a blue emitting material (or layer) is added to the orange device, and white OLED can be fabricated.

[0071] In one embodiment, the device fabricated using the organometallic complex of Structure I shows green emission with CIE of $(0.25 \pm 0.05, 0.63 \pm 0.05)$.

[0072] In another embodiment, the device fabricated using the organometallic complex of Structure I shows yellow to orange emission with CIE of $(0.40 \pm 0.1, 0.4 \pm 0.1)$.

[0073] Since the organometallic complexes of Structure I do not carry net charge and are soluble in common solvents, various device fabrication methods can be used in OLED fabrication.

[0074] The luminescent platinum(II) compounds of the present invention can be formed into thin films by vacuum deposition, spin-coating, inkjet printing or other known fabrication methods. Different multilayer OLEDs have been fabricated using the compounds of the present invention as light-emitting material or as dopant in the emitting layer. In general, the OLEDs consist on an anode and a cathode, between which are the hole transporting layer, light-emitting layer, and electron transporting or injection layer. The present invention makes use of an additional carrier confinement layer to improve the performance of the devices.

[0075] In one embodiment, the OLED is fabricated by vacuum deposition.

[0076] In another embodiment, the OLED is fabricated by solution process including spin coating and printing.

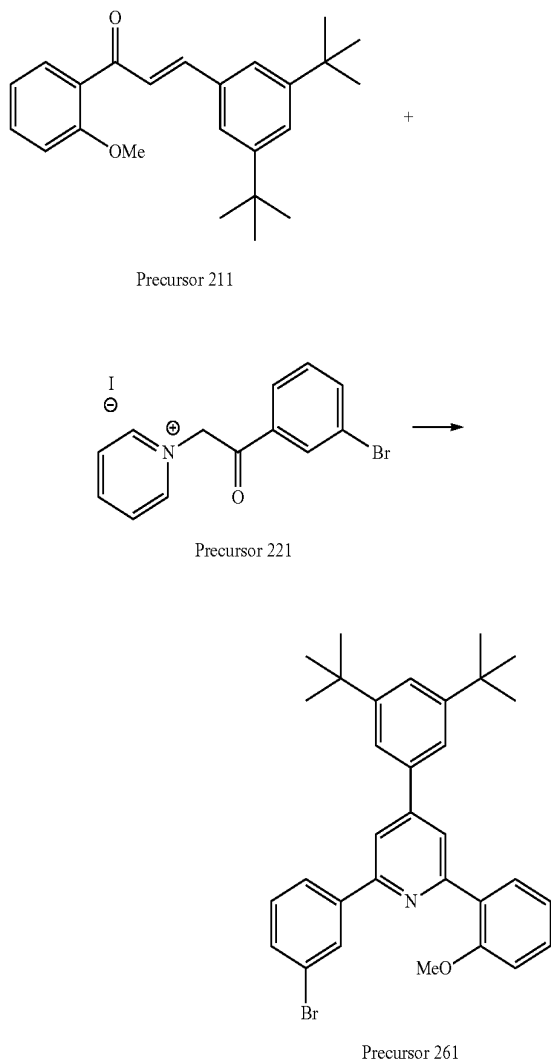
EXAMPLES

[0077] Following are examples that illustrate embodiments for practicing the invention. These examples should not be construed as limiting. All percentages are by weight and all solvent mixture proportions are by volume unless otherwise noted.

Example 1

Preparation of Precursor 261

[0078]

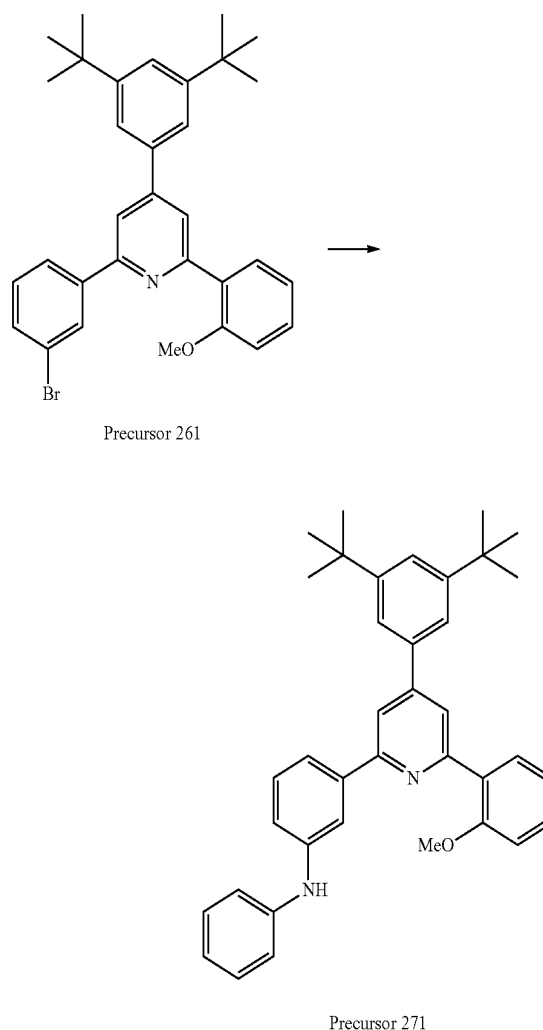


[0079] To a conical flask was charged with Precursor 221 (2.24 g, 5.5 mmol), Precursor 211 (1.95 g, 5.5 mmol), excess ammonium acetate, and methanol. The mixture was refluxed for 24 h. After cooling to room temperature, the solvent was evaporated. The crude mixture was extracted with dichloromethane and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 2.56 g of off-white solid was obtained. Yield: 88%. ¹H NMR (CDCl₃, 400 MHz): δ 8.31 (s, 1H), 8.05-8.04 (m, 2H), 8.01 (d, J=7.6 Hz, 1H), 7.78 (s, 1H), 7.55-7.53 (m, 2H), 7.52 (s, 2H), 7.42 (t, J=7.3 Hz, 1H), 7.36 (t, J=7.9 Hz, 1H), 7.15 (t, J=7.5 Hz, 1H), 7.05 (d, J=8.2 Hz, 1H), 3.90 (s, 3H), 1.41 (s, 18H).

Example 2

Preparation of Precursor 271

[0080]

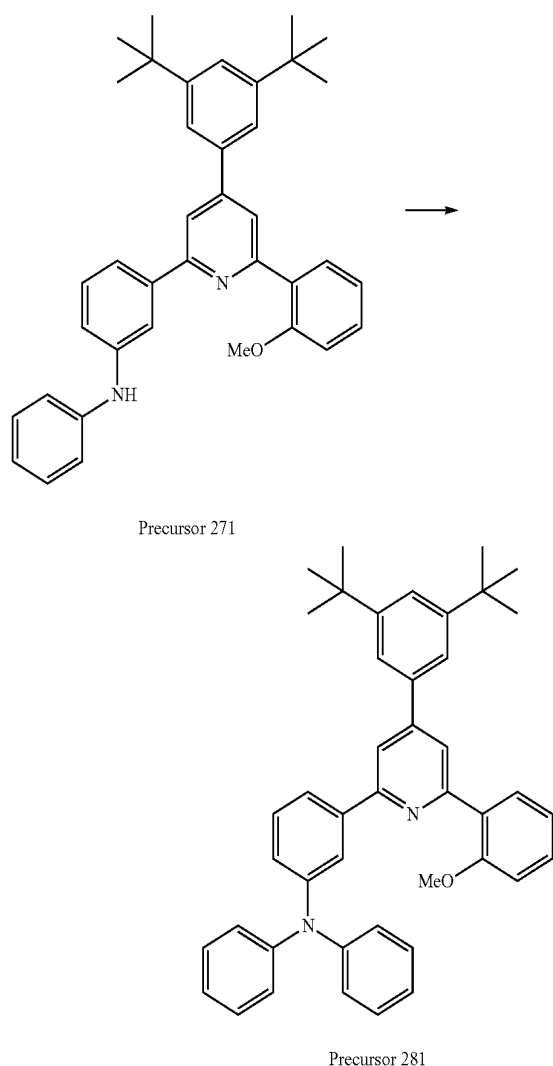


[0081] To a dry, nitrogen-flushed flask was charged with Precursor 261 (1.44 g, 2.7 mmol), potassium tert-butoxide (0.42 g, 3.8 mmol), Pd(dba)₂ (0.25 g, 0.27 mmol), DPE-phos (bis[2-(diphenylphosphino)phenyl]ether) (0.29 g, 0.55 mmol), aniline (0.25 g, 2.7 mmol), and anhydrous toluene. The mixture was refluxed for 24 h. After cooling to room temperature, ethyl acetate was added, and the mixture was stirred for five minutes. The crude mixture was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 1.31 g of yellow solid was obtained. Yield: 90%. ¹H NMR (CDCl₃, 400 MHz): δ 8.03 (s, 2H), 7.88 (s, 1H), 7.79 (s, 1H), 7.62 (m, 1H), 7.53 (s, 3H), 7.42-7.39 (m, 2H), 7.38-7.36 (m, 1H), 7.30-7.28 (m, 2H), 7.13-7.11 (m, 2H), 7.05-7.03 (m, 2H), 6.93 (m, 1H), 5.86 (s, 1H), 3.89 (s, 3H), 1.40 (s, 18H).

Example 3

Preparation of Precursor 281

[0082]

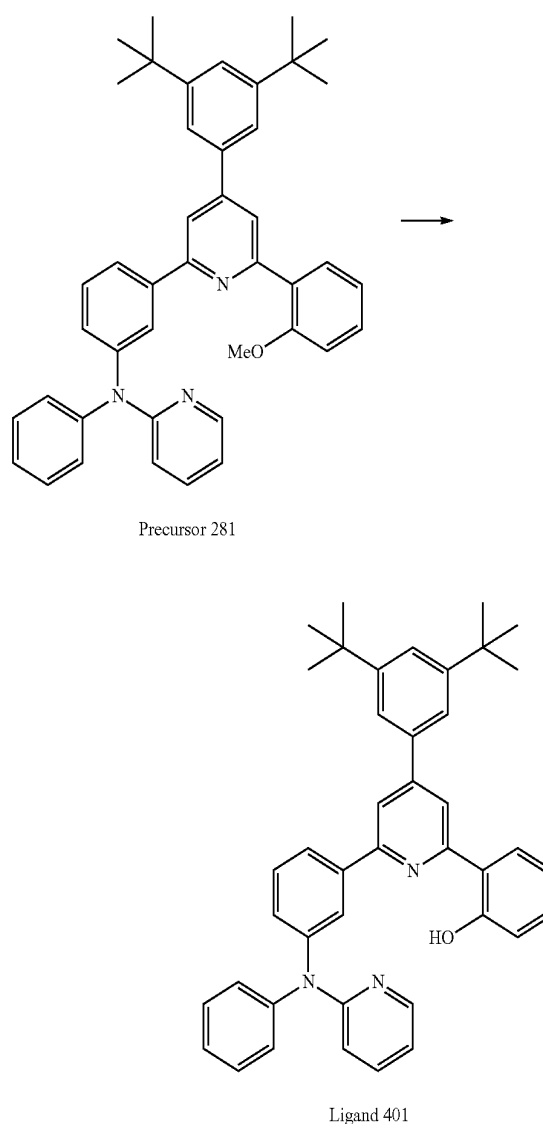


[0083] To a dry, nitrogen-flushed flask was charged with Precursor 271 (1.31 g, 2.4 mmol), potassium tert-butoxide (0.33 g, 2.9 mmol), Pd(dba)₂ (0.22 g, 0.24 mmol), DPE-phos, 2-iodopyridine (0.26 g, 0.48 mmol), and anhydrous toluene. The mixture was refluxed for 24 h. After cooling to room temperature, ethyl acetate was added, and the mixture was stirred for five minutes. The crude mixture was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 1.29 g of yellow solid was obtained. Yield: 87%. ¹H NMR (CDCl₃, 400 MHz): δ 8.26 (d, J=4.92 Hz, 1H), 8.01 (s, 1H), 7.96 (d, J=7.6 Hz, 1H), 7.93-7.89 (m, 2H), 7.70 (s, 1H), 7.52 (t, J=1.97 Hz, 1H), 7.49 (s, 2H), 7.45-7.23 (m, 8H), 7.11 (q, J=7.5 Hz, 2H), 7.03 (d, J=8.2 Hz, 1H), 6.84 (d, J=8.4 Hz, 1H), 6.78-6.80 (m, 1H), 3.86 (s, 3H), 1.38 (s, 18H).

Example 4

Preparation of Ligand 401

[0084]

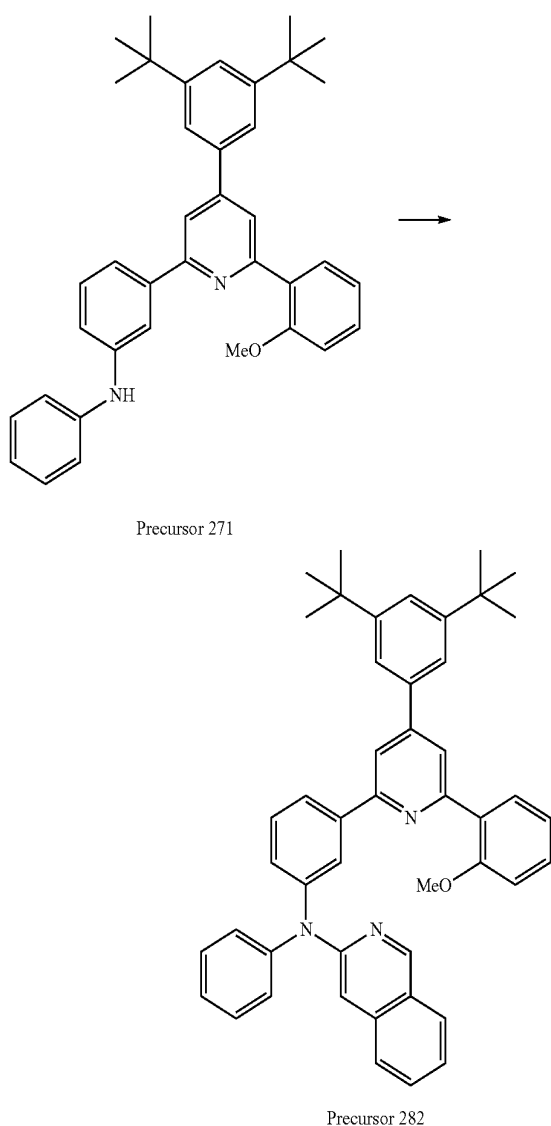


[0085] To a dry, nitrogen-flushed flask was charged with Precursor 281 (1.29 g, 2.1 mmol) and pyridine hydrochloride. The mixture was refluxed for 24 h. After cooling to room temperature, the crude mixture was extracted with dichloromethane and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 1.2 g of yellow solid was obtained. Yield: 95%. ¹H NMR (CD₂Cl₂, 500 MHz): δ 14.37 (s, 1H), 8.22 (d, J=4.9 Hz, 1H), 8.05 (s, 1H), 7.96 (d, J=8.1 Hz, 1H), 7.78 (s, 1H), 7.75 (d, J=7.7 Hz, 1H), 7.72 (s, 1H), 7.58 (s, 1H), 7.52-7.48 (m, 4H), 7.38-7.31 (m, 3H), 7.28-7.24 (m, 3H), 7.19 (t, J=5.8 Hz, 1H), 6.99 (d, J=8.3 Hz, 1H), 6.95 (t, J=7.5 Hz, 1H), 6.82-6.86 (m, 2H), 1.39 (s, 18H). MS (FAB): 604.1 (M⁺)

Example 5

Preparation of Precursor 282

[0086]

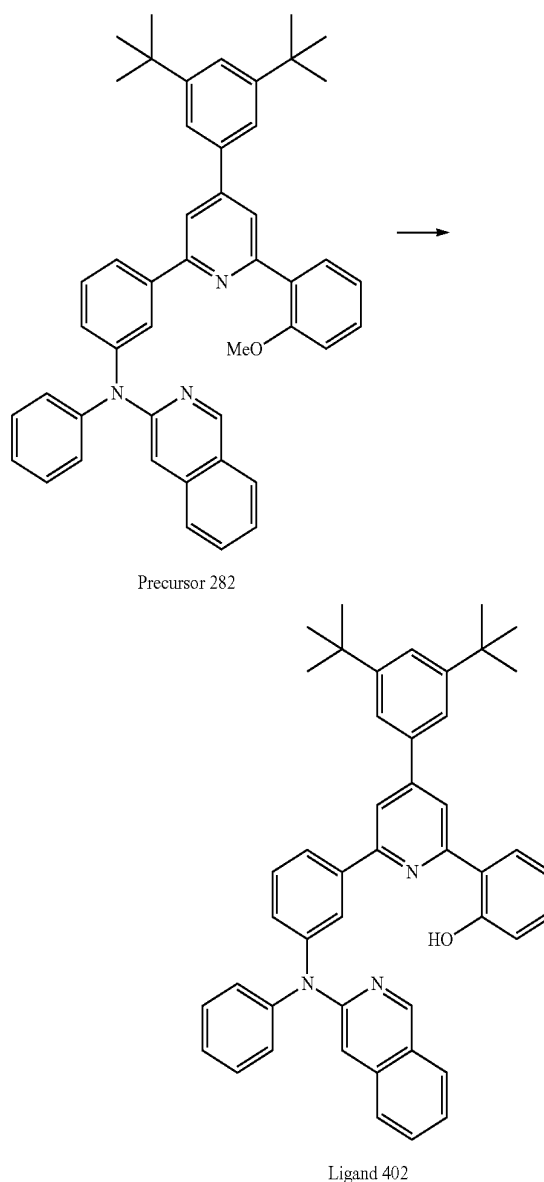


[0087] To a dry, nitrogen-flushed flask was charged with Precursor 271 (0.20 g, 0.37 mmol), potassium tert-butoxide (0.05 g, 0.44 mmol), Pd(dba)₂ (0.03 g, 0.03 mmol), DPE-phos (0.04 g, 0.07 mmol), 3-bromoisoquinoline (0.08 g, 0.86 mmol), and anhydrous toluene. The mixture was refluxed for 24 h. After cooling to room temperature, ethyl acetate was added, and the mixture was stirred for five minutes. The crude mixture was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.17 g of yellow solid was obtained. Yield: 69%. ¹H NMR (CDCl₃, 300 MHz): δ 9.03 (s, 1H), 8.00 (s, 1H), 7.83-7.96 (m, 4H), 7.69 (s, 1H), 7.53-7.45 (m, 6H), 7.39-7.30 (m, 5H), 7.25-7.23 (m, 2H), 7.15-7.02 (m, 4H), 3.85 (s, 3H), 1.37 (s, 18H).

Example 6

Preparation of Ligand 402

[0088]

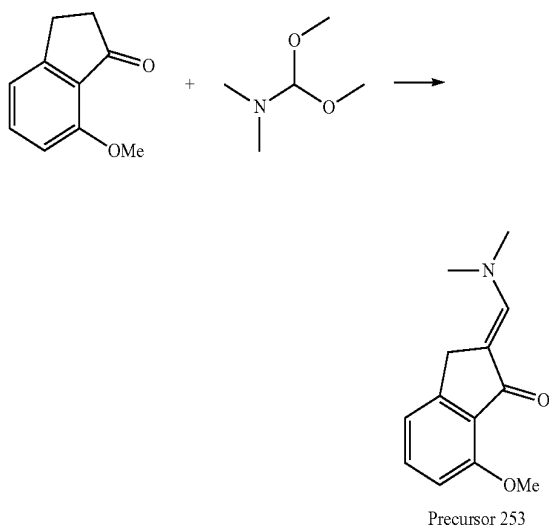


[0089] To a dry, nitrogen-flushed flask was charged with Precursor 282 (0.13 g, 0.19 mmol) and pyridine hydrochloride. The mixture was refluxed for 24 h. After cooling to room temperature, the crude mixture was extracted with dichloromethane and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.11 g of yellow solid was obtained. Yield: 90%. ¹H NMR (CD₂Cl₂, 400 MHz): δ 4.67 (s, 1H), 9.04 (s, 1H), 7.97 (s, 1H), 7.89-7.84 (m, 2H), 7.73-7.71 (m, 2H), 7.63 (s, 1H), 7.55-7.53 (m, 3H), 7.47-7.44 (m, 3H), 7.38-7.26 (m, 7H), 7.17-7.15 (m, 2H), 7.02 (d, J=8.1 Hz, 1H), 6.94 (t, J=8.1 Hz, 1H), 1.38 (s, 18H).

Example 7

Preparation of Precursor 253

[0090]

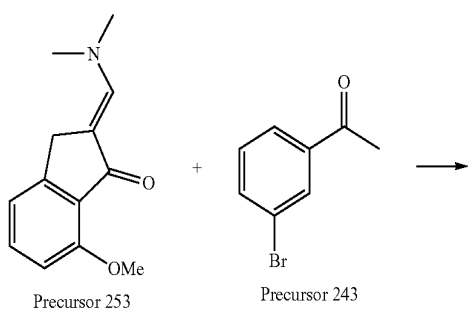


[0091] To a conical flask was charged with 7-methoxy-1-indanone (2.18 g, 13.4 mmol), 1,1-dimethoxy-N,N-dimethylmethanamine. The mixture was refluxed for 24 h. After cooling to room temperature, the solvent was evaporated. The crude mixture was purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 2.42 g of brown solid was obtained. Yield: 83%. ¹H NMR (CDCl₃, 300 MHz): δ 7.42-7.37 (m, 2H), 7.00 (d, J=7.5 Hz, 1H), 6.79 (d, J=8.2 Hz, 1H), 4.11 (s, 3H), 3.95 (s, 3H), 3.85 (s, 2H), 3.14 (s, 6H).

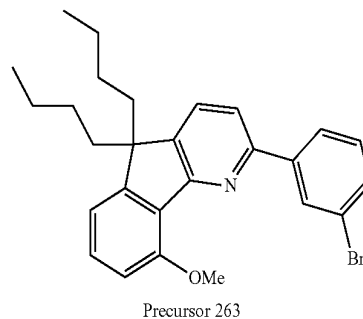
Example 8

Preparation of Precursor 263

[0092]



-continued

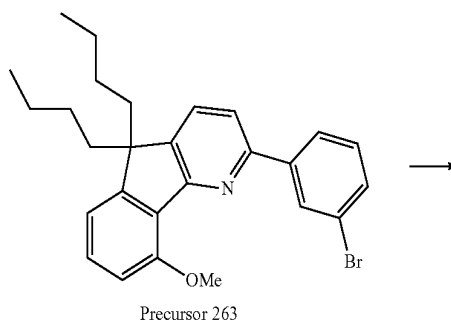


[0093] To a dry, nitrogen-flushed flask was charged with Precursor 253 (2.18 g, 10.0 mmol), Precursor 243 (1.99 g, 10.0 mmol), potassium tert-butoxide (1.35 g, 12.0 mmol), anhydrous THF. The mixture was stirred for 12 h. Excess ammonium acetate, acidic acid was added. The mixture was refluxed for 2 h. After cooling to room temperature, the crude mixture was extracted with ethyl acetate and an intermediate was purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). To a dry, nitrogen-flushed flask was charged the intermediate prepared above (0.53 g, 1.5 mmol), potassium tert-butoxide (0.37 g, 3.3 mmol), 1-iodobutane (0.38 mL, 3.3 mmol), and anhydrous THF. The mixture was stirred for 24 h. The crude mixture was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.60 g of yellow solid was obtained. Yield: 77%. ¹H NMR (CDCl₃, 400 MHz): δ 8.38 (s, 1H), 8.10 (d, J=7.8 Hz, 1H), 7.63 (q, J=7.9 Hz, 2H), 7.51 (d, J=8.0 Hz, 1H), 7.42-7.32 (m, 2H), 7.00 (d, J=7.6 Hz, 1H), 6.93 (d, J=8.0 Hz, 1H), 4.11 (s, 3H), 2.01-1.96 (s, 4H), 1.10-1.02 (m, 4H), 0.67-0.57 (m, 10H).

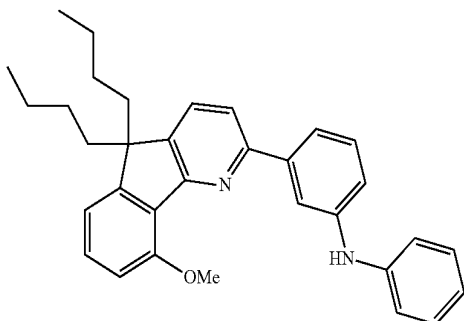
Example 9

Preparation of Precursor 273

[0094]



-continued

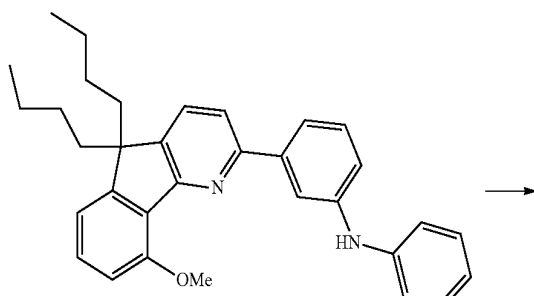


Precursor 273

[0095] To a dry, nitrogen-flushed flask was charged with Precursor 263 (0.54 g, 1.2 mmol), potassium tert-butoxide (0.16 g, 1.4 mmol), Pd(dba)₂ (0.11 g, 0.12 mmol), DPE-phos (bis[2-(diphenylphosphino)phenyl]ether) (0.13 g, 0.23 mmol), aniline (0.11 g, 1.2 mmol), and anhydrous toluene. The mixture was refluxed for 24 h. After cooling to room temperature, ethyl acetate was added, and the mixture was stirred for five minutes. The crude mixture was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.41 g of yellow solid was obtained. Yield: 74%. ¹H NMR (CDCl₃, 300 MHz): δ 8.00 (s, 1H), 7.69 (d, J=7.8 Hz, 1H), 7.62 (s, 2H), 7.41-7.33 (m, 3H), 7.30 (s, 1H), 7.15-7.13 (m, 3H), 7.00-6.90 (m, 3H), 5.82 (s, 1H), 4.05 (s, 3H), 2.00-1.95 (m, 4H), 1.10-1.02 (m, 4H), 0.67-0.57 (m, 10H).

Example 10

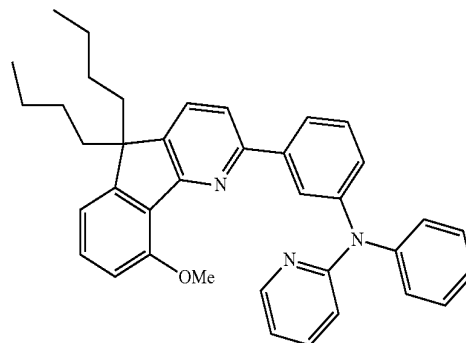
Preparation of Precursor 283

[0096]

Precursor 273



-continued

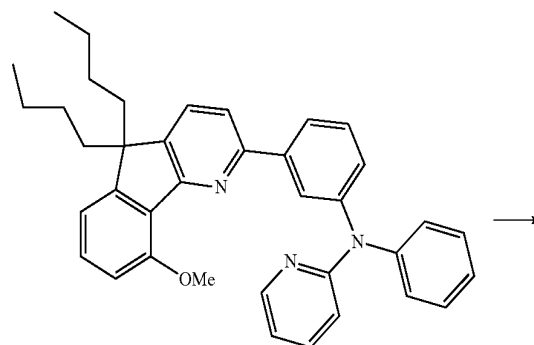


Precursor 283

[0097] To a dry, nitrogen-flushed flask was charged with Precursor 273 (0.41 g, 0.86 mmol), potassium tert-butoxide (0.12 g, 1.03 mmol), Pd(dba)₂ (0.08 g, 0.086 mmol), DPE-phos (0.09 g, 0.17 mmol), 2-iodopyridine (0.18 g, 0.86 mmol), and anhydrous toluene. The mixture was refluxed for 24 h. After cooling to room temperature, ethyl acetate was added, and the mixture was stirred for five minutes. The crude mixture was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.43 g of yellow solid was obtained. Yield: 90%. ¹H NMR (CDCl₃, 400 MHz): δ 8.26 (d, J=7.7 Hz, 1H), 8.05 (s, 1H), 7.93 (d, J=7.9 Hz, 1H), 7.60 (d, J=7.8 Hz, 2H), 7.55 (d, J=8.0 Hz, 1H), 7.45 (q, J=8.3 Hz, 2H), 7.38-7.30 (m, 4H), 7.23-7.20 (m, 2H), 7.11 (t, J=7.0 Hz, 1H), 6.97 (d, J=7.5 Hz, 1H), 6.85 (d, J=8.0 Hz, 1H), 6.81 (d, J=7.7 Hz, 1H), 6.78 (t, J=6.5 Hz, 1H), 3.95 (s, 3H), 1.97-1.55 (m, 4H), 1.07-1.00 (m, 4H), 0.65-0.53 (m, 10H).

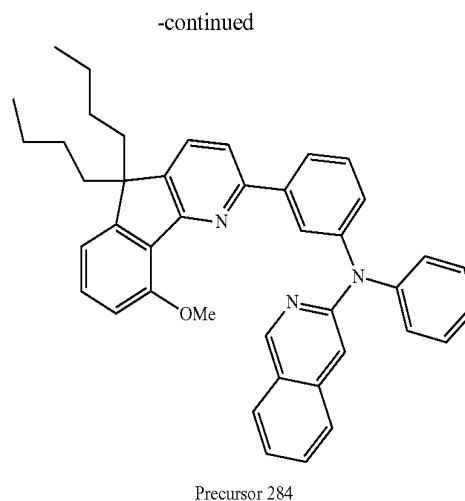
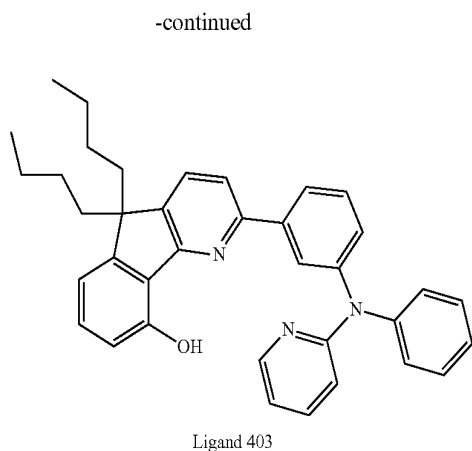
Example 11

Preparation of Ligand 403

[0098]

Precursor 283



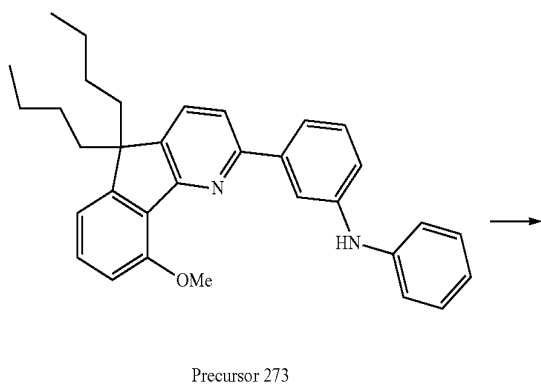


[0099] To a dry, nitrogen-flushed flask was charged with Precursor 283 (0.43 g, 0.77 mmol) and pyridine hydrochloride. The mixture was refluxed for 24 h. After cooling to room temperature, the crude mixture was extracted with dichloromethane and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.387 g of yellow solid was obtained. Yield: 90%. ¹H NMR (CD₂Cl₂, 500 MHz): δ 9.17 (s, 1H), 8.21 (d, J=5.2 Hz, 1H), 7.83 (s, 1H), 7.79 (d, J=8.0 Hz, 1H), 7.68 (d, J=7.9 Hz, 1H), 7.54 (d, J=7.9 Hz, 1H), 7.50 (t, J=7.8 Hz, 1H), 7.45 (t, J=7.9 Hz, 1H), 7.36 (t, J=7.9 Hz, 2H), 7.31 (t, J=7.9 Hz, 1H), 7.25-7.21 (m, 3H), 7.18 (t, J=7.4 Hz, 1H), 6.93 (d, J=7.3 Hz, 1H), 6.84-6.82 (m, 3H), 1.97-1.92 (m, 4H), 1.10-1.06 (m, 4H), 0.71-0.66 (m, 10H). MS (FAB): 540.3 (M⁺).

Example 12

Preparation of Precursor 284

[0100]

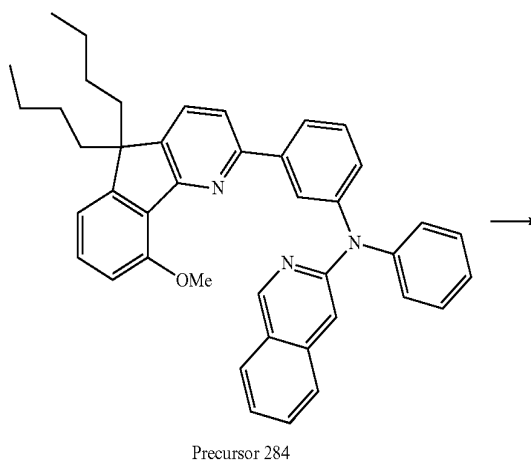


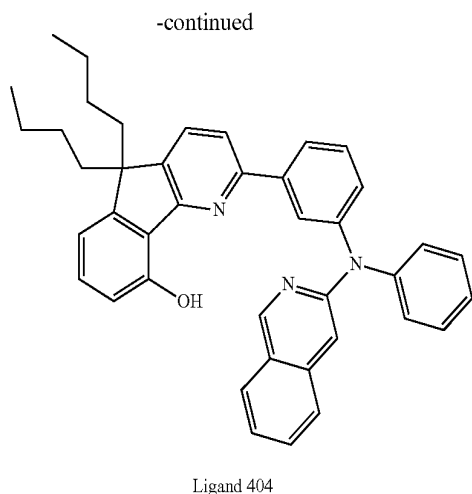
[0101] To a dry, nitrogen-flushed flask was charged with Precursor 273 (0.21 g, 0.44 mmol), potassium tert-butoxide (0.06 g, 0.52 mmol), Pd(dba)₂ (0.04 g, 0.04 mmol), DPE-phos (0.05 g, 0.08 mmol), 3-bromoisoquinoline (0.09 g, 0.44 mmol), and anhydrous toluene. The mixture was refluxed for 24 h. After cooling to room temperature, ethyl acetate was added, and the mixture was stirred for five minutes. The crude mixture was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.17 g of yellow solid was obtained. Yield: 65%. ¹H NMR (CDCl₃, 400 MHz): δ 9.03 (s, 1H), 8.05 (s, 1H), 7.95 (d, J=7.6 Hz, 1H), 7.84 (d, J=8.1 Hz, 1H), 7.60-7.50 (m, 5H), 7.46 (t, J=7.9 Hz, 1H), 7.37-7.31 (m, 5H), 7.25-7.23 (m, 2H), 7.12 (s, 1H), 6.96 (d, J=7.4 Hz, 1H), 6.84 (d, J=8.1 Hz, 1H), 3.84 (s, 3H), 1.97-1.92 (m, 4H), 1.06-1.01 (m, 4H), 0.64-0.57 (m, 10H).

Example 13

Preparation of Ligand 404

[0102]



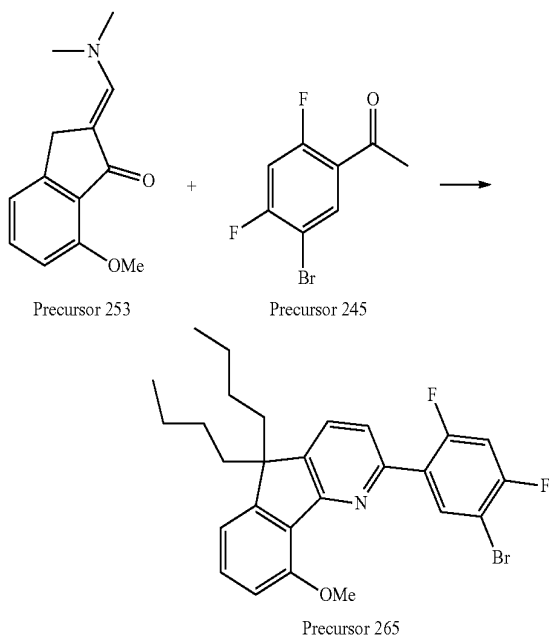


[0103] To a dry, nitrogen-flushed flask was charged with Precursor 284 (0.17 g, 0.28 mmol) and pyridine hydrochloride. The mixture was refluxed for 24 h. After cooling to room temperature, the crude mixture was extracted with dichloromethane and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.15 g of yellow solid was obtained. Yield: 90%. ¹H NMR (CDCl₃, 300 MHz): δ 9.31 (s, 1H), 9.04 (s, 1H), 7.86 (d, J=8.5 Hz, 1H), 7.80 (s, 2H), 7.54-7.45 (m, 5H), 7.42-7.31 (m, 3H), 7.29-7.23 (m, 4H), 7.15 (s, 2H), 6.87 (t, J=8.7 Hz, 2H), 1.96-1.91 (m, 4H), 1.05-1.00 (m, 4H), 0.70-0.65 (m, 10H). MS (ESI): 590.3 (M⁺).

Example 14

Preparation of Precursor 265

[0104]



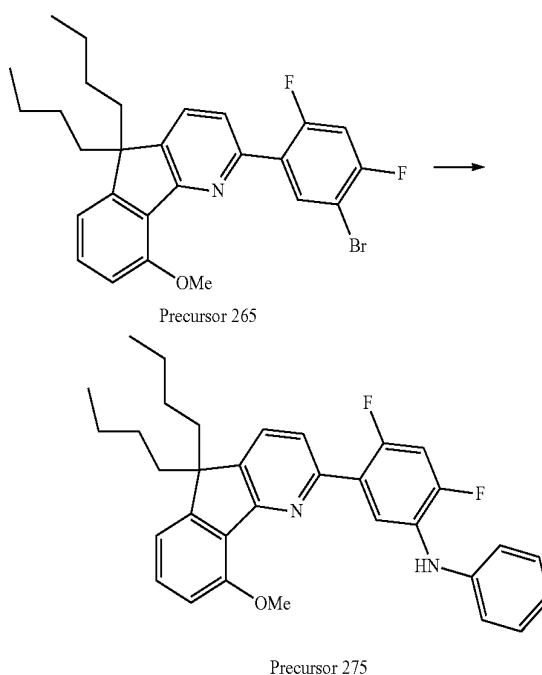
[0105] To a dry, nitrogen-flushed flask was charged with Precursor 253 (0.50 g, 2.3 mmol), Precursor 245 (0.54 g, 2.3 mmol), potassium tert-butoxide (0.31 g, 2.7 mmol), anhydrous THF. The mixture was stirred for 12 h. Excess ammonium acetate, acidic acid was added. The mixture was refluxed for 2 h. After cooling to room temperature, the crude mixture of the intermediate was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1).

[0106] To a dry, nitrogen-flushed flask was the above intermediate (0.90 g, 2.3 mmol), potassium tert-butoxide (0.57 g, 5.1 mmol), 1-iodobutane (0.58 mL, 5.1 mmol), and anhydrous THF. The mixture was stirred for 24 h. The crude mixture was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 1.04 g of yellow solid was obtained. Yield: 81%. ¹H NMR (CDCl₃, 400 MHz): δ 8.65 (t, J=8.1 Hz, 1H), 7.70 (d, J=7.9 Hz, 1H), 7.65 (d, J=7.8 Hz, 1H), 7.41 (t, J=8.0 Hz, 1H), 7.02-6.94 (m, 3H), 4.11 (s, 3H), 2.02-1.96 (m, 4H), 1.10-1.04 (m, 4H), 0.68-0.56 (m, 10H).

Example 15

Preparation of Precursor 275

[0107]



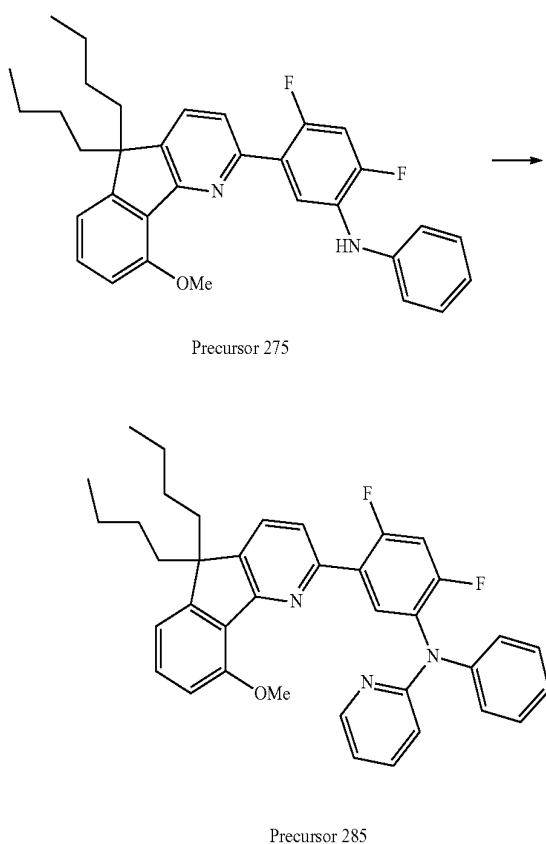
[0108] To a dry, nitrogen-flushed flask was charged with Precursor 265 (1.22 g, 2.4 mmol), potassium phosphate (0.78 g, 3.6 mmol), Pd(dba)₂ (0.22 g, 0.2 mmol), DPE-phos(bis[2-(diphenylphosphino)phenyl]ether) (0.26 g, 0.5 mmol), aniline (0.23 g, 2.4 mmol), and toluene/water mixture. The mixture was refluxed for 24 h. After cooling to room temperature, ethyl acetate was added, and the mixture was stirred for five minutes. The crude mixture was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.76 g of yellow solid was obtained. Yield: 61%. ¹H NMR (CDCl₃, 400

MHz): δ 8.39 (t, $J=8.1$ Hz, 1H), 7.72 (d, $J=6.5$ Hz, 1H), 7.62 (d, $J=7.9$ Hz, 1H), 7.39-7.30 (m, 3H), 7.17 (d, $J=8.5$ Hz, 2H), 7.00-6.96 (m, 3H), 6.88 (d, $J=8.1$ Hz, 1H), 3.92 (s, 3H), 2.00-1.94 (m, 4H), 1.09-1.03 (m, 4H), 0.67-0.58 (m, 10H).

Example 16

Preparation of Precursor 285

[0109]

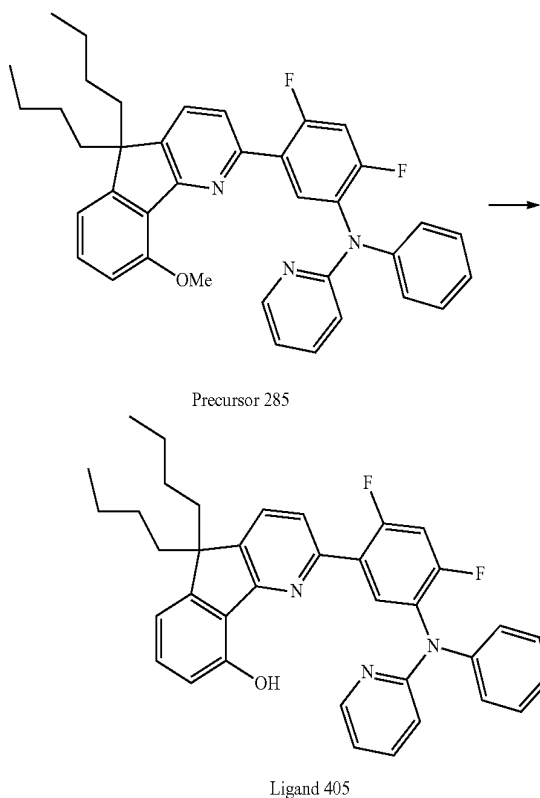


[0110] To a dry, nitrogen-flushed flask was charged with Precursor 275 (0.77 g, 1.5 mmol), potassium tert-butoxide (0.20 g, 1.8 mmol), Pd(dba)₂ (0.14 g, 0.2 mmol), DPE-phos (0.16 g, 0.3 mmol), 2-iodopyridine (0.31 g, 1.5 mmol), and anhydrous toluene. The mixture was refluxed for 24 h. After cooling to room temperature, ethyl acetate was added, and the mixture was stirred for five minutes. The crude mixture was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.49 g of yellow solid was obtained. Yield: 55%. ¹H NMR (CDCl₃, 400 MHz): δ 8.13 (d, $J=8.5$ Hz, 1H), 8.10 (d, $J=8.2$ Hz, 1H), 7.62-7.57 (m, 2H), 7.44 (m, 1H), 7.36-7.31 (m, 3H), 7.29-7.25 (m, 2H), 7.16 (t, $J=7.2$ Hz, 1H), 7.00 (d, $J=10.7$ Hz, 1H), 6.94 (d, $J=7.5$ Hz, 1H), 6.81 (d, $J=8.0$ Hz, 1H), 6.75-6.70 (m, 2H), 3.74 (s, 3H), 1.94-1.88 (m, 4H), 1.03-0.97 (m, 4H), 0.60-0.48 (m, 10H).

Example 17

Preparation of Ligand 405

[0111]

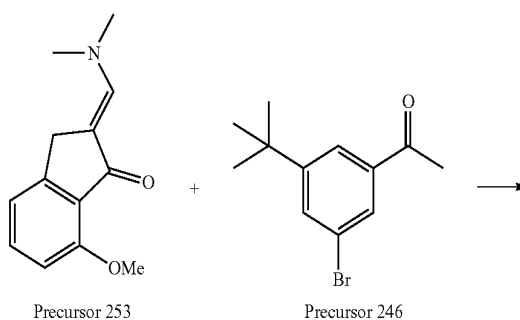


[0112] To a dry, nitrogen-flushed flask was charged with Precursor 285 (0.22 g, 0.3 mmol) and BBr₃ (0.4 mL, 3.0 mmol). The mixture was stirred for 3 h. Water was added to quench the reaction. The crude mixture was extracted with dichloromethane and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.18 g of yellow solid was obtained. Yield: 85%. ¹H NMR (CDCl₃, 400 MHz): δ 8.87 (s, 1H), 8.12 (s, 1H), 7.82 (t, $J=8.5$ Hz, 1H), 7.66 (d, $J=7.9$ Hz, 1H), 7.56 (d, $J=7.6$ Hz, 1H), 7.44 (t, $J=6.8$ Hz, 1H), 7.37-7.15 (m, 5H), 7.03 (t, $J=8.5$ Hz, 2H), 6.89 (d, $J=7.4$ Hz, 1H), 7.78-7.72 (m, 3H), 1.98-1.89 (m, 4H), 1.08-1.01 (m, 4H), 0.66-0.58 (m, 10H).

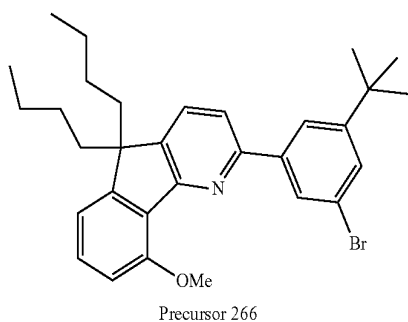
Example 18

Preparation of Precursor 266

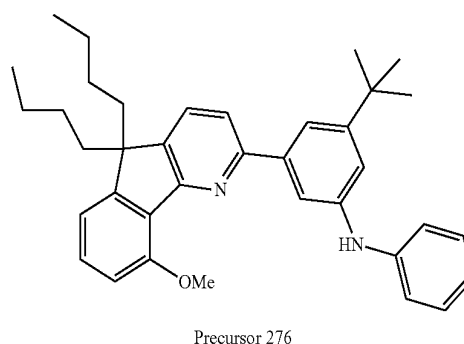
[0113]



-continued



-continued

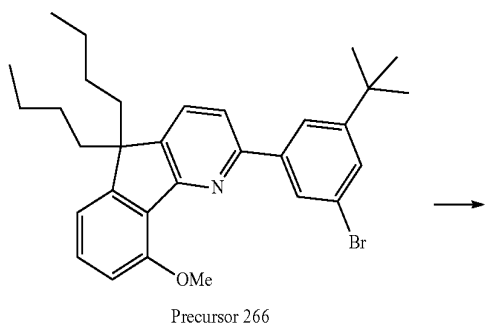


[0114] To a dry, nitrogen-flushed flask was charged with Precursor 253 (1.21 g, 5.6 mmol), Precursor 246 (1.42 g, 5.6 mmol), potassium tert-butoxide (0.75 g, 6.6 mmol), anhydrous THF. The mixture was stirred for 12 h. Excess ammonium acetate, acidic acid was added. The mixture was refluxed for 2 h. After cooling to room temperature, the crude mixture of the intermediate was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1).

[0115] To a dry, nitrogen-flushed flask was charged with the intermediate above (0.67 g, 1.6 mmol), potassium tert-butoxide (0.41 g, 3.6 mmol), 1-iodobutane (0.41 mL, 3.6 mmol), and anhydrous THF (20 mL). The mixture was stirred for 24 h. The crude mixture was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.80 g of yellow solid was obtained. Yield: 72%. ¹H NMR (CDCl₃, 400 MHz): δ 8.29 (s, 1H), 8.06 (s, 1H), 7.63 (q, J=6.8 Hz, 2H), 7.53 (s, 1H), 7.39 (t, J=7.8 Hz, 1H), 7.00 (d, J=7.4 Hz, 1H), 6.92 (d, J=8.1 Hz, 1H), 4.10 (s, 3H), 2.00-1.97 (m, 4H), 1.40 (s, 9H), 1.09-1.03 (m, 4H), 0.66-0.57 (m, 10H).

Example 19

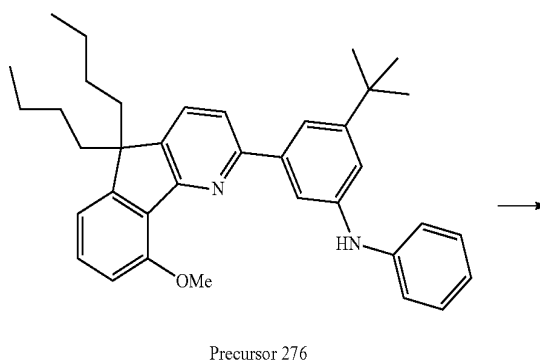
Preparation of Precursor 276

[0116]

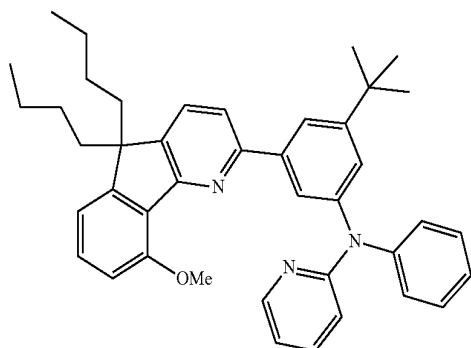
[0117] To a dry, nitrogen-flushed flask was charged with Precursor 266 (0.80 g, 1.5 mmol), potassium tert-butoxide (0.21 g, 1.8 mmol), Pd(dba)₂ (0.14 g, 0.2 mmol), DPE-phos (bis[2-(diphenylphosphino)phenyl]ether) (0.17 g, 0.3 mmol), aniline (0.16 g, 1.5 mmol), and anhydrous toluene (20 mL). The mixture was refluxed for 24 h. After cooling to room temperature, ethyl acetate was added, and the mixture was stirred for five minutes. The crude mixture was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.66 g of yellow solid was obtained. Yield: 81%. ¹H NMR (CDCl₃, 400 MHz): δ 7.91 (s, 1H), 7.74 (s, 1H), 7.59 (s, 2H), 7.36 (t, J=7.9 Hz, 1H), 7.29-7.27 (m, 2H), 7.13 (t, J=8.6 Hz, 3H), 6.98 (d, J=7.5 Hz, 1H), 6.92-6.90 (m, 2H), 4.06 (s, 3H), 1.99-1.94 (m, 4H), 1.40 (s, 9H), 1.09-1.04 (m, 4H), 0.67-0.62 (m, 10H).

Example 20

Preparation of Precursor 286

[0118]

-continued

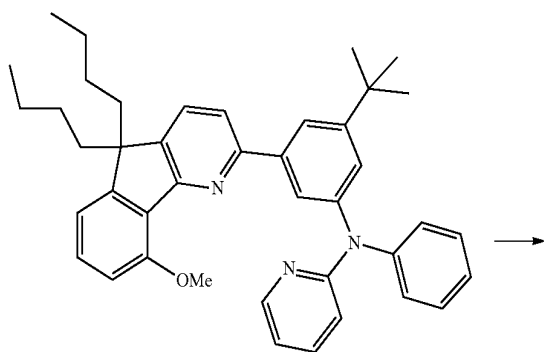


Precursor 286

[0119] To a dry, nitrogen-flushed flask was charged with Precursor 276 (0.65 g, 1.2 mmol), potassium tert-butoxide (0.17 g, 1.5 mmol), Pd(dba)₂ (0.11 g, 0.1 mmol), DPE-phos (0.13 g, 0.2 mmol), 2-iodopyridine (0.30 g, 1.2 mmol), and anhydrous toluene (20 mL). The mixture was refluxed for 24 h. After cooling to room temperature, ethyl acetate was added, and the mixture was stirred for five minutes. The crude mixture was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.65 g of yellow solid was obtained. Yield: 86%. ¹H NMR (CDCl₃, 400 MHz): δ 8.24 (d, J=4.5 Hz, 1H), 8.13 (s, 1H), 7.73 (s, 1H), 7.58 (d, J=7.9 Hz, 1H), 7.52 (d, J=7.9 Hz, 1H), 7.44 (t, J=7.0 Hz, 1H), 7.36 (t, J=7.8 Hz, 1H), 7.30 (t, J=8.3 Hz, 2H), 7.25-7.22 (m, 3H), 7.10 (t, J=7.2 Hz, 1H), 6.97 (d, J=7.8 Hz, 1H), 6.88 (d, J=8.1 Hz, 1H), 6.81-6.75 (m, 2H), 3.99 (s, 3H), 1.98-1.93 (m, 4H), 1.36 (s, 9H), 1.07-1.02 (m, 4H), 0.65-0.55 (m, 10H).

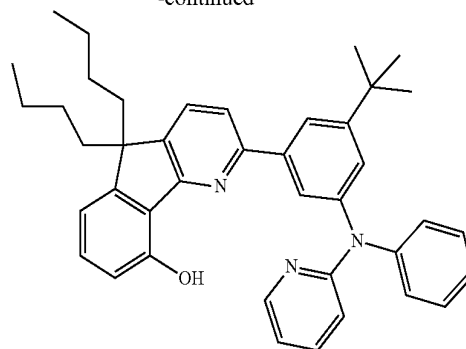
Example 21

Preparation of Ligand 406

[0120]

Precursor 286

-continued

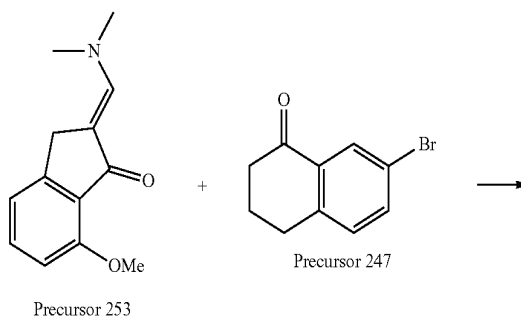


Ligand 406

[0121] To a dry, nitrogen-flushed flask was charged with Precursor 286 (0.65 g, 1.1 mmol) and pyridine hydrochloride (5 g). The mixture was refluxed for 24 h. After cooling to room temperature, the crude mixture was extracted with dichloromethane and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.59 g of yellow solid was obtained. Yield: 94%. ¹H NMR (CDCl₃, 400 MHz): δ 9.19 (s, 1H), 8.14 (s, 1H), 7.78 (s, 1H), 7.61 (d, J=7.8 Hz, 1H), 7.53 (s, 1H), 7.47-7.42 (m, 2H), 7.30-7.24 (m, 4H), 7.24-7.16 (m, 2H), 7.11-7.09 (m, 1H), 6.87 (d, J=8.0 Hz, 1H), 6.75 (d, J=7.9 Hz, 3H), 1.94-1.89 (m, 4H), 1.29 (s, 9H), 1.06-1.01 (m, 4H), 0.65-0.59 (m, 10H).

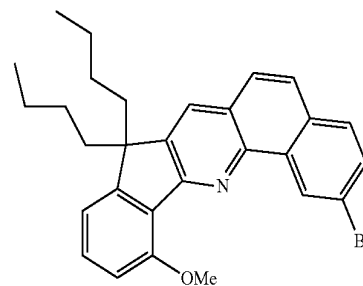
Example 22

Preparation of Precursor 267

[0122]

Precursor 253

Precursor 247



Precursor 267

[0123] To a dry, nitrogen-flushed flask was charged with Precursor 253 (1.97 g, 9.0 mmol), Precursor 247 (2.04 g, 9.0 mmol), potassium tert-butoxide (1.22 g, 10.9 mmol), anhydrous THF (40 mL). The mixture was stirred for 12 h. Excess

ammonium acetate, acidic acid was added. The mixture was refluxed for 2 h. After cooling to room temperature, the crude mixture of the first intermediate was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1).

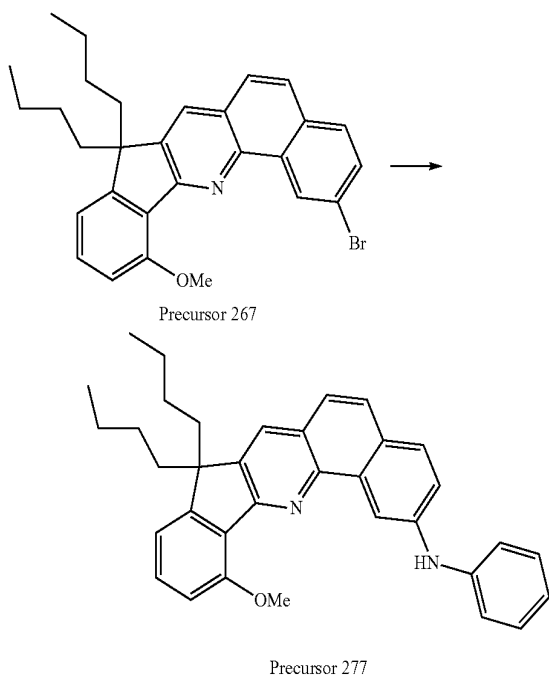
[0124] To a dry, nitrogen-flushed flask was charged the first intermediate (0.53 g, 1.4 mmol), potassium tert-butoxide (0.35 g, 3.1 mmol), 1-iodobutane (0.35 mL, 3.1 mmol), and anhydrous THF (20 mL). The mixture was stirred for 24 h. The crude mixture of the second intermediate was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1).

[0125] To a dry, nitrogen-flushed flask was charged with the second intermediate (0.64 g, 1.3 mmol), 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile(DDQ) (0.42 g, 1.8 mmol), and anhydrous 1,4-dioxane (40 mL). The mixture was refluxed for 24 h. After cooling to room temperature, ethyl acetate was added, and the mixture was stirred for five minutes. The crude mixture was extracted with saturated sodium dicarbonate solution, dichloromethane and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.61 g of yellow solid was obtained. Yield: 79.5%. ¹H NMR (CDCl₃, 400 MHz): δ 9.62 (s, 1H), 8.00 (s, 1H), 7.77-7.75 (m, 4H), 7.48 (t, J=7.9 Hz, 1H), 7.06 (d, J=7.5 Hz, 1H), 6.99 (d, J=8.1 Hz, 1H), 4.23 (s, 3H), 2.17-2.00 (m, 4H), 1.08-1.03 (m, 4H), 0.67-0.57 (m, 10H).

Example 23

Preparation of Precursor 277

[0126]



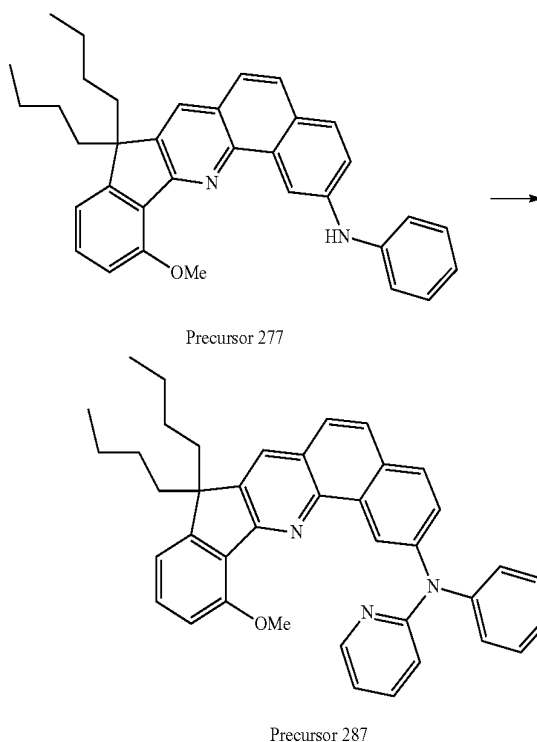
[0127] To a dry, nitrogen-flushed flask was charged with Precursor 267 (0.61 g, 1.2 mmol), potassium tert-butoxide (0.17 g, 1.5 mmol), Pd(dba)₂ (0.11 g, 0.1 mmol), DPE-phos (bis[2-(diphenylphosphino)phenyl]ether) (0.13 g, 0.2 mmol), aniline (0.13 g, 1.2 mmol), and anhydrous toluene (20 mL).

The mixture was refluxed for 24 h. After cooling to room temperature, ethyl acetate was added, and the mixture was stirred for five minutes. The crude mixture was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.51 g of yellow solid was obtained. Yield: 83%. ¹H NMR (CDCl₃, 300 MHz): δ 9.15 (s, 1H), 7.96 (s, 1H), 7.80 (d, J=8.5 Hz, 1H), 7.70 (d, J=8.7 Hz, 1H), 7.55 (d, J=8.7 Hz, 1H), 7.46-7.30 (m, 6H), 7.04 (d, J=7.5 Hz, 2H), 6.95 (d, J=8.2, 1H), 6.09 (s, 1H), 4.09 (s, 3H), 2.08-2.04 (m, 4H), 1.07-1.02 (m, 4H), 0.65-0.58 (m, 10H).

Example 24

Preparation of Precursor 287

[0128]

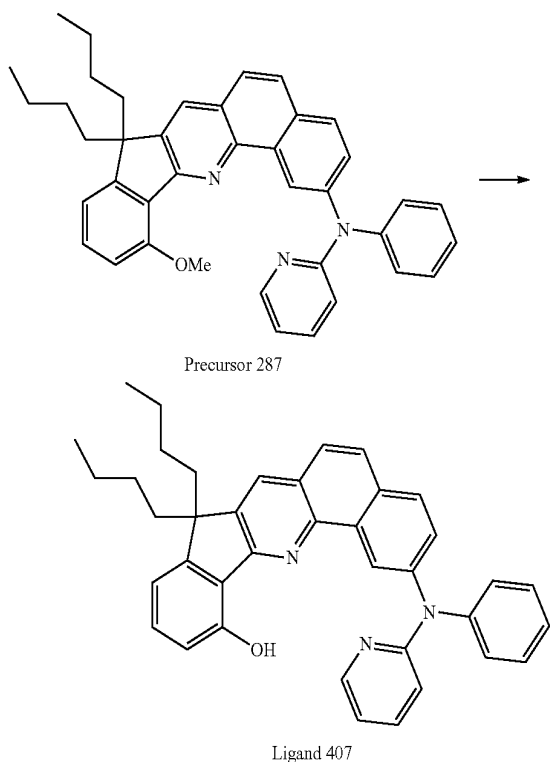


[0129] To a dry, nitrogen-flushed flask was charged with Precursor 277 (0.51 g, 1.0 mmol), potassium tert-butoxide (0.14 g, 1.2 mmol), Pd(dba)₂ (0.09 g, 0.1 mmol), DPE-phos (0.11 g, 0.2 mmol), 2-iodopyridine (0.23 g, 1.0 mmol), and anhydrous toluene (20 mL). The mixture was refluxed for 24 h. After cooling to room temperature, ethyl acetate was added, and the mixture was stirred for five minutes. The crude mixture was extracted with ethyl acetate and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.52 g of yellow solid was obtained. Yield: 89%. ¹H NMR (CDCl₃, 400 MHz): δ 9.24 (s, 1H), 8.30 (s, 1H), 7.95 (s, 1H), 7.85 (d, J=8.5 Hz, 1H), 7.74 (d, J=8.7 Hz, 1H), 7.54 (d, J=8.6 Hz, 1H), 7.51 (t, J=8.3 Hz, 2H), 7.42-7.31 (m, 5H), 7.17 (m, 1H), 7.01 (d, J=7.5 Hz, 1H), 6.91 (t, J=8.3 Hz, 2H), 6.85 (t, J=8.0 Hz, 1H), 3.89 (s, 3H), 2.09-2.04 (m, 4H), 1.08-1.00 (m, 4H), 0.65-0.54 (m, 10H).

Example 25

Preparation of Ligand 407

[0130]

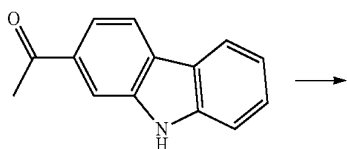


[0131] To a dry, nitrogen-flushed flask was charged with Precursor 287 (0.52 g, 0.9 mmol) and pyridine hydrochloride (5 g). The mixture was refluxed for 24 h. After cooling to room temperature, the crude mixture was extracted with dichloromethane and purified by chromatography on silica gel with mixture of hexane and ethyl acetate (v/v=10:1). 0.48 g of yellow solid was obtained. Yield: 95%. ¹H NMR (CDCl₃, 400 MHz): δ 9.39 (s, 1H), 8.90 (s, 1H), 8.30 (s, 1H), 7.99 (s, 1H), 7.88 (d, J=8.5 Hz, 1H), 7.77 (d, J=8.7 Hz, 1H), 7.67 (d, J=8.6 Hz, 1H), 7.57 (d, J=8.5 Hz, 1H), 7.51 (t, J=7.0 Hz, 1H), 7.42-7.30 (m, 5H), 7.23 (s, 1H), 6.94-6.85 (m, 4H), 2.08-2.01 (m, 4H), 1.12-1.06 (m, 4H), 0.71-0.64 (m, 10H).

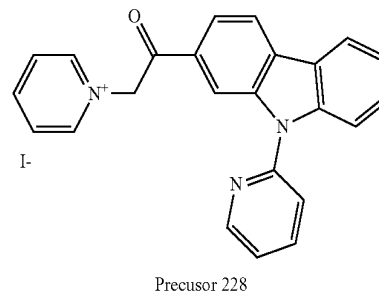
Example 26

Preparation of Precursor 228

[0132]



-continued



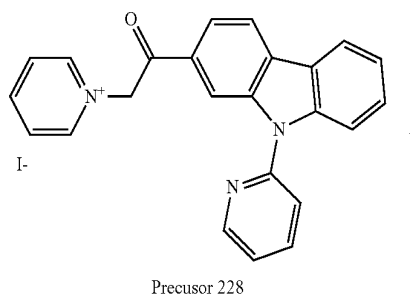
[0133] A mixture of 2-acetylcarbazole, copper powder and potassium carbonate was degassed by three pump-fill cycles. To the solid mixture was added 50 mL DMF and 2-iodopyridine. The mixture was heated to 130° C. overnight. After cooling down to room temperature, dichloromethane was added to the mixture and filtered through celite. The organic solvent was extracted with water and dried with magnesium sulfate. The crude 1-(9-(pyridin-2-yl)carbazol-2-yl)ethanone was then purified by column chromatography using dichloromethane as eluent. The product was obtained as an off-white solid.

[0134] To a mixture of 1-(9-(pyridin-2-yl)carbazol-2-yl)ethanone and iodide was added 10 mL pyridine. The mixture was heated at 90° C. overnight. The solution was cooled down to room temperature and the volatiles were removed under vacuum. The solid was filtered and washed with cold acetone. The product was obtained as a yellow solid. Yield: 1.12 g (2.28 mmol, 65%). ¹H NMR (d₆-DMSO, 300 MHz): δ 9.01 (d, J=5.6 Hz, 2H), 8.80-8.72 (m, 2H), 8.55 (d, J=8.2 Hz, 1H), 8.48 (s, 1H), 8.43 (d, J=7.7 Hz, 1H), 8.29 (t, J=7.1 Hz, 2H), 8.20 (t, J=7.8 Hz, 1H), 8.06 (d, J=8.2 Hz, 1H), 7.86 (t, J=8.6 Hz, 2H), 7.65-7.47 (m, 2H), 7.42 (t, J=7.5 Hz, 1H), 6.60 (s, 2H).

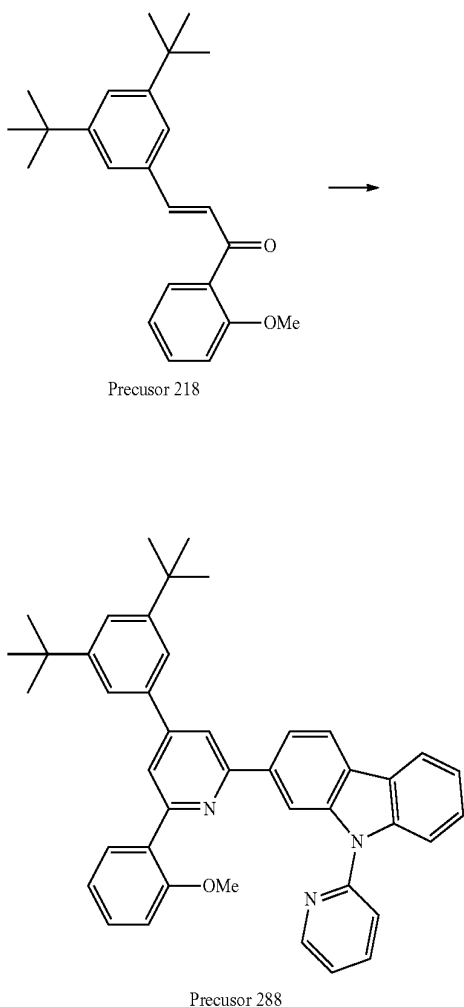
Example 27

Preparation of Precursor 288

[0135]



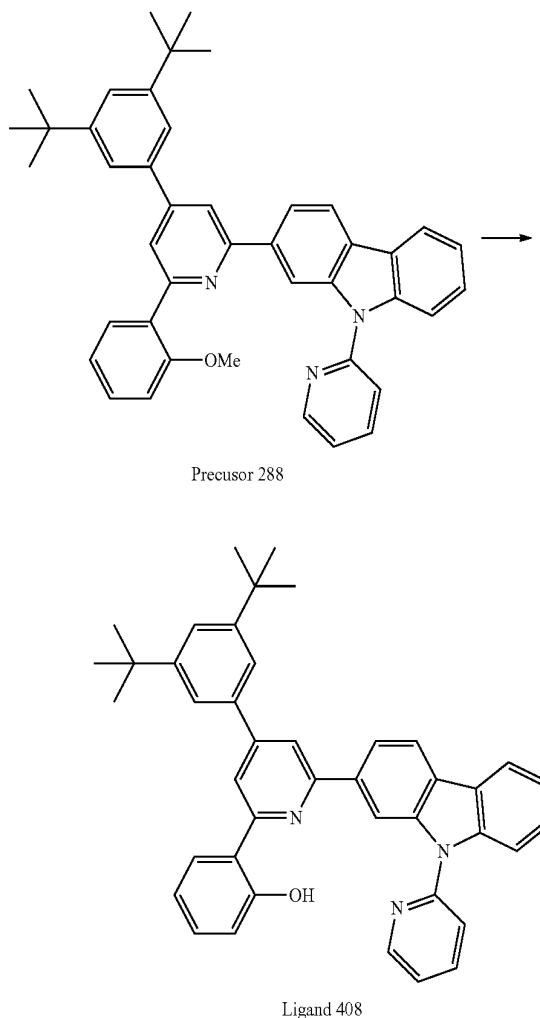
-continued



Example 28

Preparation of Ligand 408

[0137]



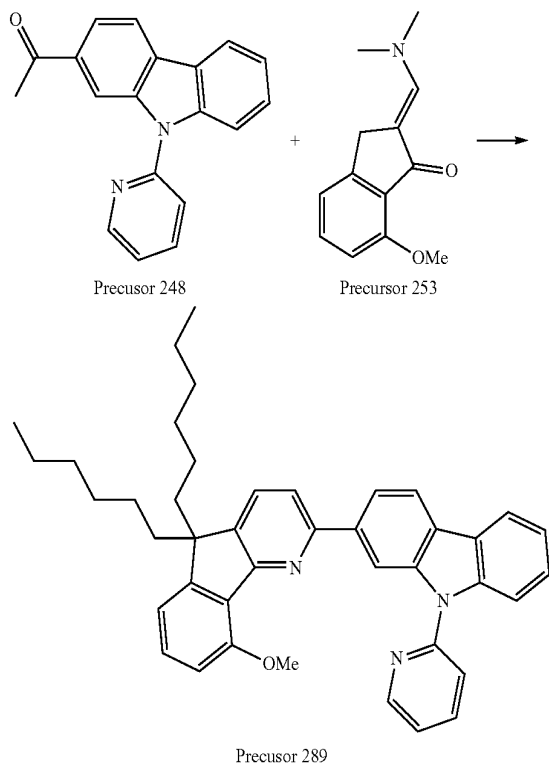
[0136] To a mixture of Precursor 218 (0.80 g, 2.28 mmol) and Precursor 228 (1.12 g, 2.28 mmol) was added 30 g ammonium acetate and 20 mL methanol. The mixture was refluxed overnight. The reaction mixture was partitioned with dichloromethane and water. The organics were dried with magnesium sulfate and evaporated under vacuum. The crude product was purified with column chromatography using dichloromethane as eluent. The product was obtained as a yellow solid. Yield: 0.75 g (1.22 mmol, 53%). ¹H NMR (CDCl₃, 400 MHz): δ 8.76-8.75 (m, 1H), 8.63 (s, 1H), 8.23 (d, J=8.2 Hz, 1H), 8.18-8.13 (m, 2H), 8.06-8.02 (m, 2H), 7.95-7.93 (m, 2H), 7.90 (d, J=8.2 Hz, 1H), 7.74 (d, J=8.1 Hz), 7.57-7.56 (m, 3H), 7.47 (t, J=7.7 Hz, 1H), 7.41 (t, J=7.8 Hz, 1H), 7.36-7.32 (m, 2H), 7.14 (t, J=7.1 Hz, 1H), 7.06 (d, J=8.0 Hz, 1H), 3.91 (s, 2H), 1.42 (s, 18H).

[0138] A mixture of Precursor 288 (0.75 g, 1.22 mmol) and 20 g pyridinium hydrochloride was heated to around 200° C. under nitrogen atmosphere. The reaction progress was monitored by TLC. When all the starting material was consumed, the reaction was quenched with water when hot. The solution was then partitioned with dichloromethane and water. The organic layer was dried with magnesium sulfate and the volatiles were removed under vacuum. The crude product was purified by column chromatography using dichloromethane as eluent. The product was obtained as a yellow solid. Yield: 0.54 g (0.90 mmol, 74%). ¹H NMR (CDCl₃, 500 MHz): δ 14.82 (s, 1H), 8.69 (dd, J=4.9 Hz, 1.3 Hz, 1H), 8.43 (s, 1H), 8.18 (d, J=8.1 Hz, 1H), 8.10 (d, J=7.7 Hz, 1H), 7.95-7.90 (m, 3H), 7.88 (dd, J=8.0 Hz, 1.4 Hz, 1H), 7.84-7.82 (m, 2H), 7.69 (d, J=8.1 Hz, 1H), 7.52 (s, 1H), 7.47 (s, 2H), 7.42 (t, J=7.7 Hz, 1H), 7.30-7.25 (m, 3H), 7.02 (dd, J=8.2 Hz, 1.0 Hz, 1H), 6.89 (t, J=7.5 Hz, 1H), 1.36 (s, 18H).

Example 29

Preparation of Precursor 289

[0139]



[0140] To a degassed 250 mL round-bottom Schlenk flask was added Precursor 248 (1.48 g, 5.16 mmol), potassium tert-butoxide (0.69 g, 6.19 mmol) and 50 mL anhydrous THF. The mixture was stirred at room temperature for 2 hours under nitrogen atmosphere. A solution of Precursor 253 (1.12 g, 5.16 mmol) in 50 mL THF was then added to the above mixture through a cannula. The reaction mixture was stirred overnight at room temperature under nitrogen. To the mixture was then added 50 g ammonium acetate and 25 mL glacial acetic acid. The volatile organics was then removed by distillation at about 100° C. The crude product was then partitioned between dichloromethane and water. The organic layer was dried with magnesium sulfate and the volatiles were removed under vacuum. The crude product of 9-methoxy-2-(9-(pyridin-2-yl)-9H-carbazol-2-yl)-5H-indeno[1,2-b]pyridine was purified by column chromatography using dichloromethane as eluent.

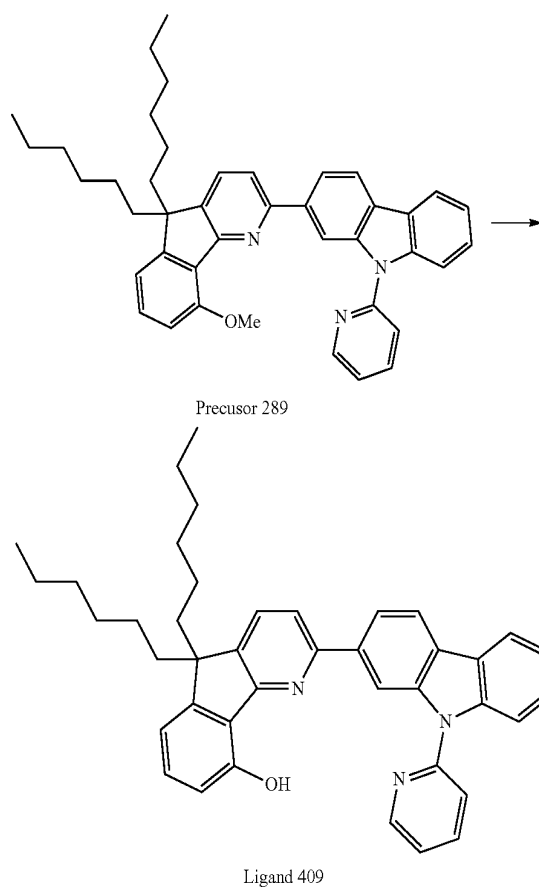
[0141] To a degassed round bottom flask with 9-methoxy-2-(9-(pyridin-2-yl)-9H-carbazol-2-yl)-5H-indeno[1,2-b]pyridine (0.45 g, 1.02 mmol), potassium tert-butoxide (0.27 g, 2.45 mmol) dissolved in 50 mL anhydrous THF was added 1-bromohexane (0.50 g, 3.05 mmol). The resulting solution was refluxed for 2 hours and then cooled down to room temperature. The crude product was then partitioned between dichloromethane and water. The organic layer was dried with magnesium sulfate and the volatiles were removed under vacuum. The crude product was purified by column chromatography using dichloromethane as eluent. The product was obtained as yellow oil. Yield: 0.59 g (0.97 mmol, 95%). ¹H

NMR (CDCl₃, 400 MHz): δ 8.81-8.78 (m, 2H), 8.20 (d, J=8.2 Hz, 1H), 8.14 (d, J=9.5 Hz, 2H), 8.00 (t, J=7.7 Hz, 1H), 7.88 (d, J=8.2 Hz, 1H), 7.83-7.778 (m, 2H), 7.65 (d, J=8.0 Hz, 1H), 7.45 (t, J=7.7 Hz, 1H), 7.40-7.31 (m, 3H), 7.00 (d, J=7.4 Hz, 1H), 6.91 (d, J=8.1 Hz, 1H), 4.06 (s, 3H), 2.01-1.94 (m, 4H), 1.11-0.99 (m, 12H), 0.74 (t, J=7.1 Hz, 6H), 0.64-0.60 (m, 4H).

Example 30

Preparation of Ligand 409

[0142]



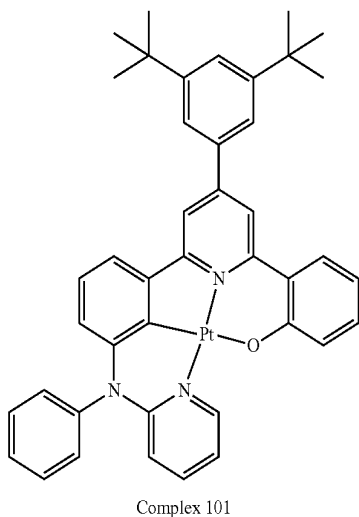
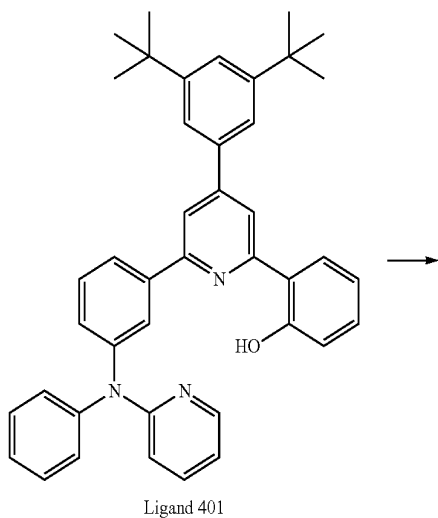
[0143] A degassed 100 mL round bottom flask charged with Precursor 289 (0.59 g, 0.97 mmol) and 20 g pyridinium hydrochloride was heated to around 200° C. The reaction was monitored by TLC. When all the starting material was consumed, the reaction was quenched with water when hot. The solution was then partitioned between dichloromethane and water. The organic layer was dried with magnesium sulfate and the volatiles were removed under vacuum. The crude product was purified by column chromatography using dichloromethane as eluent. The product was obtained as yellow oil. Yield: 0.47 g (0.79 mmol, 82%). ¹H NMR (CDCl₃, 500 MHz): δ 9.47 (s, 1H), 8.80 (d, J=4.9 Hz, 1H), 8.60 (s, 1H), 8.21 (d, J=8.1 Hz, 1H), 8.16 (d, J=7.7 Hz, 1H), 8.02-7.98 (m, 2H), 7.88 (d, J=8.3 Hz, 1H), 7.75 (d, J=8.1 Hz, 1H), 7.71-7.67 (m, 2H), 7.48 (t, J=7.7 Hz, 1H), 7.37-7.30 (m, 3H), 6.92-6.89 (m, 2H), 2.02-1.92 (m, 4H), 1.17-1.03 (m, 12H), 0.79-0.71 (m, 10H). ¹³C NMR (CDCl₃, 126 MHz): δ 161.20, 155.55,

154.47, 152.51, 151.76, 149.81, 141.75, 140.39, 140.11, 138.64, 137.09, 130.96, 130.84, 126.60, 124.95, 124.42, 124.03, 121.49, 121.15, 120.49, 120.40, 119.88, 119.15, 117.90, 114.24, 113.45, 111.30, 109.64, 54.30, 39.72, 31.49, 29.68, 24.04, 22.55, 13.98.

Example 31

Preparation of Complex 101

[0144]



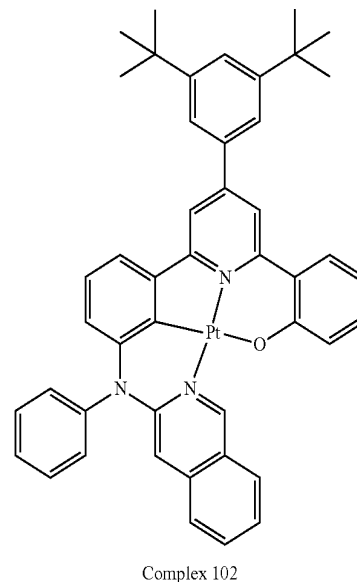
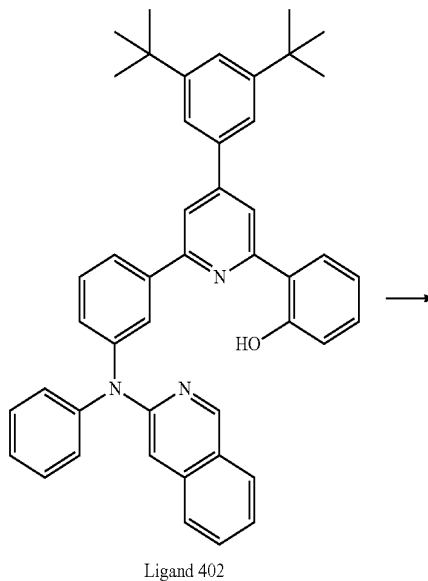
[0145] To a round bottom flask was charged with Ligand 401 (0.42 g, 0.69 mmol), K_2PtCl_4 (0.35 g, 0.83 mmol), and mixture of glacial acetic acid (140 mL) and chloroform (5 mL). The mixture was refluxed under argon for 24 h. After cooling to room temperature, the crude mixture was extracted with dichloromethane and purified by chromatography on alumina with mixture of hexane and ethyl acetate (v/v=10:1). 0.5 g of orange solid was obtained. Yield: 90%. 1H NMR (CD_2Cl_2 , 500 MHz): δ 10.18 (d, J=6.3 Hz, 1H), 8.23 (s, 1H), 7.99 (d, J=8.4 Hz, 1H), 7.90 (s, 1H), 7.72-7.69 (m, 2H), 7.64-7.59 (m, 4H), 7.54-7.51 (m, 2H), 7.49-7.34 (m, 3H), 7.25 (d, J=8.4 Hz, 1H), 6.98 (t, J=7.9 Hz, 1H), 6.85 (t, J=6.6

Hz, 1H), 6.72 (t, J=7.5 Hz, 1H), 6.41 (d, J=8.7 Hz, 1H), 6.14 (d, J=8.3 Hz, 1H), 1.43 (s, 18H). MS (FAB): 797.3 (M^+)

Example 32

Preparation of Complex 102

[0146]



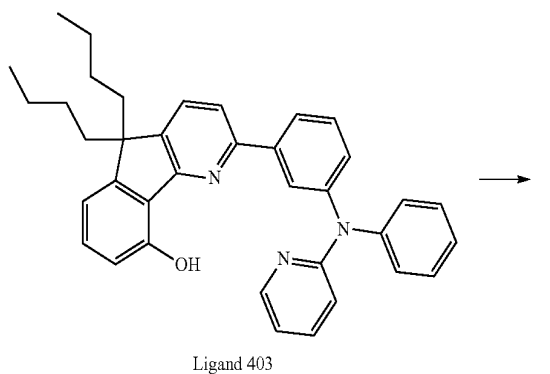
[0147] To a round bottom flask were charged with Ligand 402 (0.09 g, 0.13 mmol), K_2PtCl_4 (0.07 g, 0.16 mmol), and mixture of glacial acetic acid (24 mL) and chloroform (0.9 mL). The mixture was refluxed under nitrogen for 24 h. After cooling to room temperature, the crude mixture was extracted with dichloromethane and purified by chromatography on alumina with mixture of hexane and ethyl acetate (v/v=10:1). 0.10 g of yellow solid was obtained. Yield: 91%. 1H NMR (CD_2Cl_2 , 300 MHz): δ 11.05 (s, 1H), 8.16 (s, 1H), 7.98-7.93 (m, 2H), 7.83 (s, 1H), 7.67 (t, J=7.2 Hz, 2H), 7.56-7.54 (m, 4H), 7.50 (t, J=7.4 Hz, 1H), 7.40-7.32 (m, 3H), 7.30-7.25 (m,

4H), 6.90 (t, J=7.9 Hz, 1H), 6.67 (t, J=7.2 Hz, 1H), 6.55 (s, 1H), 6.06 (d, J=8.3 Hz, 1H), 1.36-1.32 (m, 18H). MS (ESI): 847.6 (M⁺).

Example 33

Preparation of Complex 103

[0148]

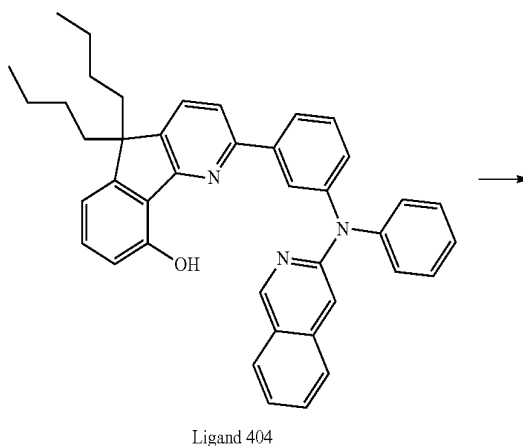


[0149] To a round bottom flask was charged with Ligand 403 (0.34 g, 0.63 mmol), K₂PtCl₄ (0.31 g, 0.76 mmol), and mixture of glacial acetic acid (100 mL) and chloroform (5 mL). The mixture was refluxed under argon for 24 h. After cooling to room temperature, the crude mixture was extracted with dichloromethane and purified by chromatography on alumina with mixture of hexane and ethyl acetate (v/v=10:1). 0.42 g of yellow solid was obtained. Yield: 90%. ¹H NMR (CD₂Cl₂, 500 MHz): δ 10.28 (d, J=6.1 Hz, 1H), 7.86 (d, J=7.6 Hz, 1H), 7.71 (t, J=7.5 Hz, 2H), 7.61 (t, J=8.7 Hz, 2H), 7.52 (t, J=7.0 Hz, 1H), 7.44-7.47 (m, 2H), 7.38 (d, J=7.2 Hz, 2H), 7.05 (d, J=8.3 Hz, 1H), 6.98 (t, J=8.2 Hz, 1H), 6.86 (t, J=6.8 Hz, 1H), 6.68 (d, J=7.1 Hz, 1H), 6.42 (d, J=8.1 Hz, 1H), 6.12 (d, J=8.3 Hz, 1H), 1.92-1.97 (m, 4H), 1.06-1.10 (m, 4H), 0.66-0.71 (m, 10H).

Example 34

Preparation of Complex 104

[0150]

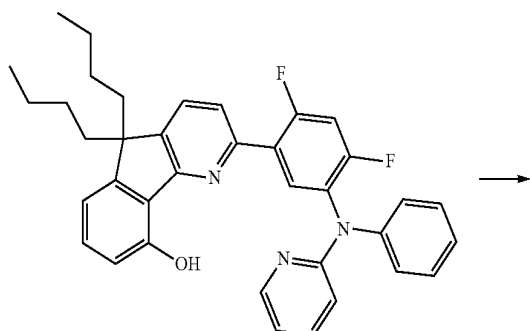


[0151] To a round bottom flask were charged with Ligand 404 (0.04 g, 0.06 mmol), K₂PtCl₄ (0.03 g, 0.08 mmol), and mixture of glacial acetic acid (13 mL) and chloroform (0.5 mL). The mixture was refluxed under nitrogen for 24 h. After cooling to room temperature, the crude mixture was extracted with dichloromethane and purified by chromatography on alumina with mixture of hexane and ethyl acetate (v/v=10:1). 0.05 g of yellow solid was obtained. Yield: 95%. ¹H NMR (CDCl₃, 300 MHz): δ 11.16 (s, 1H), 7.98 (d, J=8.2 Hz, 1H), 7.79 (d, J=7.7 Hz, 1H), 7.66 (t, J=7.2 Hz, 2H), 7.58-7.45 (m, 3H), 7.42 (t, J=7.2 Hz, 1H), 7.35 (t, J=8.4 Hz, 3H), 7.27 (q, J=7.2 Hz, 2H), 7.09 (d, J=8.3 Hz, 1H), 6.89 (t, J=7.9 Hz, 1H), 6.63 (d, J=6.9 Hz, 1H), 6.57 (s, 1H), 6.05 (d, J=8.0 Hz, 1H), 2.01-1.95 (m, 4H), 1.12-1.03 (m, 4H), 0.71-0.61 (m, 10H). MS (ESI): 782.5 (M⁺).

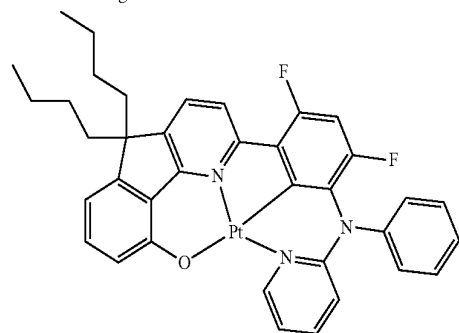
Example 35

Preparation of Complex 105

[0152]



Ligand 405



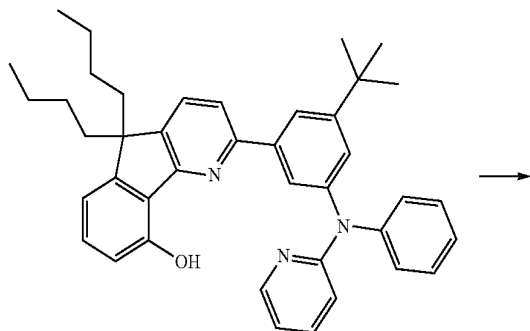
Complex 105

[0153] To a round bottom flask was charged with Ligand 405 (0.09 g, 0.2 mmol), K_2PtCl_4 (0.08 g, 0.2 mmol), and mixture of glacial acetic acid (30 mL) and chloroform (1.2 mL). The mixture was refluxed under nitrogen for 24 h. After cooling to room temperature, the crude mixture was extracted with dichloromethane and purified by chromatography on alumina with mixture of hexane and ethyl acetate (v/v=10:1). 0.1 g of yellow solid was obtained. Yield: 90%. 1H NMR (CD_2Cl_2 , 400 MHz): δ 9.92 (d, $J=6.2$ Hz, 1H), 7.87-7.87 (m, 2H), 7.57 (t, $J=7.9$ Hz, 1H), 7.46-7.25 (m, 7H), 7.03 (d, $J=8.2$ Hz, 1H), 6.99 (t, $J=7.9$ Hz, 1H), 6.67 (d, $J=7.0$ Hz, 1H), 6.55 (t, $J=8.5$ Hz, 1H), 2.06-1.98 (m, 4H), 1.11-1.04 (m, 4H), 0.71-0.63 (m, 10H). MS (ESI): 769.3 (M^+).

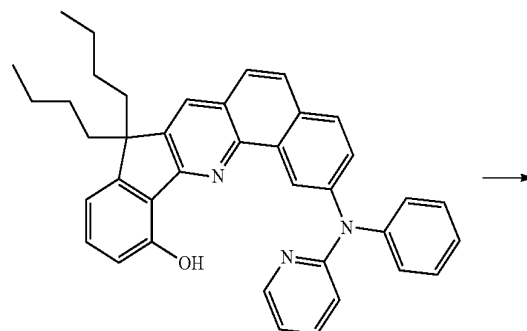
Example 36

Preparation of Complex 106

[0154]

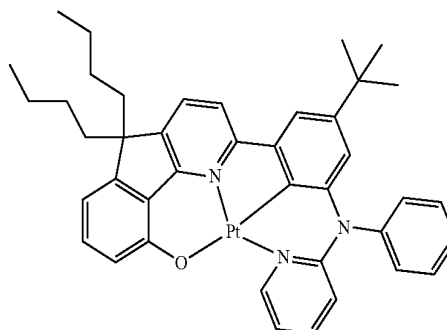


Ligand 406



Ligand 407

-continued



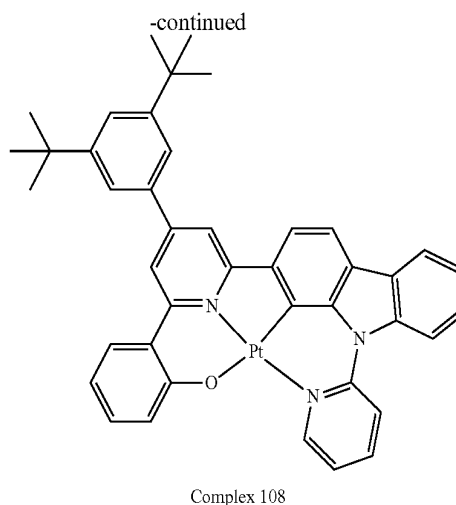
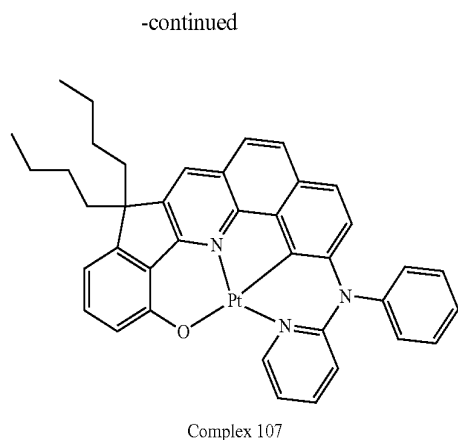
Complex 106

[0155] To a round bottom flask were charged with Ligand 406 (0.59 g, 1.0 mmol), K_2PtCl_4 (0.50 g, 1.2 mmol), and mixture of glacial acetic acid (180 mL) and chloroform (6.5 mL). The mixture was refluxed under nitrogen for 24 h. After cooling to room temperature, the crude mixture was extracted with dichloromethane and purified by chromatography on alumina with mixture of hexane and ethyl acetate (v/v=10:1). 0.75 g of yellow solid was obtained. Yield: 95%. 1H NMR (CD_2Cl_2 , 500 MHz): δ 10.25 (d, $J=5.8$ Hz, 1H), 7.85 (d, $J=7.7$ Hz, 1H), 7.72 (t, $J=6.9$ Hz, 2H), 7.63-7.60 (m, 2H), 7.52 (t, $J=7.9$ Hz, 1H), 7.49 (s, 1H), 7.45 (t, $J=7.7$ Hz, 1H), 7.39 (d, $J=7.2$ Hz, 1H), 7.04 (d, $J=8.1$ Hz, 1H), 6.84 (t, $J=6.5$ Hz, 1H), 6.67 (d, $J=6.9$ Hz, 1H), 6.46 (d, $J=8.9$ Hz, 1H), 6.17 (s, 1H), 2.10-1.98 (m, 4H), 1.14-1.09 (m, 13H), 0.80-0.68 (m, 10H). MS (ESI): 788.9 (M^+).

Example 37

Preparation of Complex 107

[0156]

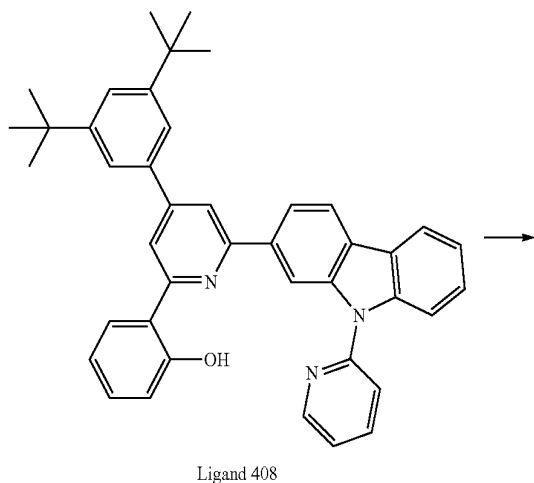


[0157] To a round bottom flask were charged with Ligand 407 (0.25 g, 0.4 mmol), K_2PtCl_4 (0.22 g, 0.5 mmol), and mixture of glacial acetic acid (80 mL) and chloroform (3 mL). The mixture was refluxed under nitrogen for 24 h. After cooling to room temperature, the crude mixture was extracted with dichloromethane and purified by chromatography on alumina with mixture of hexane and ethyl acetate (v/v=10:1). 0.32 g of yellow solid was obtained. Yield: 96%. 1H NMR (CD_2Cl_2 , 500 MHz): δ 10.32 (d, $J=6.0$ Hz, 1H), 8.26 (s, 1H), 7.77-7.72 (m, 4H), 7.66 (t, $J=7.6$ Hz, 1H), 7.64-7.51 (m, 3H), 7.45 (d, $J=8.1$ Hz, 2H), 7.16 (d, $J=8.4$ Hz, 1H), 6.88 (t, $J=6.9$ Hz, 1H), 6.76 (d, $J=7.1$ Hz, 1H), 6.56-6.51 (m, 2H), 2.23-2.09 (m, 4H), 1.18-1.11 (m, 4H), 0.89-0.66 (m, 10H). MS (ESI): 756.8 (M^+).

Example 38

Preparation of Complex 108

[0158]

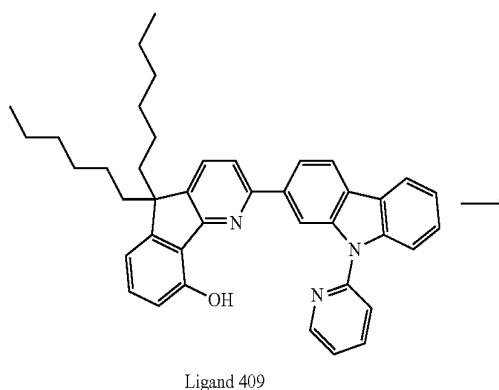


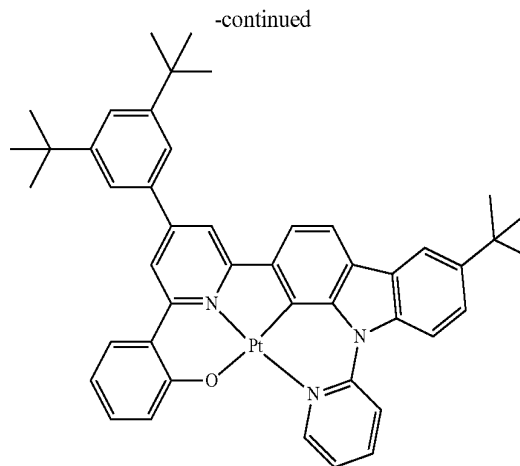
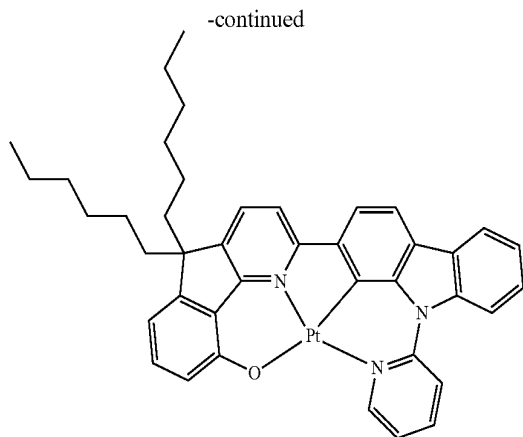
[0159] A mixture of Ligand 408 (0.54 g, 0.90 mmol), potassium tetrachloroplatinate (0.45 g, 1.08 mmol) in 50 mL glacial acetic acid and 10 mL chloroform was refluxed for 2 days. The solution was cooled down to room temperature and was partitioned between dichloromethane and water. The organic layer was dried with magnesium sulfate and the volatiles were removed under vacuum. The crude product was purified by column chromatography using dichloromethane as eluent. The product was obtained as an orange solid. Yield: 0.44 g (62%). 1H NMR ($CDCl_3$, 500 MHz): δ 9.97 (dd, $J=6.0$ Hz, 1.3 Hz, 1H), 8.07 (s, 1H), 7.97-7.94 (m, 2H), 7.90 (d, $J=8.4$ Hz, 1H), 7.87 (d, $J=7.4$ Hz, 1H), 7.76 (t, $J=7.8$ Hz, 1H), 7.64 (s, 1H), 7.59 (s, 2H), 7.51 (s, 1H), 7.45 (d, $J=8.0$ Hz, 1H), 7.39 (t, $J=7.4$ Hz, 1H), 7.36-7.31 (m, 2H), 7.26 (t, $J=7.4$ Hz, 1H), 7.20 (dd, $J=8.3$ Hz, 1.1 Hz, 1H), 6.83 (t, $J=6.2$ Hz, 1H), 6.74 (t, $J=7.4$ Hz, 1H), 1.49 (s, 18H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 164.76, 164.27, 153.13, 151.87, 150.21, 149.45, 149.39, 147.04, 142.74, 139.64, 138.29, 137.41, 136.85, 131.07, 130.09, 128.50, 126.17, 124.64, 124.23, 123.56, 122.78, 122.09, 121.47, 121.45, 118.75, 118.24, 117.58, 115.14, 114.55, 114.15, 113.62, 113.47, 35.18, 31.63

Example 39

Preparation of Complex 109

[0160]



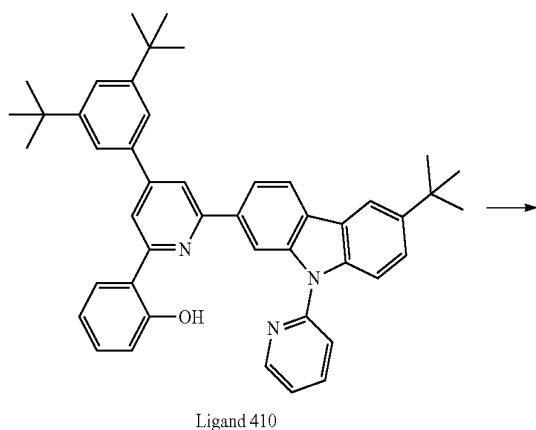


[0161] A mixture of Ligand 409 (0.47 g, 0.79 mmol), potassium tetrachloroplatinate (0.39 g, 0.95 mmol) in 50 mL glacial acetic acid and 10 mL chloroform was refluxed for 2 days. The solution was cooled down to room temperature and was partitioned between dichloromethane and water. The organic layer was dried with magnesium sulfate and the volatiles were removed under vacuum. The crude product was purified by column chromatography using dichloromethane as eluent. The product was obtained as an orange solid. Yield: 0.32 g (51%). ¹H NMR (CD₂Cl₂, 500 MHz): δ 10.31 (d, J=6.0 Hz, 1H), 8.18 (d, J=8.6 Hz, 1H), 8.08 (d, J=7.5 Hz, 1H), 8.03 (d, J=8.3 Hz, 1H), 8.01-8.97 (m, 1H), 7.84 (d, J=7.6 Hz, 1H), 7.70 (d, J=7.9 Hz, 1H), 7.61 (d, J=8.0 Hz, 1H), 7.53 (d, J=7.6 Hz, 1H), 7.50-7.46 (m, 2H), 7.39 (t, J=7.4 Hz, 1H), 7.18-7.15 (m, 1H), 7.08 (d, J=8.3 Hz, 1H), 6.71 (d, J=6.7 Hz, 1H), 2.11-1.99 (m, 4H), 1.16-1.05 (m, 12H), 0.83-0.75 (m, 10H). ¹³C NMR (CD₂Cl₂, 126 MHz): δ 161.73, 160.24, 154.76, 153.50, 150.23, 147.53, 142.79, 142.19, 139.79, 138.15, 137.63, 132.43, 129.54, 128.37, 126.47, 126.04, 123.09, 122.79, 121.53, 121.10, 118.78, 118.36, 118.13, 115.80, 114.18, 114.12, 113.11, 108.18, 55.38, 39.91, 31.50, 29.68, 24.03, 22.53, 13.71.

Example 40

Preparation of Complex 110

[0162]

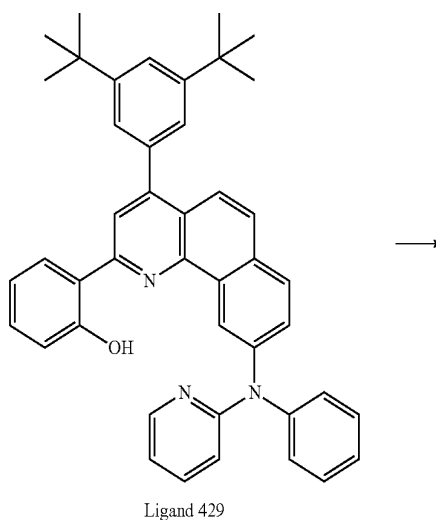


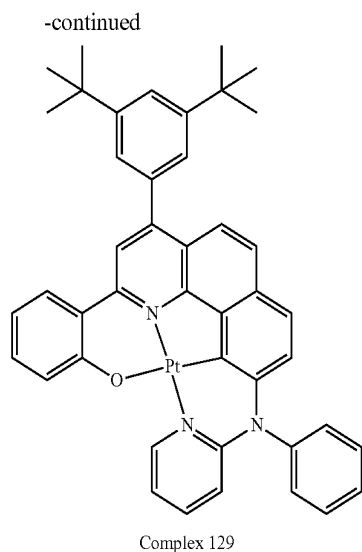
[0163] A mixture of Ligand 410 (0.12 g, 0.18 mmol), potassium tetrachloroplatinate (0.08 g, 0.20 mmol) in 50 mL glacial acetic acid and 10 mL chloroform was refluxed for 2 days. The solution was cooled down to room temperature and was partitioned between dichloromethane and water. The organic layer was dried with magnesium sulfate and the volatiles were removed under vacuum. The crude product was purified by column chromatography using dichloromethane as eluent. The product was obtained as an orange-red solid. Yield: 0.11 g (72%). ¹H NMR (CD₂Cl₂, 500 MHz): δ 10.06 (dd, J=6.1 Hz, 1.5 Hz, 1H), 8.11 (s, 1H), 8.05 (d, J=8.7 Hz, 1H), 8.00-7.97 (m, 2H), 7.91-7.88 (m, 2H), 7.67 (s, 1H), 7.65 (s, 3H), 7.61 (d, J=8.0 Hz, 1H), 7.53-7.50 (m, 2H), 7.33 (t, J=7.5 Hz, 1H), 7.19 (d, J=8.4 Hz, 1H), 6.97 (t, J=6.6 Hz, 1H), 6.72 (t, J=7.5 Hz, 1H), 1.47 (s, 18H), 1.43 (s, 9H). ¹³C NMR (CD₂Cl₂, 126 MHz): δ 165.49, 164.82, 153.62, 152.55, 150.96, 149.74, 147.84, 146.84, 143.06, 138.76, 138.41, 138.29, 137.62, * 131.68, 130.70, 128.69, 125.04, 124.92, 124.84, 124.31, 123.77, 122.42, 122.05, 119.42, 118.76, 118.47, 118.14, 115.81, 115.07, 114.38, 114.14, 114.09, 35.63, 35.19, 31.99, 31.89.

Example 41

Preparation of Complex 129

[0164]

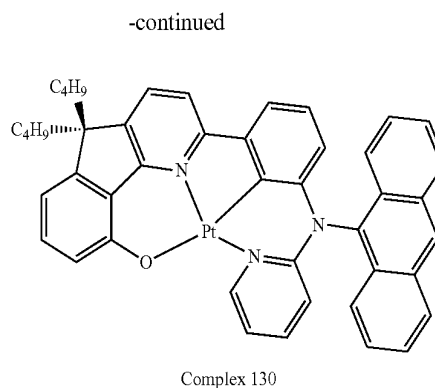
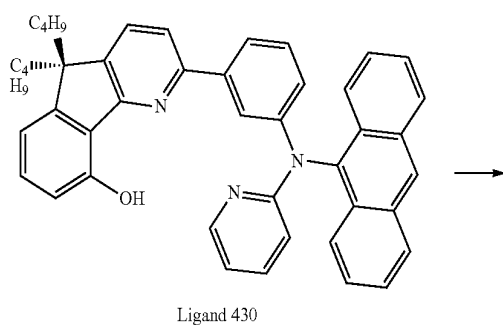




[0165] A mixture of Ligand ONCN09 (0.038 g, 0.06 mmol), potassium tetrachloroplatinate (0.03 g, 0.07 mmol) in 10.4 mL glacial acetic acid and 0.4 mL chloroform was refluxed for 12 hours. The solution was cooled down to room temperature and was partitioned between dichloromethane and water. The organic layer was dried with magnesium sulfate and the volatiles were removed under vacuum. The crude product was purified by column chromatography using hexane and ethyl acetate (v/v=10:1) as eluent. The product was obtained as an orange solid. Yield: 0.046 g (94%). ¹H NMR (600 MHz, CD₂Cl₂) δ 10.36 (d, J=6.2 Hz, 1H), 8.47 (s, 1H), 8.30 (d, J=8.4 Hz, 1H), 7.77 (d, J=7.9 Hz, 2H), 7.73 (d, J=11.9 Hz, 1H), 7.66 (s, 2H), 7.59 (d, J=8.8 Hz, 1H), 7.54 (t, J=5.3 Hz, 3H), 7.47 (d, J=7.3 Hz, 2H), 7.42 (s, 2H), 6.92 (t, J=6.5 Hz, 1H), 6.79 (d, J=8.2 Hz, 1H), 6.59 (d, J=8.8 Hz, 1H), 6.56 (d, J=8.9 Hz, 1H), 1.44 (s, 18H).

Example 42

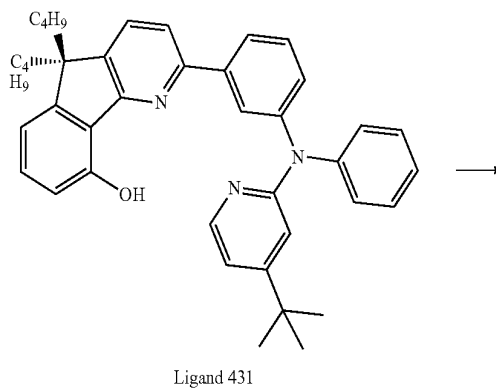
Preparation of Complex 130

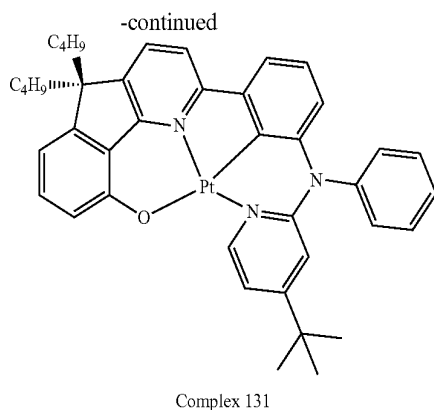
[0166]

[0167] A mixture of Ligand ONCN12 (0.044 g, 0.07 mmol), potassium tetrachloroplatinate (0.03 g, 0.08 mmol) in 12.5 mL glacial acetic acid and 0.4 mL chloroform was refluxed for 12 hours. The solution was cooled down to room temperature and was partitioned between dichloromethane and water. The organic layer was dried with magnesium sulfate and the volatiles were removed under vacuum. The crude product was purified by column chromatography using hexane and ethyl acetate (v/v=10:1) as eluent. The product was obtained as an orange solid. Yield: 0.054 g (95%). ¹H NMR (600 MHz, CD₂Cl₂) δ 10.40 (d, J=4.9 Hz, 1H), 8.76 (s, 1H), 8.21 (d, J=8.6 Hz, 2H), 7.88 (d, J=7.6 Hz, 1H), 7.84 (d, J=8.6 Hz, 2H), 7.62 (d, J=7.6 Hz, 1H), 7.54 (d, J=7.8 Hz, 2H), 7.49 (s, 1H), 7.47-7.39 (m, 3H), 7.35-7.27 (m, 1H), 7.10 (d, J=8.2 Hz, 1H), 6.87 (t, J=6.6 Hz, 1H), 6.72 (d, J=7.1 Hz, 2H), 6.02 (d, J=8.9 Hz, 1H), 5.71 (d, J=8.2 Hz, 1H), 2.07 (m, 4H), 1.15 (m, 5H), 0.72 (m, 10H).

Example 43

Preparation of Complex 13

[0168]



[0169] A mixture of Ligand ONCN14 (0.086 g, 0.14 mmol), potassium tetrachloroplatinate (0.03 g, 0.16 mmol) in 25.5 mL glacial acetic acid and 1 mL chloroform was refluxed for 12 hours. The solution was cooled down to room temperature and was partitioned between dichloromethane and water. The organic layer was dried with magnesium sulfate and the volatiles were removed under vacuum. The crude product was purified by column chromatography using hexane and ethyl acetate (v/v=10:1) as eluent. The product was obtained as an orange solid. Yield: 0.107 g (93%). ¹H NMR (600 MHz, CD₂Cl₂) δ 10.10 (d, J=6.6 Hz, 1H), 7.86 (d, J=7.6 Hz, 1H), 7.72 (t, J=7.8 Hz, 2H), 7.65-7.54 (m, 2H), 7.46 (t, J=7.6 Hz, 2H), 7.41-7.35 (m, 2H), 7.04 (d, J=8.2 Hz, 1H), 7.01-6.95 (m, 1H), 6.90 (d, J=6.7 Hz, 1H), 6.68 (d, J=7.1 Hz, 1H), 6.35 (s, 1H), 6.15 (d, J=8.2 Hz, 1H), 2.04 (m, 4H), 1.27 (m, 3H), 1.19-1.04 (m, 10H), 0.82-0.63 (m, 9H).

Example 44

Photophysical Properties for Complexes 101, 102, 103, 105, 106, 107, 108, 109 and 129

[0170]

| | Absorption | | Emission (dichloromethane solution) | | | |
|-------------|--|---|-------------------------------------|--------|--------------|---------------------------|
| | λ_{max}/nm | molar extinction coefficient/ $10^4 mol^{-1}dm^3 cm^{-1}$ | λ_{max}/nm | ϕ | $\tau/\mu s$ | $K_d/mol^{-1}dm^3 s^{-1}$ |
| Complex 101 | 330 (2.16), 370 (1.13), 450 (0.27), 481 (0.21) | | 551 | 0.91 | 4.31 | 2×10^7 |
| Complex 102 | 342 (1.96), 370 (0.99), 432 (0.21), 492 (0.14) | | 540, 605, 659 | 0.092 | 12.5 | 2×10^7 |
| Complex 103 | 321 (1.87), 337 (1.31), 365 (1.17), 393 (0.79), 434 (0.44), 458 (0.38) | | 511, 540 | 0.92 | 13.0 | 2×10^8 |
| Complex 105 | 336 (0.85), 355 (0.97), 386 (0.56), 416 (0.42), 438 (0.34), 469 (0.04) | | 505, 530, 574 | 0.54 | 31.6 | 2×10^6 |
| Complex 106 | 325 (2.30), 368 (1.44), 396 (1.03), 438 (0.54), 464 (0.46) | | 515, 552, 596 | 0.97 | 10.9 | 4×10^7 |
| Complex 107 | 334 (1.99), 355 (1.40), 375 (1.02), 433 (0.98), 474 (0.36) | | 531, 573 | 0.44 | 26.5 | 7×10^6 |
| Complex 108 | 264 (43213); 274 (45223); 324 (26577); 353 (18914); 369 (16897); 414 (13880); 442 (5902); 471 (4463) | | 540, 583, 625 | 0.41 | | |
| Complex 109 | 278 (5218); 298 (47859); 334 (40668); 355 (23675); 385 (15888); 413 (9370); 461 (4078); 488 (3516); | | 553, 587 | 0.86 | | |
| Complex 129 | 343 (2.09), 364 (1.51), 439 (0.66), 472 (0.37), 501 (0.31) | | 573 | 0.21 | 12.6 | 5×10^7 |

Example 45

General Procedures for Vacuum Deposition

[0171] In one embodiment, OLEDs were fabricated on glass substrates with pre-patterned ITO electrodes. The substrates were cleaned in an ultrasonic bath of detergent and deionized water, rinsed with deionized water, and then cleaned in sequential ultrasonic baths of deionized water, acetone, and isopropanol, and subsequently dried in an oven for 1 h. The substrates were then transferred into a vacuum chamber, in which functional layers were in sequence deposited by thermal evaporation at a pressure of 10^{-6} - 10^{-7} torr. The thickness of the deposited material was monitored in situ using an oscillating quartz thickness monitor. Finally a LiF buffer layer and Al cathode were vapor deposited onto the organic films. EL spectra, luminance, and CIE coordination were measured by a Photo Research Inc PR-655. Voltage-current characteristics were measured by using a Keithley 2400 source measurement unit. All devices were characterized at room temperature in the atmosphere without encapsulation.

Example 46

OLED 1

[0172] A device was fabricated according to Example 45 wherein four functional layers including MoO₃ (5 nm), CzSiCz (40 nm), CsPO₃: Complex 101 (4%, 30 nm) and DP0Si (30 nm), which were used as hole-injection layer, hole-transporting layer, emissive layer and electron-transporting layer respectively, were deposited in sequence. This device showed yellow emission with CIE coordinate of (0.42, 0.56), maximum current efficiency of 62.4 cd/A and efficiency roll-off of 11.9% at 1000 cd/m⁻².

Example 47

OLED 2

[0173] A device was fabricated according to Example 45 wherein four functional layers including MoO₃ (2 nm), DczSi (40 nm), CsPO1: Complex 101 (2%, 30 nm) and DPOSi (30 nm), which were used as hole-injection layer, hole-transporting layer, emissive layer and electron-transporting layer respectively, were deposited in sequence. This device showed yellow emission with CIE coordinate of (0.39, 0.59), maximum current efficiency of 77.0 cd/A and efficiency roll-off of 5.2% at 1000 cd/m⁻².

Example 48

OLED 3

[0174] A device was fabricated with according to 45 wherein four functional layers including MoO₃ (5 nm), CzSiCz (40 nm), CsPO3: Complex 103 (2%, 30 nm) and DPOSi (30 nm), which were used as hole-injection layer, hole-transporting layer, emissive layer and electron-transporting layer respectively, were deposited in sequence. This device showed green emission with CIE coordinate of (0.28, 0.61), maximum current efficiency of 43.6 cd/A and efficiency roll-off of 12.8% at 1000 cd/m⁻².

Example 49

OLED 4

[0175] A device was fabricated according to Example 45 wherein six functional layers including MoO₃ (5 nm), NPB (30 nm), TCTA (10 nm), TCTA: Complex 103 (10%, 15 nm), 1,3,5-tri(phenyl-2-benzimidazolyl)-benzene (TPBi): Complex 103 (10%, 15 nm) and TPBi (30 nm) which were used as hole-injection layer, hole-transporting layer, electron-blocking layer, emissive layer 1, emissive layer 2 and electron-transporting layer respectively, were deposited in sequence. This device showed green emission with CIE coordinate of (0.27, 0.60), maximum current efficiency of 60.0 cd/A and efficiency roll-off of 33.3% at 1000 cd/m⁻².

Example 50

OLED 5

[0176] A device was fabricated according to Example 45 wherein six functional layers including MoO₃ (5 nm), NPB (30 nm), TCTA (10 nm), CBP: Complex 103 (7%, 15 nm), TAZ: Complex 103 (7%, 15 nm) and TAZ (30 nm) which were used as hole-injection layer, hole-transporting layer, electron-blocking layer, emissive layer 1, emissive layer 2 and electron-transporting layer respectively, were deposited in sequence. This device showed green emission with CIE coordinate of (0.27, 0.60), maximum current efficiency of 78.0 cd/A and efficiency roll-off of 38.5% at 1000 cd/m⁻².

Example 51

General Procedures for Solution Process Fabrication

[0177] In one embodiment, OLEDs were fabricated on glass substrates with pre-patterned indium tin oxide (ITO) electrodes. The substrates were cleaned in an ultrasonic bath of detergent and deionized water, rinsed with deionized water, and then cleaned in sequential ultrasonic baths of dion-

ized water, acetone, and isopropanol, and subsequently dried in an oven for 1 h. The solution processable functional layers were deposition in sequence by spin coating. The samples were then then transferred into a vacuum chamber, in which the rest functional layers were in sequence deposited by thermal evaporation at a pressure of 10⁻⁶-10⁻⁷ torr. The thickness of the deposited material was monitored in situ using an oscillating quartz thickness monitor. Finally a LiF buffer layer and Al cathode were vapor deposited onto the organic films. EL spectra, luminance, and CIE coordination were measured by a Photo Research Inc PR-655. Voltage-current characteristics were measured by using a Keithley 2400 source measurement unit. All devices were characterized at room temperature in the atmosphere without encapsulation.

Example 52

OLED 6

[0178] A device was fabricated according to Example 51 wherein two solution processable functional layers including PEDOT: PPS and POSC1: Complex 101 (10%), which were used as hole-injection and hole-transporting layer and emissive layer respectively, were deposited by spin coated in sequenced. Afterward, a layer of TPBi (30 nm) was deposition by vacuum deposition as electron-transporting layer. This device showed yellow emission with CIE coordinate of (0.46, 0.54), maximum current efficiency of 35.0 cd/A and efficiency roll-off of 5.7% at 1000 cd/m⁻².

[0179] All references, including publications, patent applications and patents, cited herein are hereby incorporated by reference to the same extent as if each reference was individually and specifically indicated to be incorporated by reference and was set forth in its entirety herein.

[0180] The terms “a” and “an” and “the” and similar referents as used in the context of describing the invention are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context.

[0181] Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. Unless otherwise stated, all exact values provided herein are representative of corresponding approximate values (e.g., all exact exemplary values provided with respect to a particular factor or measurement can be considered to also provide a corresponding approximate measurement, modified by “about,” where appropriate).

[0182] The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise indicated. No language in the specification should be construed as indicating any element is essential to the practice of the invention unless as much is explicitly stated.

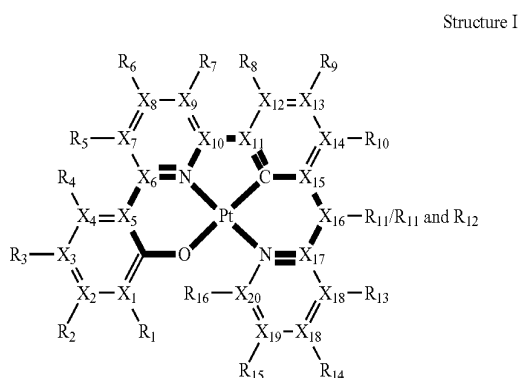
[0183] The description herein of any aspect or embodiment of the invention using terms such as “comprising”, “having”, “including” or “containing” with reference to an element or elements is intended to provide support for a similar aspect or embodiment of the invention that “consists of”, “consists essentially of”, or “substantially comprises” that particular element or elements, unless otherwise stated or clearly contradicted by context (e.g., a composition described herein as comprising a particular element should be understood as also

describing a composition consisting of that element, unless otherwise stated or clearly contradicted by context).

[0184] It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application.

What is claimed is:

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



wherein R_1 - R_{15} 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, aryloxy-carbonyl, phenoxy-carbonyl, or an alkoxy-carbonyl group;

wherein each pair of adjacent R groups of R_1 - R_{15} can be independently two separate groups or one group, and form one or more 5-8 member rings with 2 or 4 X groups; and

wherein X_1 - X_{20} are independently boron, carbon, nitrogen, oxygen, silicon, germanium, phosphorous, sulphur or selenium.

2. The organometallic complex of claim 1, wherein R_{11} is aryl or substituted aryl group, and R_{10} can be one of the carbon atoms on R_{11} thereby forming a 6-5-6 fused ring system with the adjacent aryl ring.

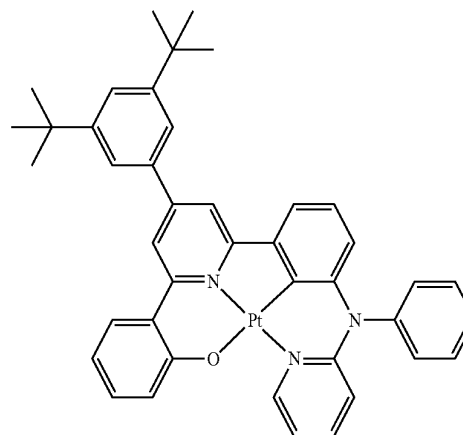
3. The organometallic complex of claim 1, wherein each R_1 - R_{15} is independently hydrogen, halogen, hydroxyl, an unsubstituted alkyl containing from 1 to 10 carbon atoms, a substituted alkyl containing from 1 to 20 carbon atoms, cycloalkyl containing from 4 to 20 carbon atoms, an unsubstituted aryl containing from 6 to 20 carbon atoms, a substituted aryl containing from 6 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, thiol, styryl, aminocarbonyl containing from 1 to 20 carbon atoms, carbamoyl containing from 1 to 20 carbon atoms, aryloxy-carbonyl containing from 1 to 20 carbon atoms, phenoxy-carbonyl containing from 1 to 20 carbon atoms, or an alkoxy-carbonyl group containing from 1 to 20 carbon atoms.

4. The organometallic complex of claim 1, wherein the complex is not in planar geometry.

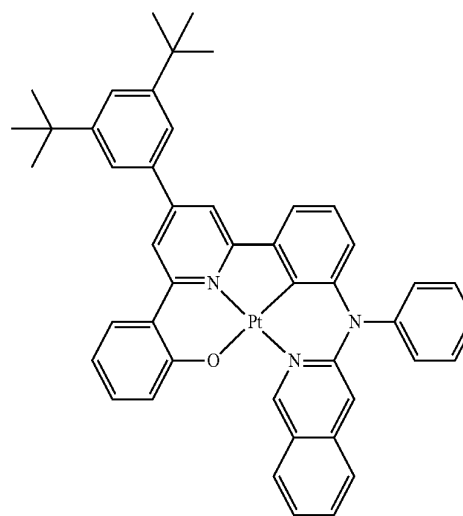
5. The organometallic complex of claim 1, wherein the complex has a self-quenching constant that is no greater than the order of 10^{-8} .

6. The organometallic complex of claim 1, wherein the complex is selected from Complex 101 to Complex 131:

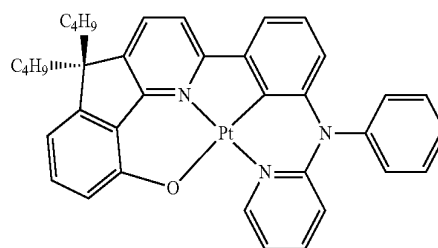
Complex 101



Complex 102

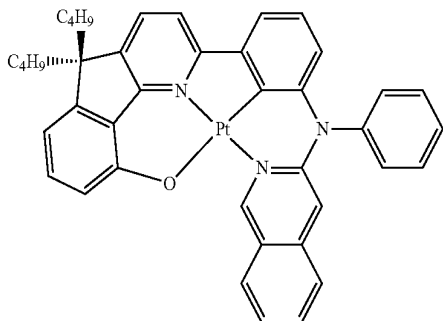


Complex 103



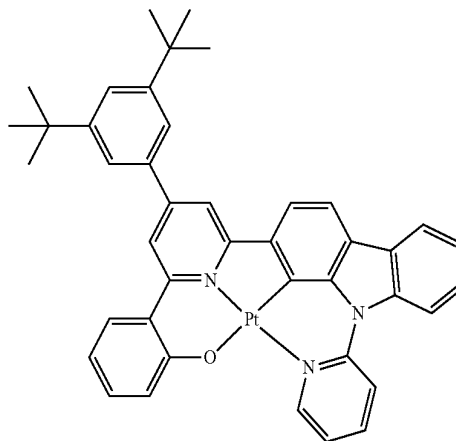
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Complex 104

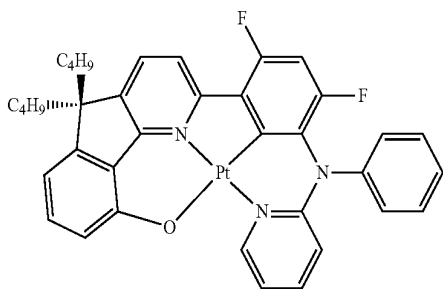


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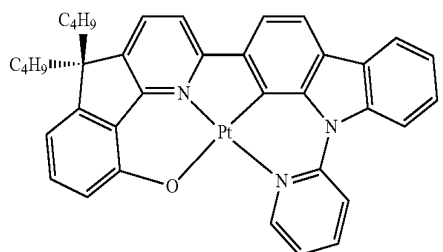
Complex 108



Complex 105

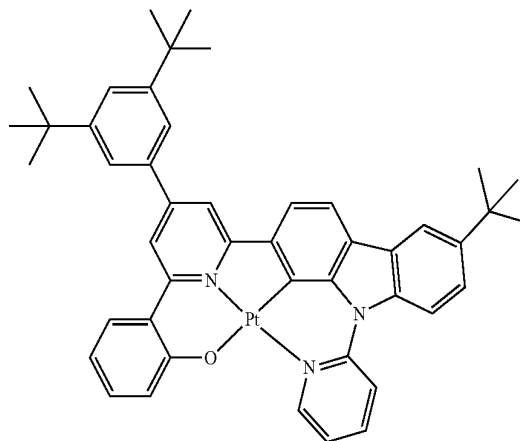
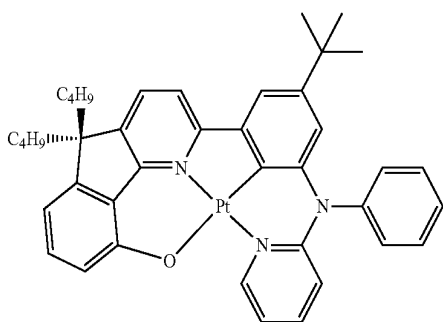


Complex 109



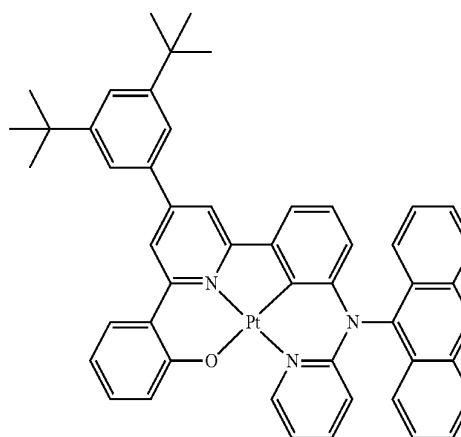
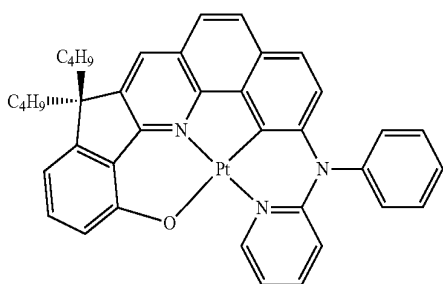
Complex 110

Complex 106



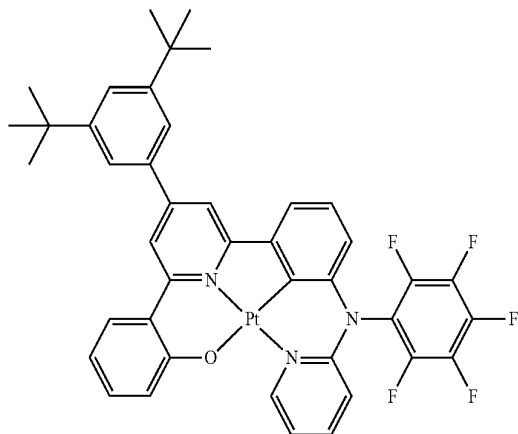
Complex 111

Complex 107



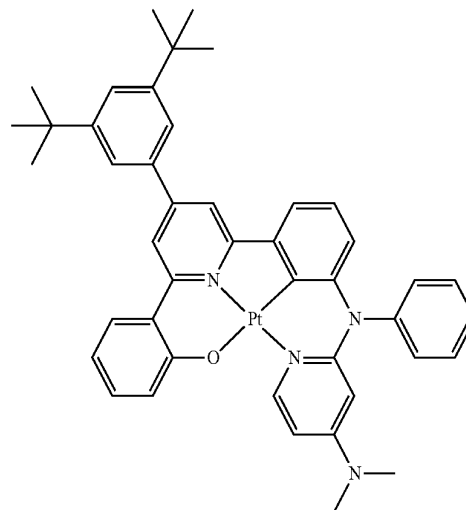
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Complex 112

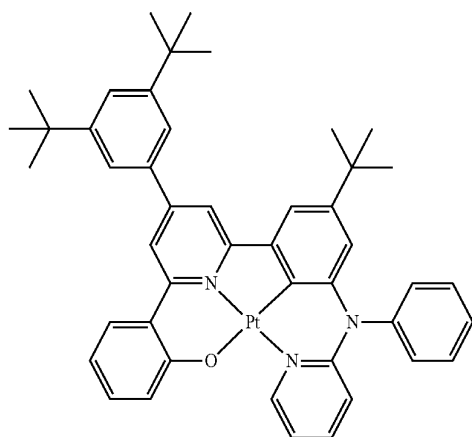


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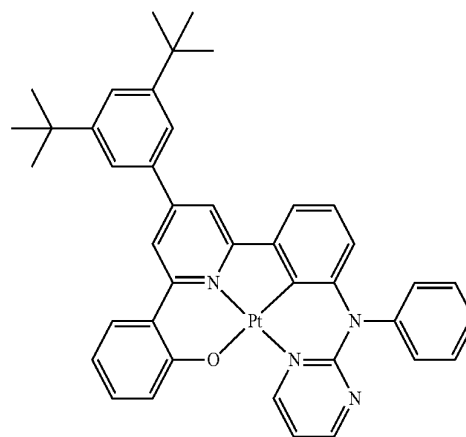
Complex 115



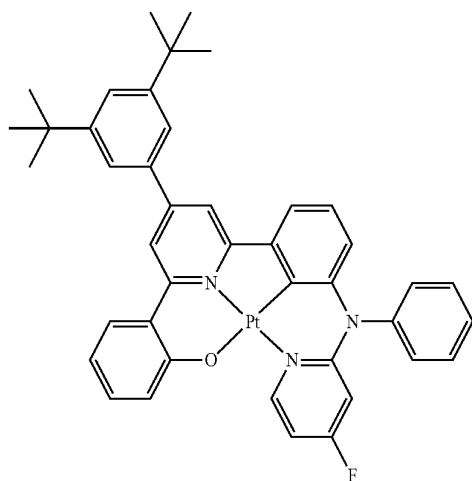
Complex 113



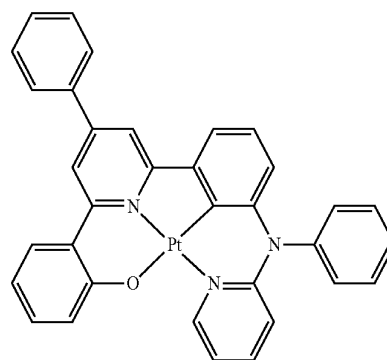
Complex 116



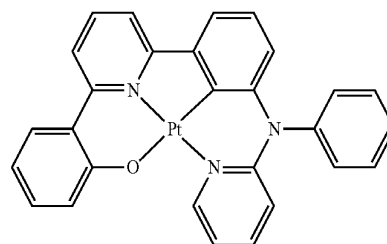
Complex 114



Complex 117

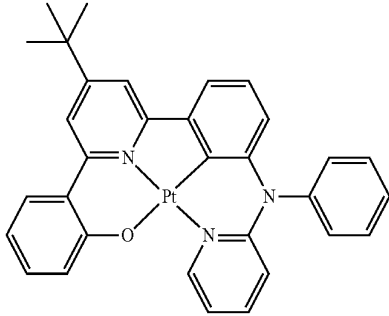


Complex 118

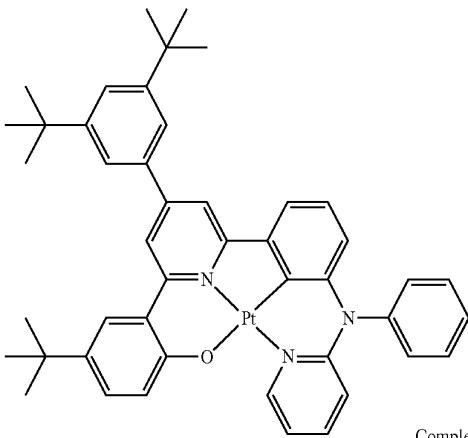


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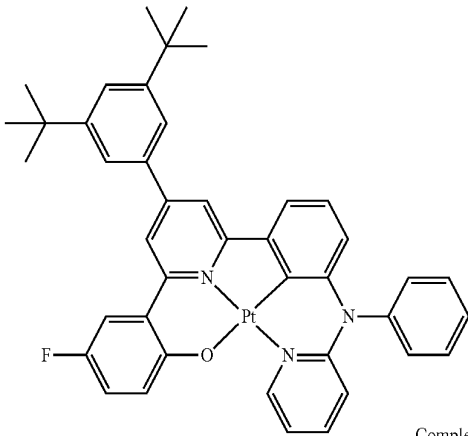
Complex 119



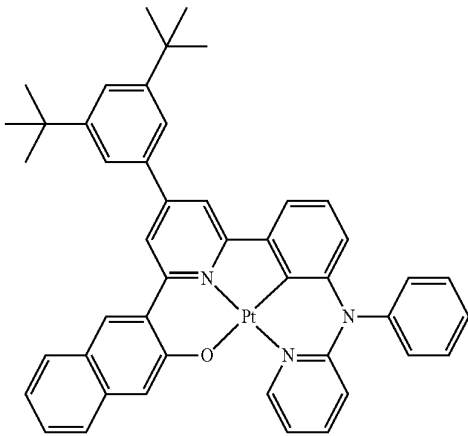
Complex 120



Complex 121

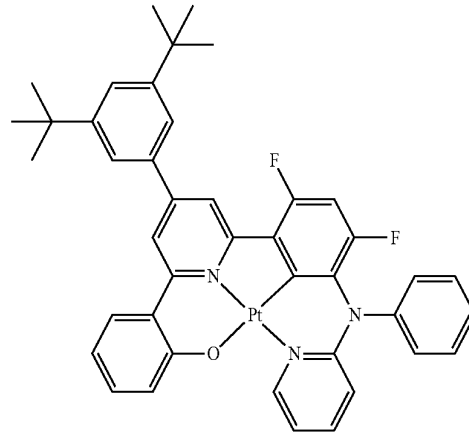


Complex 122

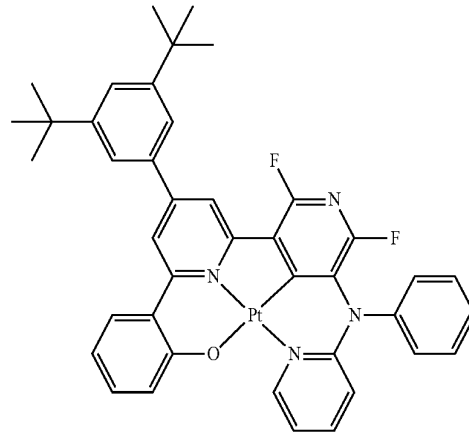


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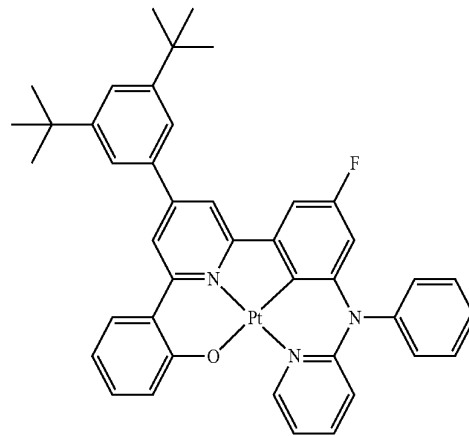
Complex 123



Complex 124

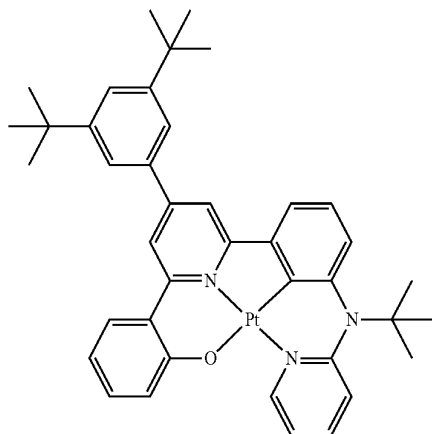


Complex 125



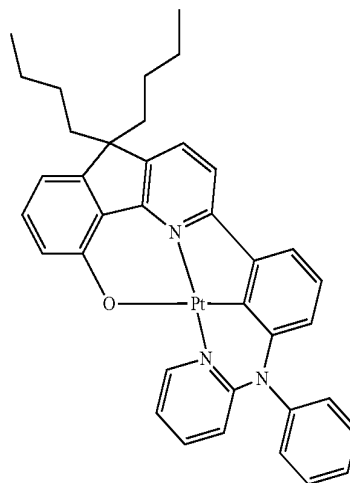
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Complex 126

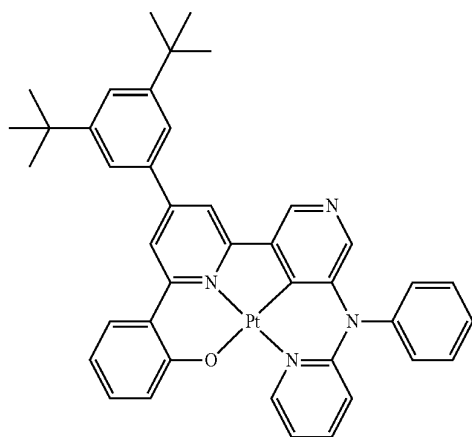


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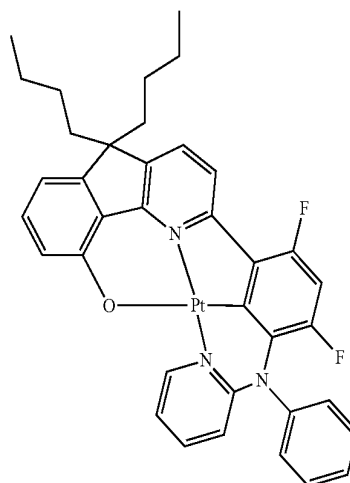
Complex 129



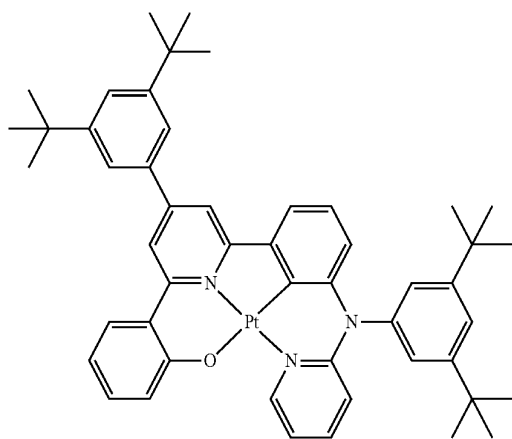
Complex 127



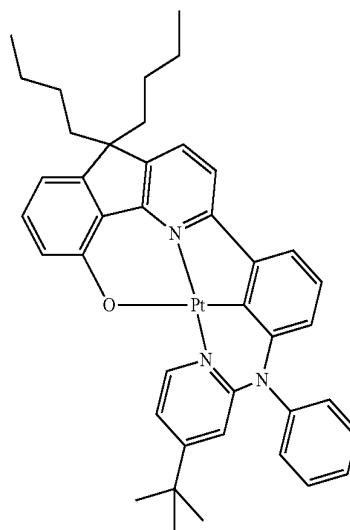
Complex 130



Complex 128

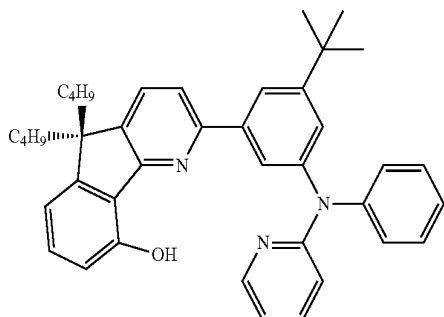


Complex 131

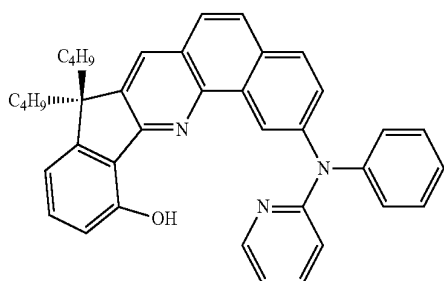


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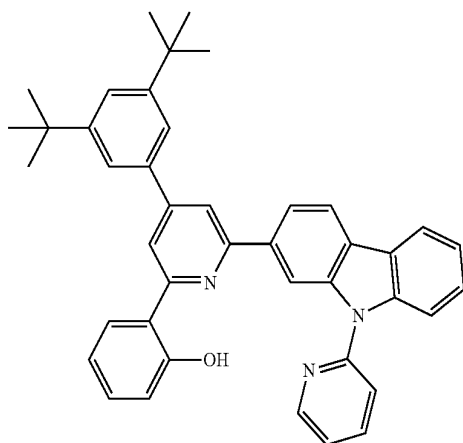
Ligand 406



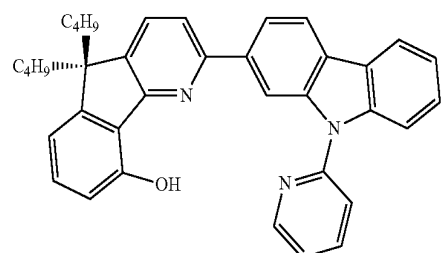
Ligand 407



Ligand 408

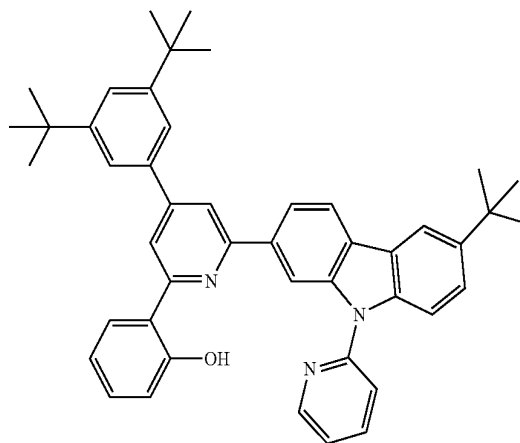


Ligand 409

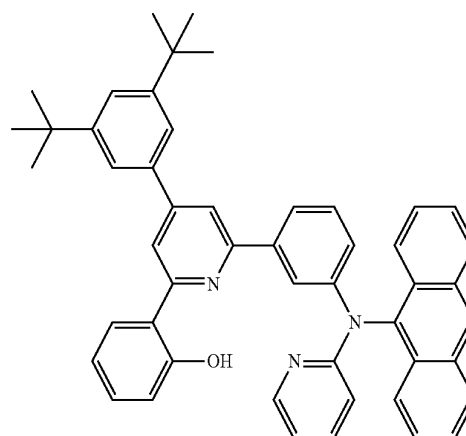


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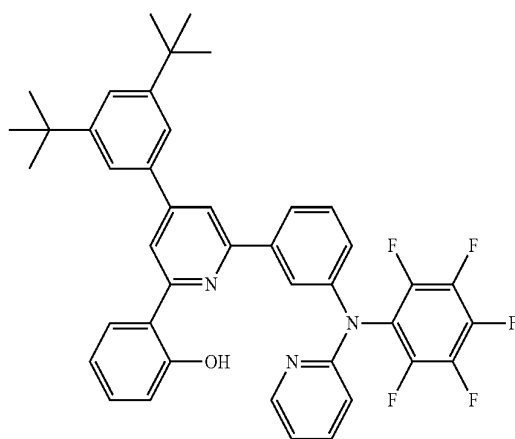
Ligand 410



Ligand 411

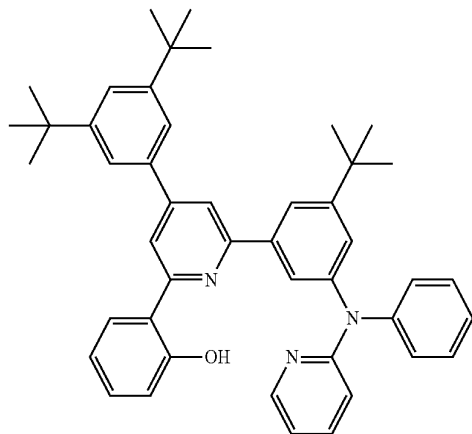


Ligand 412



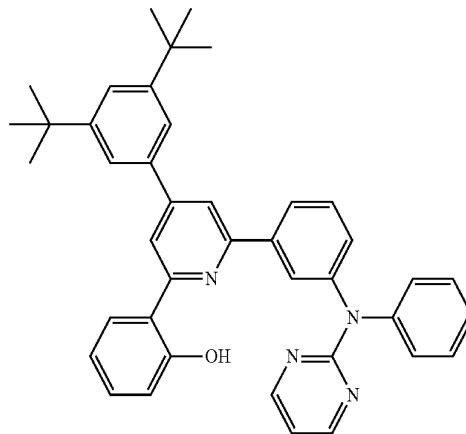
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Ligand 413

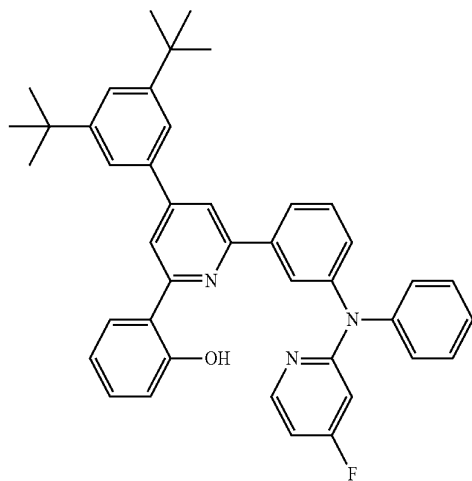


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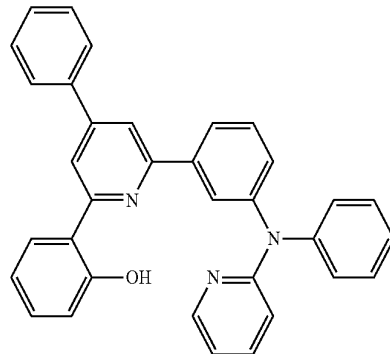
Ligand 416



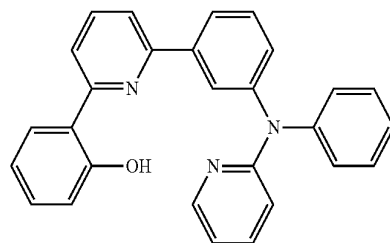
Ligand 414



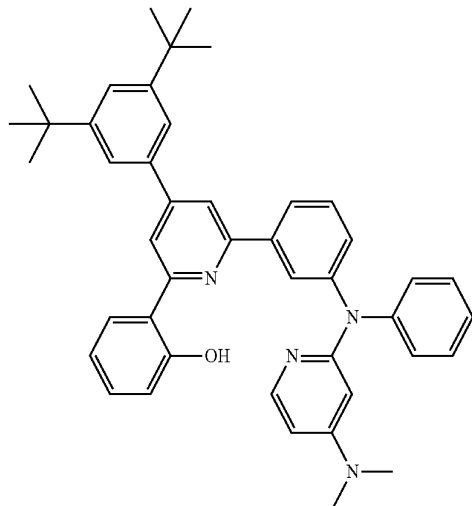
Ligand 417



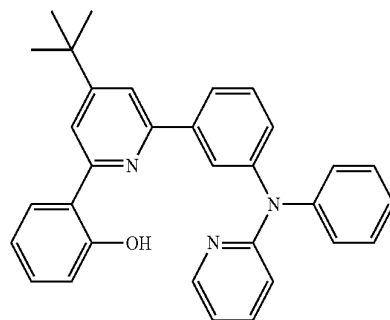
Ligand 418



Ligand 415

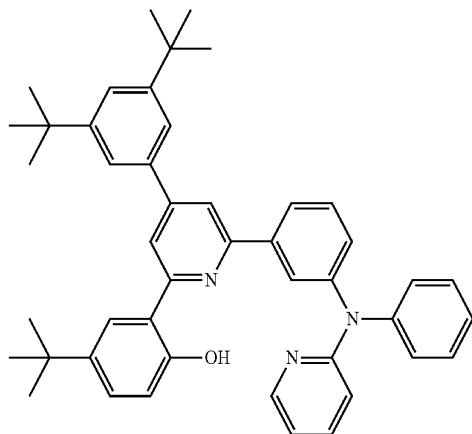


Ligand 419



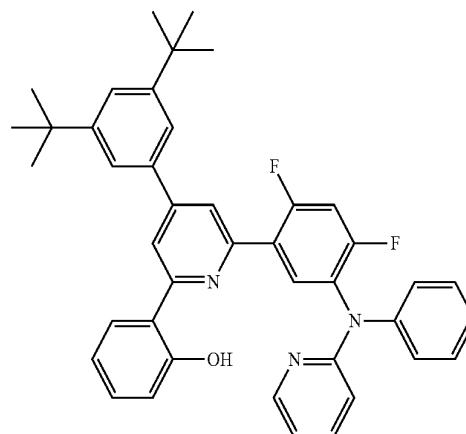
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Ligand 420

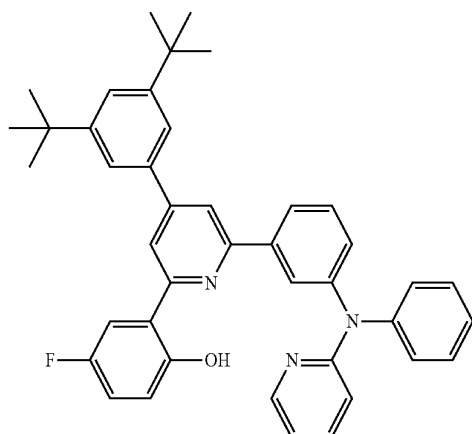


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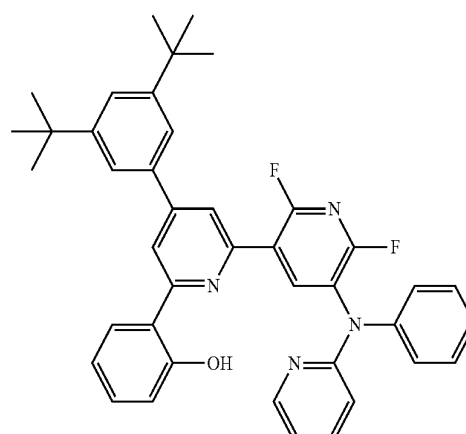
Ligand 423



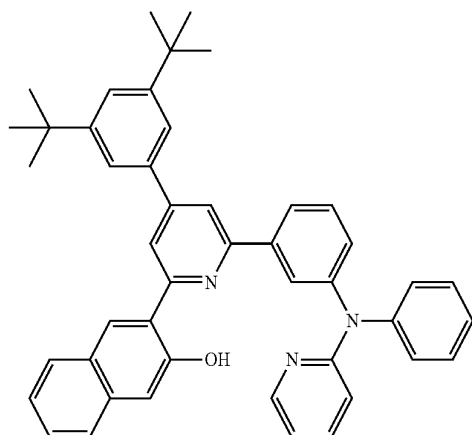
Ligand 421



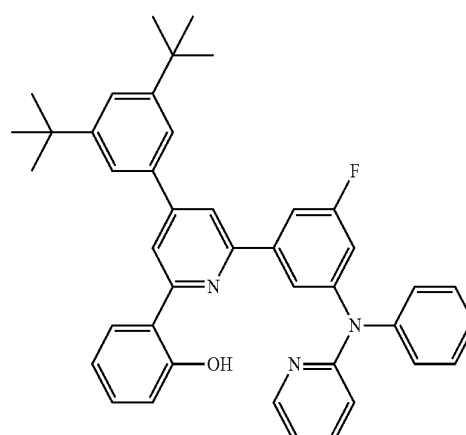
Ligand 424



Ligand 422

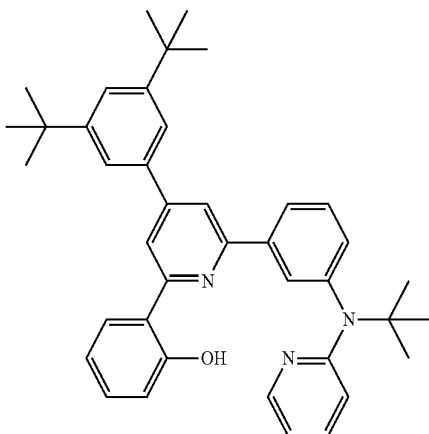


Ligand 425



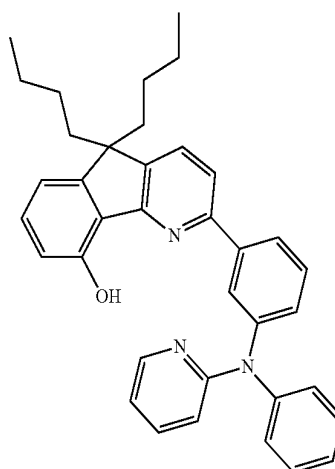
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Ligand 426

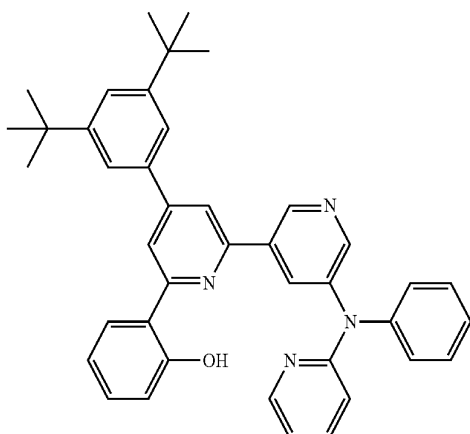


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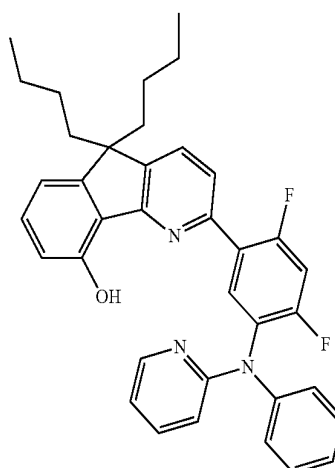
Ligand 429



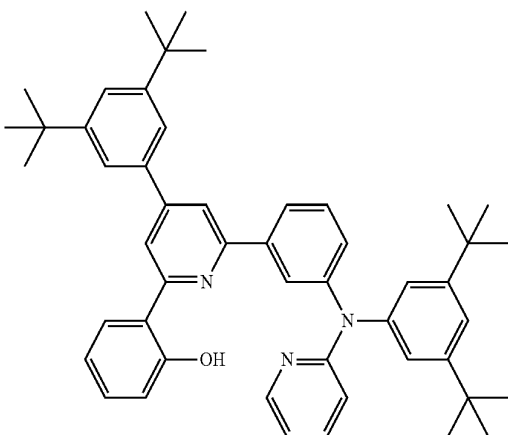
Ligand 427



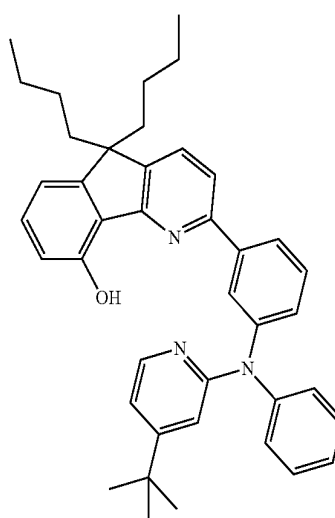
Ligand 430



Ligand 428

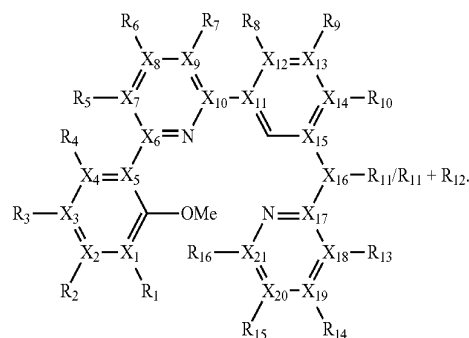
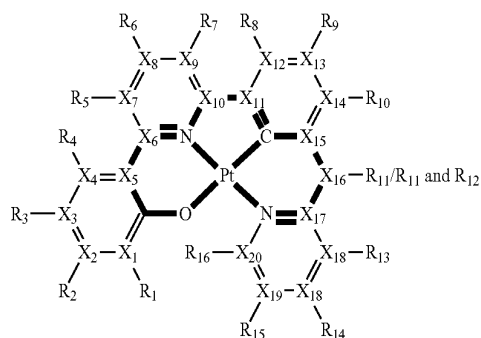


Ligand 431



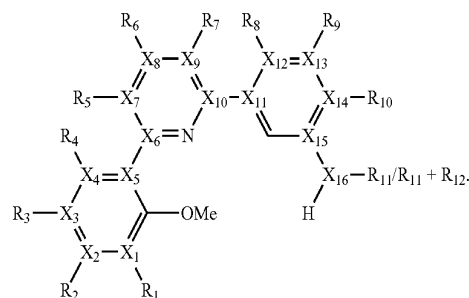
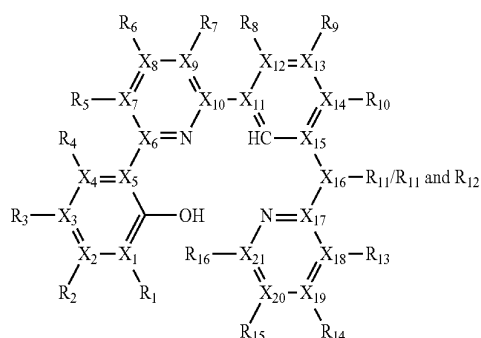
10. A method of preparing an organometallic complex of Structure I, comprising reacting a ligand compound of Structure II with a platinum(II) containing compound,

wherein said organometallic complex of Structure I is:



14. The method of claim 13, further comprising reacting Precursor 270 via a palladium coupling reaction to obtain the Precursor 280, wherein the Precursor 270 has the following structure:

wherein said ligand compound of Structure II is:



15. The method of claim 14, further comprising reacting precursor 260 via a palladium coupling reaction to obtain the Precursor 270, wherein the Precursor 260 has the following structure

wherein R_1 - R_{15} of Structure I and Structure II 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, aryloxy-carbonyl, phenoxy-carbonyl, or an alkoxy-carbonyl group;

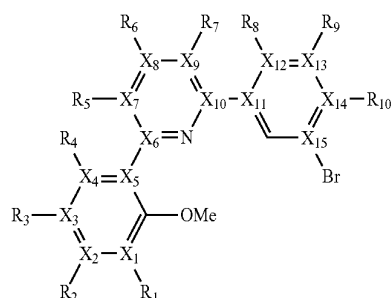
wherein each pair of adjacent R groups of R_1 - R_{15} of Structure I and Structure II can be independently two separate groups or one group, and form 5-8 member ring(s) with 2 or 4 X groups; and

wherein X_1 - X_{20} of Structure I and Structure II are independently boron, carbon, nitrogen, oxygen, silicon, germanium, phosphorous, sulphur or selenium.

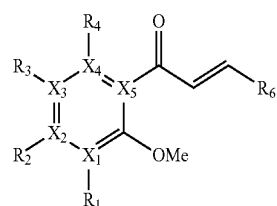
11. The method of claim 10, wherein the platinum(II) containing compound is potassium tetrachloroplatinate.

12. The method of claim 10, wherein the ligand compound of Structure II reacts with a platinum(II) containing compound in the presence of a solvent comprising acetic acid and chloroform.

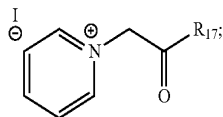
13. A method of preparing a compound of claim 7 comprising reacting Precursor 280 with carbon tetrabromide or pyridine hydrogen chloride to obtain the ligand compound of Structure II, wherein the Precursor 280 has the following structure:



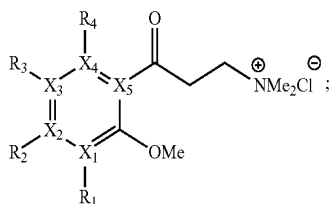
16. The method of claim 15, further comprising reacting Precursor 210 with Precursor 220 or reacting Precursor 230 with Precursor 240 to obtain the Precursor 260; wherein the Precursor 210 has the following structure:



the Precursor 220 has the following structure:

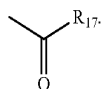


the Precursor 230 has the following structure:



and

the Precursor 240 has the following structure:



17. A light-emitting device comprising an organometallic complex of claim 1 as the emitting material.

18. The light-emitting device of claim 17, wherein the device is an organic light-emitting diode (OLED).

19. The device of claim 17, wherein the device is fabricated by vacuum deposition.

20. The device of claim 17, wherein the device is fabricated by solution processes.

21. The device of claim 17, wherein the device contains one emissive layer.

22. The device of claim 17, wherein the device contains more than one emissive layers.

23. The device of claim 17, wherein the efficiency roll-off at 1000 cd/m⁻² is less than 7%.

24. The device of claim 17, wherein the efficiency roll-off at 1000 cd/m⁻² is less than 50%.

25. The device of claim 17, wherein the device emits green light with a CIE of (0.25±0.05, 0.63±0.05).

26. The device of claim 17, wherein the device emits yellow to orange light with a CIE of (0.40±0.1, 0.4±0.1).

27. The device of claim 17, wherein the complex is not in planar geometry.

* * * * *