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[Continued on next page]

(54) Title: CHIRAL METAL COMPLEXES AS EMITTERS FOR ORGANIC POLARIZED ELECTROLUMINESCENT DEVICES

(57) Abstract: Chiral metal complexes having one of general formulae (1)-(4).

Chiral metal complexes having one of general formulae (1)-(4)

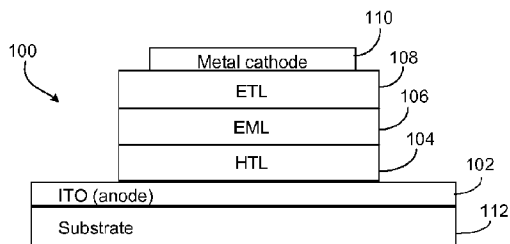
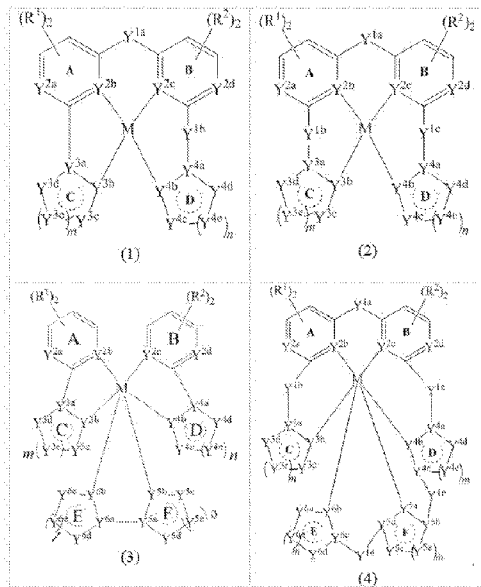


FIG. 1

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HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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CHIRAL METAL COMPLEXES AS EMITTERS FOR ORGANIC POLARIZED ELECTROLUMINESCENT DEVICES

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Patent Application Serial No. 61/945,940 entitled "CHIRAL METAL COMPLEXES AS EMITTERS FOR ORGANIC POLARIZED ELECTROLUMINESCENT DEVICES" and filed on February 28, 2014, which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] This description relates to chiral metal complexes as emitters for organic polarized electroluminescent devices.

BACKGROUND

[0003] Organic light emitting devices (OLEDs) are a new generation of display technology. As depicted in FIG. 1, a typical OLED 100 includes a layer of indium tin oxide (ITO) as an anode 102, a single layer of hole-transporting materials (HTL) 104, a single layer of emissive materials (EML) 106 including emitter and host, a single layer of electron-transporting materials (ETL) 108 and a layer of metal cathode 110. The emission color of OLED is determined by the emission energy (optical energy gap) of emitters. Emitters include phosphorescent emitters, thermal activated delayed fluorescent emitters, and metal-assisted delayed fluorescent emitters.

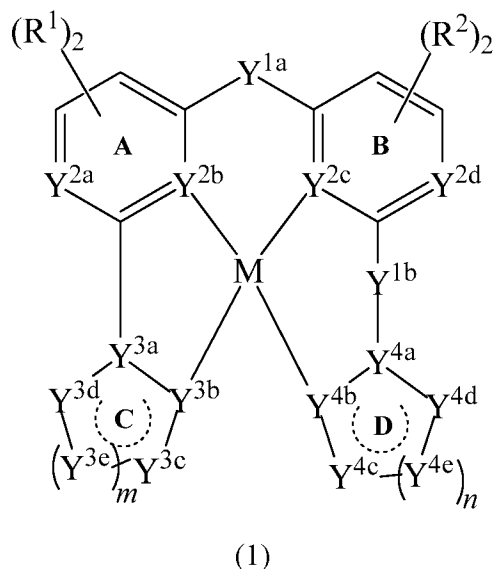
[0004] OLEDs with polarized electroluminescent spectra are desirable for mobile displays or other full color display applications. To enable a high quality of full color displays, a polarizer may be coupled to a transparent electrode of an OLED to filter unwanted reflected light from the background, thereby yielding linearly or circularly polarized light. FIG. 2A depicts a linearly polarized light wave 200. FIG. 2B depicts a circularly polarized light wave 202. This polarizer/OLED arrangement, however, decreases the device efficiency of the OLED by filtering some of the emitted photons.

SUMMARY

[0005] Chiral metal complex emitters provide various advantages over non-polarized emitters with respect to organic polarized electroluminescent devices. For example, chiral metal complex emitters generate polarized electroluminescent spectra without the use of

polarizers, thereby eliminating photon loss due to the polarizers. Specific alignment of chiral metal complex emitters may also reduce the plasmon quenching from the metal electrode and enhance the outcoupling efficiency of the device, thereby allowing more photons to exit the device and resulting in a higher illumination intensity.

[0006] Disclosed herein is an organometallic complex of general formula (1),



wherein:

M is a metal ion;

each R^1 and R^2 is independently selected from hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C_1 - C_4 alkyl;

Y^{1a} , when present, is selected from the group consisting of a direct bond, O, S, NR^{3a} , BR^{3a} , $Si(R^{3b})_2$, or $C(R^{3c})_2$;

each R^{3a} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{3b} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{3c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

Y^{1b} , when present, is selected from the group consisting of a direct bond, O, S, NR^{4a} , BR^{4a} , $Si(R^{4b})_2$, and $C(R^{4c})_2$;

each R^{4a} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{4b} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

each Y^{2a} , Y^{2b} , Y^{2c} , and Y^{2d} is independently selected from the group consisting of O, S, N, NR^{5a} , BR^{5a} , C, and CR^{5b} ;

each R^{5a} and R^{5b} is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C_1 - C_4 alkyl;

each Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , and Y^{4e} is independently selected from the group consisting of N, O, S, NR^{6a} , BR^{6a} , CR^{6b} , and $Z(R^{6c})_2$;

Z is C or Si;

each R^{6a} and R^{6b} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

each R^{6c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

m is 1 or 2;

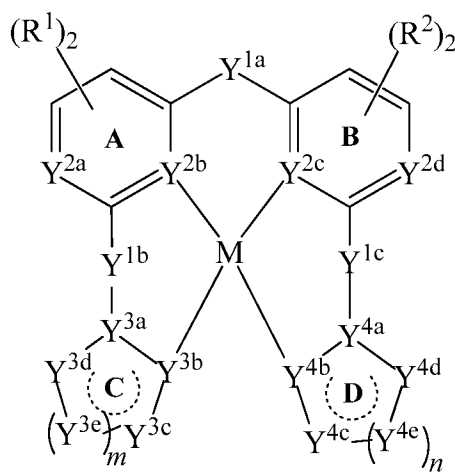
n is 1 or 2;

() represents partial or full unsaturation of the ring with which it is associated;

each ring A, B, C, and D is independently optionally fused to one or two independently selected C_{3-6} cycloalkyl, C_{6-10} aryl, or 4-10 membered heterocycloalkyl groups; and

at least one of M, R^1 , R^2 , Y^{1a} , Y^{1b} , Y^{2a} , Y^{2b} , Y^{2c} , Y^{2d} , Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} and Y^{4e} is a chiral center or comprises one or more chiral centers.

[0007] The present disclosure also provides an organometallic complex of general formula (2),



(2)

wherein:

M is a metal ion;

each R^1 and R^2 is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C₁-C₄ alkyl;

Y^{1a} , when present, is selected from the group consisting of a direct bond, O, S, NR^{3a}, BR^{3a}, Si(R^{3b})₂, and C(R^{3c})₂;

each R^{3a} is independently selected from substituted or unsubstituted C₁-C₄ alkyl;

each R^{3b} is independently selected from substituted or unsubstituted C₁-C₄ alkyl;

each R^{3c} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

Y^{1b} , when present, is selected from the group consisting of a direct bond, O, S, NR^{4a}, BR^{4a}, Si(R^{4b})₂, and C(R^{4c})₂;

each R^{4a} is independently selected from substituted or unsubstituted C₁-C₄ alkyl;

each R^{4b} is independently selected from substituted or unsubstituted C₁-C₄ alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

Y^{1c} , when present, is selected from the group consisting of a direct bond, O, S, NR^{5a}, BR^{5a}, Si(R^{5b})₂, and C(R^{5c})₂;

each R^{5a} is independently selected from substituted or unsubstituted C₁-C₄ alkyl;

each R^{5b} is independently selected from substituted or unsubstituted C₁-C₄ alkyl;

each R^{5c} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

each Y^{2a} , Y^{2b} , Y^{2c} , and Y^{2d} is independently selected from the group consisting of O, S, N, NR^{6a}, BR^{6a}, and CR^{6b};

each R^{6a} and R^{6b} is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, substituted or unsubstituted C₁-C₄ alkyl;

each Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , and Y^{4e} is independently selected from the group consisting of N, O, S, NR^{7a}, BR^{7a}, CR^{7b}, and Z(R^{7c})₂;


Z is C or Si;

each R^{7a} and R^{7b} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

each R^{7c} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

m is 1 or 2;

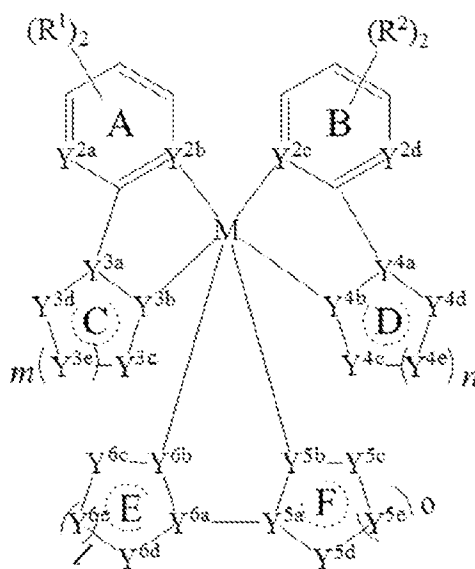
n is 1 or 2;

 represents partial or full unsaturation of the ring with which it is associated;

each ring A, B, C, and D is independently optionally fused to one or two independently selected C₃₋₆ cycloalkyl, C₆₋₁₀ aryl, or 4-10 membered heterocycloalkyl groups; and

at least one of M, R¹, R², Y^{1a}, Y^{1b}, Y^{1c}, Y^{2a}, Y^{2b}, Y^{2c}, Y^{2d}, Y^{3a}, Y^{3b}, Y^{3c}, Y^{3d}, Y^{3e}, Y^{4a}, Y^{4b}, Y^{4c}, Y^{4d}, and Y^{4e} is a chiral center or comprises one or more chiral centers.

[0008] The present disclosure also provides an organometallic complex of general formula (3),



(3)

wherein:

M is a metal ion;

each R¹ and R² is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C₁-C₄ alkyl;

each Y^{2a}, Y^{2b}, Y^{2c}, and Y^{2d} is independently selected from the group consisting of O, S, N, NR^{3a}, BR^{3a}, and CR^{3b};

each R^{3a} and R^{3b} is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C₁-C₄ alkyl;

each Y^{3a}, Y^{3b}, Y^{3c}, Y^{3d}, Y^{3e}, Y^{4a}, Y^{4b}, Y^{4c}, Y^{4d}, and Y^{4e} is independently selected from the group consisting of N, O, S, NR^{4a}, BR^{4a}, CR^{4b}, and Z(R^{4c})₂;

Z is C or Si;

each R^{4a} and R^{4b} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

m is 1 or 2;

n is 1 or 2;

l is 1 or 2;

o is 1 or 2;

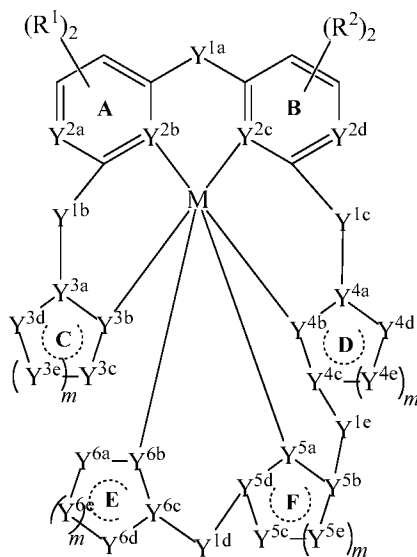
--- represents partial or full unsaturation of the ring with which it is associated;

Y^{5a} , Y^{5b} , Y^{5c} , Y^{5d} , Y^{5e} , Y^{6a} , Y^{6b} , Y^{6c} , Y^{6d} , and Y^{6e} is independently selected from the group consisting of N, O, S, NR^{6a} , and CR^{6b} ;

each ring A, B, C, D, E, and F is independently optionally fused to one or two independently selected C_{3-6} cycloalkyl, C_{6-10} aryl, or 4-10 membered heterocycloalkyl groups; and

at least one of M, R^1 , R^2 , Y^{2a} , Y^{2b} , Y^{2c} , Y^{2d} , Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , Y^{4e} , Y^{5a} , Y^{5b} , Y^{5c} , Y^{5d} , Y^{5e} , Y^{6a} , Y^{6b} , Y^{6c} , Y^{6d} , and Y^{6e} is a chiral center or comprises one or more chiral centers.

[0009] The present disclosure further provides an organometallic complex of general formula (4),



(4)

wherein:

M is a metal ion;

each R^1 and R^2 is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C_1 - C_4 alkyl;

Y^{1a} is selected from the group consisting of O, S, NR^{4a} , BR^{4a} , $Si(R^{4b})_2$, and $C(R^{4c})_2$,

R^{4a} is substituted or unsubstituted C₁-C₄ alkyl;

each R^{4b} is independently selected from substituted or unsubstituted C₁-C₄ alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C₁-

C₄ alkyl;

Y^{1b} is selected from the group consisting of O, S, NR^{5a} , BR^{5a} , $Si(R^{5b})_2$, and $C(R^{5c})_2$,

R^{5a} is substituted or unsubstituted C₁-C₄ alkyl;

each R^{5b} is independently selected from substituted and unsubstituted C₁-C₄ alkyl;

each R^{5c} is independently selected from hydrogen and substituted or unsubstituted C₁-

C₄ alkyl;

Y^{1c} is selected from the group consisting of O, S, NR^{4a} , BR^{4a} , $Si(R^{4b})_2$, and $C(R^{4c})_2$;

R^{4a} is substituted or unsubstituted C₁-C₄ alkyl;

each R^{4b} is independently selected from substituted and unsubstituted C₁-C₄ alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C₁-

C₄ alkyl;

Y^{1d} is selected from the group consisting of O, S, NR^{4a} , BR^{4a} , $Si(R^{4b})_2$, and $C(R^{4c})_2$;

R^{4a} is substituted or unsubstituted C₁-C₄ alkyl;

each R^{4b} is independently selected from substituted and unsubstituted C₁-C₄ alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C₁-

C₄ alkyl;

Y^{1e} , when present, is selected from the group consisting of a direct bond, O, S, NR^{4a} , BR^{4a} , $Si(R^{4b})_2$, and $C(R^{4c})_2$;

R^{4a} is substituted or unsubstituted C₁-C₄ alkyl;

each R^{4b} is independently selected from substituted and unsubstituted C₁-C₄ alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C₁-

C₄ alkyl;

each Y^{2a} , Y^{2b} , Y^{2c} , and Y^{2d} is independently selected from the group consisting of O, S, N, NR^{6a} , BR^{6a} , and CR^{6b} ;

each R^{6a} and R^{6b} is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C₁-C₄ alkyl;


each Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , and Y^{4e} is independently selected from the group consisting of N, O, S, NR^{6a} , BR^{6a} , CR^{6b} , and $Z(R^{6c})_2$;

Z is C or Si;

each R^{6a} and R^{6b} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

each R^{6c} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

each *m* is independently 1 or 2;

 represents partial or full unsaturation of the ring with which it is associated;

each Y^{5a}, Y^{5b}, Y^{5c}, Y^{5d}, Y^{5e}, Y^{6a}, Y^{6b}, Y^{6c}, Y^{6d}, and Y^{6e} is independently selected from the group consisting of N, O, S, NR^{6a}, and CR^{6b};

each ring A, B, C, D, E, and F is independently optionally fused to one or two independently selected C₃₋₆ cycloalkyl, C₆₋₁₀ aryl, or 4-10 membered heterocycloalkyl groups; and

at least one of M, R¹, R², Y^{1a}, Y^{1b}, Y^{1c}, Y^{1d}, Y^{1e}, Y^{2a}, Y^{2b}, Y^{2c}, Y^{2d}, Y^{3a}, Y^{3b}, Y^{3c}, Y^{3d}, Y^{3e}, Y^{4a}, Y^{4b}, Y^{4c}, Y^{4d}, Y^{4e}, Y^{5a}, Y^{5b}, Y^{5c}, Y^{5d}, Y^{5e}, Y^{6a}, Y^{6b}, Y^{6c}, Y^{6d}, and Y^{6e} is a chiral center or comprises one or more chiral centers.

[0010] Also disclosed herein are compositions including one or more chiral metal complexes disclosed herein.

[0011] Also disclosed herein are devices, such as OLEDs, including one or more chiral metal complexes disclosed herein.

[0012] Thus, particular embodiments have been described. Variations, modifications, and enhancements of the described embodiments and other embodiments can be made based on what is described and illustrated. In addition, one or more features of one or more embodiments may be combined. The details of one or more implementations and various features and aspects are set forth in the accompanying drawings, the description, and the claims below.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. 1 depicts an organic light emitting device (OLED).

[0014] FIGS. 2A and 2B depict linearly polarized and circularly polarized light waves, respectively.

[0015] FIGS. 3A and 3B depict chiral isomers of an octahedral metal complex.

[0016] FIGS. 4A-4D depict structures with chiral centers.

[0017] FIGS. 5A-5D depict general schemes for chiral metal complex based emitters.

[0018] FIG. 6 depicts synthesis of a chiral metal complex.

- [0019] FIG. 7 depicts synthesis of a chiral metal complex.
- [0020] FIG. 8 depicts synthesis of a chiral metal complex.
- [0021] FIGS. 9A and 9B depict chiral isomers of an octahedral metal complex.
- [0022] FIG. 10 shows a chiral HPLC analysis representative of a mixture of *mer*-Ir(fppy)₂(ppy*).
- [0023] FIGS. 11A and 11B show chiral HPLC analyses representative of the chiral isomers of *mer*-Ir(fppy)₂(ppy*).
- [0024] FIG. 12 shows circular dichroism (CD) spectra representative of a mixture and individual isomers of *mer*-Ir(fppy)₂(ppy*) in a solution of dichloromethane at room temperature.
- [0025] FIG. 13 depicts synthesis of a chiral metal complex.
- [0026] FIGS. 14A and 4B depict chiral isomers of an octahedral metal complex.
- [0027] FIG. 15 shows a chiral HPLC analysis representative of the mixture of *fac*-Ir(fppy)₂(ppy*).
- [0028] FIG. 16 shows CD spectra representative of the mixture and one isomer of *fac*-Ir(fppy)₂(ppy*) in a solution of dichloromethane at room temperature.
- [0029] FIG. 17 shows a chiral HPLC analysis representative of racemic *mer*-Ir(fppy)₂(ppy).
- [0030] FIG. 18 shows CD spectra representative of the mixture of *mer*-Ir(fppy)₂(ppy) in a solution of dichloromethane at room temperature.
- [0031] FIG. 19 shows CD spectra representative of the mixture of PtN1N* in a solution of dichloromethane at room temperature.

DETAILED DESCRIPTION

- [0032] The present disclosure can be understood more readily by reference to the following detailed description and Examples.
- [0033] Before the present compounds, devices, and/or methods are disclosed and described, it is to be understood that they are not limited to specific synthetic methods unless otherwise specified, or to particular reagents unless otherwise specified, as such can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing, example methods and materials are now described.

[0034] As used in the specification and the appended claims, the singular forms “a”, “an”, and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a component” includes mixtures of two or more components.

[0035] As used herein, the terms “optional” and “optionally” mean that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

[0036] Disclosed are the components to be used to prepare the compositions described herein as well as the compositions themselves to be used within the methods disclosed herein. These and other materials are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these materials are disclosed that while specific reference of each various individual and collective combinations and permutation of these compounds cannot be explicitly disclosed, each is specifically contemplated and described herein. For example, if a particular compound is disclosed and discussed and a number of modifications that can be made to a number of molecules including the compounds are discussed, specifically contemplated is each and every combination and permutation of the compound and the modifications that are possible unless specifically indicated to the contrary. Thus, if a class of molecules A, B, and C are disclosed as well as a class of molecules D, E, and F and an example of a combination molecule, A-D is disclosed, then even if each is not individually recited each is individually and collectively contemplated meaning combinations, A-E, A-F, B-D, B-E, B-F, C-D, C-E, and C-F are considered disclosed. Likewise, any subset or combination of these is also disclosed. Thus, for example, the sub-group of A-E, B-F, and C-E would be considered disclosed. This concept applies to all aspects of this application including, but not limited to, steps in methods of making and using the compositions. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps can be performed with any specific embodiment or combination of embodiments of the methods.

[0037] As referred to herein, a linking atom or group connects two atoms such as, for example, a N atom and a C atom. The linking atom or group can optionally, if valency permits, have other chemical moieties attached. For example, in one aspect, an oxygen would not have any other chemical groups attached as the valency is satisfied once it is bonded to two groups (e.g., N and/or C groups). In another aspect, when carbon is the linking atom, two additional chemical moieties can be attached to the carbon. Suitable chemical moieties include, for example, amine, amide, thiol, aryl, heteroaryl, cycloalkyl, and heterocyclyl.

[0038] The term “cyclic structure” or the like terms used herein refer to any cyclic chemical structure which includes, but is not limited to, aryl, heteroaryl, cycloalkyl, cycloalkenyl, heterocyclyl, carbene, and *N*-heterocyclic carbene.

[0039] As used herein, the term “substituted” is contemplated to include all permissible substituents of organic compounds. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, and aromatic and nonaromatic substituents of organic compounds. Illustrative substituents include, for example, those described below. The permissible substituents can be one or more and the same or different for appropriate organic compounds. For purposes of this disclosure, the heteroatoms, such as nitrogen, can have hydrogen substituents and/or any permissible substituents of organic compounds described herein which satisfy the valences of the heteroatoms. This disclosure is not intended to be limited in any manner by the permissible substituents of organic compounds. Also, the terms “substitution” or “substituted with” include the implicit proviso that such substitution is in accordance with permitted valence of the substituted atom and the substituent, and that the substitution results in a stable compound, *e.g.*, a compound that does not spontaneously undergo transformation such as by rearrangement, cyclization, elimination, etc. It is also contemplated that, in certain aspects, unless expressly indicated to the contrary, individual substituents can be further optionally substituted (*i.e.*, further substituted or unsubstituted).

[0040] In defining various terms, “A¹,” “A²,” “A³,” and “A⁴” are used herein as generic symbols to represent various specific substituents. These symbols can be any substituent, not limited to those disclosed herein, and when they are defined to be certain substituents in one instance, they can, in another instance, be defined as some other substituents.

[0041] The term “alkyl” as used herein is a branched or unbranched saturated hydrocarbon group of 1 to 24 carbon atoms, such as methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *s*-butyl, *t*-butyl, *n*-pentyl, isopentyl, *s*-pentyl, neopentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, eicosyl, tetracosyl, and the like. The alkyl group can be cyclic or acyclic. The alkyl group can be branched or unbranched. The alkyl group can also be substituted or unsubstituted. For example, the alkyl group can be substituted with one or more groups including, but not limited to, alkyl, cycloalkyl, alkoxy, amino, ether, halide, hydroxy, nitro, silyl, sulfo-oxo, or thiol, as described herein. A “lower alkyl” group is an alkyl group containing from one to six (*e.g.*, from one to four) carbon atoms.

[0042] Throughout the specification “alkyl” is generally used to refer to both unsubstituted alkyl groups and substituted alkyl groups; however, substituted alkyl groups are

also specifically referred to herein by identifying the specific substituent(s) on the alkyl group. For example, the term “halogenated alkyl” or “haloalkyl” specifically refers to an alkyl group that is substituted with one or more halide, *e.g.*, fluorine, chlorine, bromine, or iodine. The term “alkoxyalkyl” specifically refers to an alkyl group that is substituted with one or more alkoxy groups, as described below. The term “alkylamino” specifically refers to an alkyl group that is substituted with one or more amino groups, as described below, and the like. When “alkyl” is used in one instance and a specific term such as “alkylalcohol” is used in another, it is not meant to imply that the term “alkyl” does not also refer to specific terms such as “alkylalcohol” and the like.

[0043] The terms “alkoxy” and “alkoxyl” as used herein to refer to an alkyl or cycloalkyl group bonded through an ether linkage; that is, an “alkoxy” group can be defined as $-OA^1$ where A^1 is alkyl or cycloalkyl as defined above. “Alkoxy” also includes polymers of alkoxy groups as just described; that is, an alkoxy can be a polyether such as $-OA^1-OA^2$ or $-OA^1-(OA^2)_a-OA^3$, where “a” is an integer of from 1 to 200 and A^1 , A^2 , and A^3 are alkyl and/or cycloalkyl groups.

[0044] The term “aldehyde” as used herein is represented by the formula $-C(O)H$. Throughout this specification “C(O)” is a short hand notation for a carbonyl group, *i.e.*, $C=O$.

[0045] This practice is also used for other groups described herein. That is, while a term such as “cycloalkyl” refers to both unsubstituted and substituted cycloalkyl moieties, the substituted moieties can, in addition, be specifically identified herein; for example, a particular substituted cycloalkyl can be referred to as, *e.g.*, an “alkylcycloalkyl.” Similarly, a substituted alkoxy can be specifically referred to as, *e.g.*, a “halogenated alkoxy,” a particular substituted alkenyl can be, *e.g.*, an “alkenylalcohol,” and the like. Again, the practice of using a general term, such as “cycloalkyl,” and a specific term, such as “alkylcycloalkyl,” is not meant to imply that the general term does not also include the specific term.

[0046] The terms “amine” or “amino” as used herein are represented by the formula $-NA^1A^2$, where A^1 and A^2 can be, independently, hydrogen or alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein.

[0047] The term “alkylamino” as used herein is represented by the formula $-NH(-alkyl)$ where alkyl is a described herein. Representative examples include, but are not limited to, methylamino group, ethylamino group, propylamino group, isopropylamino group, butylamino group, isobutylamino group, (*sec*-butyl)amino group, (*tert*-butyl)amino group, pentylamino group, isopentylamino group, (*tert*-pentyl)amino group, hexylamino group, and the like.

[0048] The term “aryl” as used herein is a group that contains any carbon-based aromatic group including, but not limited to, benzene, naphthalene, phenyl, biphenyl, phenoxybenzene, and the like. The term “aryl” also includes “heteroaryl,” which is defined as a group that contains an aromatic group that has at least one heteroatom incorporated within the ring of the aromatic group. Examples of heteroatoms include, but are not limited to, nitrogen, oxygen, sulfur, and phosphorus. Likewise, the term “non-heteroaryl,” which is also included in the term “aryl,” defines a group that contains an aromatic group that does not contain a heteroatom. The aryl group can be substituted or unsubstituted. The aryl group can be substituted with one or more groups including, but not limited to, alkyl, cycloalkyl, alkoxy, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, heteroaryl, aldehyde, amino, carboxylic acid, ester, ether, halide, hydroxy, ketone, azide, nitro, silyl, sulfo-oxo, or thiol as described herein. The term “biaryl” is a specific type of aryl group and is included in the definition of “aryl.” Biaryl refers to two aryl groups that are bound together *via* a fused ring structure, as in naphthalene, or are attached *via* one or more carbon-carbon bonds, as in biphenyl. In some aspects, an aryl group has from 6 to 20 carbons. In some aspects, an aryl group has from 6 to 10 carbons.

[0049] The term “cycloalkyl” as used herein is a non-aromatic carbon-based ring composed of at least three carbon atoms. Examples of cycloalkyl groups include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, norbornyl, and the like. In some aspects, a cycloalkyl group comprises 3 to 20 carbons. In some aspects, a cycloalkyl group comprises 3 to 10 atoms carbons. The term “heterocycloalkyl” is a type of cycloalkyl group as defined above, and is included within the meaning of the term “cycloalkyl,” where at least one of the carbon atoms of the ring is replaced with a heteroatom such as, but not limited to, nitrogen, oxygen, sulfur, or phosphorus. The cycloalkyl group and heterocycloalkyl group can be substituted or unsubstituted. The cycloalkyl group and heterocycloalkyl group can be substituted with one or more groups including, but not limited to, alkyl, cycloalkyl, alkoxy, amino, ether, halide, hydroxy, nitro, silyl, sulfo-oxo, or thiol as described herein. In some aspects, a heterocycloalkyl group comprises from 4 to 10 atoms (e.g., C, N, S, and O). In some aspects, a heterocycloalkyl group comprises 4 to 10 atoms (e.g., C, N, S, and O).

[0050] The term “carboxylic acid” as used herein is represented by the formula $-C(O)OH$.

[0051] The term “ester” as used herein is represented by the formula $-OC(O)A^1$ or $-C(O)OA^1$, where A^1 can be alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein. The term “polyester” as used herein is represented by the formula $-(A^1O(O)C-A^2-C(O)O)_a-$ or $-(A^1O(O)C-A^2-OC(O))_a-$, where A^1

and A² can be, independently, an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group described herein and “a” is an integer from 1 to 500. “Polyester” is as the term used to describe a group that is produced by the reaction between a compound having at least two carboxylic acid groups with a compound having at least two hydroxyl groups.

[0052] The term “ether” as used herein is represented by the formula A¹OA², where A¹ and A² can be, independently, an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group described herein. The term “polyether” as used herein is represented by the formula -(A¹O-A²O)_a, where A¹ and A² can be, independently, an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group described herein and “a” is an integer of from 1 to 500. Examples of polyether groups include polyethylene oxide, polypropylene oxide, and polybutylene oxide.

[0053] The term “dialkylamino” as used herein is represented by the formula -N(-alkyl)₂ where alkyl is a described herein. Representative examples include, but are not limited to, dimethylamino group, diethylamino group, dipropylamino group, diisopropylamino group, dibutylamino group, diisobutylamino group, di(sec-butyl)amino group, di(tert-butyl)amino group, dipentylamino group, diisopentylamino group, di(tert-pentyl)amino group, dihexylamino group, N-ethyl-N-methylamino group, N-methyl-N-propylamino group, N-ethyl-N-propylamino group and the like.

[0054] The term “halogen” as used herein refers to the halogens fluorine, chlorine, bromine, and iodine.

[0055] The term “heterocyclyl,” as used herein refers to single and multi-cyclic non-aromatic ring systems and “heteroaryl as used herein refers to single and multi-cyclic aromatic ring systems: in which at least one of the ring members is other than carbon. The terms includes azetidine, dioxane, furan, imidazole, isothiazole, isoxazole, morpholine, oxazole, oxazole, including, 1,2,3-oxadiazole, 1,2,5-oxadiazole and 1,3,4-oxadiazole, piperazine, piperidine, pyrazine, pyrazole, pyridazine, pyridine, pyrimidine, pyrrole, pyrrolidine, tetrahydrofuran, tetrahydropyran, tetrazine, including 1,2,4,5-tetrazine, tetrazole, including 1,2,3,4-tetrazole and 1,2,4,5-tetrazole, thiadiazole, including, 1,2,3-thiadiazole, 1,2,5-thiadiazole, and 1,3,4-thiadiazole, thiazole, thiophene, triazine, including 1,3,5-triazine and 1,2,4-triazine, triazole, including, 1,2,3-triazole, 1,3,4-triazole, and the like.

[0056] The term “hydroxyl” as used herein is represented by the formula -OH.

[0057] The term “ketone” as used herein is represented by the formula $A^1C(O)A^2$, where A^1 and A^2 can be, independently, an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein.

[0058] The term “nitro” as used herein is represented by the formula $-NO_2$.

[0059] The term “thiol” as used herein is represented by the formula $-SH$.

[0060] The term “nitrile” as used herein is represented by the formula $-CN$.

[0061] The term “silyl” as used herein is represented by the formula $-SiA^1A^2A^3$, where A^1 , A^2 , and A^3 can be, independently, hydrogen or an alkyl, cycloalkyl, alkoxy, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein.

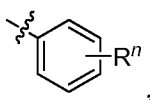
[0062] The term “sulfo-oxo” as used herein is represented by the formulae $-S(O)A^1$, $-S(O)_2A^1$, $-OS(O)_2A^1$, or $-OS(O)_2OA^1$, where A^1 can be hydrogen or an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein. Throughout this specification “S(O)” is a short hand notation for $S=O$. The term “sulfonyl” is used herein to refer to the sulfo-oxo group represented by the formula $-S(O)_2A^1$, where A^1 can be hydrogen or an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein. The term “sulfone” as used herein is represented by the formula $A^1S(O)_2A^2$, where A^1 and A^2 can be, independently, an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein. The term “sulfoxide” as used herein is represented by the formula $A^1S(O)A^2$, where A^1 and A^2 can be, independently, an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein.

[0063] “R,” “R¹,” “R²,” “R³,” “Rⁿ,” where n is an integer, as used herein can, independently, possess one or more of the groups listed above. For example, if R¹ is a straight chain alkyl group, one of the hydrogen atoms of the alkyl group can optionally be substituted with a hydroxyl group, an alkoxy group, an alkyl group, a halide, and the like. Depending upon the groups that are selected, a first group can be incorporated within second group or, alternatively, the first group can be pendant (*i.e.*, attached) to the second group. For example, with the phrase “an alkyl group comprising an amino group,” the amino group can be incorporated within the backbone of the alkyl group. Alternatively, the amino group can be attached to the backbone of the alkyl group. The nature of the group(s) that is (are) selected will determine if the first group is embedded or attached to the second group.

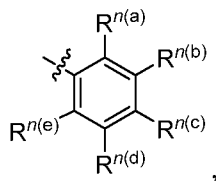
[0064] Compounds described herein may contain “optionally substituted” moieties. In general, the term “substituted,” whether preceded by the term “optionally” or not, means that one or more hydrogens of the designated moiety are replaced with a suitable substituent.

Unless otherwise indicated, an “optionally substituted” group may have a suitable substituent at each substitutable position of the group, and when more than one position in any given structure may be substituted with more than one substituent selected from a specified group, the substituent may be either the same or different at every position. Combinations of substituents envisioned by this invention are preferably those that result in the formation of stable or chemically feasible compounds. It is also contemplated that, in certain aspects, unless expressly indicated to the contrary, individual substituents can be further optionally substituted (i.e., further substituted or unsubstituted).

[0065] In some aspects, a structure of a compound can be represented by a formula:



which is understood to be equivalent to a formula:



wherein n is typically an integer. That is, R^n is understood to represent five independent substituents, $R^{n(a)}$, $R^{n(b)}$, $R^{n(c)}$, $R^{n(d)}$, $R^{n(e)}$. By “independent substituents,” it is meant that each R substituent can be independently defined. For example, if in one instance $R^{n(a)}$ is halogen, then $R^{n(b)}$ is not necessarily halogen in that instance.

[0066] Several references to variables (e.g., R^1 , M , Y^{1a} , Y^{1b} , etc.) are made in chemical structures and moieties disclosed and described herein. Any description of variables in the specification is applicable to any structure or moiety reciting said variables, respectively.

[0067] The following abbreviations may be used herein: aq. (aqueous); calc. (calculated); d (doublet); dd (doublet of doublets); DCM (dichloromethane); DMF (*N,N*-dimethylformamide); DMSO (dimethyl sulfoxide) eq. (equivalents); Et (ethyl); EtOAc (ethyl acetate); g (gram(s)); h (hour(s)); Hz (hertz); HCl (hydrochloric acid / hydrogen chloride); HPLC (high performance liquid chromatography); J (coupling constant); K_2PtCl_4 (potassium tetrachloroplatinate); m (multiplet); MHz (megahertz); MS (Mass spectrometry); Me (methyl); mg (milligram(s)); min. (minutes(s)); mL (milliliter(s)); mmol (millimole(s)); mol% (mole percent); n Bu (*n*-butyl); n Bu₄NBr (tetra-*n*-butylammonium bromide); NMR (nuclear magnetic resonance spectroscopy); Pd (palladium); pM (picomolar); s (singlet); t (triplet or tertiary); μ g (microgram(s)); μ L (microliter(s)); μ M (micromolar); wt% (weight percent).

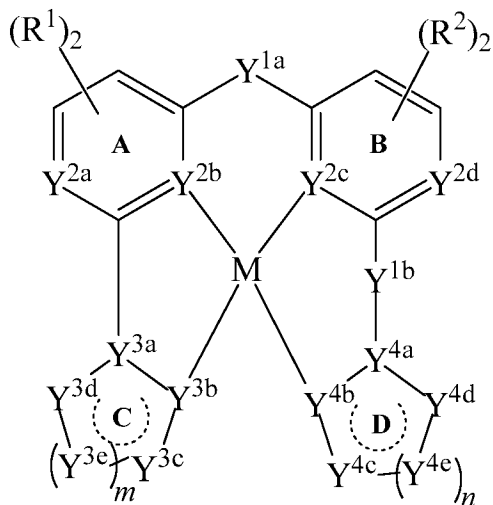
Compounds

[0068] A chiral structure, such as a molecule or organometallic complex, is not superimposable on its mirror image. FIGS. 3A and 3B depict chiral isomers of an octahedral metal complex. A chiral center is an atom in a structure, such as an organic molecule, that has four or more unique atoms or groups attached to it.

[0069] Examples of chiral centers are shown in FIGS. 4A-4D, 9A, 9B, 14A, and 14B. In FIGS. 4A, 4B, 9A, 9B, 14A, and 14B, the iridium is a chiral center. In FIG. 4C, the platinum is a chiral center. In FIG. 4D, the carbon is a chiral center. FIGS. 4A-4C depict three classes of chiral metal complexes. FIG. 4A depicts an octahedral metal complex with three different cyclometalating ligands (e.g., Ir(CN)(C'N')(C''N'')). FIG. 4B depicts an octahedral metal complex with two different cyclometalating ligands, i.e. Ir(CN)₂(C'N'). FIG. 4C depicts a non-planar asymmetric tetrahedral metal complex.

[0070] FIGS. 5A-5D depict general schemes for chiral metal complex based emitters, where at least one of M or other functional group such as C, C', C'', N, N', and N'' includes one or more chiral centers.

[0071] The present disclosure provides an organometallic complex of general formula (1),



wherein:

M is a metal ion;

each R¹ and R² is independently selected from hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C₁-C₄ alkyl;

Y^{1a} , when present, is selected from the group consisting of a direct bond, O, S, NR^{3a} , BR^{3a} , $Si(R^{3b})_2$, or $C(R^{3c})_2$;

each R^{3a} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{3b} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{3c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

Y^{1b} , when present, is selected from the group consisting of a direct bond, O, S, NR^{4a} , BR^{4a} , $Si(R^{4b})_2$, and $C(R^{4c})_2$;

each R^{4a} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{4b} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

each Y^{2a} , Y^{2b} , Y^{2c} , and Y^{2d} is independently selected from the group consisting of O, S, N, NR^{5a} , BR^{5a} , C, and CR^{5b} ;

each R^{5a} and R^{5b} is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C_1 - C_4 alkyl;

each Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , and Y^{4e} is independently selected from the group consisting of N, O, S, NR^{6a} , BR^{6a} , CR^{6b} , and $Z(R^{6c})_2$;

Z is C or Si;

each R^{6a} and R^{6b} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

each R^{6c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

m is 1 or 2;

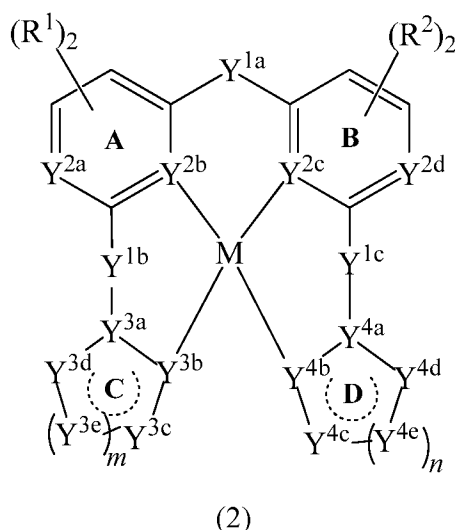
n is 1 or 2;

--- represents partial or full unsaturation of the ring with which it is associated;

each ring A, B, C, and D is independently optionally fused to one or two independently selected C_{3-6} cycloalkyl, C_{6-10} aryl, or 4-10 membered heterocycloalkyl groups; and

at least one of M, R^1 , R^2 , Y^{1a} , Y^{1b} , Y^{2a} , Y^{2b} , Y^{2c} , Y^{2d} , Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} and Y^{4e} is a chiral center or includes one or more chiral centers.

[0072] The present disclosure also provides an organometallic complex of general formula (2),



wherein:

M is a metal ion;

each R^1 and R^2 is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C_1 - C_4 alkyl;

Y^{1a} , when present, is selected from the group consisting of a direct bond, O, S, NR^{3a} , BR^{3a} , $Si(R^{3b})_2$, and $C(R^{3c})_2$,

each R^{3a} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{3b} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{3c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

Y^{1b} , when present, is selected from the group consisting of a direct bond, O, S, NR^{4a} , BR^{4a} , $Si(R^{4b})_2$, and $C(R^{4c})_2$;

each R^{4a} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{4b} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

Y^{1c} , when present, is selected from the group consisting of a direct bond, O, S, NR^{5a} , BR^{5a} , $Si(R^{5b})_2$, and $C(R^{5c})_2$;

each R^{5a} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{5b} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{5c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

each Y^{2a} , Y^{2b} , Y^{2c} , and Y^{2d} is independently selected from the group consisting of O, S, N, NR^{6a} , BR^{6a} , and CR^{6b} ;

each R^{6a} and R^{6b} is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C_1 - C_4 alkyl;

each Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , and Y^{4e} is independently selected from the group consisting of N, O, S, NR^{7a} , BR^{7a} , CR^{7b} , and $Z(R^{7c})_2$;

Z is C or Si;

each R^{7a} and R^{7b} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

each R^{7c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

m is 1 or 2;

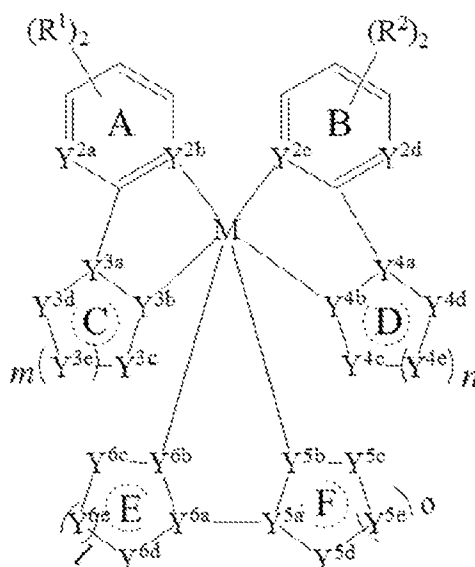
n is 1 or 2;

() represents partial or full unsaturation of the ring with which it is associated;

each ring A, B, C, and D is independently optionally fused to one or two independently selected C_{3-6} cycloalkyl, C_{6-10} aryl, or 4-10 membered heterocycloalkyl groups; and

at least one of M, R^1 , R^2 , Y^{1a} , Y^{1b} , Y^{1c} , Y^{2a} , Y^{2b} , Y^{2c} , Y^{2d} , Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , and Y^{4e} is a chiral center or comprises one or more chiral centers.

[0073] The present disclosure also provides an organometallic complex of general formula (3),



(3)

wherein:

M is a metal ion;

each R^1 and R^2 is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C_1 - C_4 alkyl;

each Y^{2a} , Y^{2b} , Y^{2c} , and Y^{2d} is independently selected from the group consisting of O, S, N, NR^{3a} , BR^{3a} , and CR^{3b} ;

each R^{3a} and R^{3b} is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C_1 - C_4 alkyl;

each Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , and Y^{4e} is independently selected from the group consisting of N, O, S, NR^{4a} , BR^{4a} , CR^{4b} , and $Z(R^{4c})_2$;

Z is C or Si;

each R^{4a} and R^{4b} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

m is 1 or 2;

n is 1 or 2;

l is 1 or 2;

o is 1 or 2;

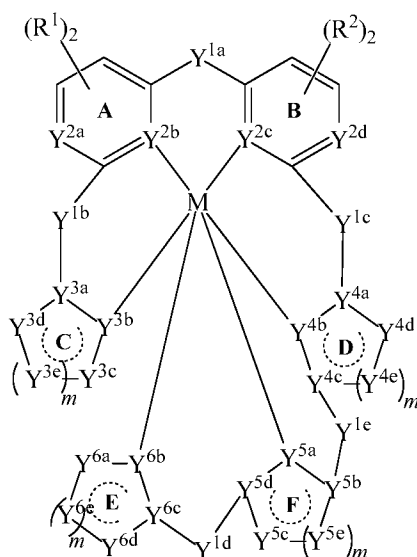
--- represents partial or full unsaturation of the ring with which it is associated;

each Y^{5a} , Y^{5b} , Y^{5c} , Y^{5d} , Y^{5e} , Y^{6a} , Y^{6b} , Y^{6c} , Y^{6d} , and Y^{6e} is independently selected from the group consisting of N, O, S, NR^{6a} , and CR^{6b} ;

each ring A, B, C, D, E, and F is independently optionally fused to one or two independently selected C_{3-6} cycloalkyl, C_{6-10} aryl, or 4-10 membered heterocycloalkyl groups; and

at least one of M, R^1 , R^2 , Y^{2a} , Y^{2b} , Y^{2c} , Y^{2d} , Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , Y^{4e} , Y^{5a} , Y^{5b} , Y^{5c} , Y^{5d} , Y^{5e} , Y^{6a} , Y^{6b} , Y^{6c} , Y^{6d} , and Y^{6e} is a chiral center or includes one or more chiral centers.

[0074] The present disclosure further provides an organometallic complex of general formula (4),



wherein:

M is a metal ion;

each R^1 and R^2 is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C_1 - C_4 alkyl;

Y^{1a} is selected from the group consisting of O, S, NR^{4a} , BR^{4a} , $Si(R^{4b})_2$, and $C(R^{4c})_2$,

R^{4a} is substituted or unsubstituted C_1 - C_4 alkyl;

each R^{4b} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C_1 -

C_4 alkyl;

Y^{1b} is selected from the group consisting of O, S, NR^{5a} , BR^{5a} , $Si(R^{5b})_2$, and $C(R^{5c})_2$,

R^{5a} is substituted or unsubstituted C_1 - C_4 alkyl;

each R^{5b} is independently selected from substituted and unsubstituted C_1 - C_4 alkyl;

each R^{5c} is independently selected from hydrogen and substituted or unsubstituted C_1 -

C_4 alkyl;

Y^{1c} is selected from the group consisting of O, S, NR^{4a} , BR^{4a} , $Si(R^{4b})_2$, and $C(R^{4c})_2$;

R^{4a} is substituted or unsubstituted C_1 - C_4 alkyl;

each R^{4b} is independently selected from substituted and unsubstituted C_1 - C_4 alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C_1 -

C_4 alkyl;

Y^{1d} is selected from the group consisting of O, S, NR^{4a} , BR^{4a} , $Si(R^{4b})_2$, and $C(R^{4c})_2$,

R^{4a} is substituted or unsubstituted C_1 - C_4 alkyl;

each R^{4b} is independently selected from substituted and unsubstituted C_1 - C_4 alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

Y^{1c} , when present, is selected from the group consisting of a direct bond, O, S, NR^{4a}, BR^{4a}, Si(R^{4b})₂, and C(R^{4c})₂;

R^{4a} is substituted or unsubstituted C₁-C₄ alkyl;

each R^{4b} is independently selected from substituted and unsubstituted C₁-C₄ alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

each Y^{2a} , Y^{2b} , Y^{2c} , and Y^{2d} is independently selected from the group consisting of O, S, N, NR^{6a}, BR^{6a}, and CR^{6b};

each R^{6a} and R^{6b} is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C₁-C₄ alkyl;

each Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , and Y^{4e} is independently selected from the group consisting of N, O, S, NR^{6a}, BR^{6a}, CR^{6b}, and Z(R^{6c})₂;

Z is C or Si;

each R^{6a} and R^{6b} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

each R^{6c} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

each m is independently 1 or 2;

(-)- represents partial or full unsaturation of the ring with which it is associated;

each Y^{5a} , Y^{5b} , Y^{5c} , Y^{5d} , Y^{5e} , Y^{6a} , Y^{6b} , Y^{6c} , Y^{6d} , and Y^{6e} is independently selected from the group consisting of N, O, S, NR^{6a}, and CR^{6b};

each ring A, B, C, D, E, and F is independently optionally fused to one or two independently selected C₃₋₆ cycloalkyl, C₆₋₁₀ aryl, or 4-10 membered heterocycloalkyl groups; and

at least one of M, R¹, R², Y^{1a}, Y^{1b}, Y^{1c}, Y^{1d}, Y^{1e}, Y^{2a}, Y^{2b}, Y^{2c}, Y^{2d}, Y^{3a}, Y^{3b}, Y^{3c}, Y^{3d}, Y^{3e}, Y^{4a}, Y^{4b}, Y^{4c}, Y^{4d}, Y^{4e}, Y^{5a}, Y^{5b}, Y^{5c}, Y^{5d}, Y^{5e}, Y^{6a}, Y^{6b}, Y^{6c}, Y^{6d}, and Y^{6e} is a chiral center or includes one or more chiral centers.

[0075] In some aspects of general formulae (1)-(4), M is selected from the group consisting of Pt²⁺, Pd²⁺, Ir⁺, Rh⁺, Au³⁺, Ir³⁺, Rh³⁺, Ru²⁺, Pt⁴⁺, and Os²⁺. In some aspects of general formulae (1)-(4), M is selected from the group consisting of Pt²⁺, Pt⁴⁺, Ir⁺, and Ir³⁺. In some aspects of general formulae (1)-(4), M is Pt²⁺ or Pt⁴⁺. In some aspects of general

formulae (1)-(4), M is Ir⁺ or Ir³⁺. In some aspects of general formulae (1)-(4), M is a chiral center.

[0076] In some aspects of general formula (1), each Y^{1a} and Y^{1b}, when present, is independently selected from the group consisting of a direct bond, NH, and CH₂. In some aspects of general formula (1), each Y^{2a}, Y^{2b}, Y^{2c}, Y^{2d}, Y^{3a}, Y^{3b}, Y^{3c}, Y^{3d}, Y^{3e}, Y^{4a}, Y^{4b}, Y^{4c}, Y^{4d} and Y^{4e} is independently selected from C, CH, N, and NH.

[0077] In some aspects of general formula (2), each Y^{1a}, Y^{1b}, and Y^{1c}, when present, is independently selected from the group consisting of a direct bond, NH, and CH₂. In some aspects of general formula (2), each Y^{2a}, Y^{2b}, Y^{2c}, Y^{2d}, Y^{3a}, Y^{3b}, Y^{3c}, Y^{3d}, Y^{3e}, Y^{4a}, Y^{4b}, Y^{4c}, Y^{4d}, and Y^{4e} is independently selected from C, CH, N, and NH.

[0078] In some aspects of general formula (3), each Y^{2a}, Y^{2b}, Y^{2c}, Y^{2d}, Y^{3a}, Y^{3b}, Y^{3c}, Y^{3d}, Y^{3e}, Y^{4a}, Y^{4b}, Y^{4c}, Y^{4d}, Y^{4e}, Y^{5a}, Y^{5b}, Y^{5c}, Y^{5d}, Y^{5e}, Y^{6a}, Y^{6b}, Y^{6c}, Y^{6d}, and Y^{6e} is independently selected from C, CH, N, and NH.

[0079] In some aspects of general formula (4), each Y^{1a}, Y^{1b}, Y^{1c}, Y^{1d}, and Y^{1e}, when present, is independently selected from the group consisting of a direct bond, NH, and CH₂. In some aspects of general formula (4), each Y^{2a}, Y^{2b}, Y^{2c}, Y^{2d}, Y^{3a}, Y^{3b}, Y^{3c}, Y^{3d}, Y^{3e}, Y^{4a}, Y^{4b}, Y^{4c}, Y^{4d}, Y^{4e}, Y^{5a}, Y^{5b}, Y^{5c}, Y^{5d}, Y^{5e}, Y^{6a}, Y^{6b}, Y^{6c}, Y^{6d}, and Y^{6e} is independently selected from C, CH, N, and NH.

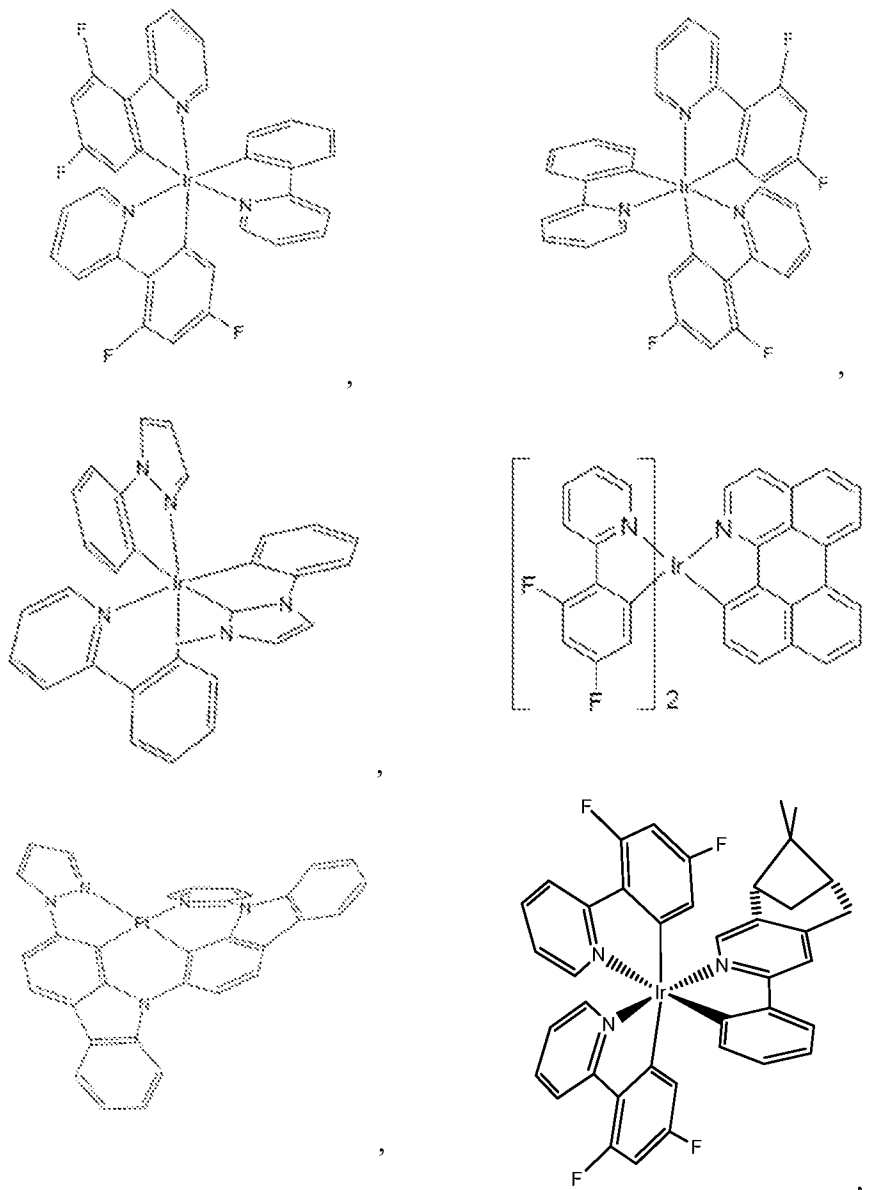
[0080] In some aspects of general formulae (1)-(4), $\left(\begin{array}{c} \text{---} \\ \text{---} \end{array} \right)$ represents full unsaturation of the ring with which it is associated or partial unsaturation of the ring with which it is associated.

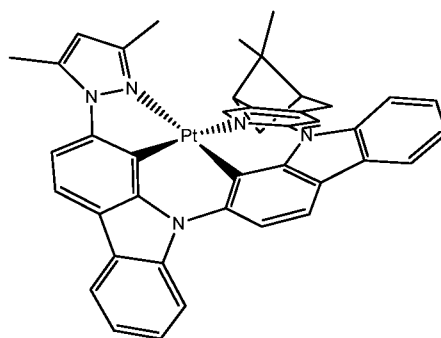
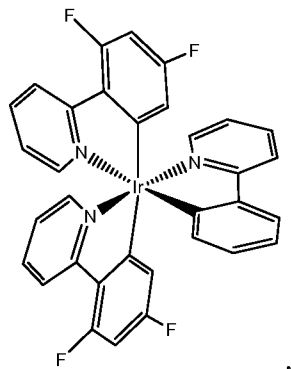
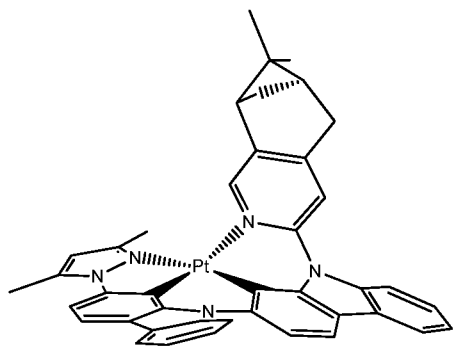
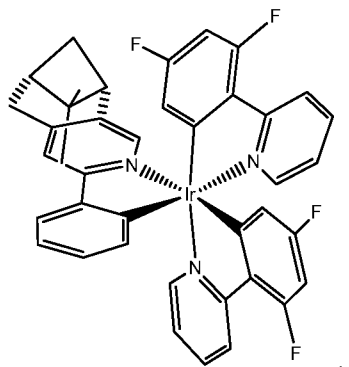
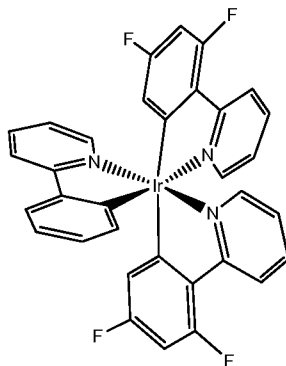
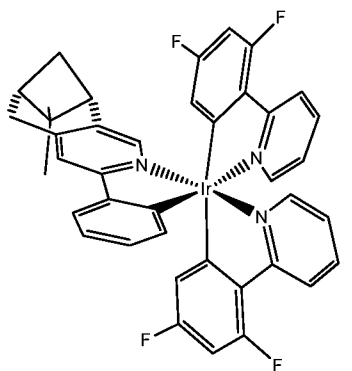
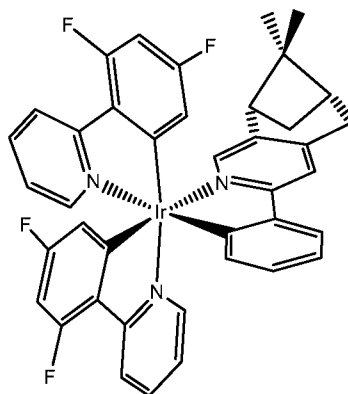
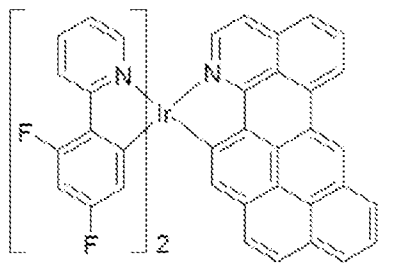
[0081] In some aspects of general formulae (1)-(2), each ring A, B, C, and D is independently selected from optionally substituted phenyl, optionally substituted pyridinyl, optionally substituted pyrazolyl, and optionally substituted imidazolyl. In some aspects of general formulae (1)-(2), each ring A, B, C, and D is independently selected from phenyl, difluorophenyl, pyridinyl, pyrazolyl, dimethylpyrazolyl, and methylimidazolyl. In some aspects of general formulae (1)-(2), at least one of rings A, B, C, and D is optionally fused to one or two C₃₋₆ cycloalkyl, C₆₋₁₀ aryl or 4-10 member heterocycloalkyl groups. In some aspects of general formulae (1)-(2), at least one of rings A, B, C, and D is optionally fused to one C₃₋₆ cycloalkyl group or one 4-10 member heterocycloalkyl group.

[0082] In some aspects of general formulae (3)-(4), each ring A, B, C, D, E, and F is independently selected from optionally substituted phenyl, optionally substituted pyridinyl, and optionally substituted pyrazolyl. In some aspects of general formulae (3)-(4), each ring

A, B, C, D, E, and F is independently selected from phenyl, difluorophenyl, pyridinyl, and dimethylpyrazolyl. In some aspects of general formulae (3)-(4), at least one of rings A, B, C, D, E, and F is optionally fused to one or two C₃₋₆ cycloalkyl, C₆₋₁₀ aryl or 4-10 member heterocycloalkyl groups. In some aspects of general formulae (3)-(4), at least one of rings A, B, C, D, E, and F is optionally fused to one C₃₋₆ cycloalkyl group or one C₆₋₁₀ aryl group.

[0083] In some aspects, the chiral metal complex disclosed herein is selected from the group consisting of:





and

Light Emitting Devices

[0084] The compounds disclosed herein are useful in a variety of applications. As light emitting materials, the compounds can be useful in organic light emitting diodes (OLEDs), luminescent devices and displays, and other light emitting devices.

[0085] Opto-electronic devices that make use of organic materials are becoming increasingly desirable for a number of reasons. Many of the materials used to make such devices are relatively inexpensive, so organic opto-electronic devices have the potential for cost advantages over inorganic devices. In addition, the inherent properties of organic materials, such as their flexibility, may make them well suited for particular applications such as fabrication on a flexible substrate. Examples of organic opto-electronic devices include organic light emitting devices (OLEDs), organic phototransistors, organic photovoltaic cells, and organic photodetectors. For OLEDs, the organic materials may have performance advantages over conventional materials. For example, the wavelength at which an organic emissive layer emits light may generally be readily tuned with appropriate dopants.

[0086] Chiral emitters described herein generate circularly polarized electroluminescent emission. OLEDs that comprise said chiral emitters in the emissive materials layer (EML) provide circularly polarized electroluminescence without the use of polarizers and the accompanying loss of efficiency.

[0087] Circularly polarized emission is generated when greater than 50 wt% or mol% of the emissive material in the emissive materials layer (EML) is a selected single enantiomer or a selected single diastereomer of the chiral metal complex emitters of general formulae (1)-(4). In some aspects, greater than 60, 70, 80, 90, 95, or 99 wt% or mol% of the emissive material in the emissive materials layer is a selected single enantiomer or a selected single diastereomer of the chiral metal complex emitters of general formulae (1)-(4). In some aspects, greater than 60, 70, 80, 90, 95, or 99 wt% of the emissive material in the emissive materials layer is a selected single enantiomer or a selected single diastereomer of the chiral metal complex emitters of general formulae (1)-(4). In some aspects, greater than 60, 70, 80, 90, 95, or 99 mol% of the emissive material in the emissive materials layer is a selected single enantiomer or a selected single diastereomer of the chiral metal complex emitters of general formulae (1)-(4). The chiral metal complex emitters in the emissive materials layer may be present as a single chiral structure, an isomeric mixture, or two or more different chiral metal complexes. In some aspects, the chiral metal complex emitter in the emissive materials layer is present as a single chiral structure. In some aspects, the chiral metal complex emitter in the emissive materials layer is present as an isomeric mixture. In some

aspects, two or more different chiral metal complexes are present in the emissive materials layer.

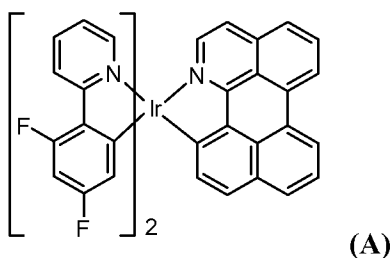
[0088] NMR spectra were recorded on a Varian Gemini-300, Varian Gemini-400 and other instrument and chemical shifts were referenced to residual protiated solvent. HPLC was performed on HPLC Agilent Technologies 1200 Series equipped with CHIRALPAK ID-3 and other chiral columns. Circular dichroism (CD) spectra were recorded on a JASCO J-710 CD spectropolarimeter.

EXAMPLES

[0089] The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compounds, compositions, articles, devices and/or methods claimed herein are made and evaluated, and are intended to be purely exemplary and not intended to limit the scope of the disclosure. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric.

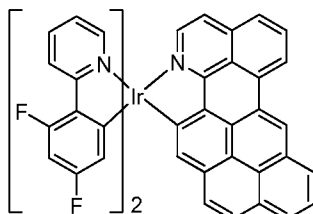
[0090] Various methods for the preparation method of the compounds described herein are recited in the examples. These methods are provided to illustrate various methods of preparation, but this disclosure is not intended to be limited to any of the methods recited herein. Accordingly, one of skill in the art in possession of this disclosure could readily modify a recited method or utilize a different method to prepare one or more of the compounds. The following aspects are only exemplary and are not intended to limit the scope of the disclosure. Temperatures, catalysts, concentrations, reactant compositions, and other process conditions can vary, and one of skill in the art, in possession of this disclosure, could readily select appropriate reactants and conditions for a desired complex.

[0091] **Example 1.** The chiral metal complex shown in structural formula (A) was synthesized as shown in FIG. 6, according to the process described below:



[0092] A mixture of chloride-bridged Ir(III) dimer $[(dfppy)_2Ir(\mu-Cl)]_2$ (0.3 g), azaperylene ligand (0.15 g), silver triflate (0.3 g), and 2–3 eq. of triethylamine was stirred in a solution of 50 mL dichloroethane for 2 h at room temperature. The reaction mixture was heated at reflux for an additional 12 h. Then the mixture was cooled to room temperature, and the precipitate was filtered off. The filtrate was evaporated to dryness under reduced pressure, and the dark red crystalline product (yield: 35%) was obtained from column chromatography on silica using a CH_2Cl_2 mobile phase. The final product can be further purified in a thermal gradient sublimation method. 1H NMR (300 MHz, $CDCl_3$), 8.31 (d, $J = 7.8$ Hz, 1 H), 8.27–8.15 (m, 3 H), 7.97 (d, $J = 5.3$ Hz, 1 H), 7.75–7.64 (m, 3 H), 7.59–7.41 (m, 6 H), 7.28 (d, $J = 8.4$ Hz, 1 H), 7.14 (d, $J = 5.7$ Hz, 1 H), 6.69 (dd, $J = 6.0$ Hz, 6.6 Hz, 1 H), 6.65 (dd, $J = 6.6$ Hz, 6.6 Hz, 1 H), 6.52–6.41 (m, 2 H), 6.06 (dd, $J = 7.5$ Hz, $J = 2.4$ Hz, 1 H), 5.93 (dd, $J = 8.4$ Hz, $J = 2.4$ Hz, 1 H). Anal. for $C_{41}H_{22}F_4IrN_3$, found: C 59.83, H 2.36, N 5.11; calcd: C 59.70, H 2.69, N 5.09.

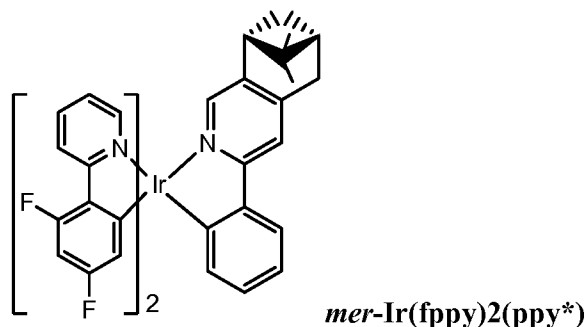
[0093] Example 2. The chiral metal complex shown in structural formula **(B)** was synthesized as shown in FIG. 7 according to the process described below:



(B)

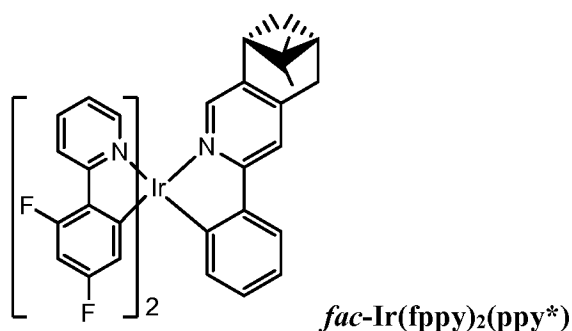
[0094] A mixture of chloride-bridged Ir(III) dimer $[(dfppy)_2Ir(\mu-Cl)]_2$ (0.3 g), benzo[*de*]pyreno[10,1-*gh*]quinolone (0.19 g), silver triflate (0.3 g), and 2–3 eq. of triethylamine was stirred in a solution of 50 mL dichloroethane for 2 h at room temperature. The reaction mixture was heated at reflux for an additional 12 h. Then the mixture was cooled to room temperature, and the precipitate was filtered off. The filtrate was evaporated to dryness under reduced pressure, and the dark red crystalline product (yield: 20%) was obtained from column chromatography on silica using a CH_2Cl_2 mobile phase. In some aspects, the final product was further purified using a thermal gradient sublimation method. 1H NMR (400 MHz, $CDCl_3$, δ) 9.30 (s, 1 H), 8.92 (d, $J = 7.9$ Hz, 1 H), 8.37 (d, $J = 7.4$ Hz, 1 H), 8.26–8.16 (m, 3 H), 8.08–7.77 (m, 8 H), 7.74 (t, $J = 8.1$ Hz, 1 H), 7.65 (s, 1 H), 7.56 (d, $J = 6.4$ Hz, 1 H), 7.54 (d, $J = 6.4$ Hz, 1 H), 7.01 (t, $J = 6.4$ Hz, 1 H), 6.91 (t, $J = 6.6$ Hz, 1 H), 6.88–6.78 (m, 2 H), 5.98 (dd, $J = 7.1, 2.4$ Hz, 1 H), 5.87 (dd, $J = 8.8, 1.9$ Hz, 1 H).

[0095] **Example 3.** The chiral metal complex *mer*-Ir(fppy)₂(ppy*) was synthesized as shown in FIG. 8, according to the process described below:



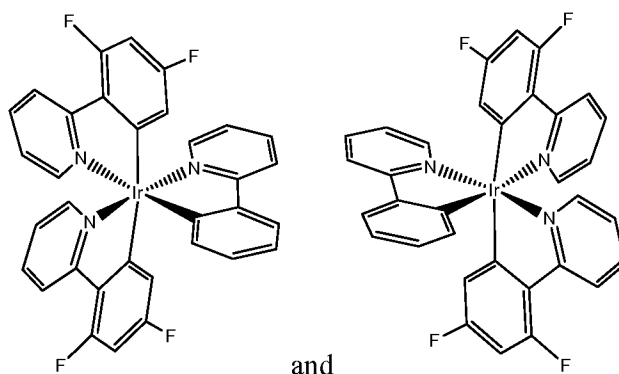
[0096] A mixture of 0.3 g chloride-bridged Ir(III) dimer, [(fppy)₂Ir(μ-Cl)]₂, about 0.1 g ppy* ligand, 0.3 g silver triflate, and 2-3 eq. triethylamine was stirred in a solution of 50 mL dichloroethane for 2 h at room temperature. The reaction mixture was heated at reflux for an additional 12 h. Then the mixture was cooled to room temperature and the precipitate was filtered off. The filtrate was evaporated to dryness under reduced pressure and the raw product of *mer*-Ir(fppy)₂(ppy*) was obtained from column chromatography on silica using a CH₂Cl₂ mobile phase. ¹H NMR for *mer*-Ir(fppy)₂(ppy*) (2 isomers in approx. 1:1 ratio, not assigned). 400 MHz, DMSO-*d*₆: δ 8.25-8.11 (m, 2 H), 8.10-7.97 (m, 2 H), 7.91-7.72 (m, 3 H), 7.66 (d, *J* = 6.2 Hz, 0.5 H), 7.48 (d, *J* = 5.5 Hz, 0.5 H), 7.30 (s, 0.5 H), 7.26 (s, 0.5 H), 7.14-7.01 (m, 2 H), 6.99-6.83 (m, 2 H), 6.79-6.58 (m, 3 H), 5.89-5.82 (m, 1 H), 5.71-5.61 (m, 1 H), 3.20-2.96 (m, 2 H), 2.70-2.38 (m, 2 H, overlapped with solvent residual peak), 2.29-2.15 (m, 1 H), 1.33 (s, 1.5 H), 1.27 (s, 1.5 H), 1.22 (d, *J* = 9.8 Hz, 0.5 H), 1.00 (d, *J* = 9.3 Hz, 0.5 H), 0.68 (s, 1.5 H), 0.31 (s, 1.5 H). By running the bulk samples through HPLC equipped with selected chiral column (e.g. CHIRALPAK ID-3) for multiple times, both isomers of *mer*-Ir(fppy)₂(ppy*), as shown in FIG. 9, were separated from the mixture. HPLC traces and circular dichroism (CD) spectra of the mixture of *mer*-Ir(fppy)₂(ppy*) and the isolated isomers are shown in FIGS. 10-12.

[0097] **Example 4.** The chiral metal complex *fac*-Ir(fppy)₂(ppy*) was synthesized as shown in FIG. 13, according to the process described below:



[0098] 0.2 g of *mer*-Ir(fppy)₂(ppy*) was dissolved in 50 mL toluene in a sealed quartz container, which was thoroughly bubbled in a nitrogen atmosphere for 2 h. Then the mixture, under nitrogen environment, was exposed to UV radiation for 2 days. The mixture was cooled to room temperature and was evaporated to dryness under reduced pressure. The raw product of *fac*-Ir(fppy)₂(ppy*) was obtained from column chromatography on silica using a CH₂Cl₂ mobile phase. ¹H NMR for *fac*-Ir(fppy)₂(ppy*) (2 isomers in approx. 1:1 ratio, not assigned). 500 MHz, DMSO-*d*₆: δ 8.28-8.17 (m, 2 H), 8.02 (d, *J* = 7.3 Hz, 1 H), 7.94-7.83 (m, 2 H), 7.79-7.70 (m, 1 H), 7.56 (t, *J* = 5.9 Hz, 1 H), 7.54-7.37 (m, 1 H), 7.28-7.10 (m, 4 H), 6.96 (d, *J* = 12.6 Hz, 1 H), 6.90-6.81 (m, 1 H), 6.80-6.73 (m, 1 H), 6.70-6.58 (m, 2 H), 5.56-6.49 (m, 1 H), 6.15-6.10 (m, 1 H), 6.09-6.03 (m, 1 H), 3.20-2.98 (m, 2 H), 2.68-2.45 (m, 2 H, overlapped with solvent residual peak), 2.28-2.18 (m, 1 H), 1.32 (s, 1.5 H), 1.27 (s, 1.5 H), 1.22 (d, *J* = 9.8 Hz, 0.5 H), 1.04 (d, *J* = 9.4 Hz, 0.5 H), 0.68 (s, 1.5 H), 0.40 (s, 1.5 H). By running the bulk samples through HPLC equipped with selected chiral column (e.g. CHIRALPAK ID-3) multiple times, one isomer of *fac*-Ir(fppy)₂(ppy*) was separated from the mixture. ¹H NMR (400 MHz, DMSO-*d*₆, δ): 8.35-8.18 (m, 2 H), 7.77-7.39 (m, 6 H), 6.98-6.68 (m, 6 H), 6.45-6.16 (m, 4 H), 3.18-2.96 (m, 2 H), 2.72-2.56 (m, 1 H), 2.52-2.37 (m, 1 H), 2.35-2.19 (m, 1 H), 1.35-1.19 (m, 4 H), 0.49 (s, 3 H). The chemical structures of *R*- and *S*- isomers of *fac*-Ir(fppy)₂(ppy*) (based on the chirality of the Iridium(III) metal ion) are shown in FIG. 14. A chiral HPLC trace of the mixture of *fac*-Ir(fppy)₂(ppy*) is shown in FIG. 15, and a CD spectra of the mixture of *fac*-Ir(fppy)₂(ppy*) and isolated isomer is shown in FIG. 16.

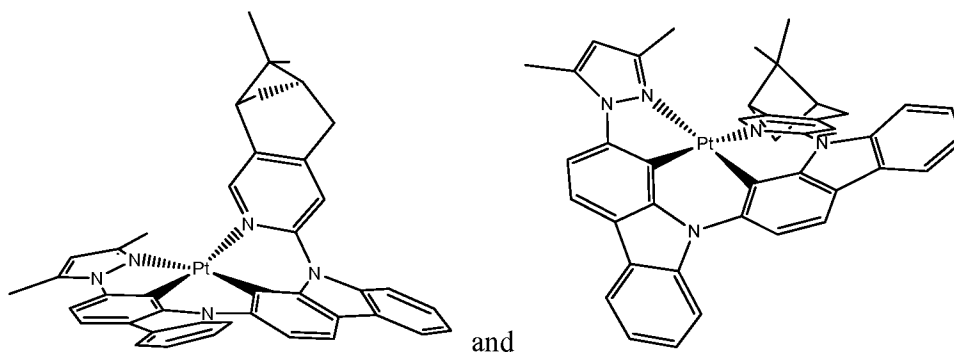
[0099] **Example 5.** The chiral metal complex *mer*-Ir(fppy)₂(ppy) was prepared as a racemic mixture (individual isomers shown below) according to the synthetic procedure for the preparation of *mer*-Ir(fppy)₂(ppy*), as described in Example 3.



***R/S*- isomers of *mer*-Ir(fppy)₂(ppy)**

¹H NMR (400 MHz, CDCl₃, δ): 8.30-8.11 (m, 3 H), 8.03-7.97 (m, 1 H), 7.96-7.72 (m, 5 H), 7.60 (d, *J* = 5.5 Hz, 1 H), 7.21 (t, *J* = 6.6 Hz, 1 H), 7.13-7.04 (m, 2 H), 7.02-6.85 (m, 2 H), 6.81-6.61 (m, 3 H), 5.88 (dd, *J* = 7.5, 2.4 Hz, 1 H), 5.67 (dd, *J* = 9.0, 2.3 Hz, 1 H). A chiral HPLC trace for the racemic mixture of *mer*-Ir(fppy)₂(ppy) is shown in FIG. 17 and a CD spectrum of a *mer*-Ir(fppy)₂(ppy) is shown in FIG. 18.

[00100] Example 6. The chiral metal complex PtN1N* was prepared according to the procedure described below:



R/S*- isomers of PtN1N

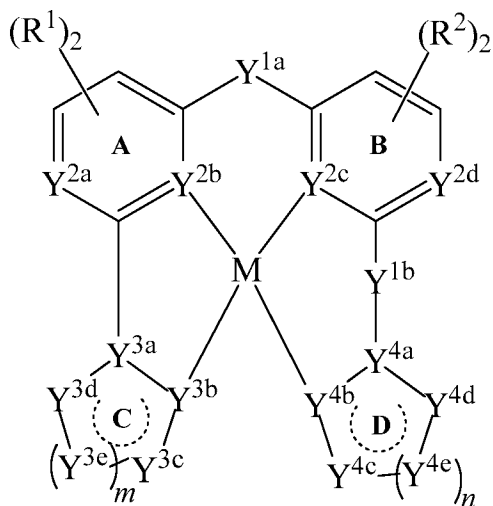
To a dry pressure tube equipped with a magnetic stir bar, ligand N1N* (3.0 mmol, 1.0 eq), K₂PtCl₄ (3.15 mmol, 1.05 eq), ⁿBu₄NBr (97 mg, 0.3 mmol, 0.1 eq) and acetic acid (180 mL) were added, in a nitrogen filled glove box. The mixture was bubbled with nitrogen for 30 min, sealed before being taken out of the glove box and stirred at room temperature for 20 h followed by three days at 105-115°C. The mixture was cooled to ambient temperature and water (180 mL) was added slowly. After stirring at room temperature for 10 min, the precipitate was filtered off and washed with water three times. Then the solid was dried in air under reduced pressure. The collected solid was purified via column chromatography on silica gel using dichloromethane as eluent to obtain the desired product PtN1N* as a yellow solid 872 mg in 44% yield. ¹H NMR for PtN1N* (2 isomers in approx. 1:1 ratio, not

assigned). 400 MHz, CDCl₃: δ 8.80 (d, $J = 4.3$ Hz, 1 H), 8.28 (d, $J = 8.6$ Hz, 1 H), 8.21-8.13 (m, 1 H), 8.10 (d, $J = 7.9$ Hz, 1 H), 8.07 (d, $J = 7.4$ Hz, 1 H), 7.98-7.90 (m, 2 H), 7.90-7.80 (m, 2 H), 7.49-7.31 (m, 4 H), 7.30-7.21 (m, 1 H, overlapped with solvent residual peak), 6.08 (s, 1 H), 3.15-3.02 (m, 1 H), 2.98-2.86 (m, 1 H), 2.85-2.57 (m, 5 H), 2.46 (s, 1.5 H), 2.43 (s, 1.5 H), 2.37-2.28 (m, 1 H), 1.45 (s, 1.5 H), 1.40 (d, $J = 9.4$ Hz, 0.5 H), 1.35 (s, 1.5 H), 1.06 (d, $J = 9.8$ Hz, 0.5 H), 0.87 (s, 1.5 H). A CD spectrum of a mixture of PtN1N* is shown in FIG. 19.

[00101] A number of embodiments of the invention have been described. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of the invention. Accordingly, other embodiments are within the scope of the following claims.

WHAT IS CLAIMED IS:

1. An organometallic complex of general formula (1),



(1)

wherein:

M is a metal ion;

each R^1 and R^2 is independently selected from hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C_1 - C_4 alkyl;

Y^{1a} , when present, is selected from the group consisting of a direct bond, O, S, NR^{3a} , BR^{3a} , $Si(R^{3b})_2$, or $C(R^{3c})_2$;

each R^{3a} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{3b} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{3c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

Y^{1b} , when present, is selected from the group consisting of a direct bond, O, S, NR^{4a} , BR^{4a} , $Si(R^{4b})_2$, and $C(R^{4c})_2$;

each R^{4a} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{4b} is independently selected from substituted or unsubstituted C_1 - C_4 alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

each Y^{2a} , Y^{2b} , Y^{2c} , and Y^{2d} is independently selected from the group consisting of O, S, N, NR^{5a} , BR^{5a} , C, and CR^{5b} ;

each R^{5a} and R^{5b} is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C_1 - C_4 alkyl;

each Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , and Y^{4e} is independently selected from the group consisting of N, O, S, NR^{6a} , BR^{6a} , CR^{6b} , and $Z(R^{6c})_2$;

Z is C or Si;

each R^{6a} and R^{6b} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

each R^{6c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

m is 1 or 2;

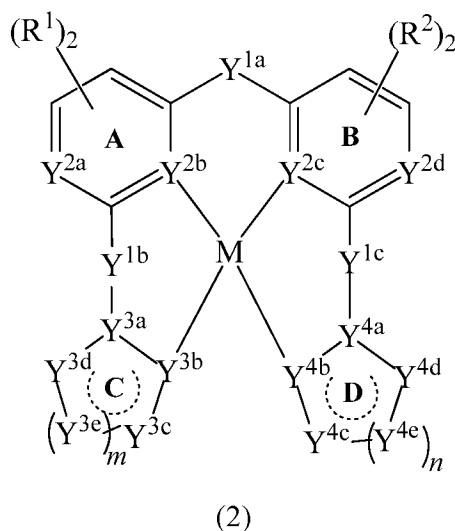
n is 1 or 2;

($_$) represents partial or full unsaturation of the ring with which it is associated; and

at least one of M, R^1 , R^2 , Y^{1a} , Y^{1b} , Y^{2a} , Y^{2b} , Y^{2c} , Y^{2d} , Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} and Y^{4e} is a chiral center or comprises one or more chiral centers.

2. The organometallic complex of claim 1, wherein each ring A, B, C, and D is independently selected from optionally substituted phenyl, optionally substituted pyridinyl, optionally substituted pyrazolyl, and optionally substituted imidazolyl.
3. The organometallic complex of claim 1, wherein each ring A, B, C, and D is independently selected from phenyl, difluorophenyl, pyridinyl, pyrazolyl, dimethylpyrazolyl, and methylimidazolyl.
4. The organometallic complex of claim 1, wherein one or more of rings A, B, C, and D is fused to one or two independently selected C_{6-10} aryl or 4-10 membered heterocycloalkyl groups.

5. An organometallic complex of general formula (2),



wherein:

M is a metal ion;

each R^1 and R^2 is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C₁-C₄ alkyl;

Y^{1a} , when present, is selected from the group consisting of a direct bond, O, S, NR^{3a} , BR^{3a} , $Si(R^{3b})_2$, and $C(R^{3c})_2$,

each R^{3a} is independently selected from substituted or unsubstituted C₁-C₄ alkyl;

each R^{3b} is independently selected from substituted or unsubstituted C₁-C₄ alkyl;

each R^{3c} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

Y^{1b} , when present, is selected from the group consisting of a direct bond, O, S, NR^{4a} , BR^{4a} , $Si(R^{4b})_2$, and $C(R^{4c})_2$;

each R^{4a} is independently selected from substituted or unsubstituted C₁-C₄ alkyl;

each R^{4b} is independently selected from substituted or unsubstituted C₁-C₄ alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

Y^{1c} , when present, is selected from the group consisting of a direct bond, O, S, NR^{5a} , BR^{5a} , $Si(R^{5b})_2$, and $C(R^{5c})_2$;

each R^{5a} is independently selected from substituted or unsubstituted C₁-C₄ alkyl;

each R^{5b} is independently selected from substituted or unsubstituted C₁-C₄ alkyl;

each R^{5c} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

each Y^{2a} , Y^{2b} , Y^{2c} , and Y^{2d} is independently selected from the group consisting of O, S, N, NR^{6a} , BR^{6a} , and CR^{6b} ;

each R^{6a} and R^{6b} is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C_1 - C_4 alkyl;

each Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , and Y^{4e} is independently selected from the group consisting of N, O, S, NR^{7a} , BR^{7a} , CR^{7b} , and $Z(R^{7c})_2$;

Z is C or Si;

each R^{7a} and R^{7b} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

each R^{7c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

m is 1 or 2;

n is 1 or 2;

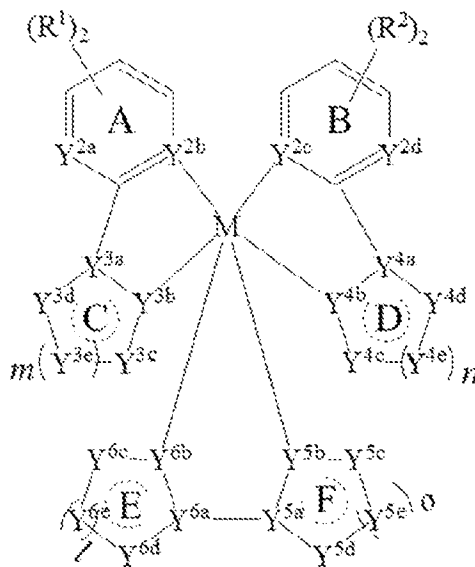
$\text{\textcircled{~}}\text{\textcircled{~}}$ represents partial or full unsaturation of the ring with which it is associated; and at least one of M, R^1 , R^2 , Y^{1a} , Y^{1b} , Y^{1c} , Y^{2a} , Y^{2b} , Y^{2c} , Y^{2d} , Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , and Y^{4e} is a chiral center or comprises one or more chiral centers.

6. The organometallic complex of claim 5, wherein each ring A, B, C, and D is independently selected from optionally substituted phenyl, optionally substituted pyridinyl, optionally substituted pyrazolyl, and optionally substituted imidazolyl.

7. The organometallic complex of claim 5, wherein each ring A, B, C, and D is independently selected from phenyl, difluorophenyl, pyridinyl, pyrazolyl, dimethylpyrazolyl, and methylimidazolyl.

8. The organometallic complex of claim 5, wherein at least one of rings A, B, C, and D is fused to one or two independently selected C_{6-10} aryl or 4-10 membered heterocycloalkyl groups.

9. An organometallic complex of general formula (3),



(3)

wherein:

M is a metal ion;

each R^1 and R^2 is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C_1 - C_4 alkyl;

each Y^{2a} , Y^{2b} , Y^{2c} , and Y^{2d} is independently selected from the group consisting of O, S, N, NR^{3a} , BR^{3a} , and CR^{3b} ;

each R^{3a} and R^{3b} is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C_1 - C_4 alkyl;

each Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , and Y^{4e} is independently selected from the group consisting of N, O, S, NR^{4a} , BR^{4a} , CR^{4b} , and $Z(R^{4c})_2$;

Z is C or Si;

each R^{4a} and R^{4b} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

m is 1 or 2;

n is 1 or 2;

l is 1 or 2;

o is 1 or 2;

--- represents partial or full unsaturation of the ring with which it is associated;

each Y^{5a} , Y^{5b} , Y^{5c} , Y^{5d} , Y^{5e} , Y^{6a} , Y^{6b} , Y^{6c} , Y^{6d} , and Y^{6e} is independently selected from the group consisting of N, O, S, NR^{6a} , and CR^{6b} ; and

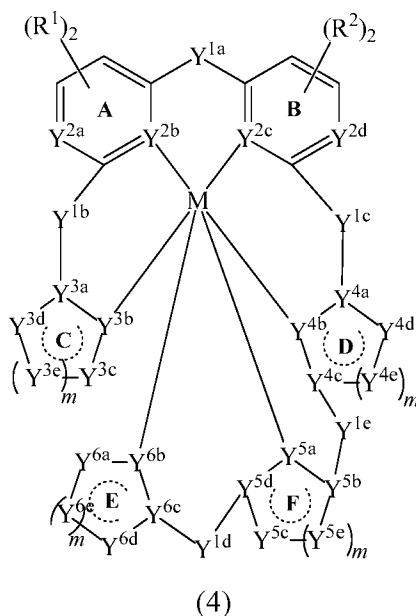
at least one of M, R^1 , R^2 , Y^{2a} , Y^{2b} , Y^{2c} , Y^{2d} , Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , Y^{4e} , Y^{5a} , Y^{5b} , Y^{5c} , Y^{5d} , Y^{5e} , Y^{6a} , Y^{6b} , Y^{6c} , Y^{6d} , and Y^{6e} is a chiral center or comprises one or more chiral centers.

10. The organometallic complex of claim 9, wherein each ring A, B, C, D, E, and F is independently selected from optionally substituted phenyl, optionally substituted pyridinyl, and optionally substituted pyrazolyl.

11. The organometallic complex of claim 9, wherein each ring A, B, C, D, E, and F is independently selected from phenyl, difluorophenyl, pyridinyl, and dimethylpyrazolyl.

12. The organometallic complex of claim 9, wherein at least one of rings A, B, C, D, E, and F is fused to one or two independently selected C_{6-10} aryl or 4-10 membered heterocycloalkyl groups.

13. An organometallic complex of general formula (4),



wherein:

M is a metal ion;

each R^1 and R^2 is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C_1 - C_4 alkyl;

Y^{1a} is selected from the group consisting of O, S, NR^{4a} , BR^{4a} , $Si(R^{4b})_2$, and $C(R^{4c})_2$,

R^{4a} is substituted or unsubstituted C₁-C₄ alkyl;

each R^{4b} is independently selected from substituted or unsubstituted C₁-C₄ alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

Y^{1b} is selected from the group consisting of O, S, NR^{5a} , BR^{5a} , $Si(R^{5b})_2$, and $C(R^{5c})_2$,

R^{5a} is substituted or unsubstituted C₁-C₄ alkyl;

each R^{5b} is independently selected from substituted and unsubstituted C₁-C₄ alkyl;

each R^{5c} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

Y^{1c} is selected from the group consisting of O, S, NR^{4a} , BR^{4a} , $Si(R^{4b})_2$, and $C(R^{4c})_2$;

R^{4a} is substituted or unsubstituted C₁-C₄ alkyl;

each R^{4b} is independently selected from substituted and unsubstituted C₁-C₄ alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

Y^{1d} is selected from the group consisting of O, S, NR^{4a} , BR^{4a} , $Si(R^{4b})_2$, and $C(R^{4c})_2$,

R^{4a} is substituted or unsubstituted C₁-C₄ alkyl;

each R^{4b} is independently selected from substituted and unsubstituted C₁-C₄ alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

Y^{1e} , when present, is selected from the group consisting of a direct bond, O, S, NR^{4a} , BR^{4a} , $Si(R^{4b})_2$, and $C(R^{4c})_2$;

R^{4a} is substituted or unsubstituted C₁-C₄ alkyl;

each R^{4b} is independently selected from substituted and unsubstituted C₁-C₄ alkyl;

each R^{4c} is independently selected from hydrogen and substituted or unsubstituted C₁-C₄ alkyl;

each Y^{2a} , Y^{2b} , Y^{2c} , and Y^{2d} is independently selected from the group consisting of O, S, N, NR^{6a} , BR^{6a} , and CR^{6b} ;

each R^{6a} and R^{6b} is independently selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, thiol, and substituted or unsubstituted C₁-C₄ alkyl;

each Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , and Y^{4e} is independently selected from the group consisting of N, O, S, NR^{6a} , BR^{6a} , CR^{6b} , and $Z(R^{6c})_2$;

Z is C or Si;

each R^{6a} and R^{6b} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

each R^{6c} is independently selected from hydrogen and substituted or unsubstituted C_1 - C_4 alkyl;

each m is independently 1 or 2;

--- represents partial or full unsaturation of the ring with which it is associated;

each Y^{5a} , Y^{5b} , Y^{5c} , Y^{5d} , Y^{5e} , Y^{6a} , Y^{6b} , Y^{6c} , Y^{6d} , and Y^{6e} is independently selected from the group consisting of N, O, S, NR^{6a} , and CR^{6b} ; and

at least one of M, R^1 , R^2 , Y^{1a} , Y^{1b} , Y^{1c} , Y^{1d} , Y^{1e} , Y^{2a} , Y^{2b} , Y^{2c} , Y^{2d} , Y^{3a} , Y^{3b} , Y^{3c} , Y^{3d} , Y^{3e} , Y^{4a} , Y^{4b} , Y^{4c} , Y^{4d} , Y^{4e} , Y^{5a} , Y^{5b} , Y^{5c} , Y^{5d} , Y^{5e} , Y^{6a} , Y^{6b} , Y^{6c} , Y^{6d} , and Y^{6e} is a chiral center or comprises one or more chiral centers.

14. The organometallic complex of claim 13, wherein each ring A, B, C, D, E, and F is independently selected from optionally substituted phenyl, optionally substituted pyridinyl, and optionally substituted pyrazolyl.

15. The organometallic complex of claim 13, wherein each ring A, B, C, D, E, and F is independently selected from phenyl, difluorophenyl, pyridinyl, and dimethylpyrazolyl.

16. The organometallic complex of claim 13, wherein at least one of rings A, B, C, D, E, and F is fused to one or two independently selected C_{6-10} aryl or 4-10 membered heterocycloalkyl groups.

17. The organometallic complex of any one of claims 1 to 16, wherein M is selected from the group consisting of Pt^{2+} , Pd^{2+} , Ir^+ , Rh^+ , Au^{3+} , Ir^{3+} , Rh^{3+} , Ru^{2+} , Pt^{4+} , and Os^{2+} .

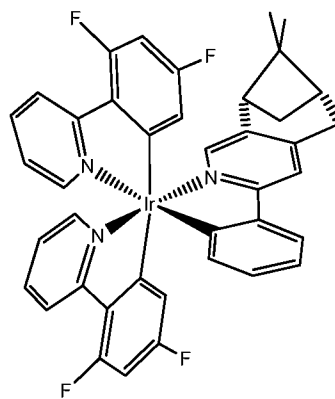
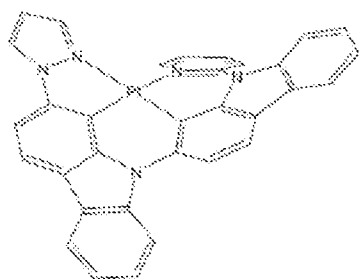
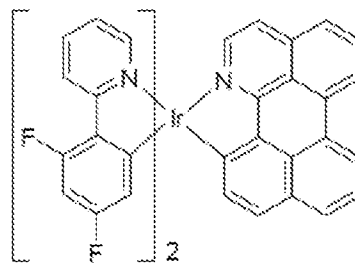
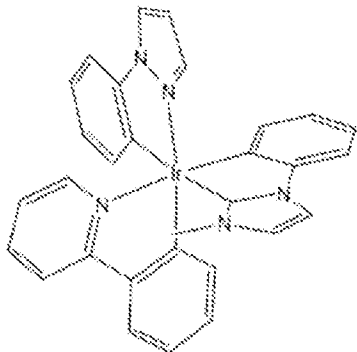
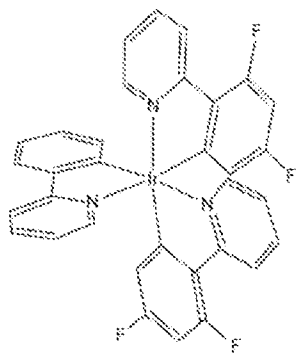
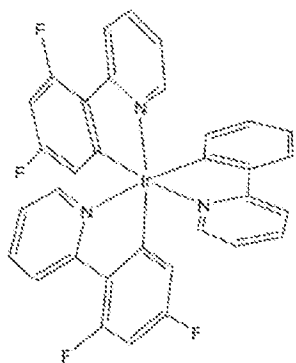
18. A light emitting device, comprising the organometallic complex of any one of claims 1 to 17.

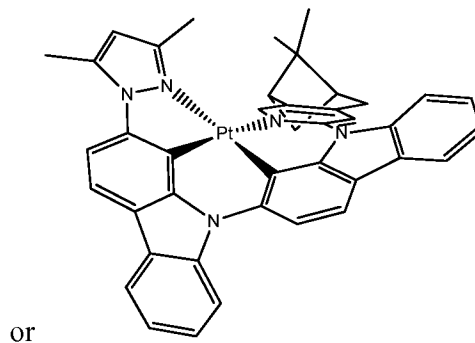
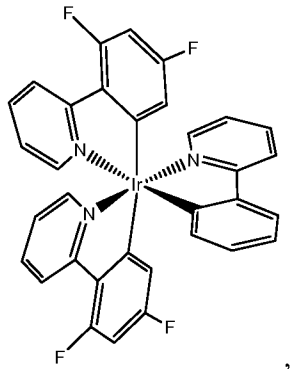
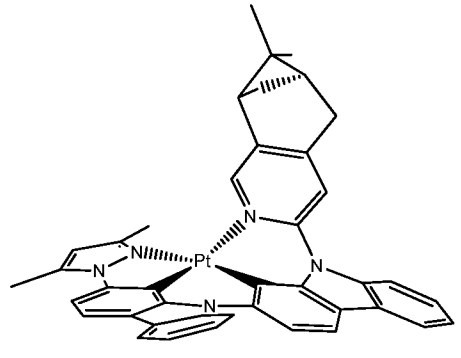
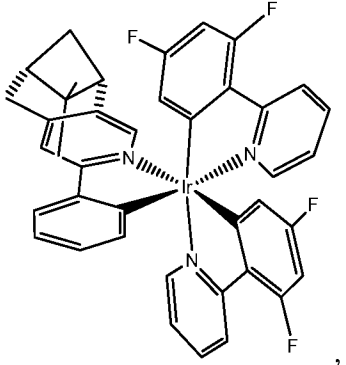
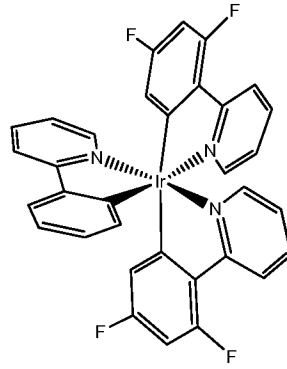
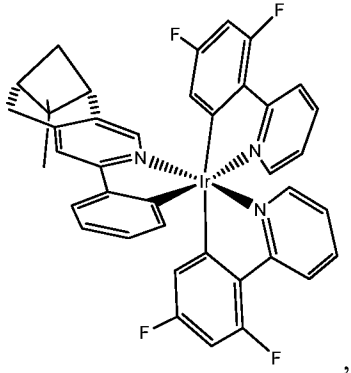
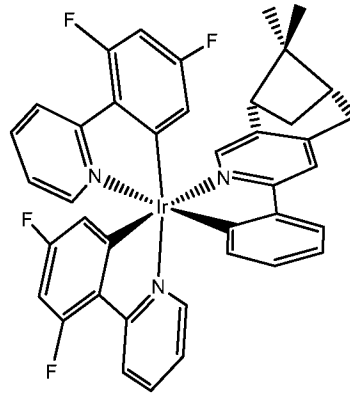
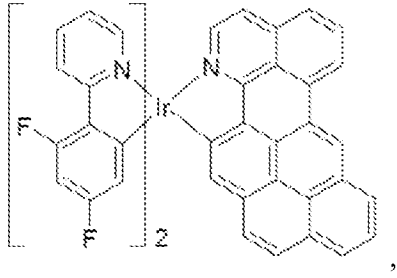
19. The light emitting device of claim 18, wherein two or more of the organometallic complexes are present in the emissive materials layer of said light emitting device.

20. The light emitting device of claim 19, wherein greater than 50, 60, 70, 80, 90, 95, or 99 wt% or mol% of the emissive material in the emissive materials layer is a selected single enantiomer or a selected single diastereomer of said organometallic complex.

21. A composition comprising one or more of the organometallic complexes of any one of claims 1 to 17.

22. An organometallic complex having one of the following structures:





or

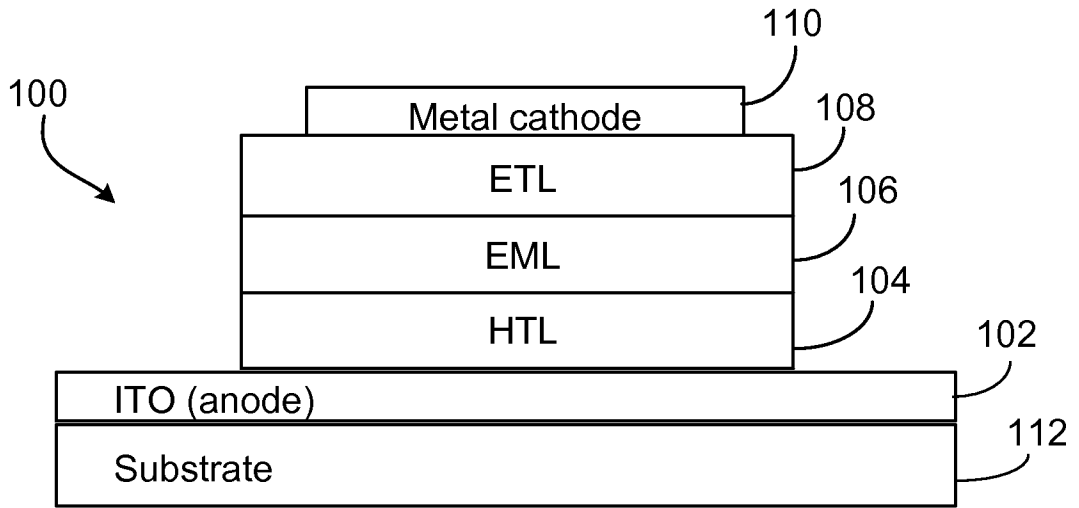


FIG. 1

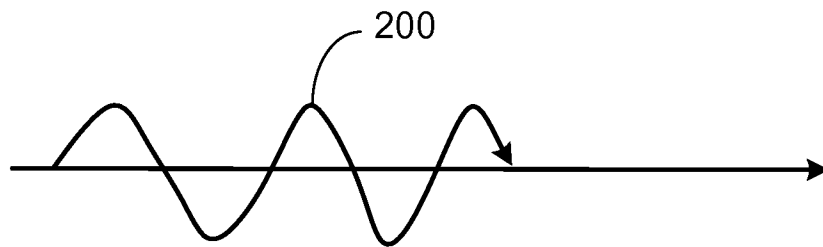


FIG. 2A

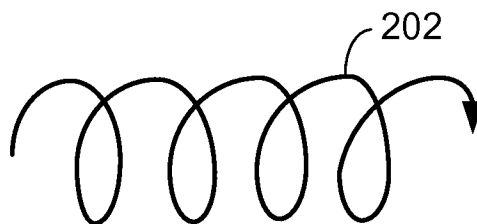
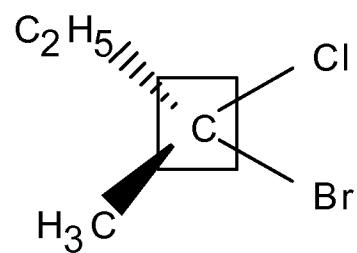
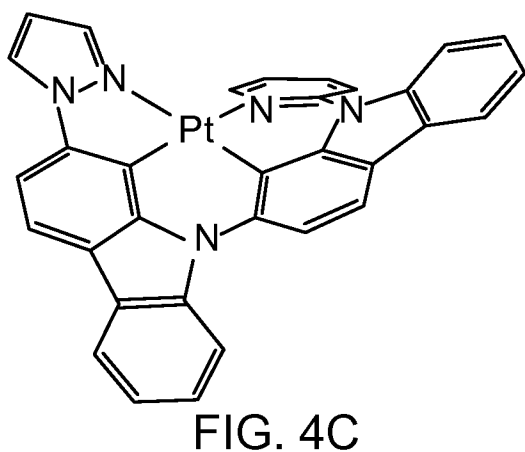
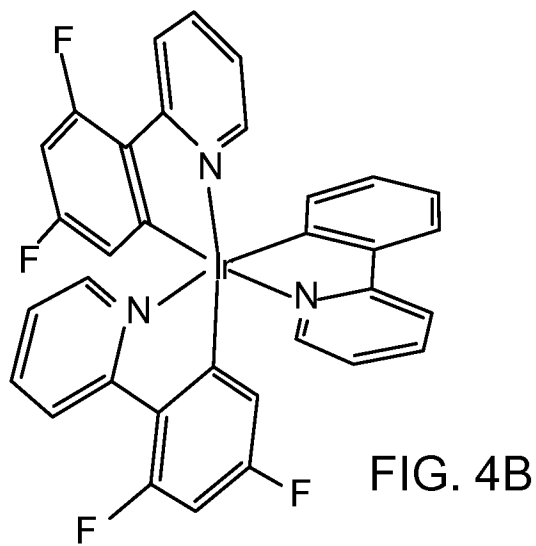
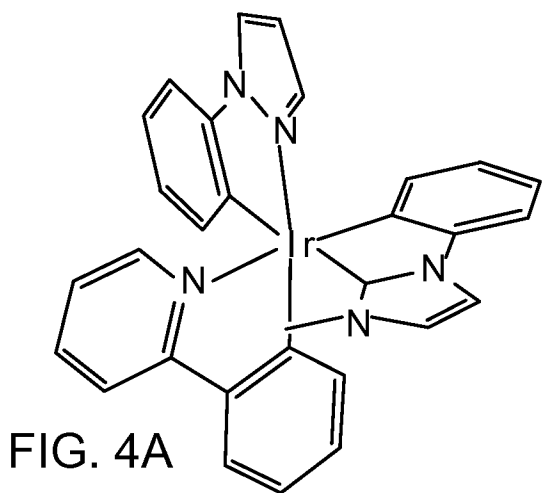
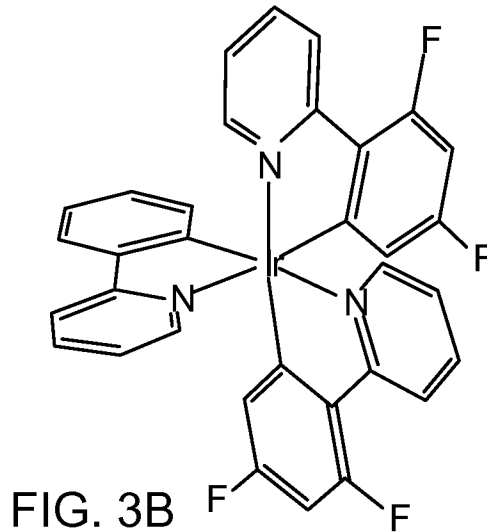
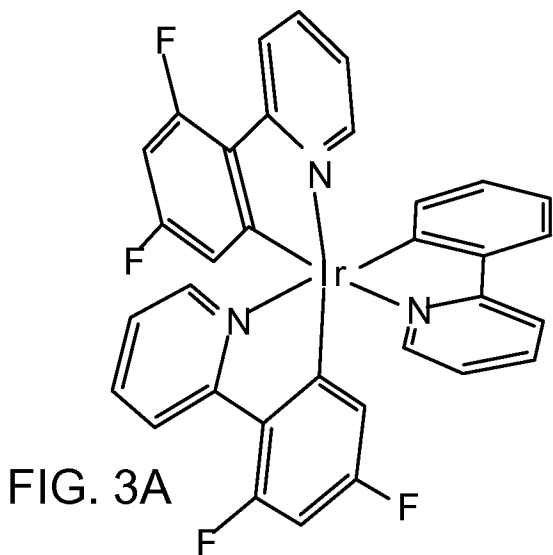


FIG. 2B



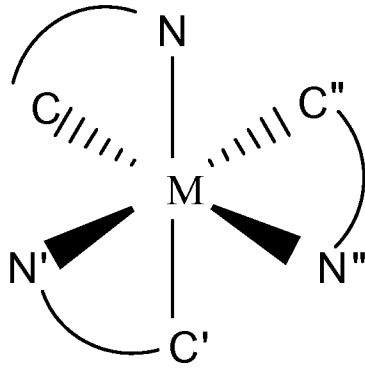


FIG. 5A

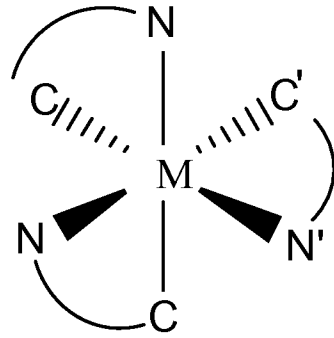


FIG. 5B

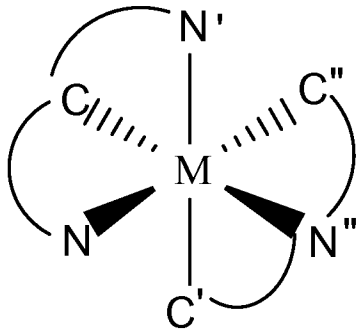


FIG. 5C

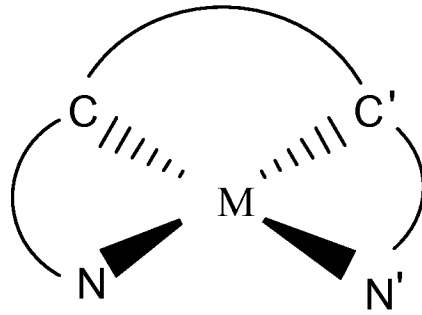
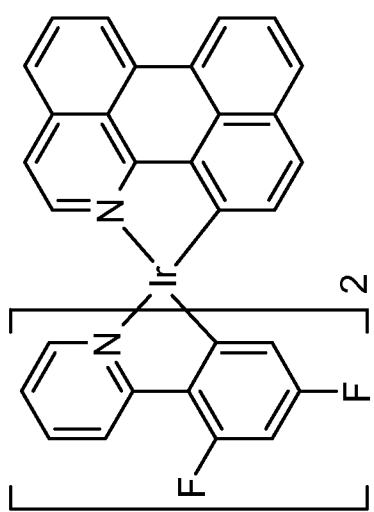
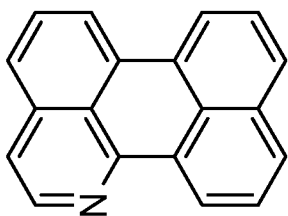


FIG. 5D



AgOTf, Et₃N
DCE, reflux
35% yield



+

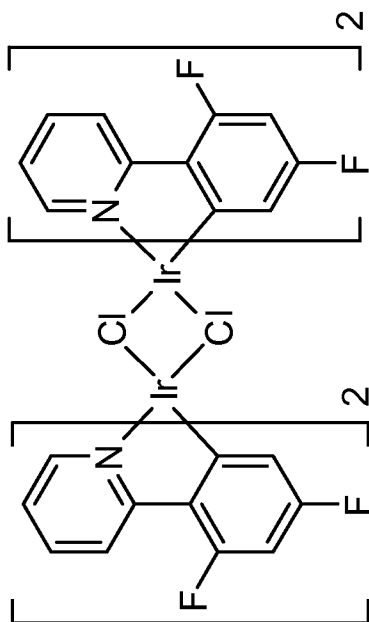
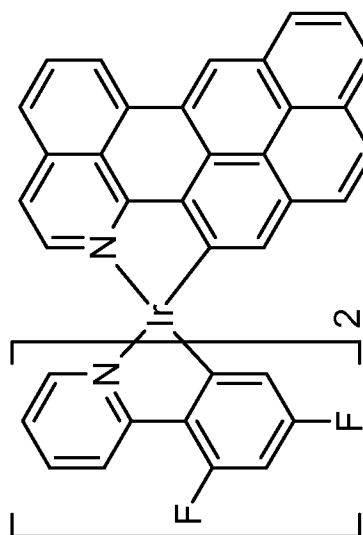
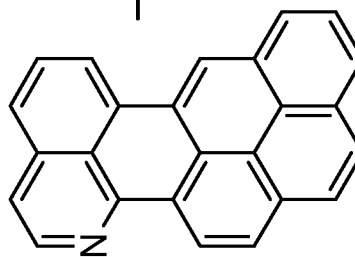


FIG. 6

[(dfppy)₂Ir(μ-Cl)]₂



AgOTf, Et₃N
DCE, reflux
20% yield



+

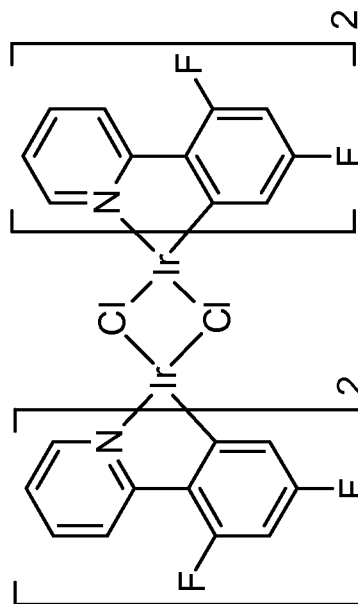


FIG. 7

[(dfppy)₂Ir(μ-Cl)]₂

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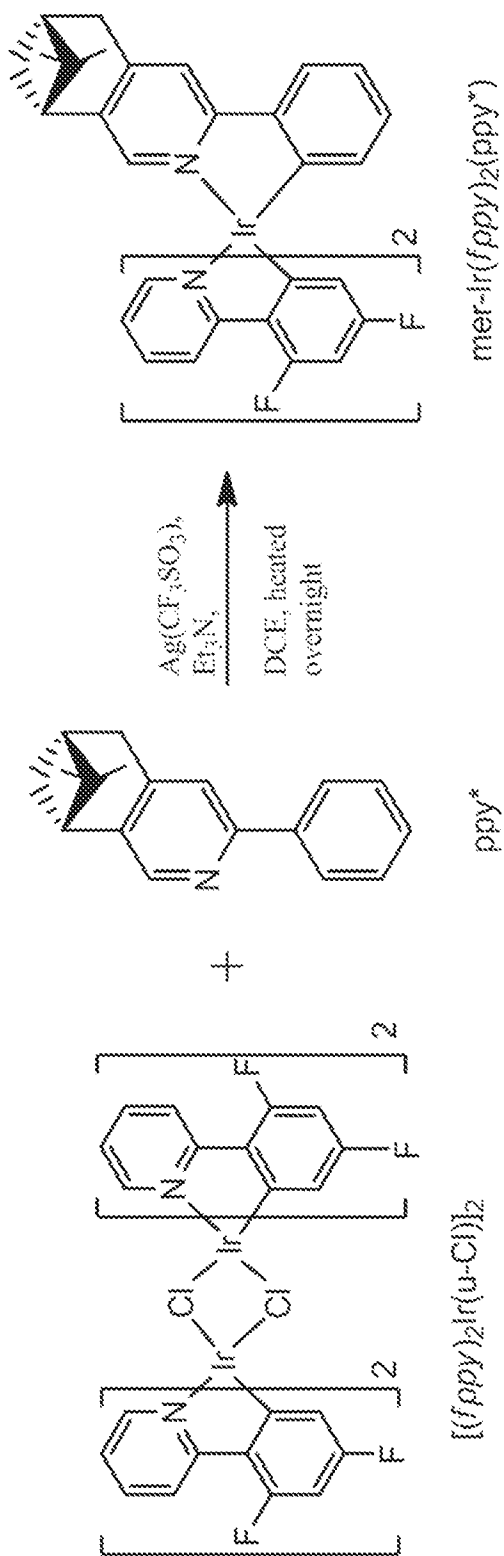


FIG. 8

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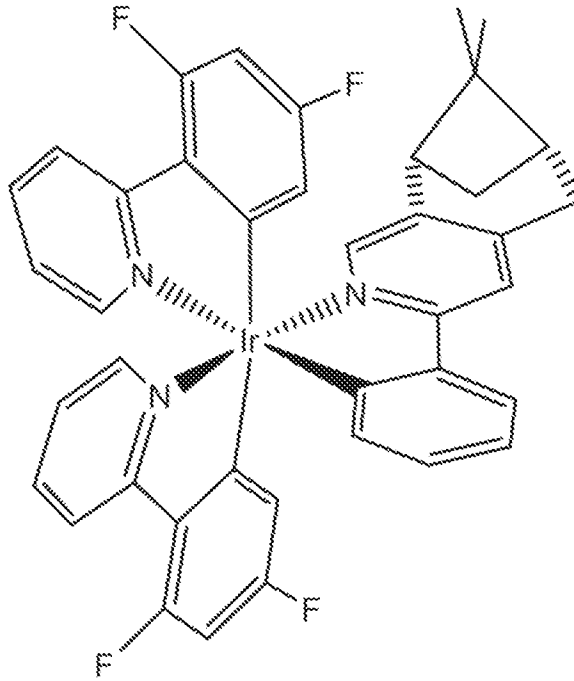


FIG. 9A

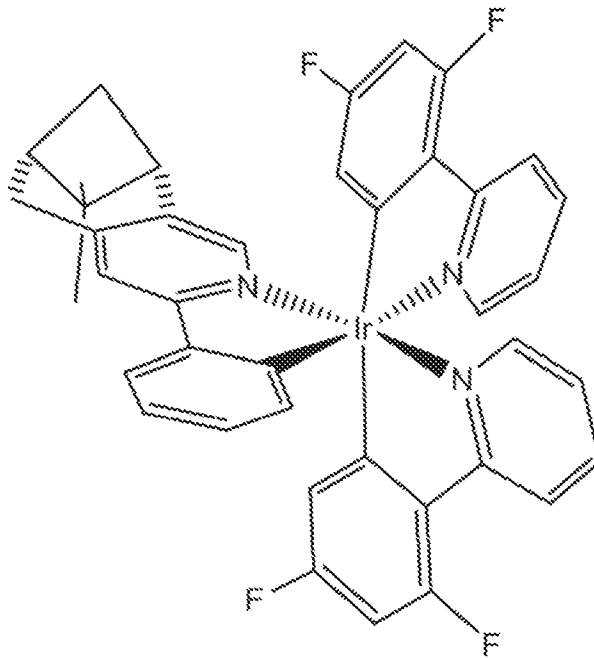


FIG. 9B

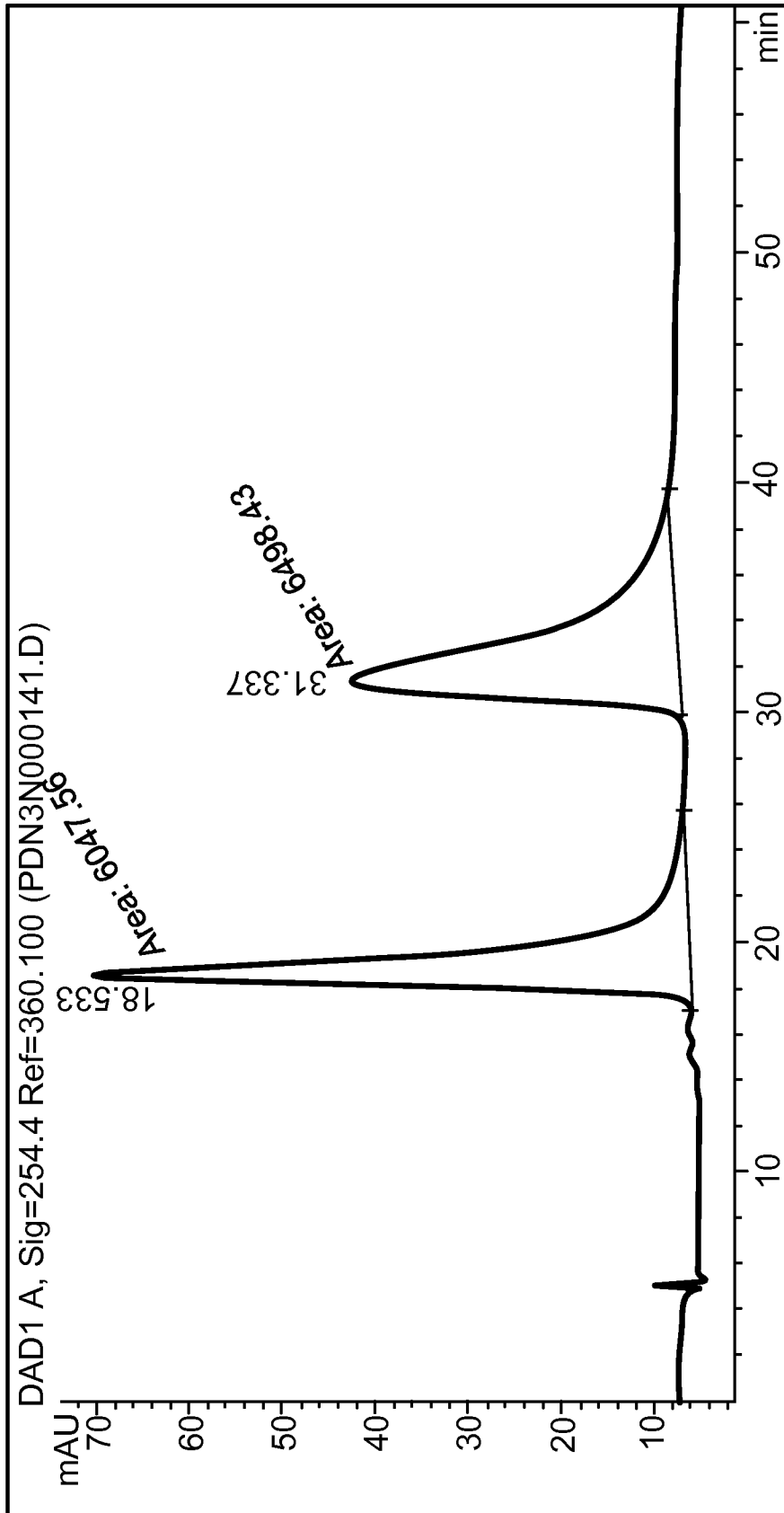


FIG. 10

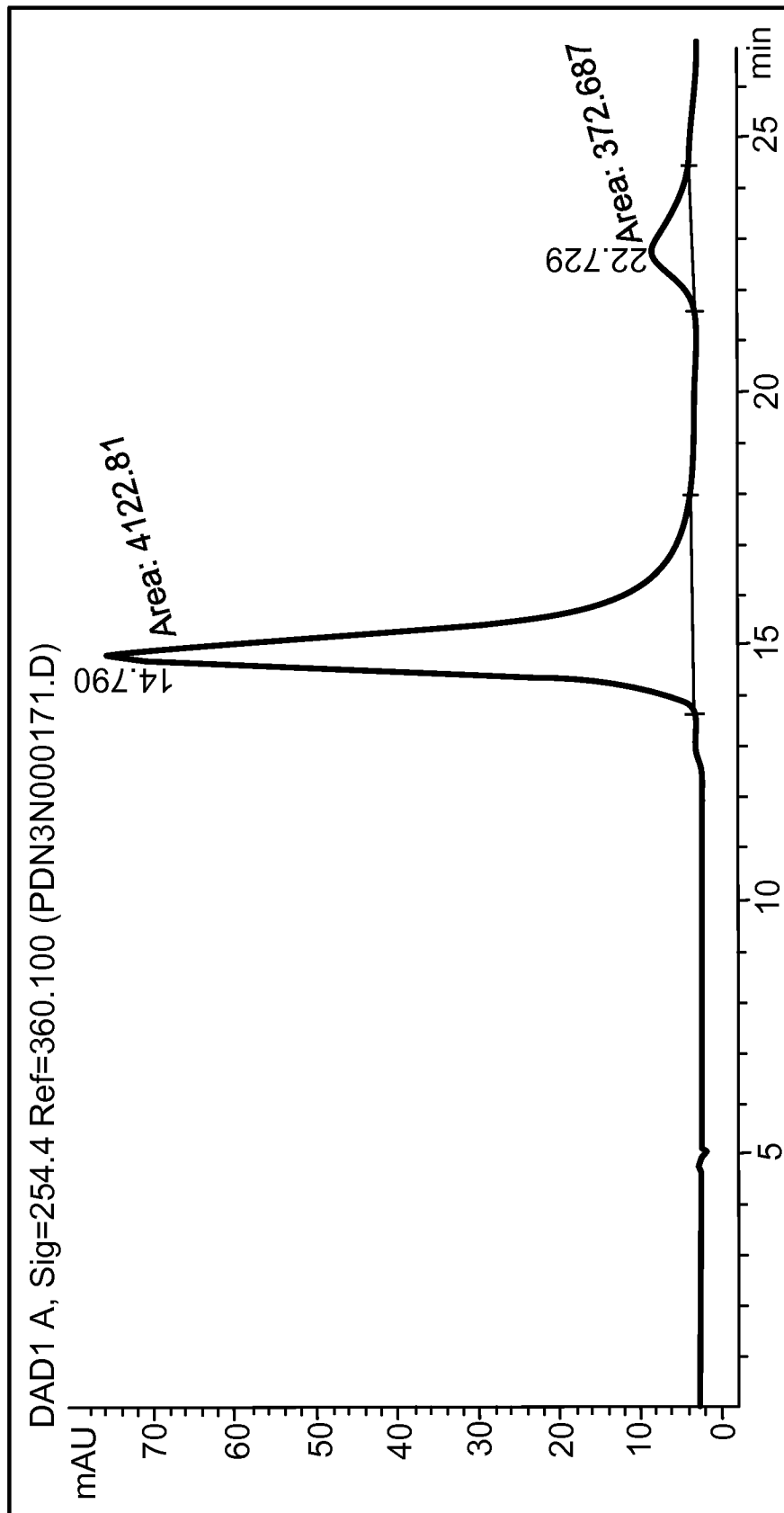


FIG. 11A

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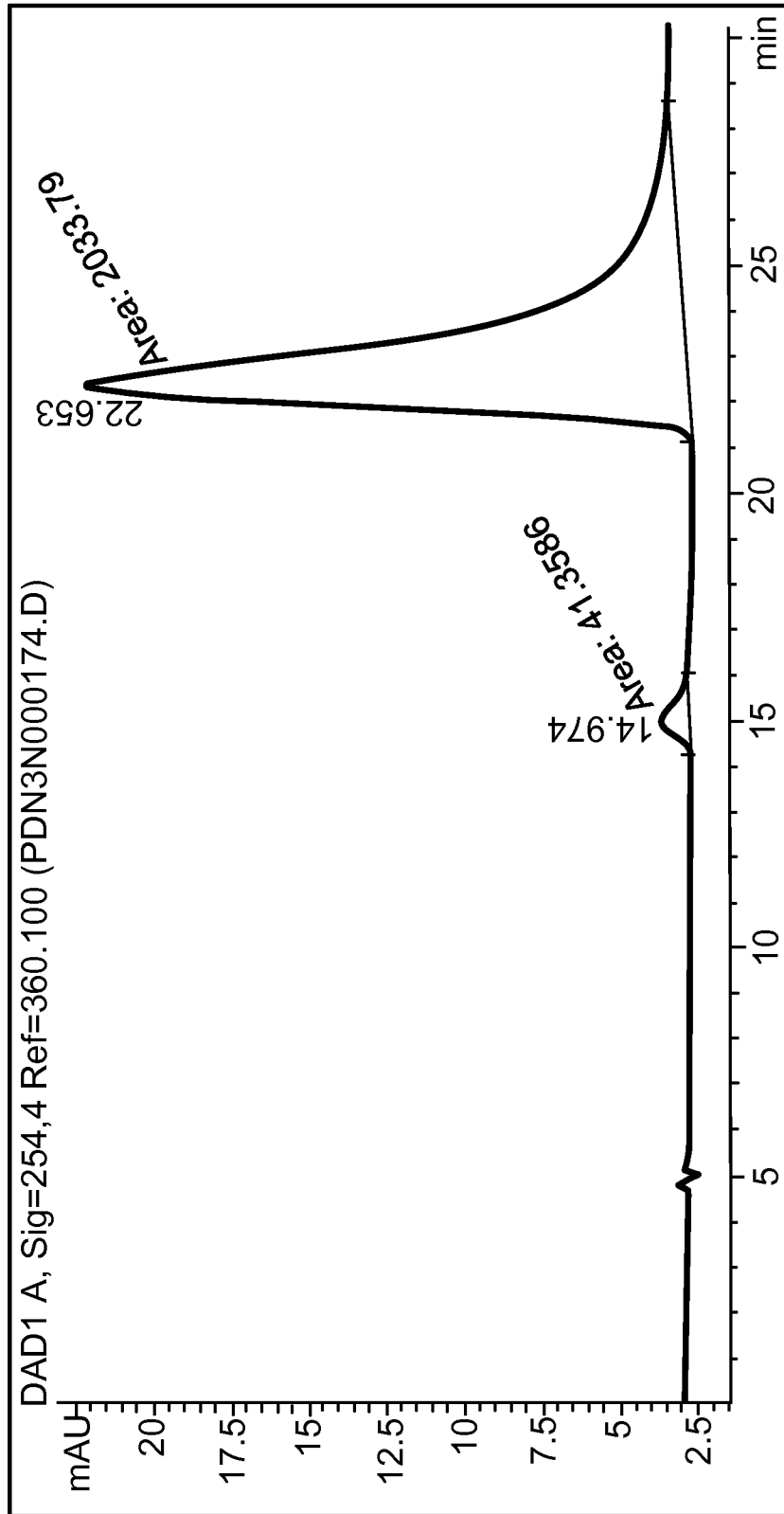


FIG. 11B

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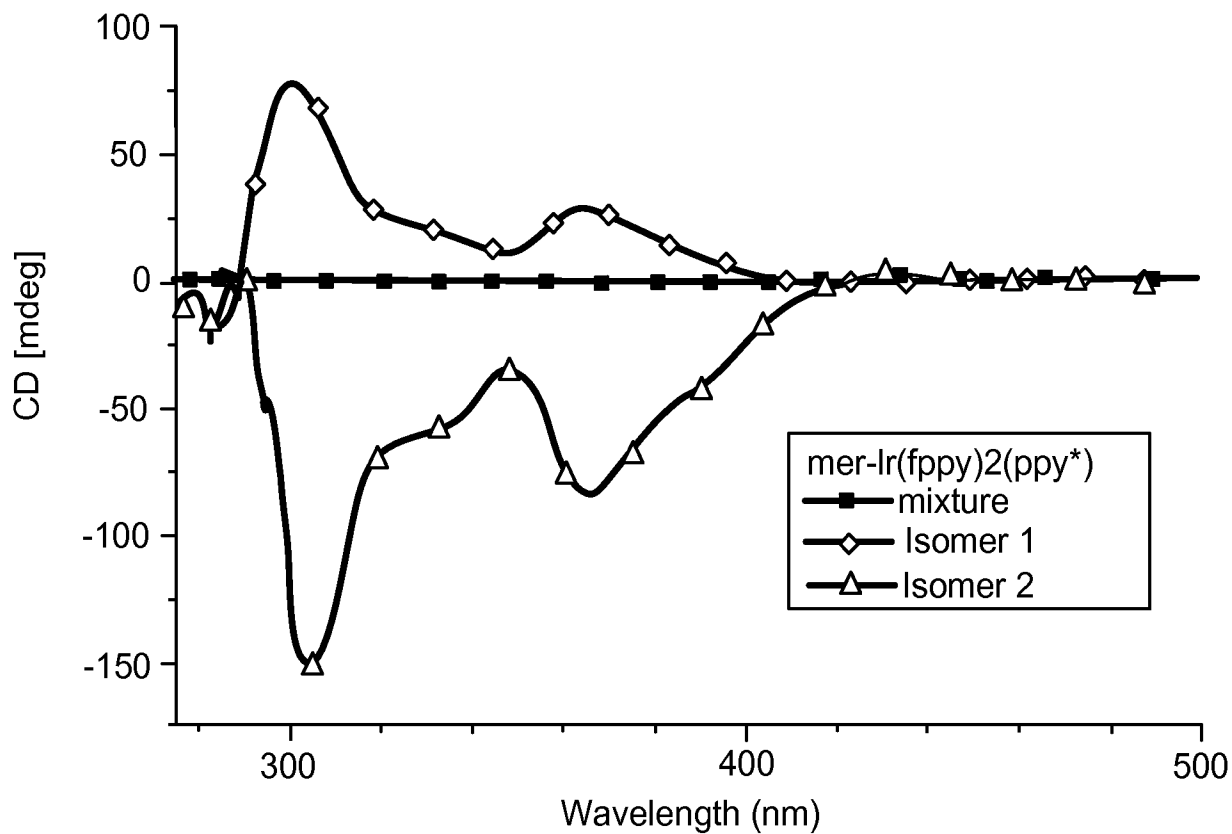


FIG. 12

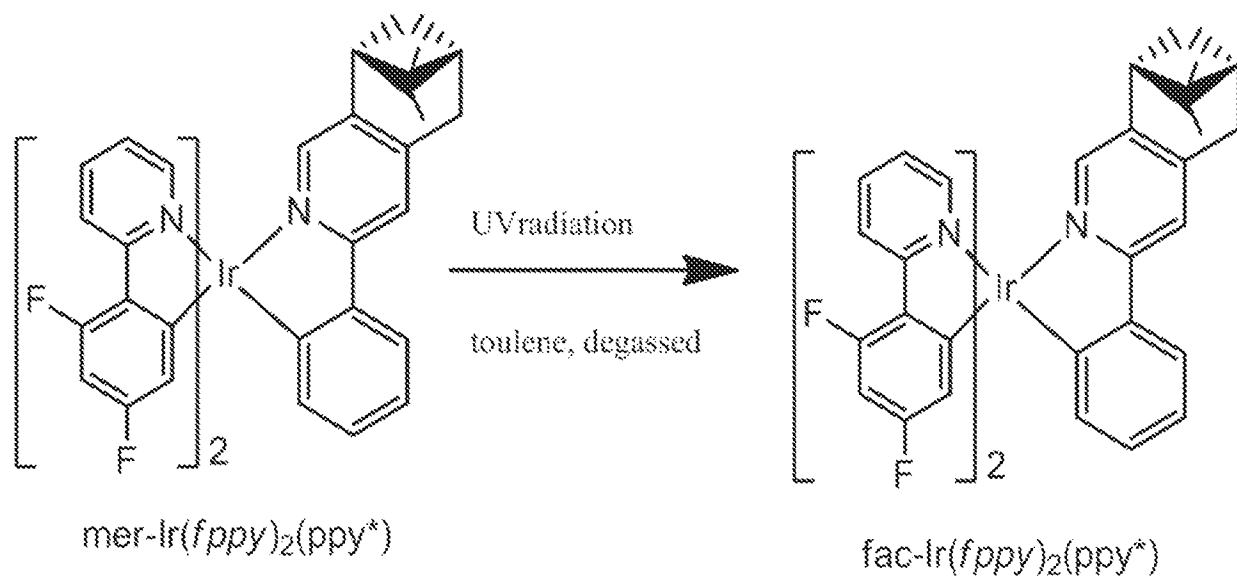


FIG. 13

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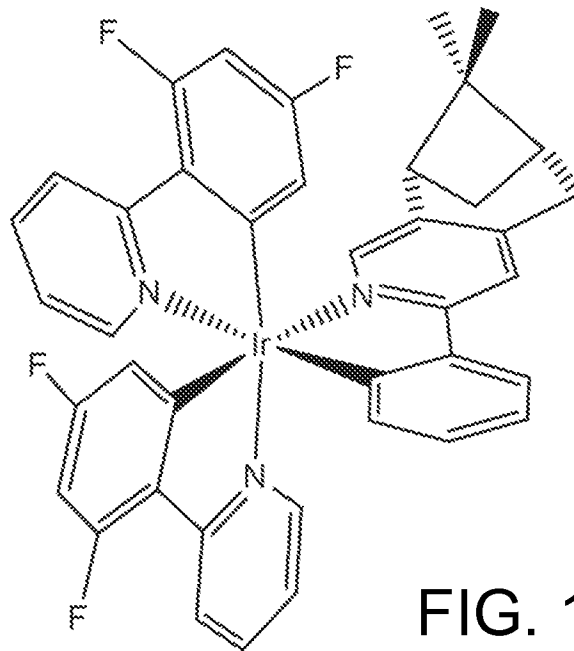


FIG. 14A

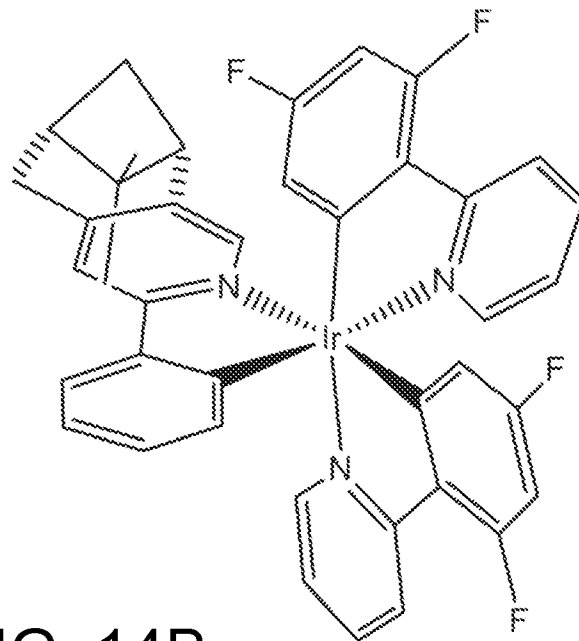


FIG. 14B

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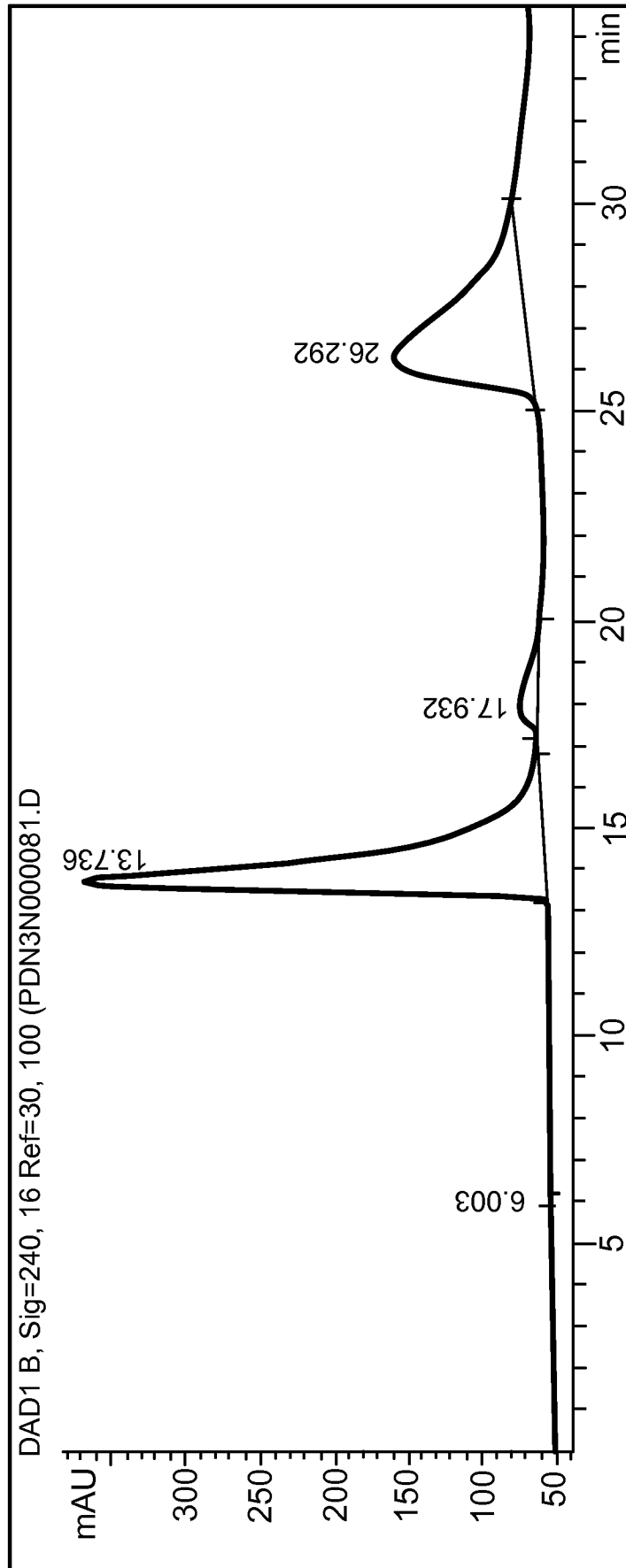


FIG. 15

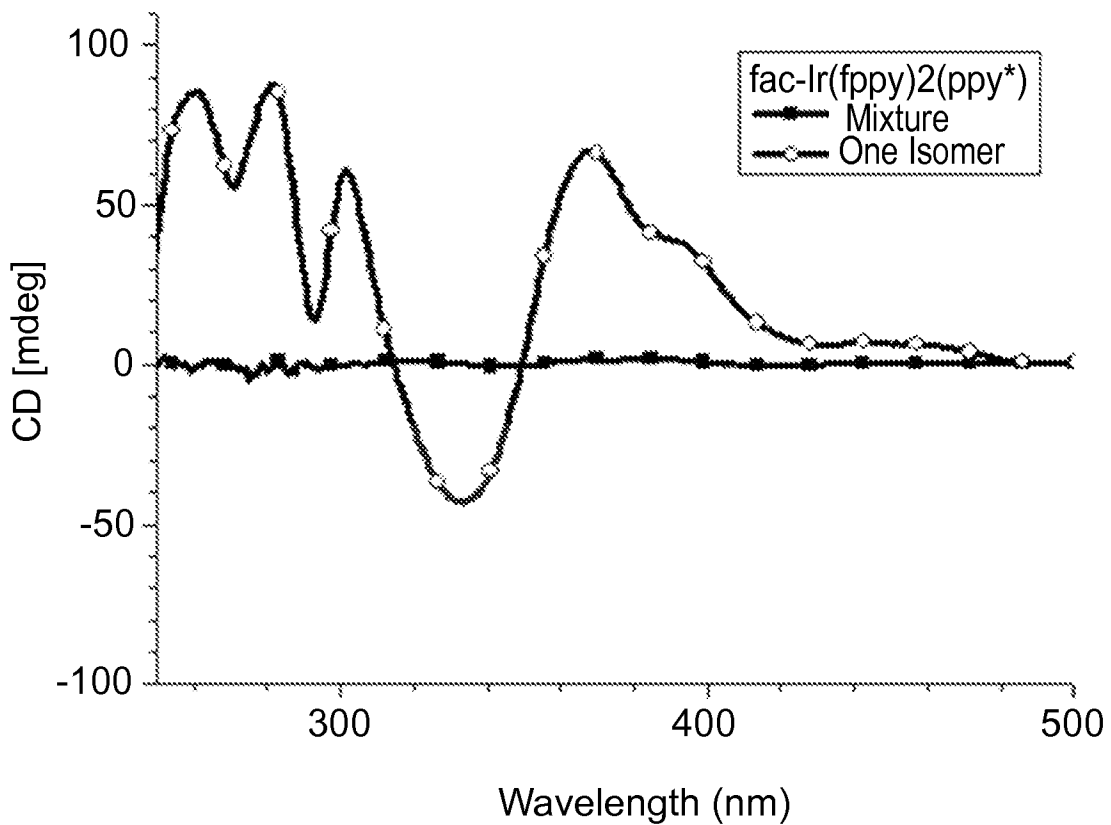


FIG. 16

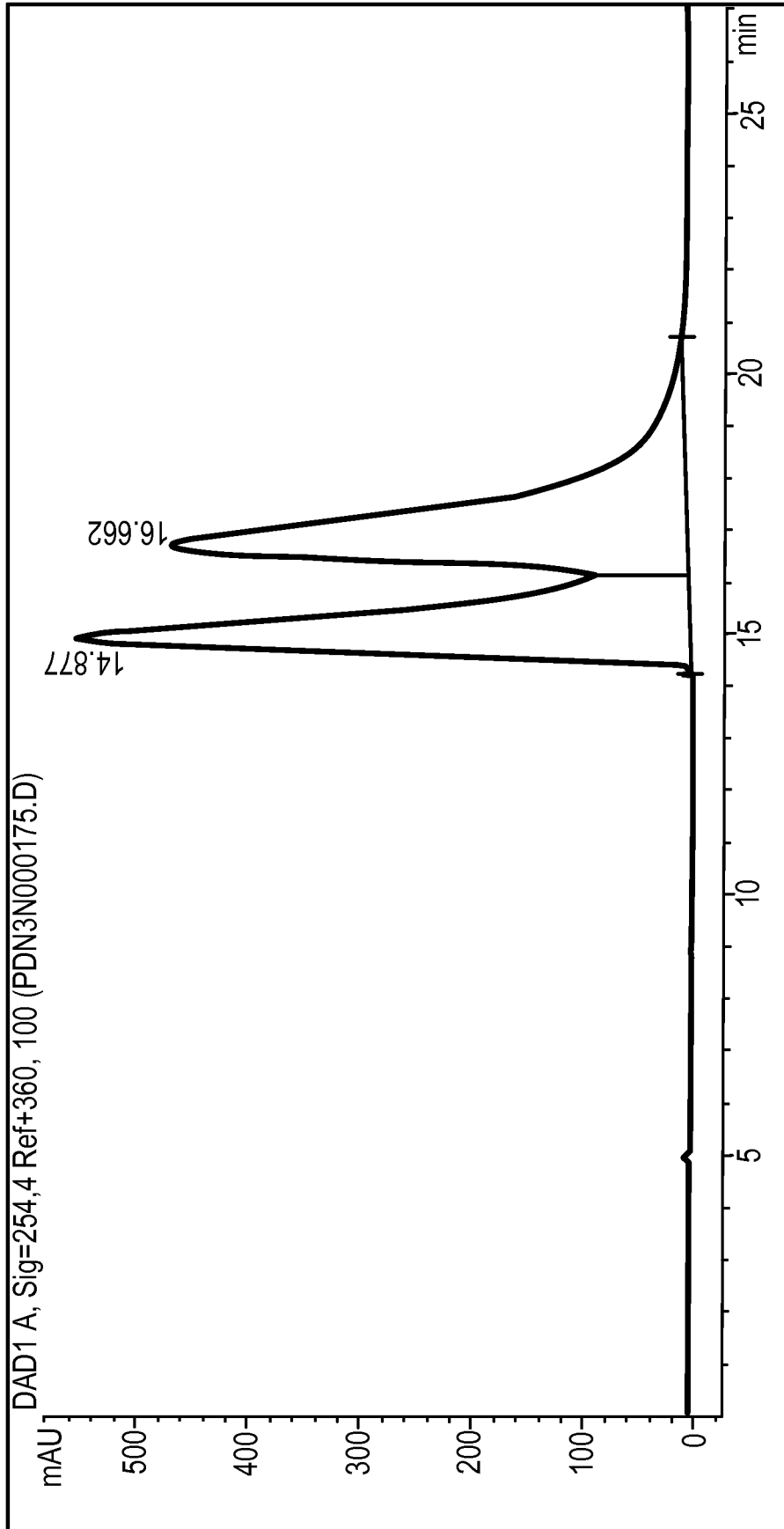


FIG. 17

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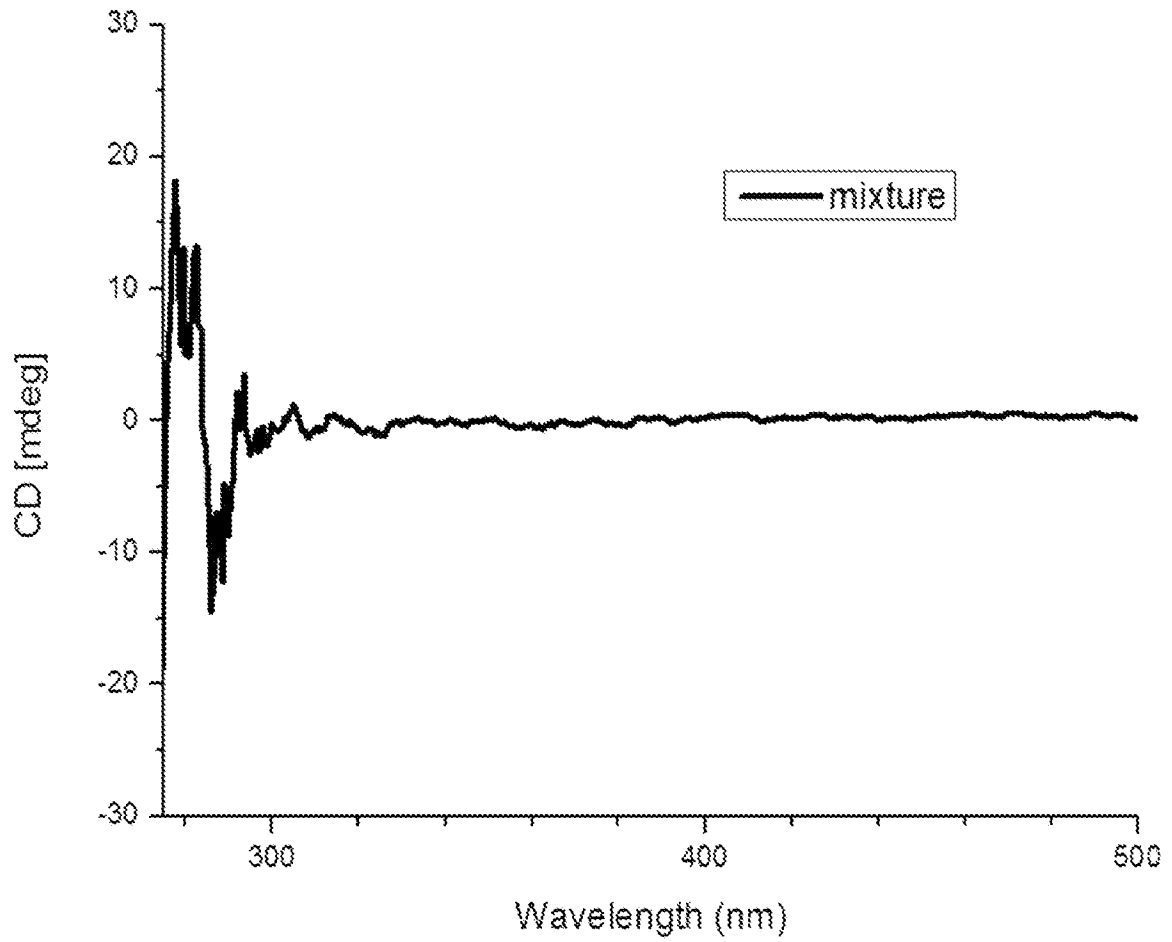


FIG. 18

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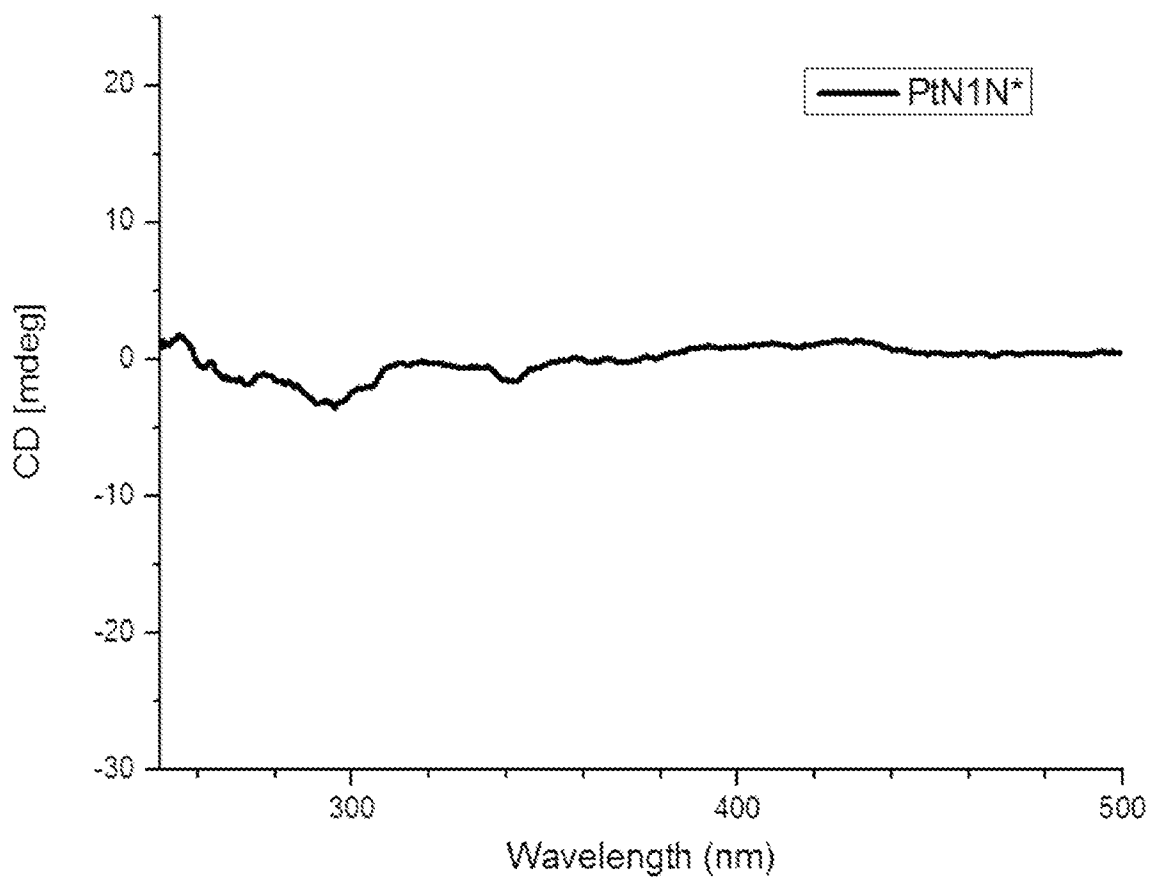


FIG. 19

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/018195**A. CLASSIFICATION OF SUBJECT MATTER**

C07F 15/00(2006.01)i, C09K 11/06(2006.01)i, H01L 51/50(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07F 15/00; C09K 11/06; H01L 51/54; C09K 11/06; H01L 51/50; C09K 11/06; H01L 51/50; C09K 11/06; H01L 51/50; C09K 11/06; H01L 51/54; C07D 471/14; H01L 51/00

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

Korean utility models and applications for utility models
Japanese utility models and applications for utility modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: chiral metal complex, iridium complex, OLED, bridged, cyclometalated**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012-0181528 A1 (TAKADA SAKI et al.) 19 July 2012 See abstract; pages 13 ~ 36 (e.g. compounds d1, e1, g1 and h1); and claims.	1-3,5-7,17
A		4,8
X	JP 2007-324309 A (FUJIFILM CORP) 13 December 2007 See paragraphs [0078] ~ [0083] (compounds 57 and 64); and claims.	1-3,5-7,17
A		4,8
X	JP 2007-053132 A (FUJIFILM CORP) 01 March 2007 See paragraphs [0039] ~ [0047] (compounds 1, 6 and 21); and claims.	1-3,5-7,17
A		4,8
X	JP 2010-135689 A (FUJIFILM CORP) 17 June 2010 See compound 57; and claims.	1,4-5,8,17
A		2-3,6-7
X	AYAN MAITY et al., 'Room-temperature synthesis of cyclometalated iridium(III) complexes: kinetic isomers and reactive functionalities', Chem. Sci., Vol.4, pp.1175-1181 (2013) See abstract; scheme1; and table 3.	9-12,17,22

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

14 May 2015 (14.05.2015)

Date of mailing of the international search report

14 May 2015 (14.05.2015)

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2015/018195

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SHIRO KOSEKI et al., `Spin-orbit coupling analyses of the geometrical effects on phosphorescence in Ir(ppy) ₃ and its derivatives`, J. Phys. Chem. C, Vol.117, pp.5314-5327 (2013) See abstract; and figure 1.	9-11,17,22
A		12
X	JI HYUN SEO et al., `Efficient blue-green organic light-emitting diodes based on heteroleptic tris-cyclometalated iridium(III) complexes`, Thin Solid Films, Vol.517, pp.1807-1810 (2009) See abstract; and Fig.1.	9-11,17,22
A		12
X	WO 2012-142387 A1 (ARIZONA BOARD OF REGENTS ACTING FOR AND ON BEHALF OF ARIZONA STATE UNIVERSITY) 18 October 2012 See abstract; paragraph [0054]; and claims.	13-17
A	US 2006-0286406 A1 (TATSUYA IGARASHI et al.) 21 December 2006 See abstract; and claims.	1-17,22
A	EP 2036907 A1 (FUJIFILM CORPORATION) 18 March 2009 See paragraph [0039]; and claims.	1-17,22

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/018195

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: 19-20
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 19 and 20 are unclear under PCT Article 6, because they refer to any one of multiple dependent claims which are not drafted in accordance with the third sentence of PCT Rule 6.4(a).

3. Claims Nos.: 18 and 21
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

- Remark on Protest**
- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
 - The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
 - No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/018195

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012-0181528 A1	19/07/2012	JP 2011-225801A KR 10-2012-0091044 A US 8426042 B2 WO 2011-040343 A1	10/11/2011 17/08/2012 23/04/2013 07/04/2011
JP 2007-324309 A	13/12/2007	JP 5144034 B2	13/02/2013
JP 2007-053132 A	01/03/2007	JP 4796802 B2	19/10/2011
JP 2010-135689 A	17/06/2010	JP 5497284 B2	21/05/2014
WO 2012-142387 A1	18/10/2012	TW 201249851 A US 2012-264938 A1	16/12/2012 18/10/2012
US 2006-0286406 A1	21/12/2006	JP 04934345 B2 JP 2006-332620 A US 07758971 B2	16/05/2012 07/12/2006 20/07/2010
EP 2036907 A1	18/03/2009	CN 101386630 A CN 101386630 B EP 2036907 B1 JP 04579320 B2 JP 2009-167162 A KR 10-2009-0028437 A US 08187729 B2 US 2009-0072726 A1	18/03/2009 31/07/2013 29/02/2012 10/11/2010 30/07/2009 18/03/2009 29/05/2012 19/03/2009