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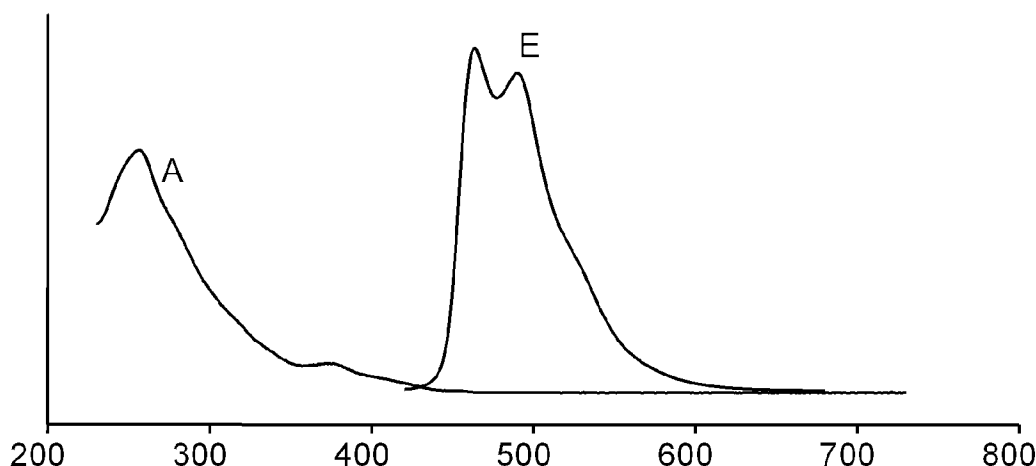
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(54) Title: LIGHT-EMITTING MATERIAL



(57) Abstract: This invention pertains to light emitting materials comprising novel ortho-metalated transition metal complexes [C^N]2ML, comprising chelate monoionic ligands (L), also called ancillary ligands. It has been surprisingly found that when the ancillary ligand comprises a substituted aromatic ring bearing a substituent possessing adequate electron-donating properties, said ligand (L) advantageously participates in the emission process, significantly shifting emission towards higher energies (blue-shift) and enabling appreciable improvement of the emission efficiency of complexes [C^N]2ML. Still objects of the invention are the use of said light emitting materials and organic light emitting device comprising said light emitting material.

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Description

LIGHT-EMITTING MATERIAL

Technical field

[0001] This invention relates to a light-emitting material, to the use of said material and to a light-emitting device capable of converting electric energy to light.

Background art

[0002] Today, various display devices have been under active study and development, in particular those based on electroluminescence (EL) from organic materials.

[0003] In the contrast to photoluminescence, i.e. the light emission from an active material as a consequence of optical absorption and relaxation by radiative decay of an excited state, electroluminescence (EL) is a non-thermal generation of light resulting from the application of an electric field to a substrate. In this latter case, excitation is accomplished by recombination of charge carriers of contrary signs (electrons and holes) injected into an organic semiconductor in the presence of an external circuit.

[0004] A simple prototype of an organic light-emitting diode (OLED), i.e. a single layer OLED, is typically composed of a thin film of the active organic material which is sandwiched between two electrodes, one of which needs to be semitransparent in order to observe light emission from the organic layer, usually an indium tin oxide (ITO)-coated glass substrate is used as anode.

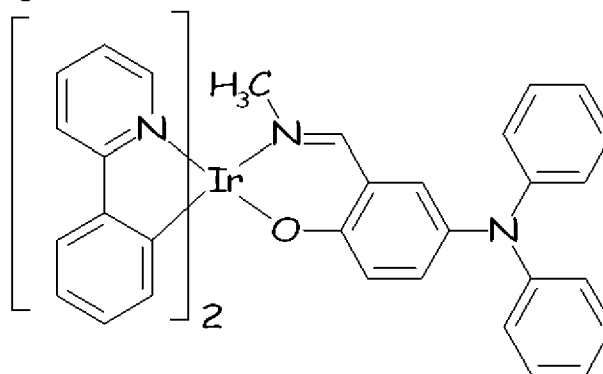
[0005] If an external voltage is applied to the two electrodes, charge carriers, i.e. holes, at the anode and electrons at the cathode are injected to the organic layer beyond a specific threshold voltage depending on the organic material applied. In the presence of an electric field, charge carriers move through the active layer and are non-radiatively discharged when they reach the oppositely charged electrode. However, if a hole and an electron encounter one another while drifting through the organic layer, excited singlet (anti-symmetric) and triplet (symmetric) states, so-called excitons, are formed. Light is thus generated in the organic material from

the decay of molecular excited states (or excitons). For every three triplet excitons that are formed by electrical excitation in an OLED, only one anti-symmetric state (singlet) exciton is created.

- [0006] Many organic materials exhibit fluorescence (i.e. luminescence from a symmetry-allowed process) from singlet excitons : since this process occurs between states of like symmetry it may be very efficient. On the contrary, if the symmetry of an exciton is different from that of the ground state, then the radiative relaxation of the exciton is disallowed and luminescence will be slow and inefficient. Because the ground state is usually anti-symmetric, decay from a triplet breaks symmetry : the process is thus disallowed and efficiency of EL is very low. Thus the energy contained in the triplet states is mostly wasted.
- [0007] Luminescence from a symmetry-disallowed process is known as phosphorescence. Characteristically, phosphorescence may persist for up to several seconds after excitation due to the low probability of the transition, in contrast to fluorescence which originates in the rapid decay.
- [0008] However, only a few organic materials have been identified which show efficient room temperature phosphorescence from triplets.
- [0009] Successful utilization of phosphorescent materials holds enormous promises for organic electroluminescent devices. For example, an advantage of utilizing phosphorescent materials is that all excitons (formed by combination of holes and electrons in an EL), which are (in part) triplet-based in phosphorescent devices, may participate in energy transfer and luminescence. This can be achieved either via phosphorescence emission itself, or using phosphorescent materials for improving efficiency of the fluorescence process as a phosphorescent host or a dopant in a fluorescent guest, with phosphorescence from a triplet state of the host enabling energy transfer from a triplet state of the host to a singlet state of the guest.
- [0010] In either case, it is important that the light emitting material provides electroluminescence emission in a relatively narrow band centered near selected spectral regions, which correspond to one of the three primary

colors, red, green and blue, so that they may be used as a colored layer in an OLED.

- [0011] As a means for improving the properties of light-emitting devices, there has been reported a green light-emitting device utilizing the emission from ortho-metalated iridium complex : . Ir(PPy)₃ : tris-ortho-metalated complex of iridium (III) with 2-phenylpyridine. Appl. phys. lett.. 1999, vol.75, p.4.
- [0012] US 2002034656 A (THOMPSON MARK E) 21/03/2002 discloses several organometallic complexes used as phosphorescent emitters in organic LEDs, preferably compounds of formula L₂MX, wherein L and X are distinct bidentate ligands, X being a monoanionic bidentate ligand and L coordinating to M via atoms of L comprising sp² hybridized carbon and a heteroatom of the ligand, and M being a metal, in general Ir. Examples of ligands L in said document are notably phenylpyridine ligands, which are claimed to participate more in the emission process than does X, the ancillary ligand. In particular, this document discloses, inter alia, a compound having formula :



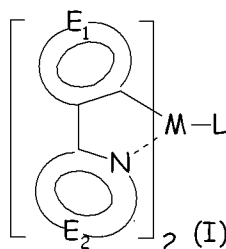
- [0013] This complex is claimed to act as a hole trap, thanks to the trapping site on the diarylamine substituent on the salicylanilide group, which is reported not to be involved in the luminescent process.
- [0014] However, since the foregoing light-emitting materials of the prior art are limited to green, the range within they can be applied as OLED active compound is narrow. It has thus been desired to develop light-emitting materials capable of emitting light with narrow emission bands centered near all primary colours, and especially in the blue region.

Disclosure of the invention

[0015] It is thus a first object of the invention to provide a light emitting material comprising an ortho-metallated complex comprising an ancillary ligand as detailed here below.

[0016] Still objects of the invention are emitting layers comprising said light emitting materials and organic light emitting device comprising said light emitting material.

[0017] A first object of the invention is to provide for a light emitting material comprising a complex of formula (I) :



wherein :

M represents a transition metal of atomic number of at least 40, preferably of groups 8 to 12, more preferably Ir or Pt, most preferably Ir;

E₁ represents a nonmetallic atoms group required to form a 5- or 6-membered aromatic or heteroaromatic ring, optionally condensed with additional aromatic moieties or non aromatic cycles, said ring optionally having one or more substituents, optionally forming a condensed structure with the ring comprising E₂, said ring coordinating to the metal M via a sp² hybridized carbon;

E₂ represents a nonmetallic atoms group required to form a 5- or 6-membered heteroaromatic ring, optionally condensed with additional aromatic moieties or non aromatic cycles, said ring optionally having one or more substituents, optionally forming a condensed structure with the ring comprising E₁, said ring coordinating to the metal M via a sp² hybridized nitrogen;

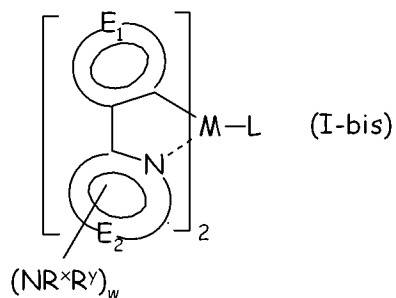
L is a chelate monoionic ligand, also designated as ancillary ligand, coordinating to the metal M through at least one oxygen atom and at least one sp² hybridized nitrogen atom, comprising at least one aromatic

and/or heteroaromatic ring, said ring comprising at least one substituent selected from the group consisting of halogens, such as $-\text{Cl}$, $-\text{F}$, $-\text{Br}$, $-\text{OR}_0$; $-\text{SR}_0$; $-\text{N}(\text{R}_0)_2$; $-\text{P}(\text{OR}_0)_2$ and $-\text{P}(\text{R}_0)_2$; wherein R_0 is a C_1 - C_6 alkyl, fluoro- or perfluoroalkyl, e.g. $-\text{CH}_3$, $-\text{nC}_4\text{H}_9$, $-\text{iC}_3\text{H}_7$, $-\text{CF}_3$, $-\text{C}_2\text{F}_5$, $-\text{C}_3\text{F}_7$ or a C_1 - C_6 alkyl, fluoro- or perfluoroalkyl having one or more ether groups, e.g. $-\text{CH}_2(\text{CH}_2\text{-O-CH}_2)_n\text{-CH}_3$, $-\text{CH}_2\text{-}[\text{CH}_2(\text{CH}_3)\text{-O-CH}_2]_n\text{-CH}_3$, $-(\text{CF}_2\text{O})_n\text{-C}_2\text{F}_5$, with n being an integer from 1 to 8; preferably said ring comprising at least one substituent selected among $-\text{OR}_0$ and $-\text{N}(\text{R}_0)_2$, wherein R_0 has the above meaning.

- [0018] The two monoanionic ligands bound to the metal as above specified in formula (I), comprising E_1 and E_2 moieties, are generally denoted as orthometalated ligands ($\text{C}^{\wedge}\text{N}$ ligands, hereinafter).
- [0019] It has been surprisingly found that when the chelate monoionic ligand (L), also called ancillary ligand, comprises a substituted aromatic ring bearing a substituent as above defined, possessing adequate electron-donating properties, said ligand (L) advantageously participates in the emission process, significantly shifting emission towards higher energies (blue-shift) and enabling appreciable improvement of the emission efficiency of complexes $[\text{C}^{\wedge}\text{N}]_2\text{ML}$ of formula (I) here above.
- [0020] Moreover, by means of the chelate monoionic ligand (L) substituted as above specified it is advantageously possible to obtain light emitting materials comprising $[\text{C}^{\wedge}\text{N}]_2\text{ML}$ complexes of formula (I) here above, having maximum emission between 430 nm and 500 nm, thus corresponding to a blue emission.
- [0021] According to an embodiment of the invention, the nonmetallic atoms group E_2 in formula (I) here above required to form a 5- or 6-membered aromatic or heteroaromatic ring as above detailed, comprises, in said ring, one or more substituents of $-\text{NR}^{\text{x}}\text{R}^{\text{y}}$ type, said ring optionally having one or more substituents different from $-\text{NR}^{\text{x}}\text{R}^{\text{y}}$, optionally forming a condensed structure with the ring comprising E_1 , wherein:
 R^{x} and R^{y} , equal or different from each other and at each occurrence, are chosen among C_1 - C_6 alkyl, fluoro- or perfluoroalkyl groups, e.g. -

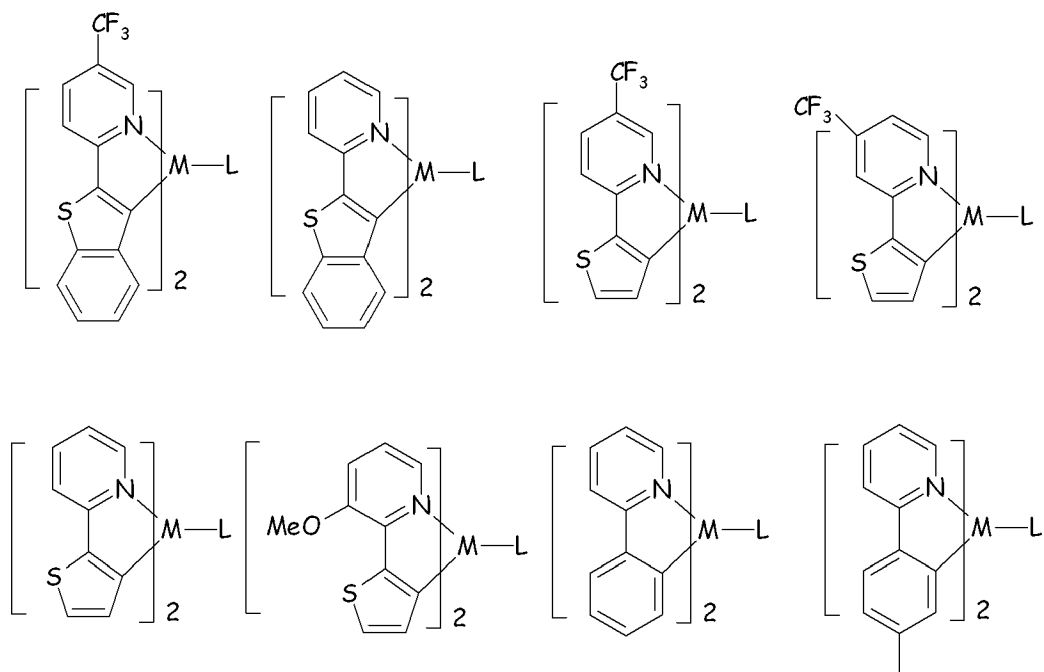
CH₃, -nC₄H₉, -iC₃H₇, -CF₃, -C₂F₅, -C₃F₇ or C₁-C₆ alkyl, fluoro- or perfluoroalkyl groups having one or more ether groups.

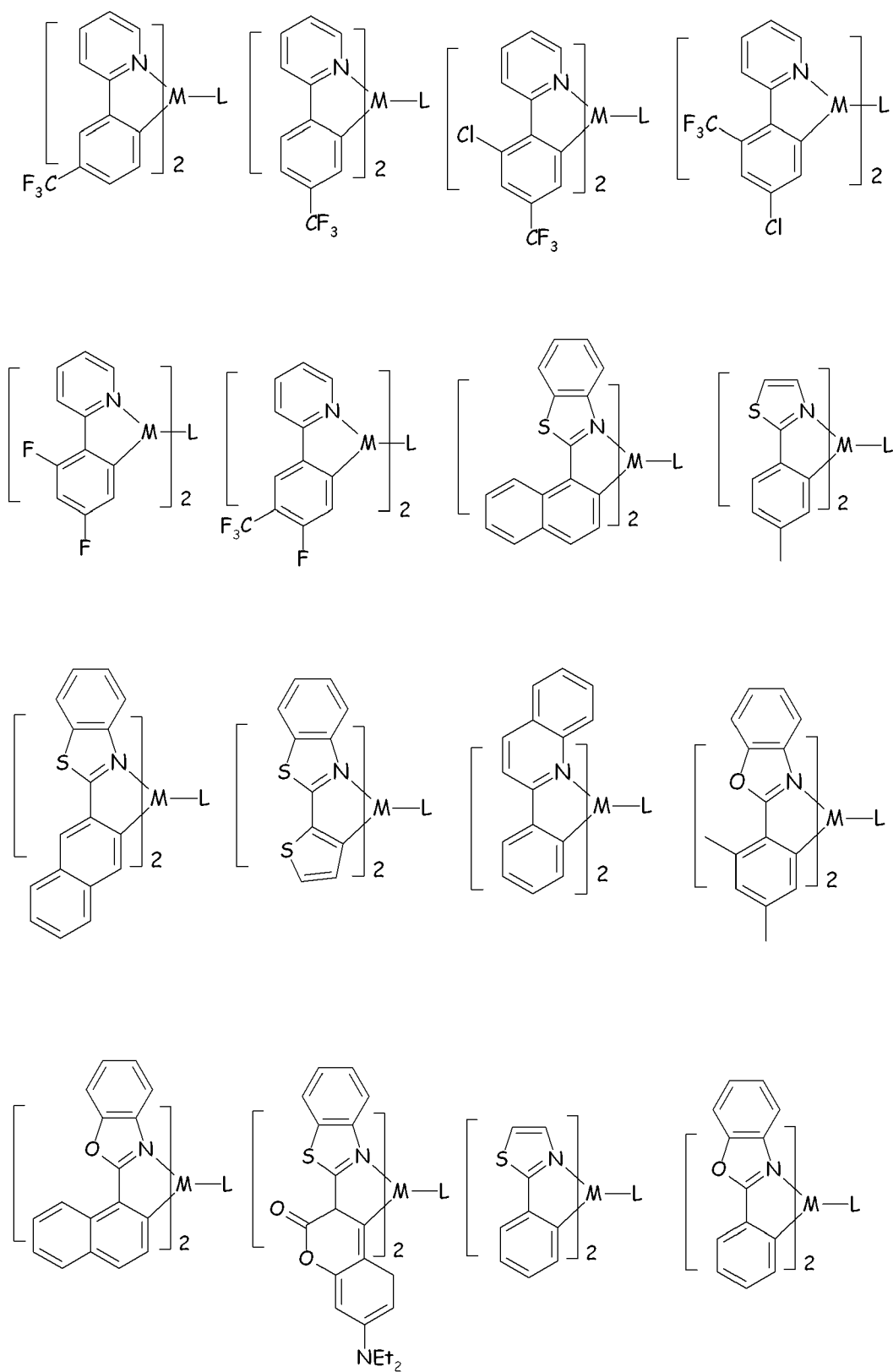
[0022] Thus, the light emitting material according to this embodiment of the invention comprises a complex of formula (I-bis) here below:

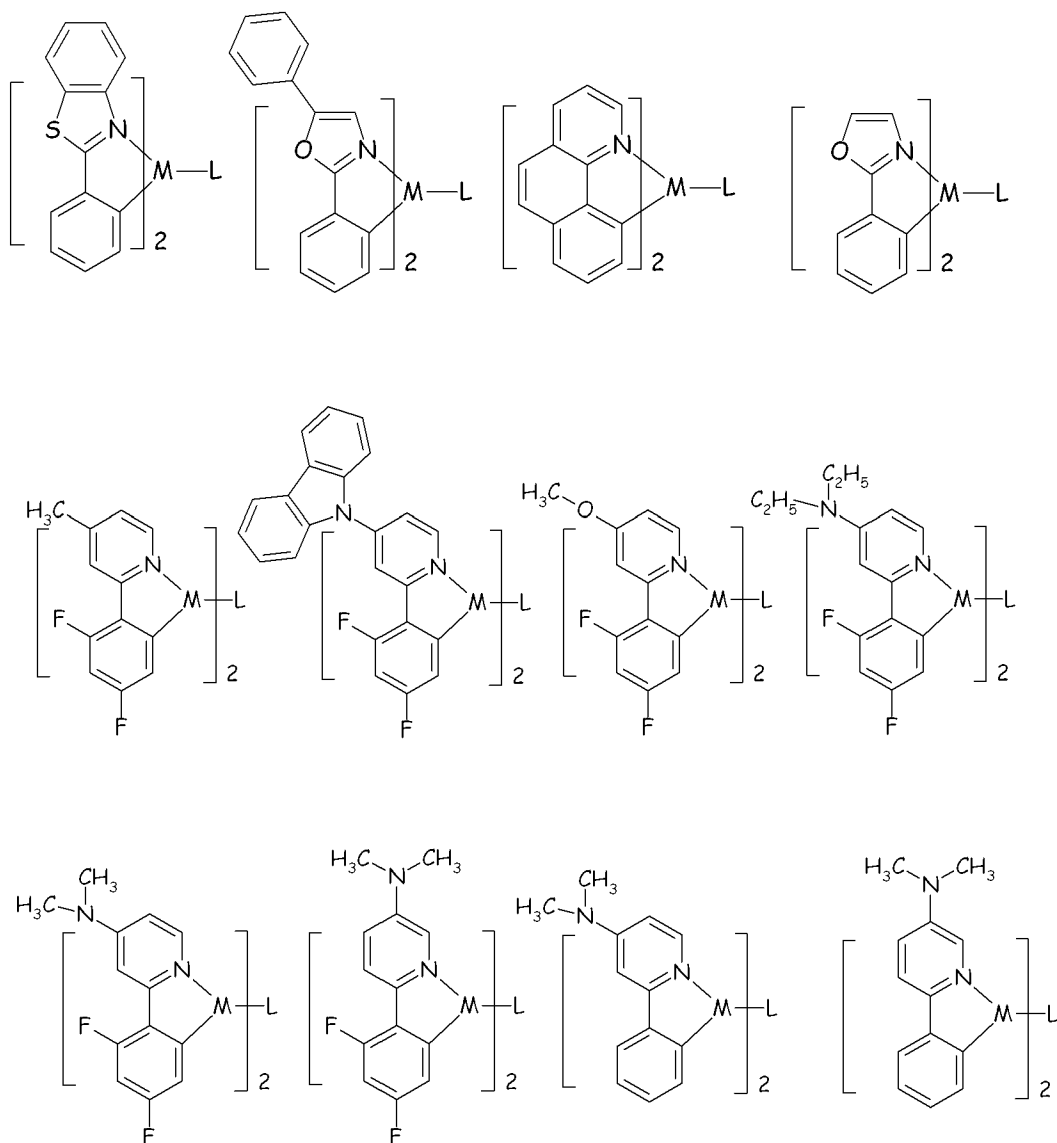


wherein E₁, E₂, M, L, R^x and R^y have the same meanings as above defined and w is an integer between 1 and 4.

[0023] Suitable examples of complexes complying with formula (I) here above are notably :

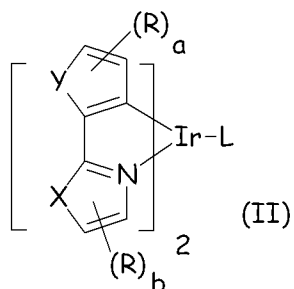






wherein L and M have the same meaning as above defined.

[0024] Preferably, the light emitting material of the invention comprises a complex complying with formula (II) here below :



wherein :

L has the same meaning as above defined;

X is a group chosen among the group consisting of $-\text{CH}=\text{CH}-$, $-\text{CR}=\text{CH}-$, $-\text{CR}=\text{CR}-$, $\text{N}-\text{H}$, $\text{N}-\text{R}^1$, O , S or Se ; preferably X is a group selected among $-\text{CH}=\text{CH}-$, $-\text{CR}=\text{CH}-$ or S ; most preferably X is $-\text{CH}=\text{CH}-$;

Y is a group chosen among the group consisting of $-\text{CH}=\text{CH}-$, $-\text{CR}=\text{CH}-$, $-\text{CR}=\text{CR}-$, $\text{N}-\text{H}$, $\text{N}-\text{R}^1$, O , S or Se ; preferably Y is a group selected among $-\text{CH}=\text{CH}-$, $-\text{CR}=\text{CH}-$ or S ; most preferably Y is $-\text{CH}=\text{CH}-$;

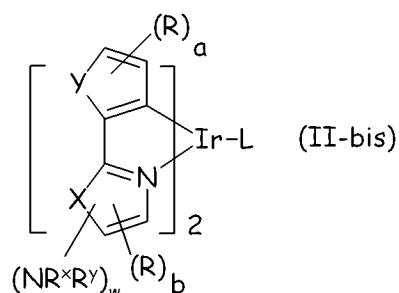
R is the same or different at each occurrence and is F , Cl , Br , NO_2 , CN ; a straight-chain or branched or cyclic alkyl or alkoxy group or dialkylamino group having from 1 to 20 carbon atoms, in each of which one or more nonadjacent $-\text{CH}_2-$ groups may be replaced by $-\text{O}-$, $-\text{S}-$, $-\text{NR}^1-$, or $-\text{CONR}^2-$, and in each of which one or more hydrogen atoms may be replaced by F ; an aryl or heteroaryl group having from 4 to 14 carbon atoms which may be substituted by one or more nonaromatic radicals $-\text{R}$; and a plurality of substituents R , either on the same ring or on the two different rings, may in turn together form a further mono- or polycyclic ring system, optionally aromatic.

R^1 and R^2 are the same or different from each other and at each occurrence and are each H or an aliphatic or aromatic hydrocarbon radical having from 1 to 20 carbon atoms;

a is an integer from 0 to 4;

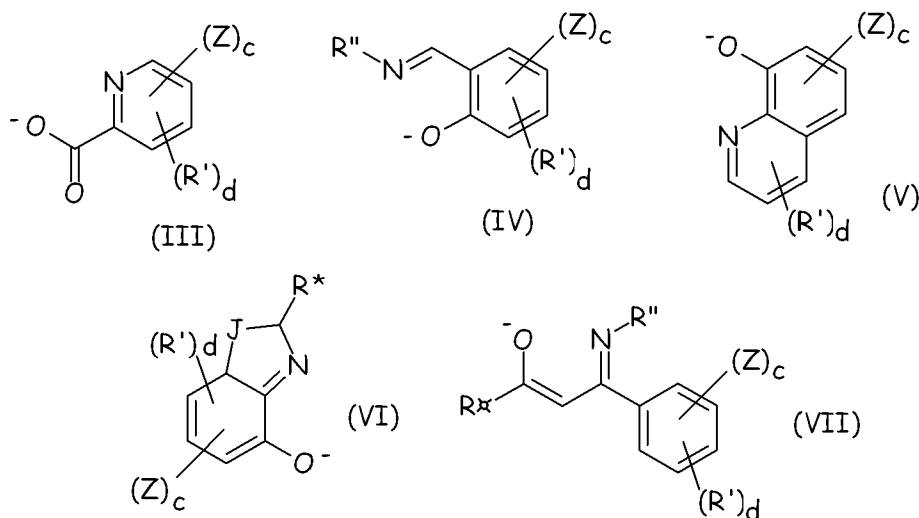
b is an integer from 0 to 4.

[0025] According to an embodiment of the invention, the preferred light emitting material of the invention comprises a complex of formula (II-bis) here below:



wherein L , R^x , R^y , X , Y , R , a , b and w have the same meaning as above defined.

[0026] More preferably, the chelate monoionic ligand (L) is selected from the structures represented by following formulae (III) to (VII) or tautomers thereof :



wherein :

Z is a substituent selected from the group consisting of halogens, such as -Cl, -F, -Br; -OR₀; -SR₀; -N(R₀)₂; -P(OR₀)₂ and -P(R₀)₂; wherein R₀ is a C₁-C₆ alkyl, fluoro- or perfluoroalkyl, e.g. -CH₃, -nC₄H₉, -iC₃H₇, -CF₃, -C₂F₅, -C₃F₇ or a C₁-C₆ alkyl, fluoro- or perfluoroalkyl having one or more ether groups, e.g. -CH₂-(CH₂-O-CH₂)_n-CH₃, -CH₂-[CH₂(CH₃)-O-CH₂]_n-CH₃, -(CF₂O)_n-C₂F₅, with n being an integer from 1 to 8; preferably Z is chosen among -OR₀ and -N(R₀)₂, wherein R₀ has the above meaning.

J is a group chosen among the group consisting of -CH=CH-, -CR=CH-, -CR=CR-, N-H, N-R¹, O, S or Se;

R', R*, R^α the same or different from each other and at each occurrence, represent F, Cl, Br, NO₂, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having from 1 to 20 carbon atoms, in each of which one or more nonadjacent -CH₂- groups may be replaced by -O-, -S-, -NR¹-, or -CONR²-, and in each of which one or more hydrogen atoms may be replaced by F; or an aryl or heteroaryl group having from 4 to 14 carbon atoms which may be substituted by one or more nonaromatic radicals -R'; and a plurality of substituents R', either on the same ring or on the two

different rings, may in turn together form a further mono- or polycyclic ring system, optionally aromatic;

R'' , R^1 and R^2 are the same or different from each other and at each occurrence and are each H or an aliphatic or aromatic hydrocarbon radical, optionally substituted, having from 1 to 20 carbon atoms;

c is an integer from 1 to 3;

d is an integer from 0 to 4.

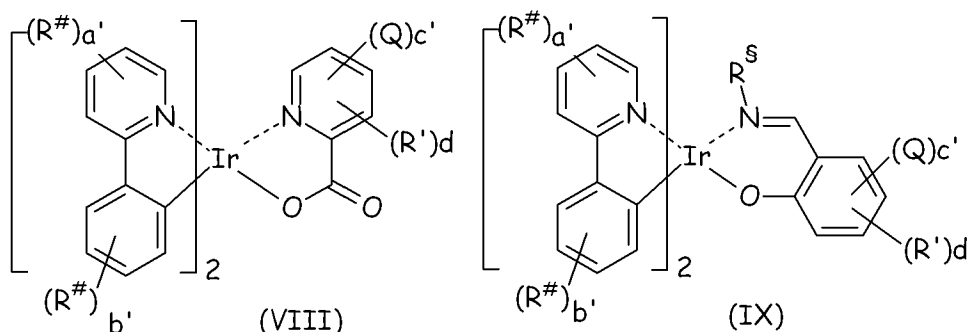
[0027] To the purpose of the invention, the term tautomer is intended to denote one of two or more structural isomers that exist in equilibrium and are readily converted from one isomeric form to another, by, for instance, simultaneous shift of electrons and/or of a hydrogen atom.

[0028] Good results have been obtained with chelate monoionic ligand (L) as above described (formulae III to VII), wherein the group Z is $-OR_0$ or $-N(R_0)_2$ wherein R_0 is a C_1 - C_6 alkyl, fluoro- or perfluoroalkyl, e.g. $-CH_3$, $-nC_4H_9$, $-iC_3H_7$, $-CF_3$, $-C_2F_5$, $-C_3F_7$ or a C_1 - C_6 alkyl, fluoro- or perfluoroalkyl having one or more ether groups, e.g. $-CH_2-(CH_2-O-CH_2)_n-CH_3$, $-CH_2-[CH_2(CH_3)-O-CH_2]_n-CH_3$, $-(CF_2O)_n-C_2F_5$, with n being an integer from 1 to 8.

[0029] Preferably the chelate monoionic ligand (L) is chosen among the group consisting of structures (III), (IV) and (V) here above.

[0030] Most preferably, the chelate monoionic ligand (L) responds to formula (III) or (IV) here above.

[0031] Light emitting materials particularly suitable for the invention comprise a complex of formula (VIII) or (IX) here below :



wherein :

R' and d have the same meaning as above defined;

Q is $-OR_0$ or $-N(R_0)_2$ wherein R_0 is a C_1 - C_6 alkyl, fluoro- or perfluoroalkyl, e.g. $-CH_3$, $-nC_4H_9$, $-iC_3H_7$, $-CF_3$, $-C_2F_5$, $-C_3F_7$ or a C_1 - C_6 alkyl, fluoro- or perfluoroalkyl having one or more ether groups, e.g. $-CH_2-(CH_2-O-CH_2)_n-CH_3$, $-CH_2-[CH_2(CH_3)-O-CH_2]_n-CH_3$, $-(CF_2O)_n-C_2F_5$, with n being an integer from 1 to 8;

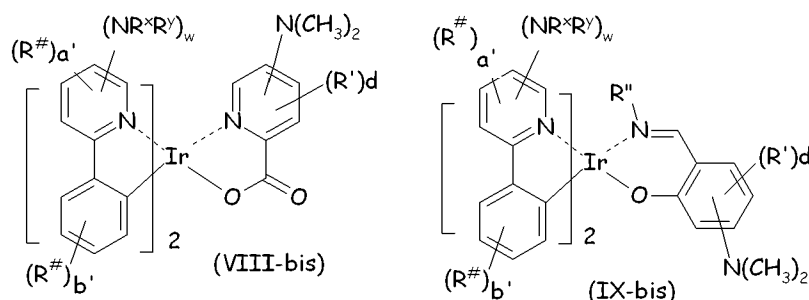
c' being an integer between 1 and 3;

$R^\#$ the same or different at each occurrence, is F, Cl, Br, NO_2 , CN, a straight-chain or branched or cyclic alkyl or alkoxy group or dialkylamino group having from 1 to 20 carbon atoms, in each of which one or more nonadjacent $-CH_2-$ groups may be replaced by $-O-$, $-S-$, $-NR^1$, or $-CONR^2$ - (with R^1 and R^2 being each H or an aliphatic or aromatic hydrocarbon radical having from 1 to 20 carbon atoms) and in each of which one or more hydrogen atoms may be replaced by F, or an aryl or heteroaryl group having from 4 to 14 carbon atoms which may be substituted by one or more nonaromatic radicals $-R^\#$; and a plurality of substituents $R^\#$, either on the same ring or on the two different rings, may in turn together form a further mono- or polycyclic ring system, optionally aromatic;

a' and b' equal or different each other, are independently an integer between 0 and 4;

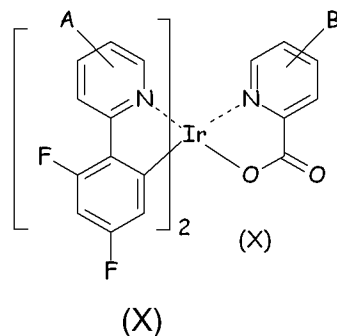
$R^\S$ is chosen among H and aliphatic or aromatic hydrocarbon radicals, optionally substituted, having from 1 to 20 carbon atoms.

[0032] According to an embodiment of the invention, said light emitting material particularly suitable comprises a complex of formula (VIII-bis) or (IX-bis) here below:



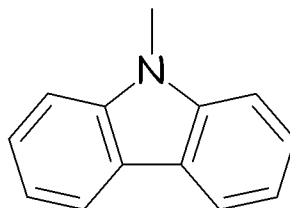
wherein a' , b' , d , w , $R^\#$, R^x , R^y , R' have the meaning as above defined.

[0033] Light emitting materials which gave good results are those complying with formula (X) here below :



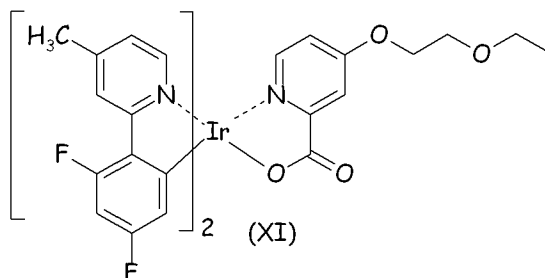
wherein :

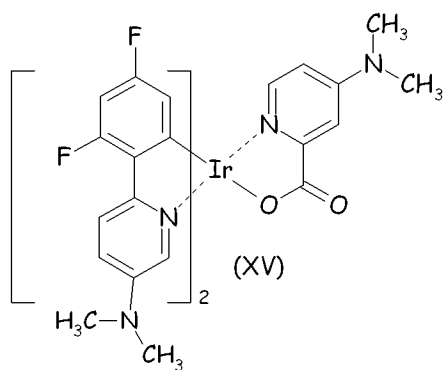
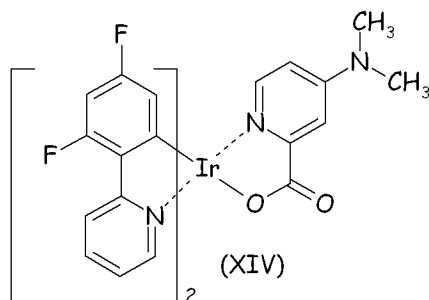
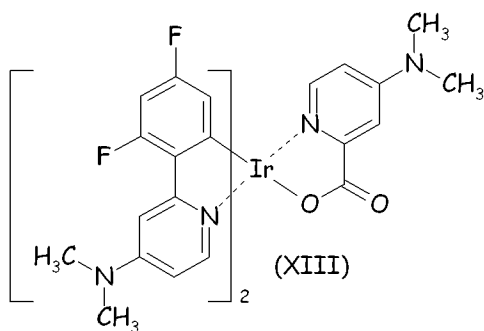
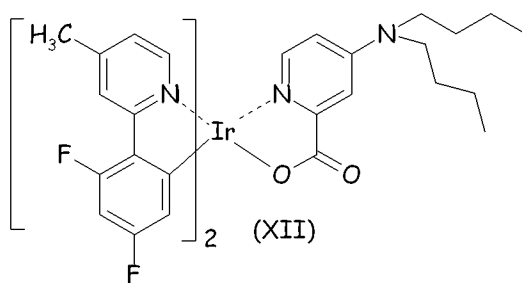
A is selected from H, $-R_H$, $-OR_H$, $-N(R_H)_2$, with R_H being a C_1 - C_{20} alkyl or alkyloxy group, preferably a methyl group; an aryl or heteroaryl group having from 4 to 14 carbon atoms, preferably a carbazole moiety of formula :

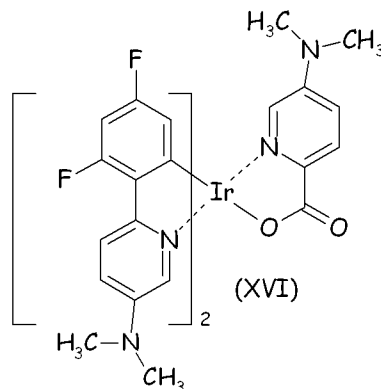


B is selected from $-OR_{H'}$ and $-N(R_{H''})_2$, with $R_{H'}$ being a C_1 - C_{20} alkyl or alkyloxy group, preferably $-\text{CH}_2-(\text{CH}_2-\text{O}-\text{CH}_2)_n-\text{CH}_3$ or $-\text{CH}_2-[\text{CH}_2(\text{CH}_3)-\text{O}-\text{CH}_2]_n-\text{CH}_3$, with n being an integer from 1 to 8, preferably $n=1$, and with $R_{H''}$ being a C_1 - C_{20} alkyl group, preferably a methyl, ethyl or n-butyl group.

[0034] Excellent results were obtained with light emitting materials comprising a complex chosen among formulae (XI) to (XVI) here below, or mixtures of two or more thereof:





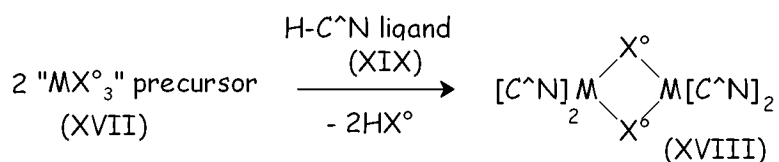


[0035] Complexes of formulae (XI) to (XVI), comprising a substituted picolinate moiety as ancillary ligand are particularly advantageous for the purposes of the invention also because of their chemical stability, which enable handling and treating them in further processing technologies without any risk of decomposition nor degradation.

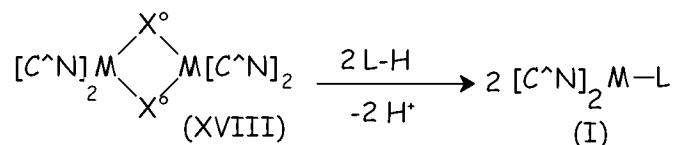
[0036] The synthesis of complexes of formula (I) here above, i.e. metal complex comprising two orthometalated ligands (C[^]N ligands) and an ancillary ligand (L), as above specified, can be accomplished by any known method. Details of synthetic methods suitable for the preparation of complexes of formula (I) here above are notably disclosed in "Inorg. Chem.", No. 30, pag. 1685 (1991); "Inorg. Chem.", No. 27, pag. 3464 (1988); "Inorg. Chem.", No. 33, pag. 545 (1994); "Inorg. Chem. Acta", No. 181, pag. 245 (1991), "J. Organomet. Chem.", No. 35, pag. 293 (1987), "J. Am. Chem. Soc.", No. 107, pag. 1431 (1985).

[0037] Typically, the synthesis is carried out in two steps, according to the following scheme :

Step 1 :



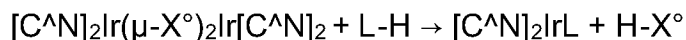
Step 2 :



wherein X° is a halogen, preferably Cl, and M, L, C[^]N have the meaning as above defined.

- [0038] Acid forms of the orthometalated ligands (H-C[^]N) and of ancillary ligands (L-H) can be either commercially available or easily synthesized by well-known organic synthesis reaction pathways.
- [0039] Should the transition metal be iridium, trihalogenated iridium (III) compounds such as $\text{IrCl}_3 \cdot \text{H}_2\text{O}$, hexahalogenated Iridium (III) compounds, such as $\text{M}^\circ_3\text{IrX}^\circ_6$, wherein X° is a halogen, preferably Cl and M° is an alkaline metal, preferably K, and hexahalogenated iridium (IV) compounds such as $\text{M}^\circ_2\text{IrX}^\circ_6$, wherein X° is a halogen, preferably Cl and M° is an alkaline metal, preferably K (Ir halogenated precursors, hereinafter) can be used as starting materials to synthesize the complexes of formula (I), as above described.
- [0040] $[\text{C}^\wedge\text{N}]_2\text{Ir}(\mu\text{-X}^\circ)_2\text{Ir}[\text{C}^\wedge\text{N}]_2$ complexes (formula XVIII, wherein $\text{M}=\text{Ir}$), with X° being a halogen, preferably Cl, can be thus prepared from said Ir halogenated precursors and the appropriate orthometalated ligand by literature procedures (S. Sprouse, K. A. King, P. J. Spellane, R. J. Watts, J. Am. Chem. Soc., 1984, 106, 6647-6653; M.E. Thompson et al., Inorg. Chem., 2001, 40(7), 1704; M.E. Thompson et al., J. Am. Chem. Soc., 2001, 123(18), 4304-4312).
- [0041] Reaction is advantageously carried out using an excess of the neutral form of the orthometalated ligand (H-C[^]N); high-boiling temperature solvent are preferred.
- [0042] To the purpose of the invention, the term high-boiling temperature solvent is intended to denote a solvent having a boiling point of at least 80 °C, preferably of at least 85 °C, more preferably of at least 90°C. Suitable solvents are for instance ethoxyethanol, glycerol, dimethylformamide (DMF), N-methylpyrrolidone (NMP), dimethylsulfoxide (DMSO), and the like; said solvents can be used as such or in admixture with water.
- [0043] Optionally reaction can be carried out in the presence of a suitable Brønsted base.
- [0044] $[\text{C}^\wedge\text{N}]_2\text{IrL}$ complexes can be finally obtained by reaction of said $[\text{C}^\wedge\text{N}]_2\text{Ir}(\mu\text{-X}^\circ)_2\text{Ir}[\text{C}^\wedge\text{N}]_2$ complex with the acid form of the ancillary ligand (L-H). The

reaction :



can be carried out in a high-boiling temperature solvent or in a low-boiling temperature solvent.

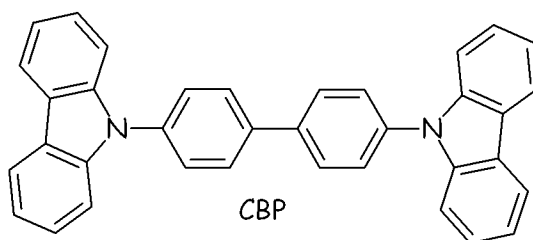
- [0045] Suitable high-boiling temperature solvents are notably alcohols such as ethoxyethanol, glycerol, DMF, NMP, DMSO and the like; said solvents can be used as such or in admixture with water.
- [0046] The reaction is preferably carried out in the presence of a Brønsted base, such as metal carbonates, in particular potassium carbonate (K_2CO_3), metal hydrides, in particular sodium hydride (NaH), metal ethoxide or metal methoxide, in particular $NaOCH_3$, $NaOC_2H_5$.
- [0047] Suitable low-boiling temperature solvents are notably chlorohydrocarbons like notably chloromethanes (eg. CH_3Cl ; CH_2Cl_2 ; $CHCl_3$); dichloromethane being preferred.
- [0048] Optionally, a precursor for ligand L can be used in the second step of the synthesis as above defined, which, in the reactive medium of said second step, advantageously reacts to yield the targeted L ligand.
- [0049] Another object of the invention is the use of the light emitting materials as above described in the emitting layer of an organic light emitting device.
- [0050] In particular, the present invention is directed to the use of the light emitting material as above described as dopant in a host layer, functioning as an emissive layer in an organic light emitting device.
- [0051] Should the light emitting material used as dopant in a host layer, it is generally used in an amount of at least 1 % wt, preferably of at least 3 % wt, more preferably of least 5 % wt with respect to the total weight of the host and the dopant and generally of at most 25 % wt, preferably at most 20 % wt, more preferably at most 15 % wt.
- [0052] The present invention is also directed to an organic light emitting device (OLED) comprising an emissive layer (EML), said emissive layer comprising the light emitting material as above described, optionally with a host material (wherein the light emitting material as above described is preferably present as a dopant), said host material being notably adapted to luminesce when a voltage is applied across the device structure.

[0053] The OLED generally comprises :

- a glass substrate;
- an anode, generally transparent anode, such as an indium-tin oxide (ITO) anode;
- a hole transporting layer (HTL);
- an emissive layer (EML);
- an electron transporting layer (ETL);
- a cathode, generally a metallic cathode, such as an Al layer.

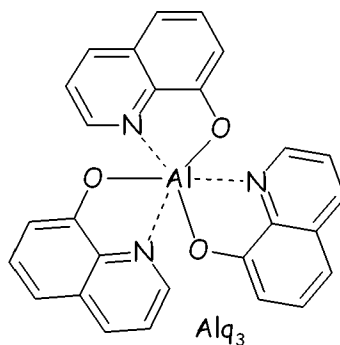
[0054] For a hole conducting emissive layer, one may have an exciton blocking layer, notably a hole blocking layer (HBL) between the emissive layer and the electron transporting layer. For an electron conducting emissive layer, one may have an exciton blocking layer, notably an electron blocking layer (EBL) between the emissive layer and the hole transporting layer. The emissive layer may be equal to the hole transporting layer (in which case the exciton blocking layer is near or at the anode) or to the electron transporting layer (in which case the exciton blocking layer is near or at the cathode).

[0055] The emissive layer may be formed with a host material in which the light emitting material as above described resides as a guest or the emissive layer may consist essentially of the light emitting material as above described itself. In the former case, the host material may be a hole-transporting material selected from the group of substituted tri-aryl amines. Preferably, the emissive layer is formed with a host material in which the light emitting material resides as a guest. The host material may be an electron-transporting material selected from the group of metal quinoxolates (e.g. aluminium quinolate (Alq_3), lithium quinolate (Liq)), oxadiazoles and triazoles. An example of a host material is 4,4'-N,N'-dicarbazole-biphenyl ["CBP"], which has the formula :

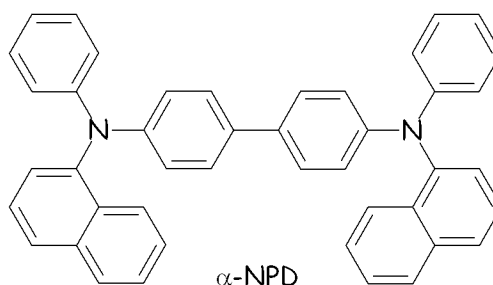


[0056] Optionally, the emissive layer may also contain a polarization molecule, present as a dopant in said host material and having a dipole moment, that generally affects the wavelength of light emitted when said light emitting material as above described, used as dopant, luminesces.

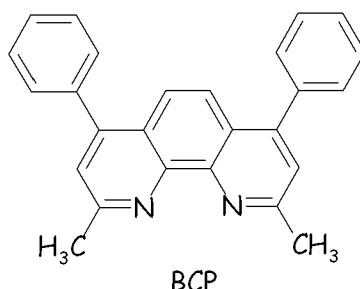
[0057] A layer formed of an electron transporting material is advantageously used to transport electrons into the emissive layer comprising the light emitting material and the (optional) host material. The electron transporting material may be an electron-transporting matrix selected from the group of metal quinoxolates (e.g. Alq₃, Liq), oxadiazoles and triazoles. An example of an electron transporting material is tris-(8-hydroxyquinoline)aluminum of formula ["Alq₃"] :



[0058] A layer formed of a hole transporting material is advantageously used to transport holes into the emissive layer comprising the light emitting material as above described and the (optional) host material. An example of a hole transporting material is 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl [" α -NPD"].



[0059] The use of an exciton blocking layer ("barrier layer") to confine excitons within the luminescent layer ("luminescent zone") is greatly preferred. For a hole-transporting host, the blocking layer may be placed between the emissive layer and the electron transport layer. An example of a material for such a barrier layer is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (also called bathocuproine or "BCP"), which has the formula



BCP

[0060] The OLED has preferably a multilayer structure, as depicted in Figure 1, wherein 1 is a glass substrate, 2 is an ITO layer, 3 is a HTL layer comprising α -NPD, 4 is an EML comprising CBP as host material and the light emitting material as above defined as dopant in an amount of about 8 % wt with respect to the total weight of host plus dopant; 5 is a HBL comprising BCP; 6 is an ETL comprising Alq₃; 7 is an Al layer cathode.

[0061] Some examples of the present invention are reported hereinafter, whose purpose is merely illustrative but not limitative of the scope of the invention itself.

[0062] NMR spectroscopy

[0063] NMR spectra have been recorded using an Oxford NMR spectrometer or a Varian Mercury Plus spectrometer, both operating at 300 MHz.

[0064] UV-VIS spectroscopy

[0065] UV-visible spectra were measured on a Shimadzu model UV-3101PC (UV-vis-nir scanning spectrophotometer). UV-visible spectra were carried out in ethanol solutions at concentration of 0.01 to 0.02 mM, unless otherwise specified.

[0066] Photoluminescence spectroscopy

[0067] Photoluminescent spectra were measured on a JASCO model FP-750 spectrofluorometer. Photoluminescent spectra measurements (at concentration of from 0.001 to 0.002 mM) were carried out at room temperature in ethanol solution using excitation wavelength of 375 nm, unless otherwise specified. Emission quantum yields were determined using fac-Ir(tpy)₃ as a reference

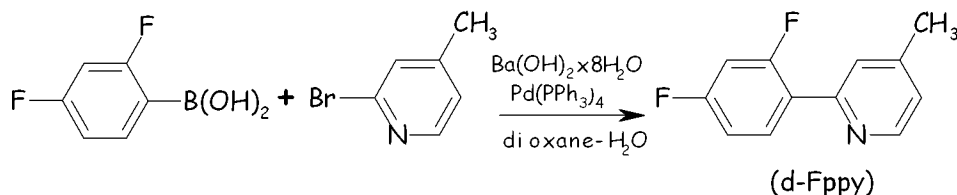
[0068] Thin layer chromatography (TLC)

[0069] Thin layer chromatography (TLC) was performed using silica plates.

[0070] Example 1

Synthesis of (2,4-difluorophenyl)-4-methylpyridine (d-Fppy)

The d-Fppy was synthesized according to the reaction scheme embedded here below :



In a 250 ml one-necked round bottom flask equipped with a condenser were placed 2,4-difluorophenylboronic acid (available from Aldrich Chem., 4 g, 25.3 mmol), $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ (available from Aldrich Chem., 24 g, 76.0 mmol), and $\text{Pd(PPh}_3)_4$ (available from TCI Co., 1.83 g, 1.6 mmol). The reaction flask was evacuated and filled with Ar gas three times. 1,4-Dioxane (90 ml), H_2O (30 ml), and 2-bromo-4-methylpyridine (available from TCI Co., 2.26 ml, 20.3 mmol) were added. The reaction mixture was refluxed for 24 hr under Ar gas and cooled to room temperature. The dioxane was removed and the contents were poured into CH_2Cl_2 (150 ml), the precipitate was removed through filter paper, and the organic layer washed with 1M-NaOH aqueous solution (2×150 ml) and saturated aqueous

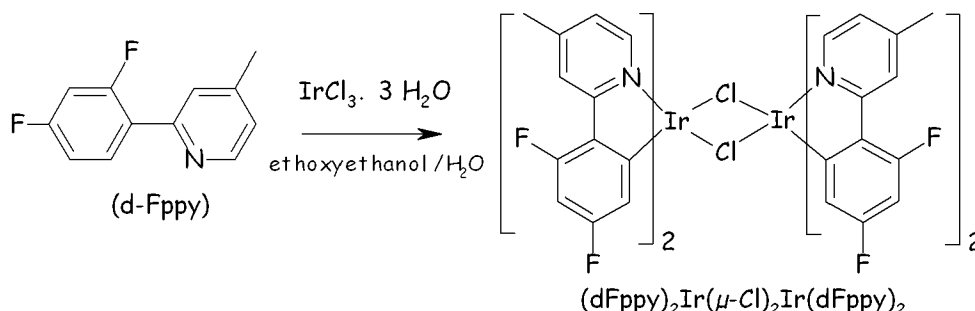
NaCl (150 ml), and dried over Na_2SO_4 . After evaporation of the solvent, purification of the product by liquid chromatography (silica gel, elution with 1:15 EtOAc/n-hexane) provided 2.91 g (70%) of d-Fppy, (2-(2,4-Difluorophenyl)-4-methylpyridine) as an oil.

TLC R_f = 0.51 (1:4 EtOAc/n-hexane); ^1H NMR (300MHz, CDCl_3) : δ 2.43 (s, 3H), 7.11-7.20 (m, 3H), 7.63 (s, 1H), 8.08 (q, 1H) 8.53 (d, 1H).

[0071] Example 2

Synthesis of cyclometalated Ir(III)- μ -chloro-bridge dimer with d-Fppy
 $[(\text{dFppy})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{dFppy})_2]$

Cyclometalated Ir(III) μ -chloro-bridge dimer, $[(\text{dFppy})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{dFppy})_2]$ was synthesized according to the method reported by Nonoyama in Bull. Chem. Soc. Jpn., No. 47, pag. 767 (1974), as depicted in the reaction scheme here below :



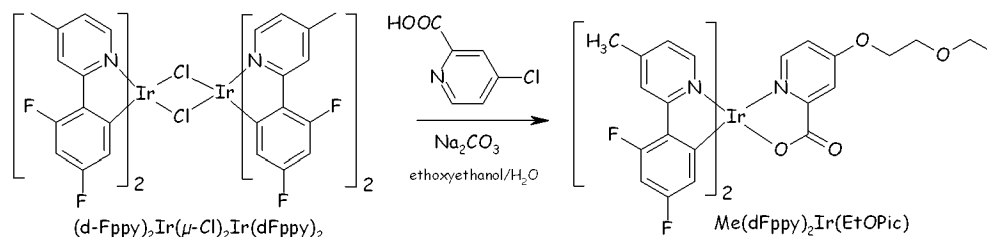
In a 100 ml one-necked round bottom flask equipped with a condenser were placed 2-(2,4-difluorophenyl)-4-methylpyridine (2.1 g, 10.3 mmol), $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (available from Across Organics, 1.80 g, 5.2 mmol), 2-ethoxyethanol (available from Aldrich Chem., 22.5 ml); finally H_2O (7.5 ml) was added. The flask was evacuated and filled with Ar gas three times. The reaction mixture was refluxed for 15 hr under Ar gas and cooled to room temperature. The coloured precipitate was filtered off and was washed with water, followed by 4 portions of ethanol (yield 80%).

^1H -NMR (300MHz, CDCl_3) δ 2.67 (s, 12H), 5.30~5.34 (m, 4H), 6.34 (t, 4H), 6.60 (d, 4H), 8.14 (s, 4H), 8.89 (q, 4H). Elemental Analysis : Found C 45.57, H 2.40 N 4.37. Calcd C 45.32, H 2.54, N 4.40.

[0072] Example 3

Synthesis of [iridium(III) bis(2-(2,4-difluorophenyl)-4-methylpyridinato- N,C^2)-4-(2-ethoxyethoxy)picolinate] $[\text{Me}(\text{dFppy})_2\text{Ir}(\text{EtOPic})]$ (formula XI)

Me(dFppy)₂Ir(EtOPic) was obtained from the reaction of (dFppy)₂Ir(μ-Cl)₂Ir(dFppy)₂ and 4-chloropicolinic acid in the solvent 2-ethoxyethanol, according to the following reaction scheme.



In a 50 ml one-necked round bottom flask equipped with a condenser were placed $[(\text{dFppy})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{dFppy})_2]$ complex (0.182 g, 0.14 mmol), 4-chloropicolinic acid (TCI Co., 0.057 g, 0.36 mmol), sodium carbonate (0.16 g, 1.86 mmol); finally 2-ethoxyethanol (Aldrich Chem., 12 ml) was added. The flask was evacuated and filled with Ar gas three times. The reaction mixture was refluxed for 24 hr under Ar gas and cooled to room temperature. The 2-ethoxyethanol was removed under reduced pressure. The product was extracted with CH_2Cl_2 . The combined organic layer was washed with brine, dried over Na_2SO_4 , filtered, and concentrated. The light yellow residue was purified by chromatography over silica gel (1:4:0.1 EtOAc/n-hexane/methanol). Further purification of the product by crystallization (methylene chloride, n-hexane) provided 0.041 g (yield 70%) of $\text{Me}(\text{dFppy})_2\text{Ir}(\text{EtOPic})$ [iridium(III) bis(2-(2,4-difluorophenyl)-4-methylpyridinato-N,C^{2'}) 4-(2-ethoxyethoxy)picolinate] (XI) as light yellow crystals.

TLC R_f = 0.16 (1:1:0.1 EtOAc/n-hexane/methanol) ; ^1H NMR (300MHz, CDCl_3) : δ 1.19-1.24 (t, 3H), 2.54 (s, 6H), 3.53-3.60 (q, 2H), 3.78-3.81 (t, 2H), 4.22-4.26 (q, 2H), 5.58-5.62 (dd, 1H), 5.79-5.83 (dd, 1H), 6.36-6.44 (m, 2H), 6.78-6.80 (dd, 1H), 6.91-6.94 (dd, 1H), 6.98-7.01 (dd, 1H), 7.27-7.29 (d, 1H), 7.48-7.50 (d, 1H), 7.82-7.83 (d, 1H), 8.02 (s, 1H) 8.09 (s, 1H), 8.51-8.53 (d, 1H).

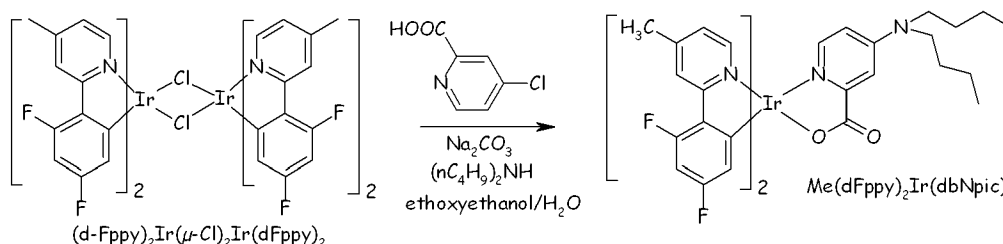
[0073] Figure 2 depicts the absorption (A) and emission (E) spectra of orthometalated complex of example 3 (formula XI) [wavelength in abscissa

in nm; intensity (arbitrary units) in ordinate], showing a maximum of emission at ($\lambda_{\max}$) 464 nm, with a quantum yield (F) of 0.69.

[0074] The luminescence spectrum of $\text{Me}(\text{dFppy})_2\text{Ir}(\text{EtOPic})$ (XI) showed the appearance of a new strong second emission peak at 464 nm; portions of emission at the blue region is increased up to 64%. Major portion of the luminescence appeared at the blue region below 500 nm with a very high luminescence quantum yield ($\Phi = 0.69$).

[0075] Example 4

Synthesis of iridium(III) bis(2-(2,4-difluorophenyl)-4-methylpyridinato-N,C^{2'})-4-dibutylaminopicolinate) [$\text{Me}(\text{dFppy})_2\text{Ir}(\text{dbNPic})$] (formula XII) $\text{Me}(\text{dFppy})_2\text{Ir}(\text{dbNPic})$ was obtained from the reaction of $(\text{dFppy})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{dFppy})_2$ and 4-chloropicolinic acid and n-butylamine in the presence of Na_2CO_3 in 2-ethoxyethanol, according to the following reaction scheme.



In a 50 ml one-necked round bottom flask equipped with a condenser were placed $[(\text{dFppy})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{dFppy})_2]$ complex (0.165 g, 0.13 mmol), 4-chloropicolinic acid (TCI Co., 0.051 g, 0.32 mmol), sodium carbonate (0.14 g, 1.69 mmol), and n-dibutylamine (Aldrich Chem., 14 ml); 2-ethoxyethanol was finally added. The flask was evacuated and filled with Ar gas three times. The reaction mixture was refluxed for 24 hr under Ar gas and cooled to room temperature. The n-dibutylamine and the solvent were removed for evaporation. The product was extracted with CH_2Cl_2 . The combined organic layer was washed with brine, dried over Na_2SO_4 , filtered, and concentrated. The light yellow residue was purified by chromatography over silica gel (1:4:0.1 EtOAc/n-hexane/methanol). Additional purification of the product by crystallization (methylene chloride, n-hexane) provided 0.038 g (yield 70%) of $\text{Me}(\text{dFppy})_2\text{Ir}(\text{dbNPic})$ (XII) [iridium(III) bis(2-(2,4-difluorophenyl)-4-methylpyridinato-N,C^{2'})-4-

dibutylamino-picolinate] as light yellow crystal.

TLC R_f = 0.44 (1:1:0.1 EtOAc/n-hexane/methanol) ; ^1H NMR (300MHz, CDCl_3) : δ 0.91-0.96 (t, 6H), 1.25-1.37 (m, 4H), 1.53-1.58 (m, 4H), 2.53-2.54 (d, 6H), 3.27-3.32 (dd, 4H), 5.59-5.63 (dd, 1H), 5.79-5.83 (dd, 1H), 6.30-6.44 (m, 2H), 6.35-6.39 (q, 1H) 6.80-6.83 (dd, 1H), 7.00-7.03 (dd, 1H), 7.18-7.20 (d, 1H), 7.43-7.47 (d, 1H), 7.45-7.46 (d, 1H), 8.02 (s, 1H), 8.07 (s, 1H), 8.56-8.58 (d, 1H)

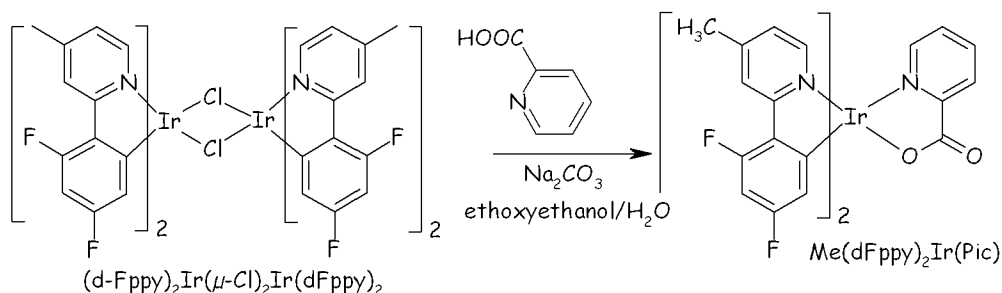
[0076] Figure 3 depicts the absorption (A) and emission (E) spectra of orthometalated complex of example 4 (XII) [wavelength in abscissa in nm; intensity (arbitrary units) in ordinate], showing a maximum of emission at (λ_{max}) 466 nm, with a quantum yield (F) of 0.57.

[0077] $\text{Me}(\text{dFppy})_2\text{Ir}(\text{dbNPic})$ having a strong electron donating dialkyl amino group on its ancillary picolinate ligand was shown to have an emission peak in its luminescence spectrum at 466 nm; roughly 66% of the luminescence intensity was found to appear at blue region below 500 nm.

[0078] Example 5 (COMPARATIVE)

Synthesis of $\text{Me}(\text{dFppy})_2\text{Ir}(\text{Pic})$ [iridium(III) bis(2-(2,4-difluorophenyl)-4-methylpyridinato-N, C^2)picolinate]

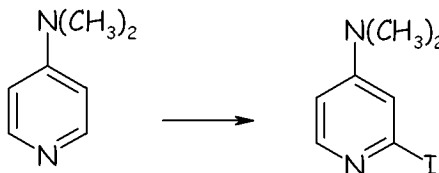
$\text{Me}(\text{dFppy})_2\text{Ir}(\text{Pic})$ was obtained from the reaction of $(\text{dFppy})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{dFppy})_2$ and 2-picolinic acid in the solvent 2-ethoxyethanol, according to the following reaction scheme:



In a 50 ml one-necked round bottom flask equipped with a condenser were placed $[(\text{dFppy})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{dFppy})_2]$ complex (0.28 g, 0.22 mmol), 2-picolinic acid (Aldrich Chem., 0.068 g, 0.55 mmol), sodium carbonate (0.24 g, 2.86 mmol); finally 2-ethoxyethanol (Aldrich Chem., 18 ml) was added. The flask was evacuated and filled with Ar gas three times. The reaction mixture was refluxed for 20 hr under Ar gas and cooled to room temperature. The 2-ethoxyethanol was removed under reduced pressure

and the product was extracted with CH_2Cl_2 . The combined organic layer was washed with brine, dried over Na_2SO_4 , filtered, and concentrated. The light yellow residue was purified by chromatography over silica gel (1:4:0.1 EtOAc/n-hexane/methanol). Further purification of the product by crystallization (methylene chloride, n-hexane) provided 0.036 g (yield 75%) of $\text{Me}(\text{dFppy})_2\text{Ir}(\text{Pic})$ [iridium(III) bis(2-(2,4-difluorophenyl) -4-methylpyridinato-N,C^{2'}) picolinate] as light yellow crystal. TLC R_f = 0.21 (1:1:0.1 EtOAc/n-hexane/methanol) ; ^1H NMR (300MHz, CDCl_3) : δ 2.52 (s, 6H), 5.56-5.60 (dd, 1H), 5.80-5.84 (dd, 1H), 6.30-6.48 (m, 2H), 6.76-6.79 (dd, 1H), 6.98-7.00 (dd, 1H), 7.22-7.24 (d, 1H), 7.36-7.42 (td, 1H), 7.74-7.76 (d, 1H), 7.88-7.94 (td, 1H), 8.03 (s, 1H), 8.08 (s, 1H), 8.29-8.31 (d, 1H), 8.52-8.54 (d, 1H).

- [0079] Figure 4 depicts the absorption (A) and emission (E) spectra of orthometalated complex of example 5 [wavelength in abscissa in nm; intensity (arbitrary units) in ordinate], showing a maximum of emission at (λ_{max}) 512 nm, with a quantum yield (F) of 0.44.
- [0080] $\text{Me}(\text{dFppy})_2\text{Ir}(\text{Pic})$ bearing no substituent on its ancillary picolinate ligand was shown to have an emission peak in its luminescence spectrum at 512 nm (green region) and a lower quantum efficiency with respect to substituted complexes of examples 3 and 4. This comparison well demonstrates that the presence of the substituent possessing adequate electron-donating properties significantly shifts emission towards higher energies (blue-shift) and enables appreciable improvement of the emission efficiency.
- [0081] Example 6
Synthesis of 2-iodo-4-dimethylaminopyridine



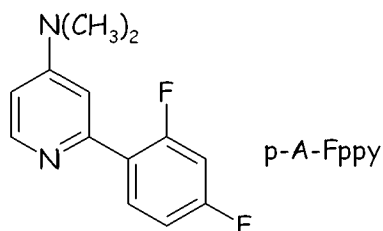
$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (8.4 g, 59 mmol) was added dropwise to a solution of 4-dimethylaminopyridine (6 g, 49 mmol) in dry THF (250 ml) at 0°C . The

resulting mixture was stirred 1 hour at 0°C under nitrogen. Temperature was cooled down to -78°C and BuLi (1.6 M in hexane, 46 ml, 74 mmol) was added dropwise. The resulting mixture was stirred for 1 hour at -78°C and a solution of I₂ (18.7 g, 74 mmol) in dry THF (50 ml) was added dropwise. The resulting mixture was stirred at -78°C for 2 hours and allowed to warm to room temperature (2 hours). THF was evaporated and a saturated Na₂S₂O₅ solution was added. The resulting slurry was extracted with EtOAc (5×150 ml). The combined organic fractions were successively washed with saturated Na₂S₂O₅ (50 ml), brine (50 ml), dried over MgSO₄, filtered and evaporated to dryness. The resulting residue was purified by chromatography column (SiO₂, EtOAc/petroleum ether, 1/1) to afford 7 g (57%) of the desired compound as colourless oil which solidified upon standing.

¹H and ¹³C NMR were found to be in agreement with those reported in the literature (Cuperly, D.; Gros, P.; Fort, Y. J. Org. Chem. 2002, 67, 238-241.)

[0082] Example 7

Synthesis of 2-(2,4-difluorophenyl)-4-dimethylamino-pyridine (p-A-Fppy)



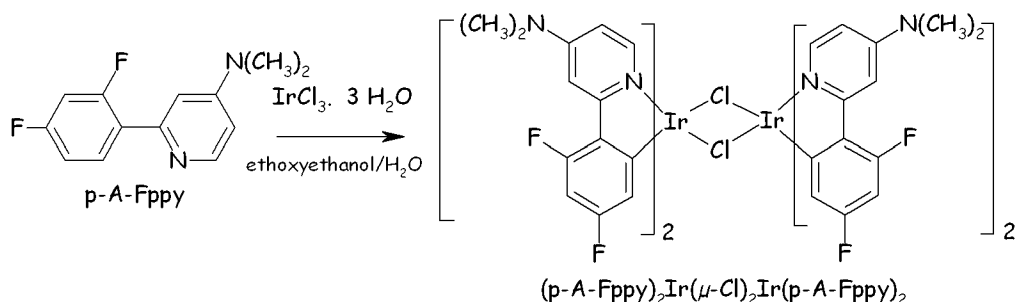
A mixture of 2-iodo-4-dimethylaminopyridine (3 g, 12 mmol), 2,4-difluorophenylboronic acid (2.3 g, 14.5 mmol) and K₂CO₃ (6 g, 43.5 mmol) in toluene (60ml) and water (10 ml) were degassed with nitrogen for 15 minutes. Pd(PPh₃)₄ (800 mg, 0.66 mmol) was added and the resulting mixture was heated to 90°C for 48 hours under nitrogen. After being cooled to room temperature, the aqueous phase was separated and extracted with EtOAc (3×100 ml). The combined organic fractions were washed with brine, dried over MgSO₄, filtered and evaporated. The crude compound was purified by column chromatography (SiO₂, CHCl₃ then

$\text{CHCl}_3/\text{MeOH}$, 97/3) to afford 2.2 g (78%) of the titled compound as slightly yellow oil which solidified upon standing.

$^1\text{H-NMR}$ (CDCl_3 , 298K, 200 MHz, δ ppm) 3.05 (s, 6H), 6.49 (dd, $J = 2.5$ and 6 Hz, 1H), 6.92 (m, 3H), 7.94 (m, 1H), 8.33 (d, $J = 6$ Hz, 1H).

[0083] Example 8

Synthesis of cyclometalated Ir(III)- μ -chloro-bridge dimer [(2-(2,4-difluorophenyl)-4-dimethylaminopyridine) $_2\text{IrCl}$] $_2$ with p-A-Fppy [(p-A-Fppy) $_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{p-A-Fppy})_2$]

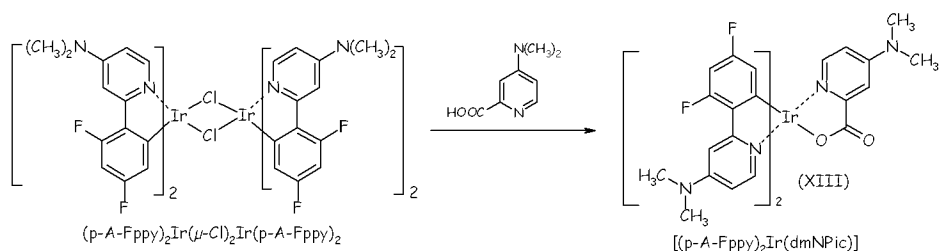


$\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ and 2.5 equivalents of 2-(2,4-difluorophenyl)-4-dimethylaminopyridine were heated at 110°C in a mixture of 2-ethoxyethanol and water (3/1, v/v) overnight under nitrogen. After being cooled to room temperature, the resulting precipitate was filtered off, successively washed with methanol than Et_2O and finally dried to afford the desired dimer. Because of the low solubility of this compound, its $^1\text{H-NMR}$ was recorded in DMSO-d_6 as its $\text{L}_2\text{Ir}(\text{Cl})(\text{DMSO})$ derivative.

$^1\text{H-NMR}$ (DMSO-d_6 , 298K, 200 MHz, δ ppm) 3.16 (s, 6H), 3.19 (s, 6H), 5.35 (dd, $J = 2$ and 8.7 Hz, 1H), 5.83 (dd, $J = 2$ and 8.7 Hz, 1H), 6.70-7.00 (m, 4H), 7.37 (m, 2H), 8.86 (d, $J = 7$ Hz, 1H), 9.21 (d, $J = 7$ Hz, 1H).

[0084] Example 9

Synthesis of iridium(III) bis(2-(2,4-difluorophenyl)-4-dimethylaminopyridinato-N,C $^{2-}$)-4-dimethylaminopicolinate) [(p-A-Fppy) $_2\text{Ir}(\text{dmNPic})$] (formula XIII)

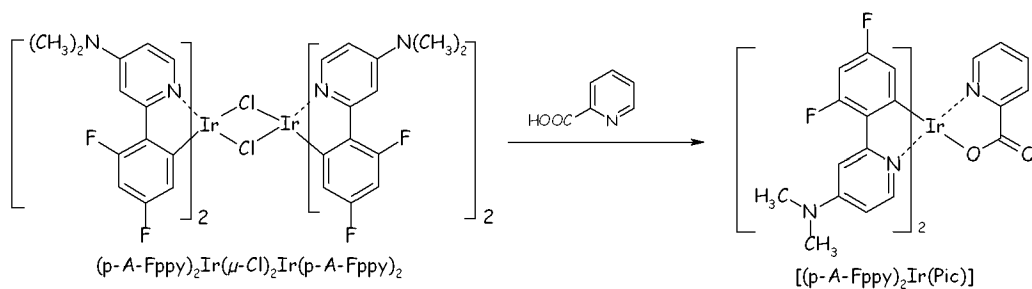


The complex $[(p\text{-A-Fppy})_2\text{Ir}(\text{dmNPic})]$ (XIII) was conveniently synthesized in the low boiling solvent dichloromethane by reacting dichloro-bridged iridium (III) dimer $[(p\text{-A-Fppy})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(p\text{-A-Fppy})_2]$ with corresponding ancillary ligand. The complex was recrystallized from ethanol petroleum ether mixture and characterized by spectroscopic techniques.

Figure 5 shows the crystal structure of complex (XIII) as determined by modelling the X-ray results. Figure 6 is the emission spectrum measured at 298 K in dichloromethane solution of complex (XIII) of example 9, obtained by exciting the complex at 380 nm; abscissa represents the wavelength in nm, while ordinate depicts the emission intensity in cps. Two emission peaks were identified having maximum of emission at (λ_{max}) 460 and 503 nm, respectively.

[0085] Example 10 (Comparative)

Synthesis of iridium(III) bis(2-(2,4-difluorophenyl)-4-dimethylaminopyridinato-N,C^{2'})-picolinate $[(p\text{-A-Fppy})_2\text{Ir}(\text{Pic})]$



The complex $[(p\text{-A-Fppy})_2\text{Ir}(\text{Pic})]$ was conveniently synthesized following the same procedure as detailed in example 9 here above, but using unsubstituted 2-picolinic acid.

Figure 7 is the emission spectrum measured at 298 K in dichloromethane solution of complex of comparative example 10, obtained by exciting the complex at 380 nm; abscissa represents the wavelength in nm, while

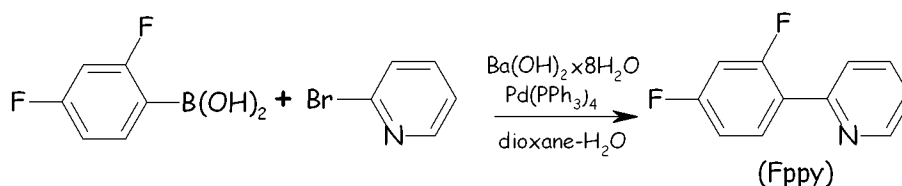
ordinate depicts the emission intensity in cps. An emission peak was identified having maximum of emission at ($\lambda_{\max}$) 565 nm.

$[(p\text{-A-Fppy})_2\text{Ir(Pic)}]$ bearing no substituent on its ancillary picolinato ligand was shown to have an emission peak in its luminescence spectrum at 565 nm (yellow region) and a lower quantum efficiency with respect to the corresponding substituted complex (XIII) of example 9. This comparison well demonstrates that the presence of the substituent possessing adequate electron-donating properties significantly shifts emission towards higher energies (blue-shift) and enables appreciable improvement of the emission efficiency.

[0086] Example 11

Synthesis of 2-(2,4-difluorophenyl)-pyridine (Fppy)

The Fppy was synthesized following the same procedure as described in example 1 here above, according to the reaction scheme embedded here below :

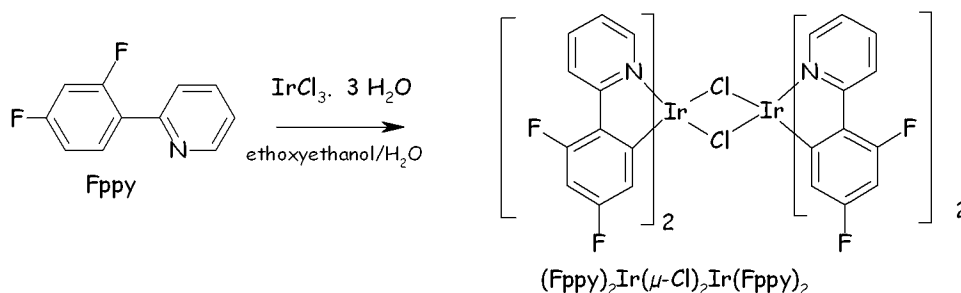


[0087] Example 12

Synthesis of cyclometalated Ir(III)- μ -chloro-bridge dimer with Fppy

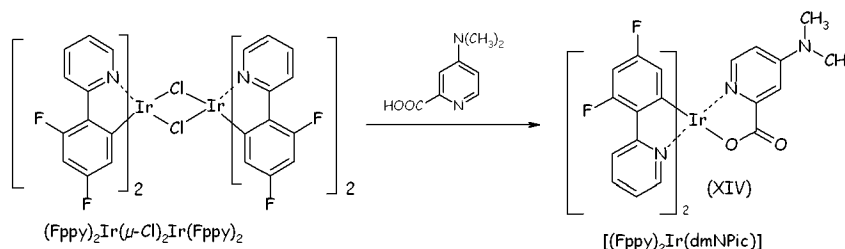
$[(\text{Fppy})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{Fppy})_2]$

The complex was synthesized following the same procedure as described in example 8, according to the following reaction scheme:



[0088] Example 13

Synthesis of iridium(III) bis(2-(2,4-difluorophenyl)-pyridinato-N,C^{2'})-4-dimethylaminopicolinate) [(Fppy)₂Ir(dmNPic)] (formula XIV)



The complex [(Fppy)₂Ir(dmNPic)] (XIV) was conveniently synthesized in the low boiling solvent dichloromethane by reacting dichloro-bridged iridium (III) dimer [(Fppy)₂Ir(μ-Cl)₂Ir(Fppy)₂] with corresponding ancillary ligand. The complex was recrystallized from ethanol petroleum ether mixture and characterized by spectroscopic techniques.

Figure 8 is the emission spectrum measured at 298 K in dichloromethane solution of complex (XIV) of example 13, obtained by exciting the complex at 380 nm; abscissa represents the wavelength in nm, while ordinate depicts the emission intensity in cps. Two emission peaks were identified having maximum of emission at (λ_{max}) 476 and 520 nm, respectively.

[0089] Example 14

Synthesis of 2-(2,4-difluorophenyl)-5-dimethylamino-pyridine (m-A-Fppy)
(1) Synthesis of 2-bromo-5-dimethylaminopyridine

2-bromo-5-aminopyridine (11.7 g, 67.6 mmol) was added portionwise to HCO₂H (20 ml) at 0°C. Formaldehyde (37% in water, 17 ml, 210 mmol) was then added and the mixture heated to reflux for hours. The reaction was then cooled to room temperature and an aqueous KOH solution (1N, ml) was added. The mixture was extracted with Et₂O (3×100 ml) and the combined extract was dried over MgSO₄, filtered and evaporated to dryness. The residual oil was purified by flash chromatography on silica (CH₂Cl₂). The yellowish solid was dissolved in the minimum volume of CH₂Cl₂, petroleum ether (150 ml) was added and the solution was stand in the fridge overnight. The white crystalline solid was filtered and washed

with small portion of cold petroleum ether to afford 5.2 g (40%) of the desired compound as white crystalline solid.

$^1\text{H-NMR}$ (CDCl_3 , 298K, 200 MHz, δ ppm) δ 2.96 (s, 6H), 6.87 (dd, $J = 2.5 \times 9$ Hz, 1H), 7.25 (d, $J = 9$ Hz, 1H), 7.84 (d, $J = 2.5$ Hz, 1H).

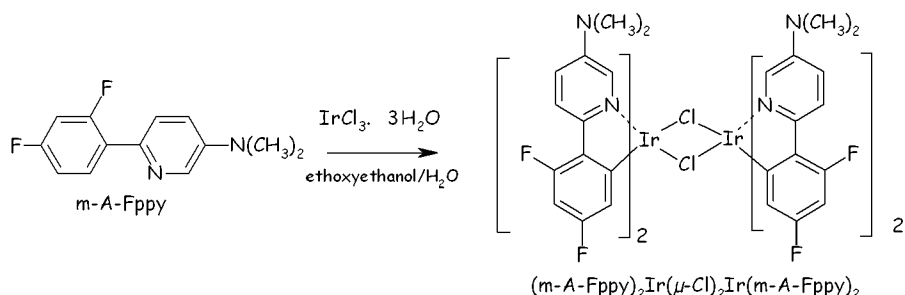
(2) Synthesis of 2-(2,4-difluorophenyl)-5-dimethylamino-pyridine

2-bromo-5-dimethylaminopyridine (3.2 g, 16 mmol), 2,4-difluorophenylboronic acid (4.8 g, 30 mmol), K_2CO_3 (13 g, 94 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (400 mg, 0.35 mmol) in a degased mixture of DME/ H_2O (60/50 ml) were refluxed 24 hours under nitrogen. After being cooled to room temperature, the organic layer was separated and the aqueous phase extracted with EtOAc (100ml). The combined organic fractions were washed with brine, dried over MgSO_4 and evaporated to dryness. The crude compound was purified by column chromatography (SiO_2 , CH_2Cl_2 then $\text{CH}_2\text{Cl}_2/\text{MeOH}$: 97/3). The resulting brown solid was dissolved in CH_2Cl_2 and decolorized with charcoal. Filtration and evaporation of the solvent afford 3 g (80%) of the desired compound as a slightly yellow crystalline solid.

$^1\text{H-NMR}$ (CDCl_3 , 298K, 200 MHz, δ ppm) δ 3.03 (s, 6H), 6.9-7.1 (m, 3H), 7.60 (dd, $J = 2.5 \times 9$ Hz, 1H), 7.95 (m, 1H), 8.24 (d, $J = 2.5$ Hz, 1H).

[0090] Example 15

Synthesis of cyclometalated Ir(III)- μ -chloro-bridge dimer [2-(2,4-difluorophenyl)-5-dimethylaminopyridine] $_2\text{IrCl}_2$ with m-A-Fppy [(m-A-Fppy) $_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{m-A-Fppy})_2$]



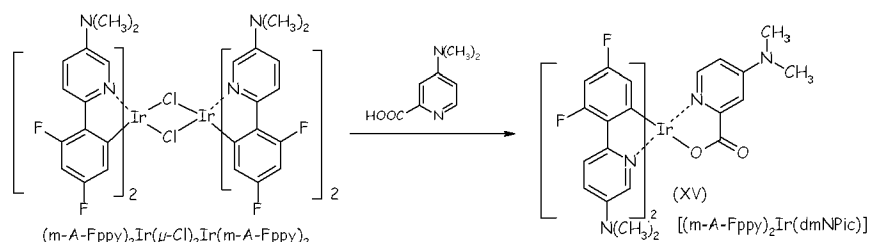
2-(2,4-difluorophenyl)-5-dimethylamino-pyridine (1.35 g, 5.76 mmol) and $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (820 mg, 2.32 mmol) were refluxed overnight in a mixture of ethoxyethanol/ H_2O (20/15 ml). After being cooled to room temperature,

water (15 ml) was added and the precipitate was filtered, washed with water and Et₂O to afford 1.4 g (87%) of the desired dimer as a yellowish powder. Because of the low solubility of this compound, its ¹H-NMR was recorded in DMSO-d₆ as its L₂Ir(Cl)(DMSO) derivative.

¹H-NMR (DMSO-d₆, 298K, 200 MHz, δ ppm) δ 3.05 (s, 6H), 3.07 (s, 6H), 5.14 (dd, J = 2.5×9 Hz, 1H), 5.71 (dd, J = 2.5×9 Hz, 1H), 6.67 (m, 2H), 7.51 (m, 2H), 8.01 (m, 2H), 9.07 (s, 1H), 9.48 (s, 1H).

[0091] Example 16

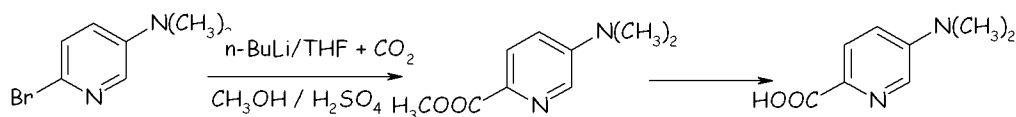
Synthesis of iridium(III) bis(2-(2,4-difluorophenyl)-5-dimethylaminopyridinato-N,C^{2'})-4-dimethylaminopicolinate) [(m-A-Fppy)₂Ir(dmNPic)] (formula XV)



The complex [(m-A-Fppy)₂Ir(dmNPic)] (XV) was conveniently synthesized in the low boiling solvent dichloromethane by reacting dichloro-bridged iridium (III) dimer [(m-A-Fppy)₂Ir(μ-Cl)₂Ir(m-A-Fppy)₂] with corresponding ancillary ligand.

Figure 9 is the emission spectrum measured at 298 K in dichloromethane solution of complex (XV) of example 16, obtained by exciting the complex at 380 nm; abscissa represents the wavelength in nm, while ordinate depicts the emission intensity in cps. Two emission peaks were identified having maximum of emission at (λ_{max}) 528 and 562 nm, respectively.

[0092] Example 17



(1) Synthesis of 5-dimethylamino-2-carboxymethyl-pyridine

To a solution of 2-bromo-5-dimethylaminopyridine (1.45 g, 7.2 mmol) in

THF (100 ml) cooled to -78°C was dropwise added $n\text{BuLi}$ (1.6M, 6.3 ml, 10 mmol). The resulting orange solution was stirred at -78°C for 40 minutes under nitrogen. CO_2 (from dry-ice) was then bubbled into the solution during 3 hours while the temperature was allowed to reach room temperature. MeOH (2 ml) was then added and the solvent removed under vacuum. MeOH (100 ml) and concentrated H_2SO_4 (4 ml) were added and the resulting mixture refluxed overnight. The solvent was removed under vacuum and water (100 ml) was added. The mixture was neutralized with aqueous K_2CO_3 and extracted with CH_2Cl_2 (3×50 ml). The combined organic fractions were washed with brine, dried over MgSO_4 and evaporated. The residue was purified by column chromatography (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{MeOH}$: 95/5). The obtained orange oil was dissolved in CH_2Cl_2 (1 ml) and petroleum ether (100 ml) was added. The solution was stand in the fridge overnight. The formed precipitate was filtered and washed with small portions of cold petroleum ether to afford 600 mg (46%) of the desired compound as a slightly yellow solid.

$^1\text{H-NMR}$ (CDCl_3 , 298K, 200 MHz, δ ppm) δ 3.09 (s, 6H), 3.96 (s, 3H), 6.94 (dd, $J = 2.5 \times 9$ Hz, 1H), 7.99 (d, $J = 9$ Hz, 1H), 8.17 (d, $J = 2.5$ Hz, 1H).

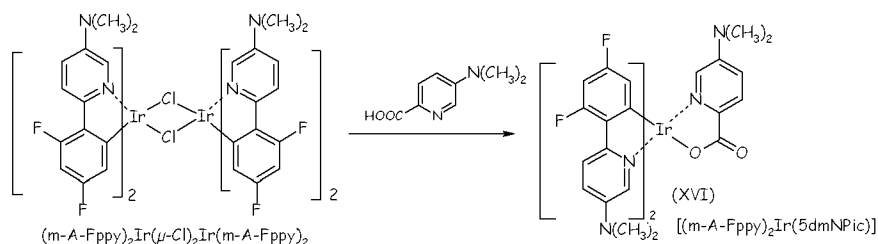
$^{13}\text{C-NMR}$ (CDCl_3 , 298K, 50 MHz, δ ppm) δ 39.7, 52.2, 116.8, 126.2, 133.9, 134.9, 147.7, 166.1.

(2) Synthesis of 5-dimethylamino-2-carboxy-pyridine

Free acid was obtained following standard hydrolysis procedures from corresponding methyl ester.

[0093] Example 18

Synthesis of iridium(III) bis(2-(2,4-difluorophenyl)-5-dimethylaminopyridinato-N, C^2)- 5-dimethylaminopyridinato) [(m-A-Fppy) $_2$ Ir(5dmNPic)] (formula XVI)



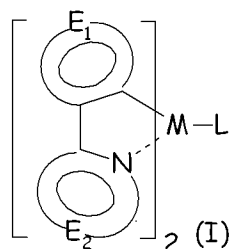
The complex [(m-A-Fppy)₂Ir(5dmNPic)] (XVI) was conveniently synthesized in the low boiling solvent dichloromethane by reacting dichloro-bridged iridium (III) dimer [(m-A-Fppy)₂Ir(μ-Cl)₂Ir(m-A-Fppy)₂] with corresponding ancillary ligand.

Figure 10 is the emission spectrum measured at 298 K in dichloromethane solution of complex (XVI) of example 18, obtained by exciting the complex at 380 nm; abscissa represents the wavelength in nm, while ordinate depicts the emission intensity in cps. Two emission peaks were identified having maximum of emission at (λ_{max}) 528 and 562 nm, respectively.

[0094]

Claims

1. A light emitting material comprising a complex of formula (I) :



wherein :

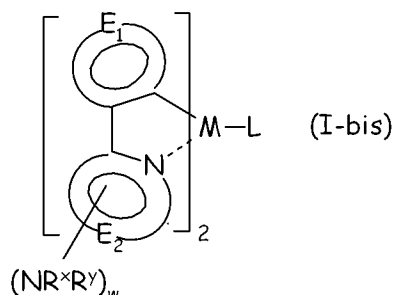
M represents a transition metal of atomic number of at least 40, preferably of groups 8 to 12, more preferably Ir or Pt, most preferably Ir;

E₁ represents a nonmetallic atoms group required to form a 5- or 6-membered aromatic or heteroaromatic ring, optionally condensed with additional aromatic moieties or non aromatic cycles, said ring optionally having one or more substituents, optionally forming a condensed structure with the ring comprising E₂, said ring coordinating to the metal M via a sp² hybridized carbon;

E₂ represents a nonmetallic atoms group required to form a 5- or 6-membered heteroaromatic ring, optionally condensed with additional aromatic moieties or non aromatic cycles, said ring optionally having one or more substituents, optionally forming a condensed structure with the ring comprising E₁, said ring coordinating to the metal M via a sp² hybridized nitrogen;

L is a chelate monoionic ligand, also designated as ancillary ligand, coordinating to the metal M through at least one oxygen atom and at least one sp² hybridized nitrogen atom, comprising at least one aromatic and/or heteroaromatic ring, said ring comprising at least one substituent selected from the group consisting of halogens, such as -Cl, -F, -Br; -OR₀; -SR₀; -N(R₀)₂; -P(OR₀)₂ and -P(R₀)₂; wherein R₀ is a C₁-C₆ alkyl, fluoro- or perfluoroalkyl, e.g. -CH₃, -nC₄H₉, -iC₃H₇, -CF₃, -C₂F₅, -C₃F₇ or a C₁-C₆ alkyl, fluoro- or perfluoroalkyl having one or more ether groups, e.g. -CH₂-(CH₂-O-CH₂)_n-CH₃, -CH₂-[CH₂(CH₃)-O-CH₂]_n-CH₃, -(CF₂O)_n-C₂F₅, with n being an integer from 1 to 8.

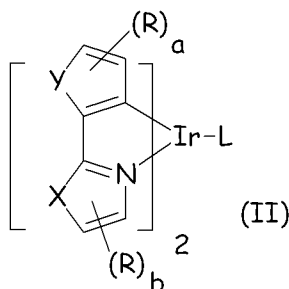
2. The light emitting material according to claim 1 comprising a complex of formula (I-bis) here below:



wherein E₁, E₂, M, L, have the meaning as above defined,

R^x and R^y, equal or different from each other and at each occurrence, are chosen among C₁-C₆ alkyl, fluoro- or perfluoroalkyl groups, e.g. -CH₃, -nC₄H₉, -iC₃H₇, -CF₃, -C₂F₅, -C₃F₇ or C₁-C₆ alkyl, fluoro- or perfluoroalkyl groups having one or more ether groups; and w is an integer between 1 and 4.

3. The light emitting material of anyone of the preceding claims, comprising a complex complying with formula (II) here below :



wherein :

L has the same meaning as above defined;

X is a group chosen among the group consisting of -CH=CH-, -CR=CH-, -CR=CR-, N-H, N-R¹, O, S or Se; preferably X is a group selected among -CH=CH-, -CR=CH- or S; most preferably X is -CH=CH-;

Y is a group chosen among the group consisting of -CH=CH-, -CR=CH-, -CR=CR-, N-H, N-R¹, O, S or Se; preferably Y is a group selected among -CH=CH-, -CR=CH- or S; most preferably Y is -CH=CH-;

R is the same or different at each occurrence and is F, Cl, Br, NO₂, CN; a straight-chain or branched or cyclic alkyl or alkoxy group or dialkylamino group having from 1 to 20 carbon atoms, in each of which one or more

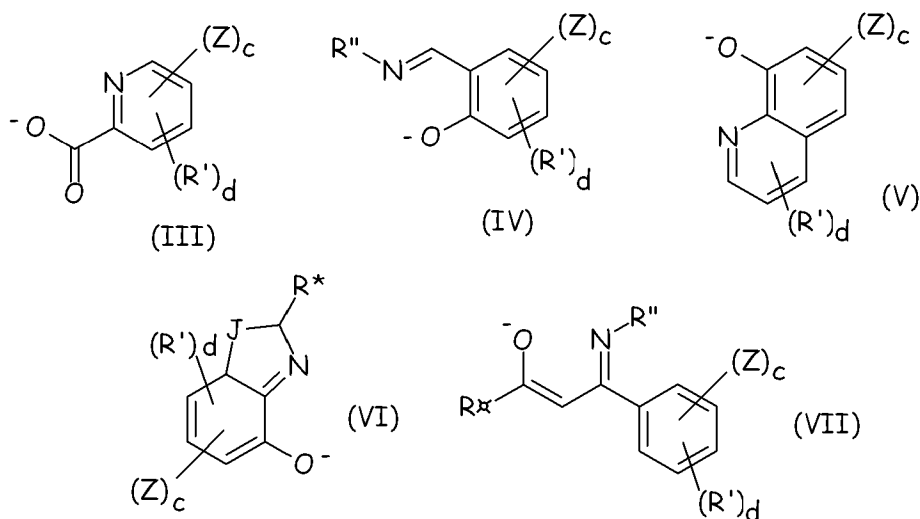
nonadjacent $-\text{CH}_2-$ groups may be replaced by $-\text{O}-$, $-\text{S}-$, $-\text{NR}^1-$, or $-\text{CONR}^2-$, and in each of which one or more hydrogen atoms may be replaced by F; an aryl or heteroaryl group having from 4 to 14 carbon atoms which may be substituted by one or more nonaromatic radicals $-\text{R}$; and a plurality of substituents R , either on the same ring or on the two different rings, may in turn together form a further mono- or polycyclic ring system, optionally aromatic.

R^1 and R^2 are the same or different from each other and at each occurrence and are each H or an aliphatic or aromatic hydrocarbon radical having from 1 to 20 carbon atoms;

a is an integer from 0 to 4;

b is an integer from 0 to 4.

4. The light emitting material according to anyone of the preceding claims, wherein the chelate monoionic ligand (L) is selected from the structures represented by following formulae (III) to (VII) or tautomers thereof :



wherein :

Z is a substituent selected from the group consisting of halogens, such as $-\text{Cl}$, $-\text{F}$, $-\text{Br}$; $-\text{OR}_0$; $-\text{SR}_0$; $-\text{N}(\text{R}_0)_2$; $-\text{P}(\text{OR}_0)_2$ and $-\text{P}(\text{R}_0)_2$; wherein R_0 is a C_1 - C_6 alkyl, fluoro- or perfluoroalkyl, e.g. $-\text{CH}_3$, $-\text{nC}_4\text{H}_9$, $-\text{iC}_3\text{H}_7$, $-\text{CF}_3$, $-\text{C}_2\text{F}_5$, $-\text{C}_3\text{F}_7$ or a C_1 - C_6 alkyl, fluoro- or perfluoroalkyl having one or more ether groups, e.g. $-\text{CH}_2(\text{CH}_2\text{OCH}_2)_n-\text{CH}_3$, $-\text{CH}_2[\text{CH}_2(\text{CH}_3)\text{OCH}_2]_n-\text{CH}_3$, $-(\text{CF}_2\text{O})_n-\text{C}_2\text{F}_5$, with n being an integer from 1 to 8;

J is a group chosen among the group consisting of $-\text{CH}=\text{CH}-$, $-\text{CR}=\text{CH}-$, $-\text{CR}=\text{CR}-$, $\text{N}-\text{H}$, $\text{N}-\text{R}^1$, O , S or Se ;

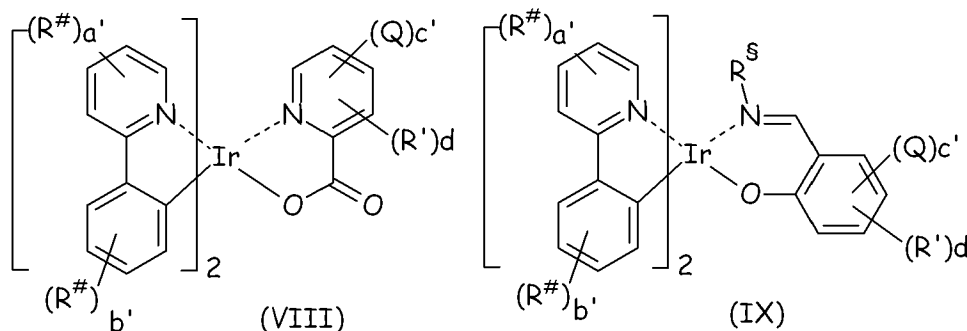
R' , R^* , R^α the same or different from each other and at each occurrence, represent F , Cl , Br , NO_2 , CN , a straight-chain or branched or cyclic alkyl or alkoxy group having from 1 to 20 carbon atoms, in each of which one or more nonadjacent $-\text{CH}_2-$ groups may be replaced by $-\text{O}-$, $-\text{S}-$, $-\text{NR}^1-$, or $-\text{CONR}^2-$, and in each of which one or more hydrogen atoms may be replaced by F ; or an aryl or heteroaryl group having from 4 to 14 carbon atoms which may be substituted by one or more nonaromatic radicals $-\text{R}'$; and a plurality of substituents R' , either on the same ring or on the two different rings, may in turn together form a further mono- or polycyclic ring system, optionally aromatic;

R'' , R^1 and R^2 are the same or different from each other and at each occurrence and are each H or an aliphatic or aromatic hydrocarbon radical, optionally substituted, having from 1 to 20 carbon atoms;

c is an integer from 1 to 3;

d is an integer from 0 to 4.

5. The light emitting material of claim 4, comprising a complex of formula (VIII) or (IX) here below :



wherein :

R' and d have the same meaning as above defined;

Q is $-\text{OR}_0$ or $-\text{N}(\text{R}_0)_2$ wherein R_0 is a C_1 - C_6 alkyl, fluoro- or perfluoroalkyl, e.g. $-\text{CH}_3$, $-\text{nC}_4\text{H}_9$, $-\text{iC}_3\text{H}_7$, $-\text{CF}_3$, $-\text{C}_2\text{F}_5$, $-\text{C}_3\text{F}_7$ or a C_1 - C_6 alkyl, fluoro- or perfluoroalkyl having one or more ether groups, e.g. $-\text{CH}_2-(\text{CH}_2-\text{O}-\text{CH}_2)_n-\text{CH}_3$, $-\text{CH}_2-[\text{CH}_2(\text{CH}_3)-\text{O}-\text{CH}_2]_n-\text{CH}_3$, $-(\text{CF}_2\text{O})_n-\text{C}_2\text{F}_5$, with n being an integer from 1 to 8;

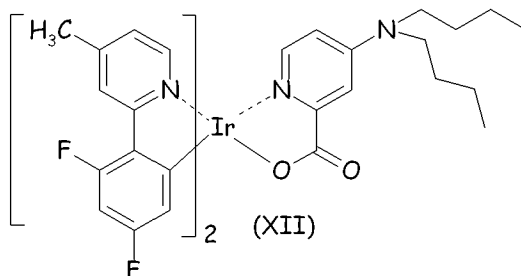
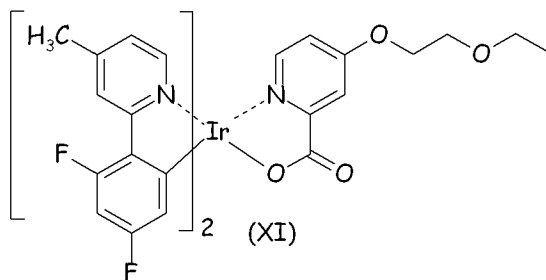
c' being an integer between 1 and 3;

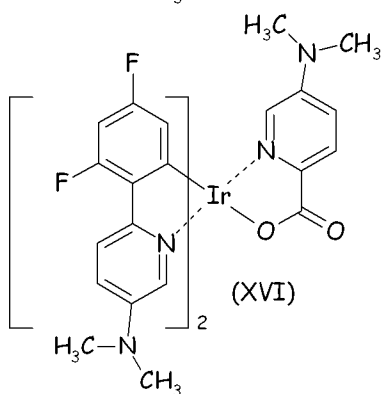
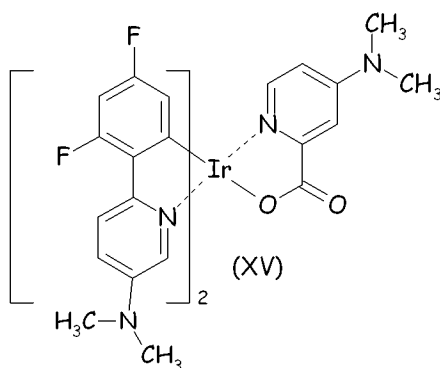
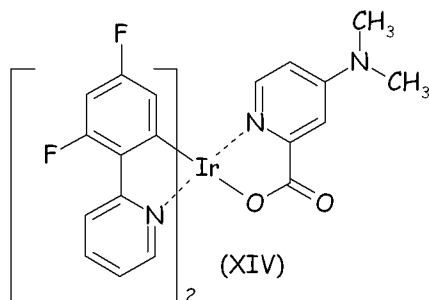
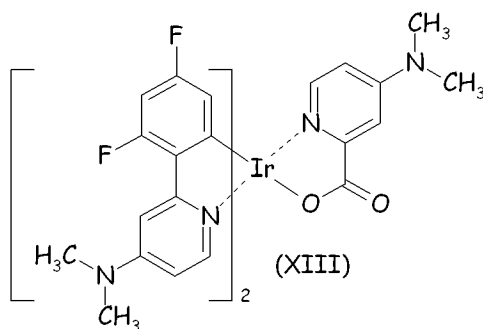
$R^\#$ the same or different at each occurrence, is F, Cl, Br, NO_2 , CN, a straight-chain or branched or cyclic alkyl or alkoxy group or dialkylamino group having from 1 to 20 carbon atoms, in each of which one or more nonadjacent $\text{-CH}_2\text{-}$ groups may be replaced by -O- , -S- , $\text{-NR}^1\text{-}$, or $\text{-CONR}^2\text{-}$ (with R^1 and R^2 being each H or an aliphatic or aromatic hydrocarbon radical having from 1 to 20 carbon atoms) and in each of which one or more hydrogen atoms may be replaced by F, or an aryl or heteroaryl group having from 4 to 14 carbon atoms which may be substituted by one or more nonaromatic radicals $\text{-R}^\#$; and a plurality of substituents $R^\#$, either on the same ring or on the two different rings, may in turn together form a further mono- or polycyclic ring system, optionally aromatic;

a' and b' equal or different each other, are independently an integer between 0 and 4;

$R^\S$ is chosen among H and aliphatic or aromatic hydrocarbon radicals, optionally substituted, having from 1 to 20 carbon atoms.

6. The light emitting material according to claim 5 comprising a complex chosen among formulae (XI) to (XVI) here below, or mixtures of two or more thereof:





7. Use of the light emitting material according to anyone of claims 1 to 6 in the emitting layer of an organic light emitting device.
8. Use of the light emitting material according to anyone of claims 1 to 6 as dopant in a host layer, functioning as an emissive layer in an organic light emitting device.

9. An organic light emitting device (OLED) comprising an emissive layer (EML), said emissive layer comprising the light emitting material according to anyone of claims 1 to 6, optionally with a host material.

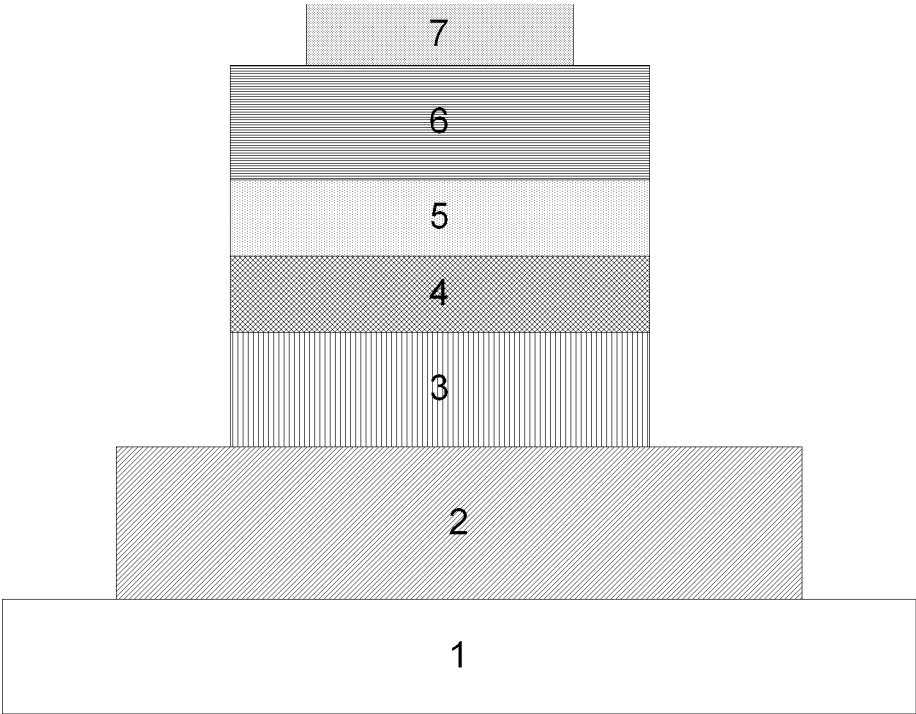


Fig. 1

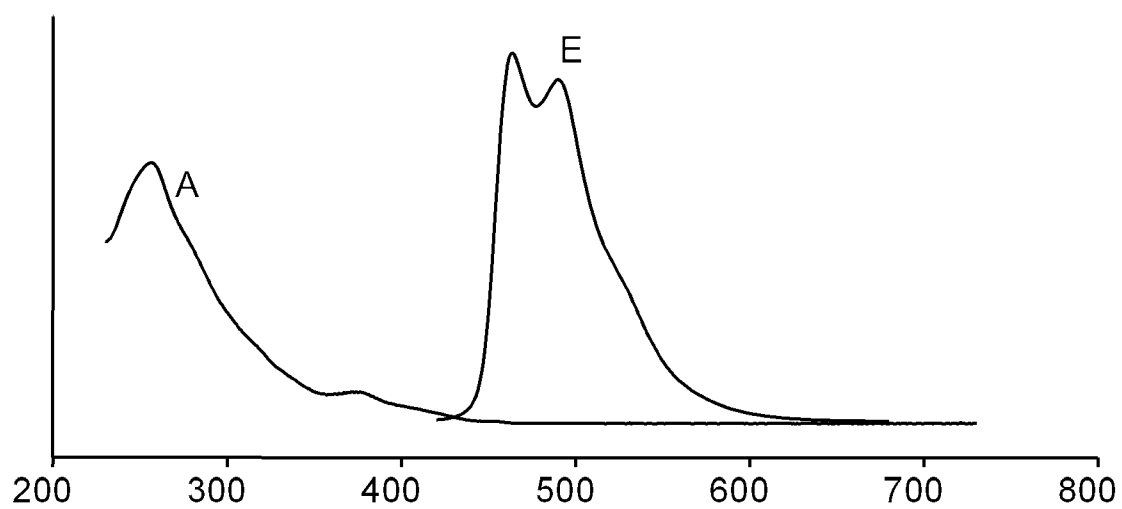


Fig. 2

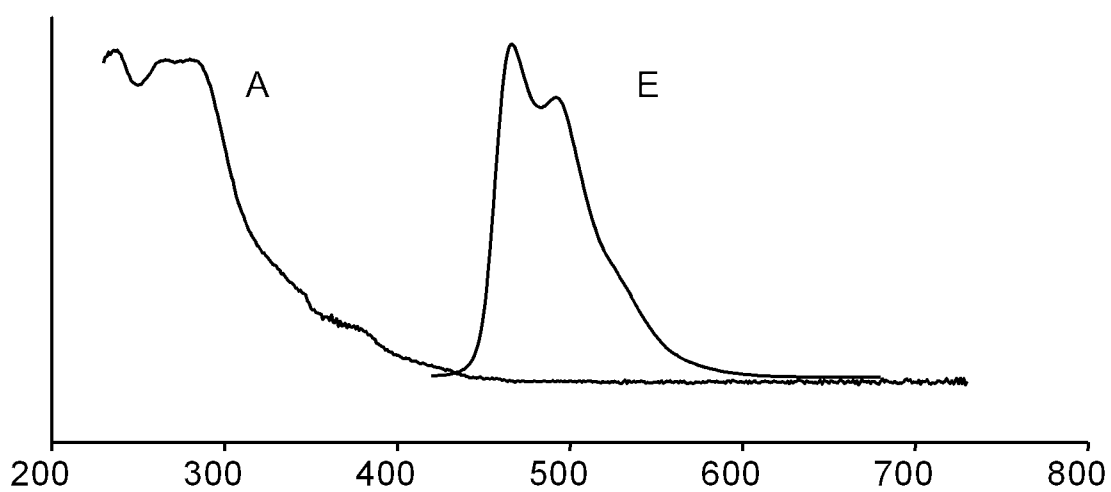


Fig. 3

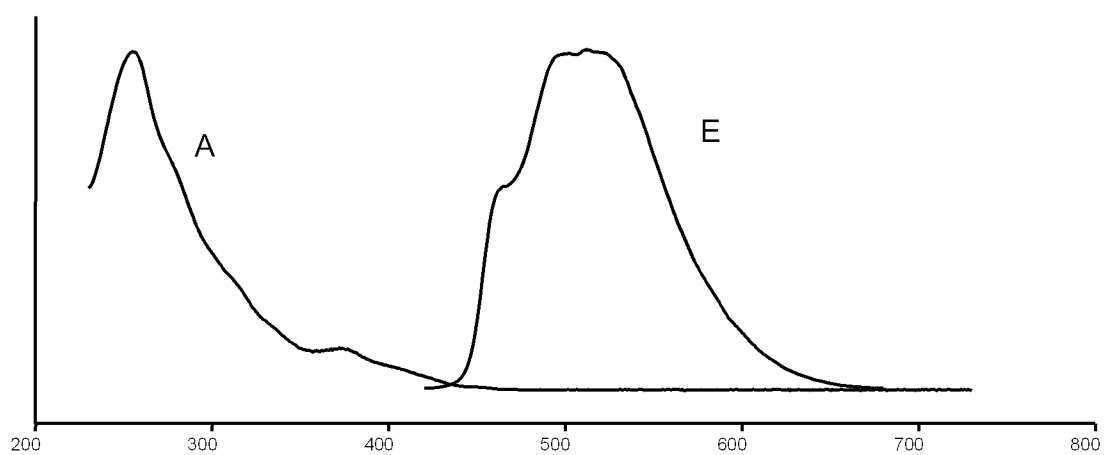


Fig. 4

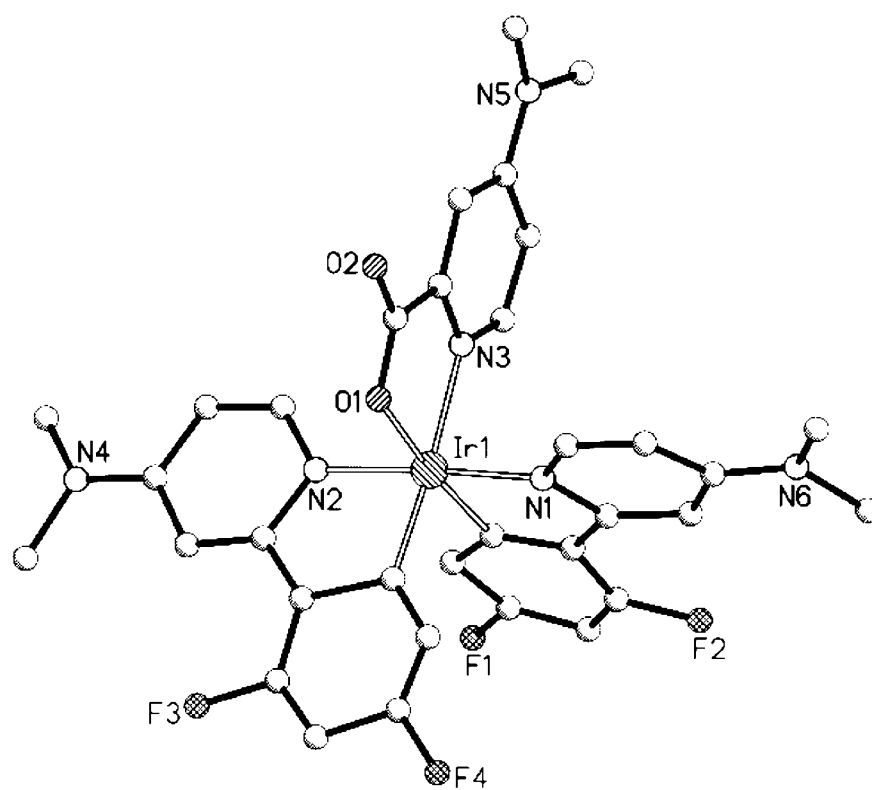


Fig. 5

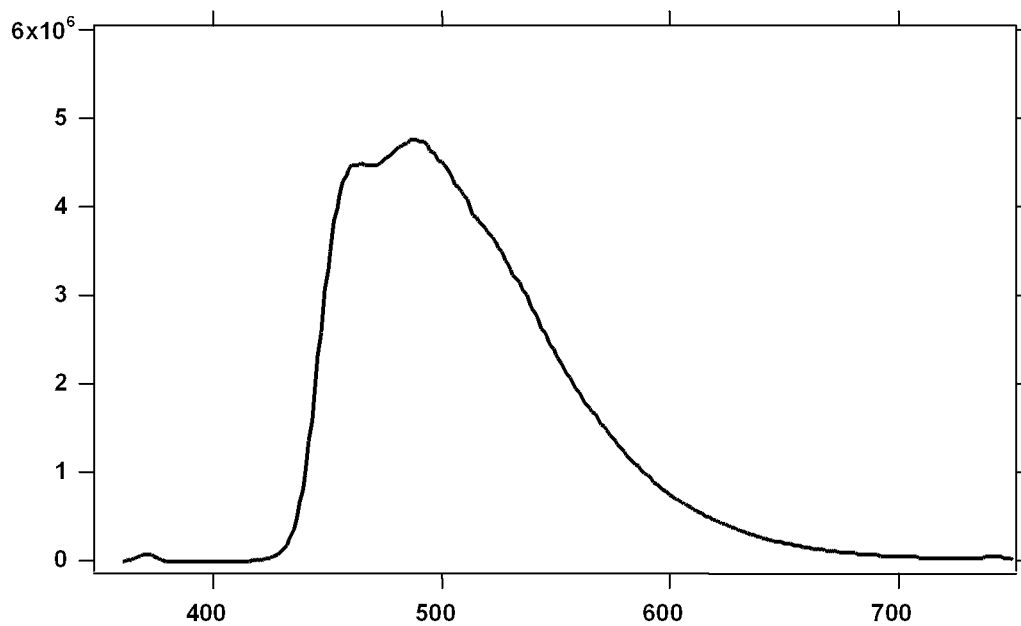


Fig. 6

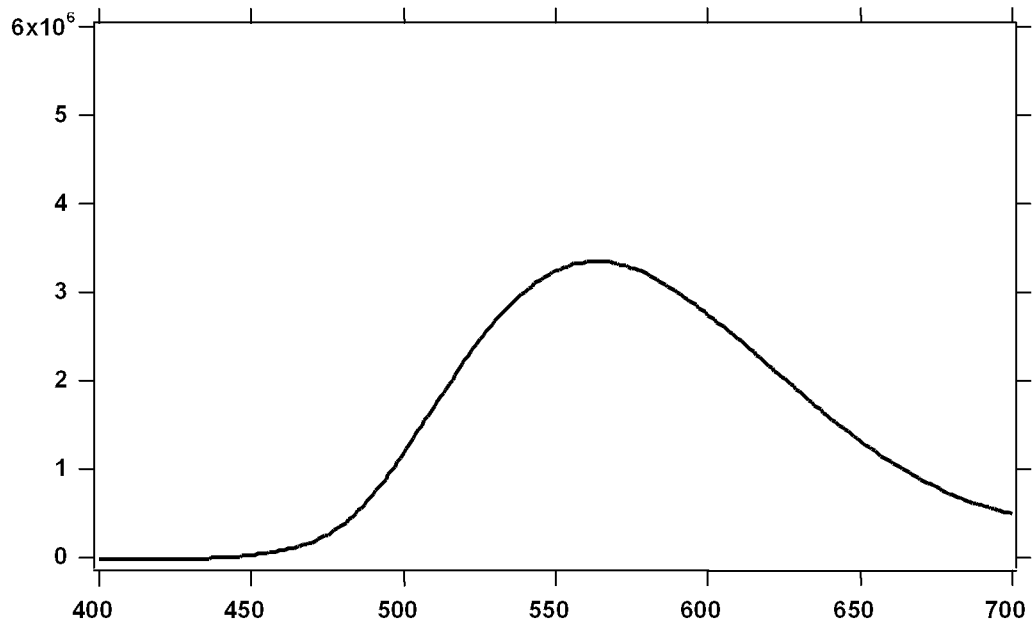


Fig. 7

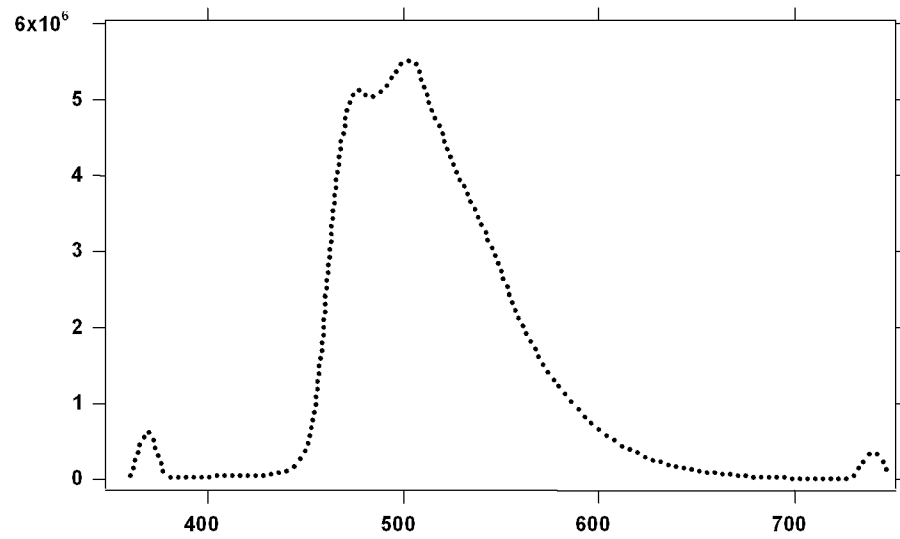


Fig. 8

6/6

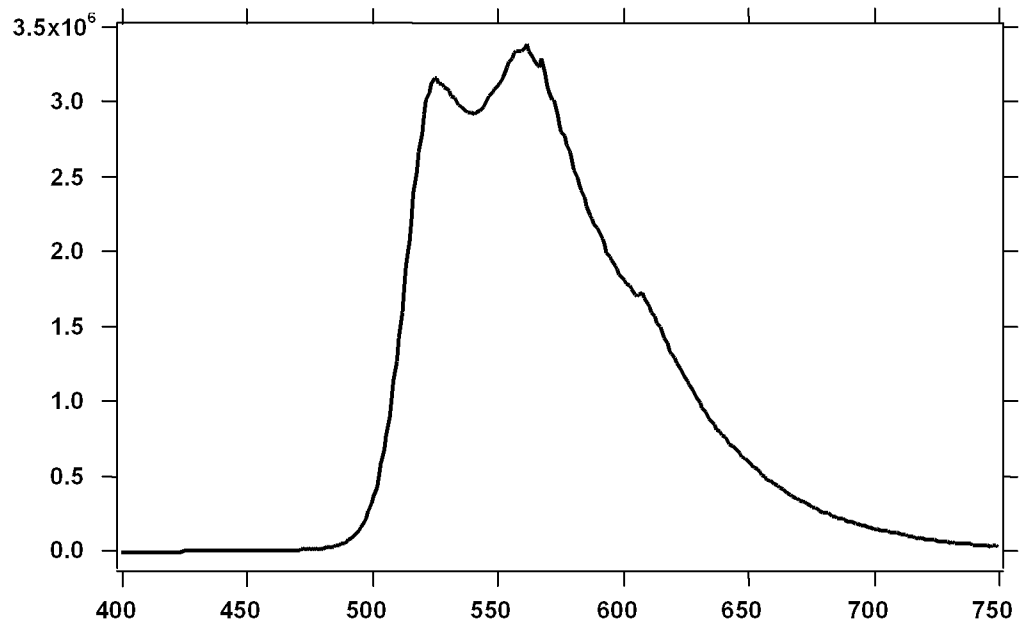


Fig. 9

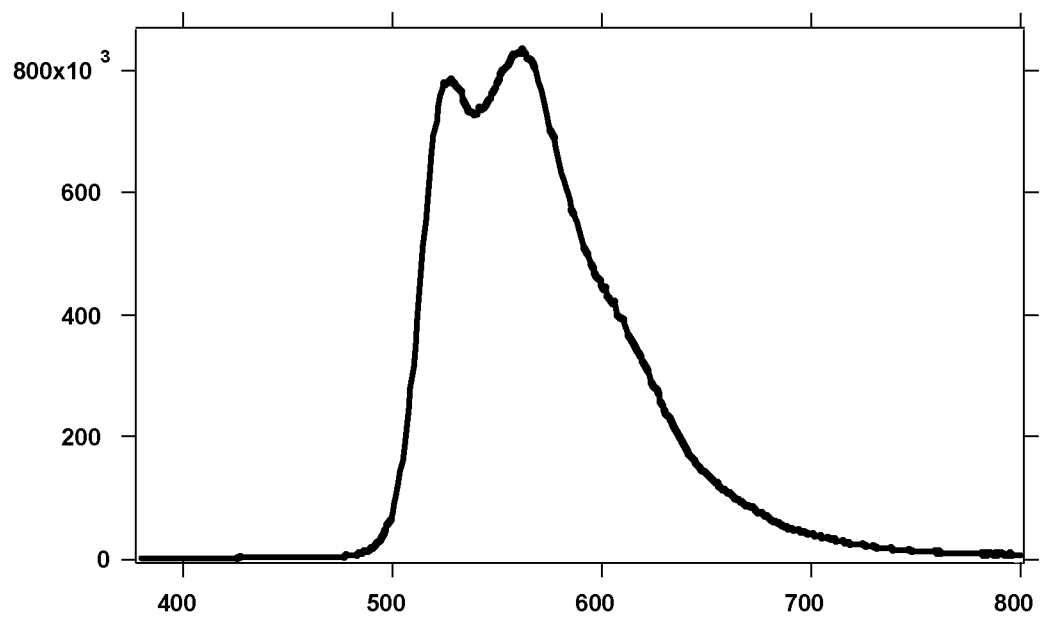


Fig. 10