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(54) **DEPOSITABLE ION ORGANIC FUNCTION MATERIAL AND USE THEREOF IN ORGANIC ELECTROLUMINESCENT DEVICE**

ABSCHIEDBARES ORGANISCHES IONENFUNKTIONSMATERIAL UND VERWENDUNG DAVON
IN EINER ORGANISCHEN ELEKTROLUMINESZENTEN VORRICHTUNG

MATÉRIAU FONCTIONNEL ORGANIQUE D'IONS POUVANT ÊTRE DÉPOSÉ ET UTILISATION
CORRESPONDANTE DANS UN DISPOSITIF ÉLECTROLUMINESCENT ORGANIQUE

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(73) Proprietors:
• **Kunshan Go-Visionox Opto-Electronics Co., Ltd.**
KunShan, Jiangsu 215300 (CN)
• **Tsinghua University**
Beijing 100084 (CN)

(72) Inventors:
• **DUAN, Lian**
Beijing 100085 (CN)

- **MA, Dongxin**
Beijing 100084 (CN)
- **LIU, Song**
Beijing 100085 (CN)
- **XIE, Jing**
Langfang
Hebei 065000 (CN)
- **ZHAO, Fei**
Beijing 100085 (CN)

(74) Representative: **Herrmann, Uwe**
Lorenz Seidler Gossel
Rechtsanwälte Patentanwälte
Partnerschaft mbB
Widenmayerstraße 23
80538 München (DE)

(56) References cited:
WO-A2-2014/094962 US-A1- 2006 177 695
US-A1- 2013 203 997

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Description

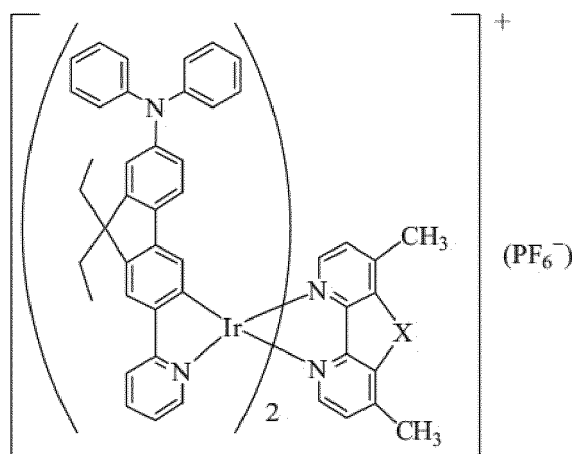
Technical Field

[0001] The present invention relates to the field of organic electroluminescent materials, and in particular relates to a depositable ionic organic functional material which can be used in an organic electroluminescent device, a preparation method thereof and use thereof in the field of organic electroluminescent materials.

Background

[0002] The organic light-emitting layer of an organic electroluminescent device OLED is prepared mainly by using a fully fluorescent material, a fully phosphorescent material, or a mixture of fluorescent material and phosphorescent material. The fluorescent light-emitting material in the prior art is prone to fluorescent quenching, and the device prepared by doping the light-emitting layer with the fluorescent light-emitting material in the prior art is prone to crystallization phenomenon, which leads to reduced service life. And it is difficult to use a phosphorescent light-emitting material to synthesize a stable dark-blue light material.

[0003] In order to solve the above-mentioned problem, cationic complex is developed to be used as light-emitting material. The synthesis conditions of this type of material are mild and easy to carry out, with high yield, and the product is simple to purify; secondly, this type of complex has good redox properties and can increase the stability of the device. However, because ionic material has poor volatilization properties and is not suitable for preparing a device by means of evaporation-deposition, which severely limits the use of this type of material in electronic devices. US 2006/0177695 A1 discloses cyclometalated transition metal complexes and their use in organic electroluminescent devices. Advanced Functional Materials, 2007, 17, 315 discloses an Iridium complex having a structure shown in the following formula (41), wherein the reported two kinds of depositable ionic complexes adopt an Iridium complex as the cation, and adopts a hexafluorophosphate anion as the counterion. This method has a deficiency of not having universality, i.e. more kinds of depositable ionic complexes cannot be developed according to this route.



X = none (1)

X = CH=CH (2)

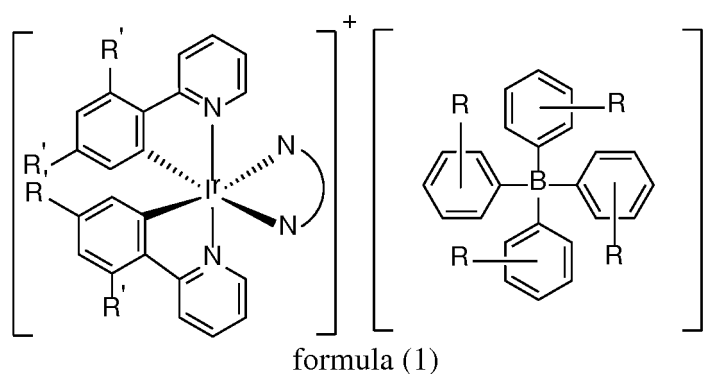
formula (41)

Summary of the Invention

[0004] An objective of the present invention is to provide a depositable ionic organic functional material wherein, when the functional material is used as a luminescent dye, the synthesis conditions are mild and easy to carry out, the yield is high, the product is simple to purify, and the functional material can be used in high-efficiency OLEDs emitting blue to red light.

[0005] In order to achieve the above-mentioned objective, the present invention adopts the following technical scheme:

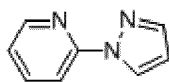
[0006] A depositable ionic organic functional material is provided, which has a structure shown in the following formula (1):



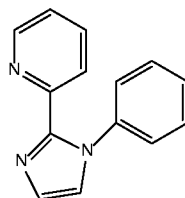
wherein, R is a hydrogen atom, a halogen atom or $-\text{CF}_3$;

R' is a hydrogen atom or a halogen atom;

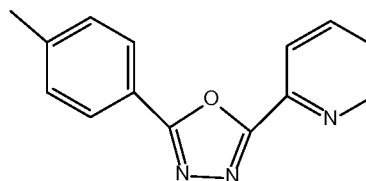
the N^N ligand is selected from **Pzpy** shown in the following formula (31), **Pyim** shown in the following formula (32), **Ptop** shown in the following formula (33), **Pop** shown in the following formula (34), and **Bpy** shown in the following formula (35):



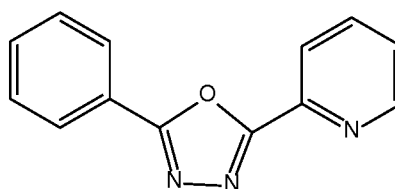
formula (31)



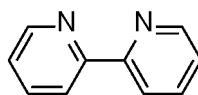
formula (32)



formula (33)

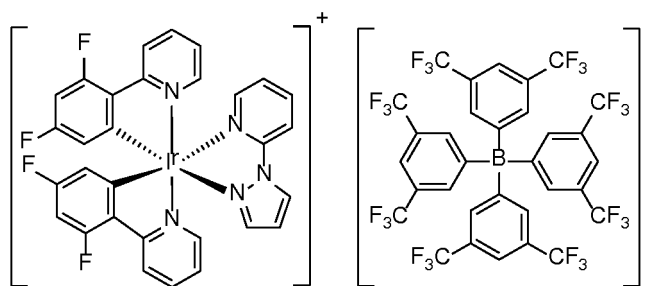


formula (34)

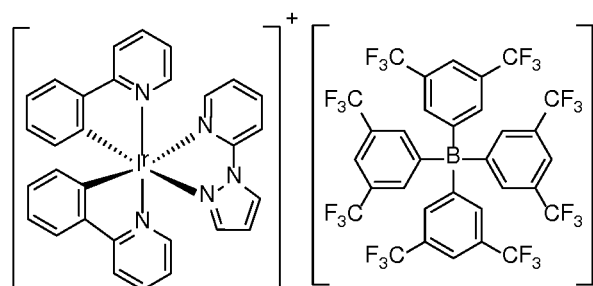


formula (35)

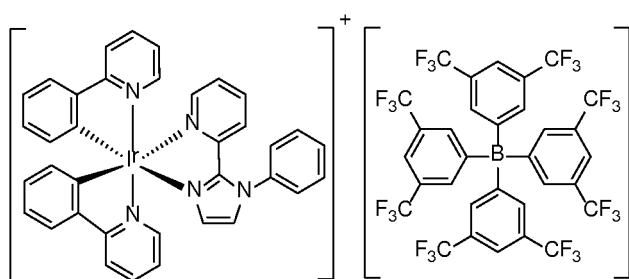
[0007] Preferable, the depositable ionic complex has a structure shown in the following formulas (11) to (16) and formulas (21) to (26):



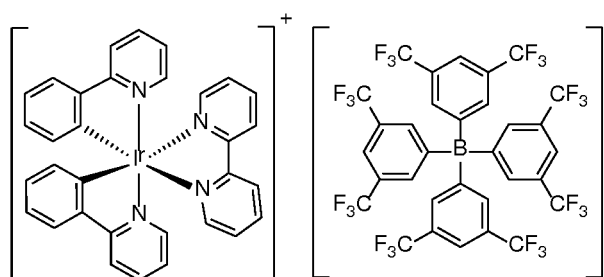
formula (11)



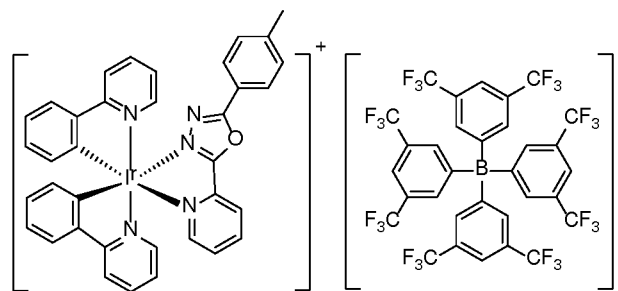
formula (12)



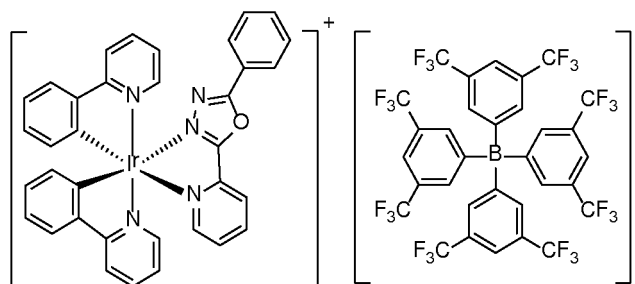
formula (13)



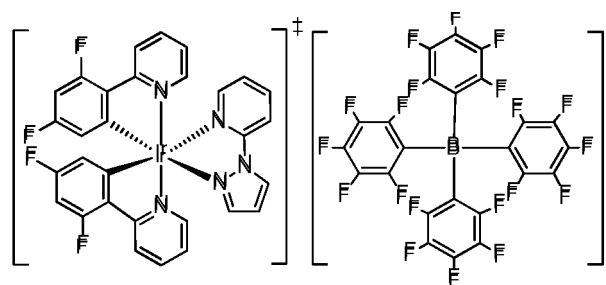
formula (14)



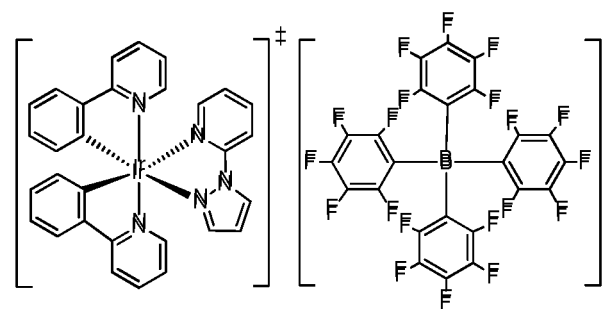
formula (15)



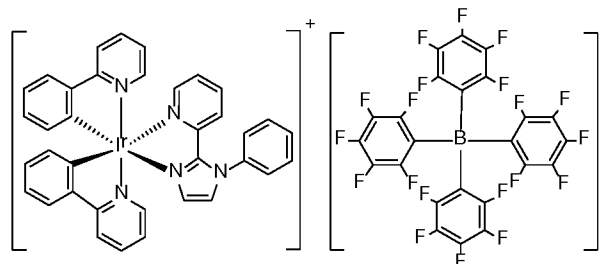
formula (16)



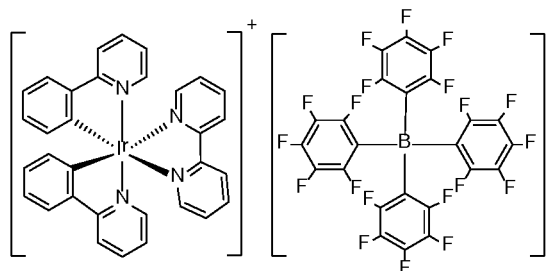
formula (21)



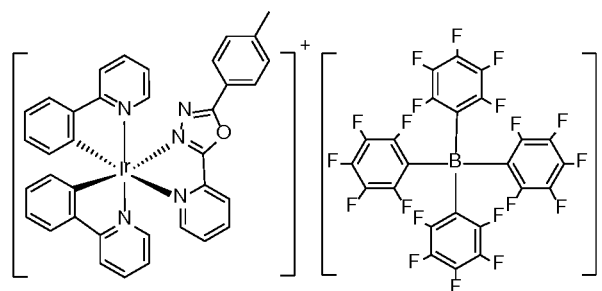
formula (22)



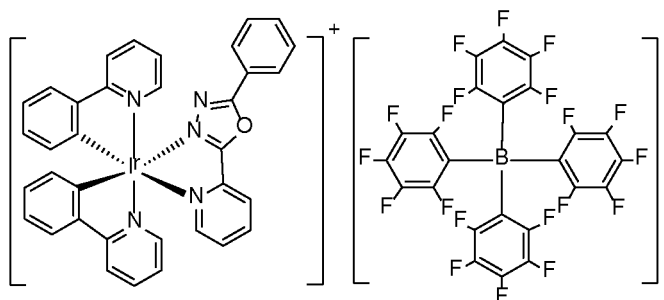
formula (23)



formula (24)



formula (25)



formula (26).

[0008] A use of the aforementioned depositable ionic organic functional material in an organic electroluminescent device is provided, wherein, the depositable ionic organic functional material is used as a dye in an organic light-emitting layer of the organic electroluminescent device.

[0009] An organic electroluminescent device is provided, which comprises a substrate, and an anode layer, an organic light-emitting functional layer, a cathode layer formed in sequence upon the substrate, wherein the organic light-emitting functional layer comprises a hole transport layer, an organic light-emitting layer and an electron transport layer, and wherein a host material of the organic light-emitting layer is doped with the aforementioned depositable ionic organic functional material.

[0010] Doping concentration of the depositable ionic organic functional material is 2wt%-10wt%.

[0011] The depositable ionic organic functional material is red, yellow, green or blue light emitting material.

[0012] The organic light-emitting layer has a thickness of 10nm-50nm, preferably 10nm-30nm.

[0013] As compared to the prior art, the depositable ionic organic functional material of the present invention has the following advantages:

A molecular design strategy for obtaining a depositable ionic organic functional material is provided for the first time by the present invention, wherein a series of depositable ionic Iridium complexes are designed and developed. In this type of depositable ionic Iridium complexes, a tetraphenylborate derivative anion, which is a counterion with large steric hindrance and good electrical charge dispersion, is introduced into a cationic Iridium complex to replace the hexafluorophosphate anion as mentioned in the background technology, thereby reducing the interactivity between anions and cations. Furthermore, the tetraphenylborate derivative anion can increase the electrical charge transport capability, reduce the drive voltage of the device, reduce the energy consumption, and thus effectively reduce the production cost. The present invention is simple and easy to carry out and has universality, depositable ionic Iridium complexes as dyes of various colors can be developed accordingly, so as to produce high-efficiency OLEDs emitting blue to red light.

Brief Description of the Drawings

[0014]

Figure 1 is a thermogravimetric analysis diagram of the complexes shown by the formulas (11) to (16) in a N₂ atmosphere;

Figure 2 is a current density-voltage spectrogram of the devices 1-6 in the application example 1;

Figure 3 is a luminance-voltage spectrogram of the devices 1-6 in the application example 1;

Figure 4 is an EL spectrogram of the devices 1-6 in the application example 1;

Figure 5 is a thermogravimetric analysis diagram of the complexes shown by the formulas (21) to (26) in a N₂ atmosphere;

Figure 6 is a current density-voltage spectrogram of the devices 7-12 in the application example 2;

Figure 7 is a luminance-voltage spectrogram of the devices 7-12 in the application example 2;

Figure 8 is an EL spectrogram of the devices 7-12 in the application example 2;

Figure 9 is a structural schematic diagram of the organic electroluminescent device; wherein,

01- substrate,

02- anode layer

03- cathode layer

04- hole injection layer

05- hole transport layer

06- organic light-emitting layer

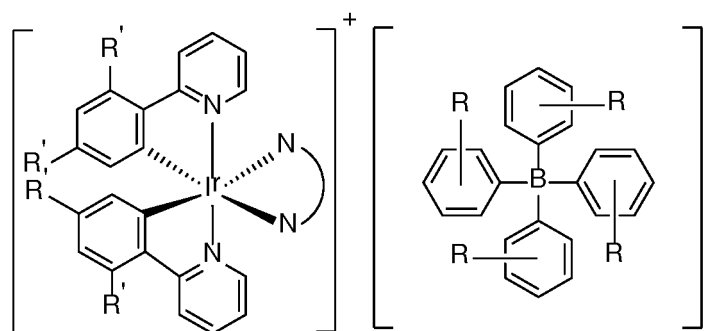
07- electron transport layer

Detailed Description of Embodiments

[0015] The present invention is further described hereinafter by illustrating specific embodiments.

[0016] The present invention can be implemented in many different forms, and should not be interpreted to be limited to the embodiments described herein. On the contrary, by providing these embodiments, the present disclosure is made complete and thorough, and the inventive concept of the present invention is sufficiently conveyed to those skilled in the art, wherein the present invention is defined by the Claims. In the accompanying drawings, for the sake of clarity, dimensions and relative sizes of layers and areas might be exaggerated. It should be understood that, when one element such as a layer, an area or a substrate is described as "formed on" or "configured on" another element, this one element may be configured directly upon that another element, or there may exist intermediate element(s). On the contrary, when one element is described as "directly formed upon" or "directly configured upon" another element, there exists no intermediate element.

[0017] The present invention provides a depositable ionic organic functional material, wherein the depositable ionic organic functional material has a structure shown in the following formula (1):

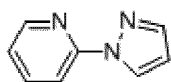


formula (1)

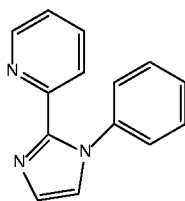
wherein, R is a hydrogen atom, a halogen atom or $-\text{CF}_3$;

R' is a hydrogen atom or a halogen atom;

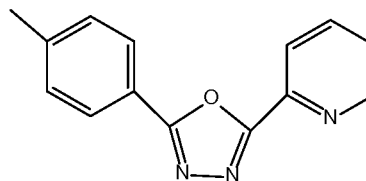
N[^]N ligand is selected from **Pzpy** shown in the following formula (31) and its derivatives, **Pyim** shown in the following formula (32), **Ptop** shown in the following formula (33), **Pbp** shown in the following formula (34), and **Bpy** shown in the following formula (35):



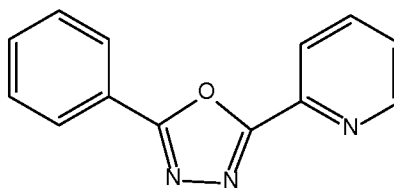
formula (31)



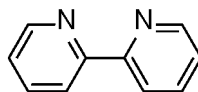
formula (32)



formula (33)

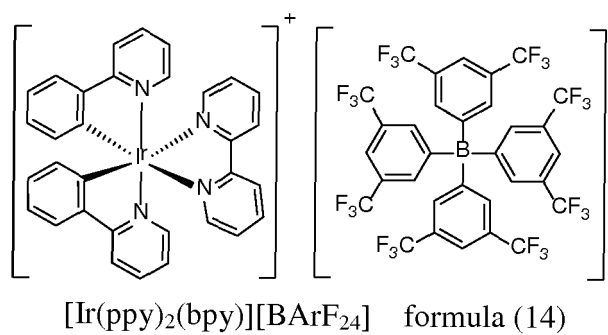
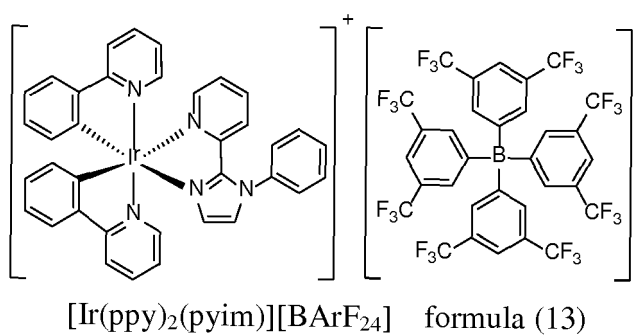
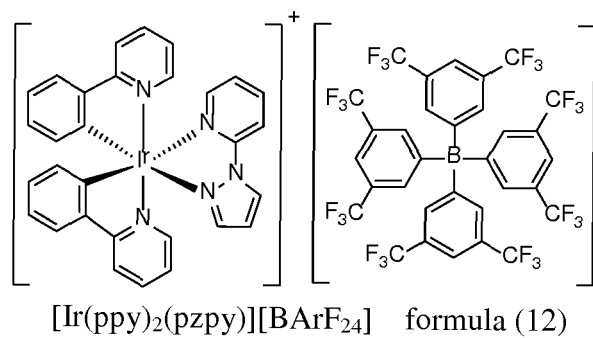
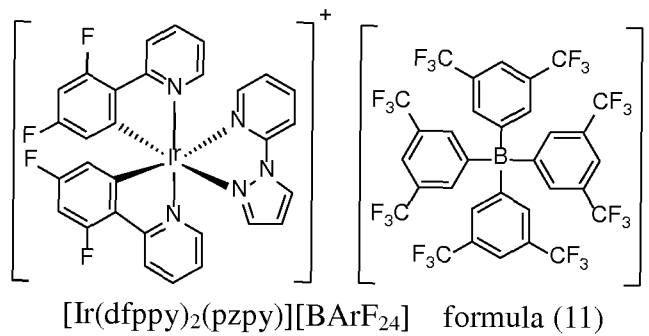


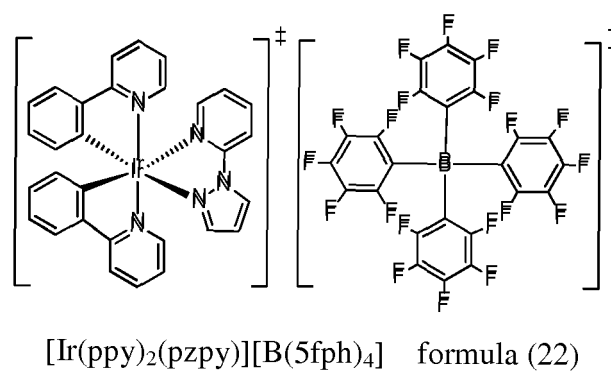
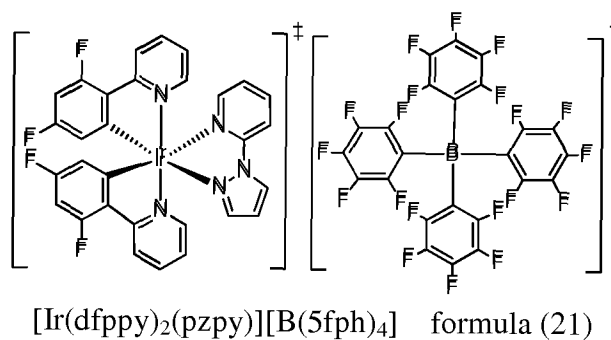
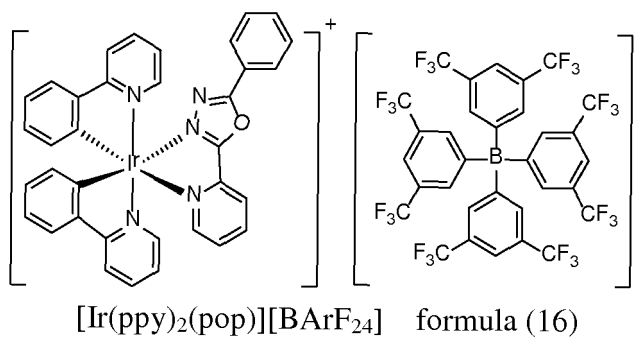
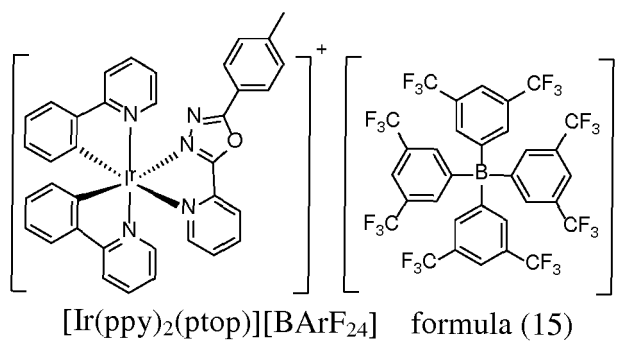
formula (34)

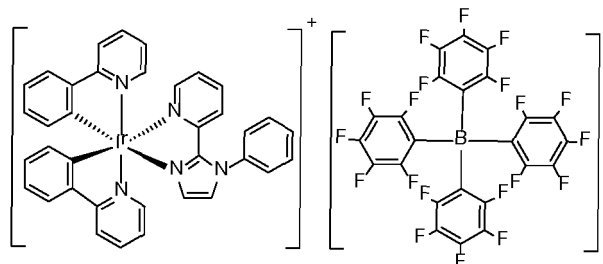
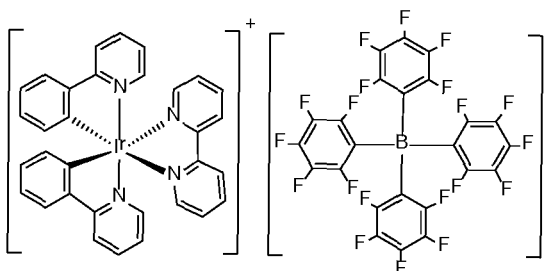
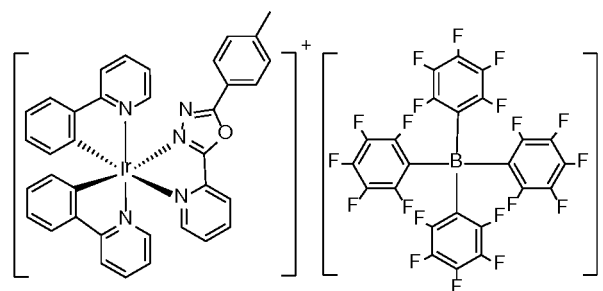
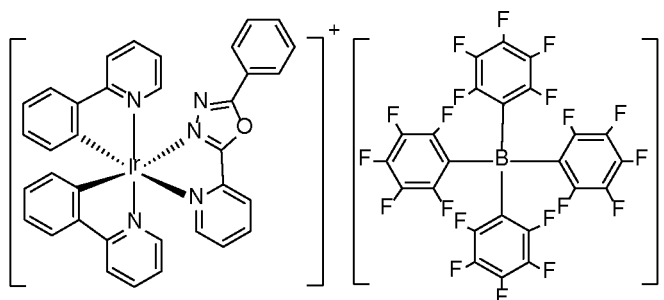


formula (35)

[0018] The depositable ionic organic functional material is preferably:





[Ir(ppy)₂(pyim)][B(5fph)₄] formula (23)[Ir(ppy)₂(bpy)][B(5fph)₄] formula (24)[Ir(ppy)₂(ptop)][B(5fph)₄] formula (25)[Ir(ppy)₂(pop)][B(5fph)₄] formula (26).

[0019] A use of the aforementioned depositable ionic organic functional material in an organic electroluminescent device is provided.

[0020] In the above-mentioned use, the depositable ionic organic functional material is used as a dye in an organic light-emitting layer of the organic electroluminescent device.

[0021] As shown in Figure 9, the organic electroluminescent device comprises a substrate 01, and an anode layer 02, an organic light-emitting functional layer, a cathode layer 03 formed in sequence upon the substrate, wherein the organic light-emitting functional layer comprises a hole injection layer 04, a hole transport layer 05, an organic light-emitting layer 06 and an electron transport layer 07, and wherein a host material of the organic light-emitting layer 06 is doped with

the aforementioned depositable ionic organic functional material.

[0022] Doping concentration of the depositable ionic organic functional material is 2wt%-10wt%.

[0023] The depositable ionic organic functional material is red, yellow, green or blue light emitting material.

[0024] The organic light-emitting layer has a thickness of 10nm-50nm, preferably 10nm-30nm.

[0025] If not particularly described otherwise, the respective layers of the device in the present invention are made of the following materials:

The anode layer may adopt inorganic material or organic conducting polymer. The inorganic material is usually selected from metal oxides such as indium tin oxide (ITO), zinc oxide (ZnO), indium zinc oxide (IZO), and metals having relatively high work function such as gold, copper, silver, and it is preferably ITO. The organic conducting polymer is preferably selected from Polythiophene / Polyvinylbenzenesulfonate sodium (hereinafter abbreviated as PEDOT:PSS), and polyaniline (hereinafter abbreviated as PANI).

[0026] The cathode layer usually adopts metals having relatively low work function such as lithium, magnesium, calcium, strontium, aluminum, indium, or their alloys with copper, gold, silver, or the cathode layer is an electrode layer formed by alternately arranged metal and metal fluoride. In the present invention, the cathode layer is preferably a mixed electrode of Mg:Ag/Ag.

[0027] The material of the hole transport layer may be selected from aromatic amine type, carbazole type and branched polymer type low molecular material, and is preferably selected from NPB and TCTA.

[0028] In the organic electroluminescent device of the present invention, there may also be a hole injection layer between the anode layer and the hole transport layer. The material of the hole injection layer may adopt, for example, 2,3,6,7,10,11-hexacyanil-1,4,5,8,9,12-hexaazatriphenylene (HAT-CN), 4,4',4"-tri-(3-methyl-phenyl-aniline)-tri-aniline doped with F4TCNQ, or may adopt copper phthalocyanine (CuPc), or may be a metal oxide such as molybdenum oxide, rhenium oxide.

[0029] The light-emitting material of the organic light-emitting layer 06 may be a fluorescent dye selected from coumarins such as DMQA or C545T, bis-pyrans such as DCJTb or DCM, or may be a metal complex containing lanthanide series or actinide series metal such as Ir, Pt, Os, Ru, Rh, Pd.

[0030] The fluorescent dye has a doping concentration no higher than 5wt% in the organic light-emitting layer 06, and the phosphorescent dye has a doping concentration no higher than 30wt% in the organic light-emitting layer 06. Said doping concentration = dye mass / (dye mass + host material mass) × 100%.

[0031] The host material of the organic light-emitting layer 06 may be selected from materials which are commonly used as a substrate material, such as 4,4'-di-(carbazole-9-yl)-biphenyl (CBP).

[0032] The material of the electron transport layer may adopt a material which is commonly used for an electron transport layer, such as aromatic fused ring compound (e.g. pentacene, perylene) or o-phenanthroline compound (e.g. Bphen, BCP).

[0033] The organic electroluminescent device of the present invention comprises an anode layer 02, a hole transport layer 05, an organic light-emitting layer 06, an electron transport layer 07 and a cathode layer 03 sequentially deposited in a stacked manner upon a substrate 01, which are then encapsulated.

[0034] The substrate may be a glass substrate or a flexible substrate, wherein the flexible substrate may adopt polyester, polyimide compound material, or a thin metal plate. The layered stacking and encapsulation may be conducted by using any suitable method known to a person skilled in the art.

[0035] A specific preparation method of the organic electroluminescent device of the present invention is as follows: Firstly, washing a glass substrate with detergent or deionized water, placing the glass substrate under an infrared lamp for drying, and sputtering a layer of anode material with a film thickness of 150nm upon the glass substrate.

[0036] Then, placing the above-mentioned glass substrate with anode layer into a vacuum chamber, vacuumizing to 1×10^{-4} Pa, continuing to evaporation coating NPB as a hole transport layer upon the anode layer, at a film coagulation speed of 0.1nm/s, to get an evaporation coated film thickness of 40nm.

[0037] Evaporation coating an organic light-emitting layer upon the hole transport layer by using a double source co-evaporation method, wherein the mass percentages of the host material and the dye are controlled by using a film thickness monitor-controller to adjust the film coagulation speed, and the evaporation coated film thickness thereof is 30nm.

[0038] Continuing to evaporation coating a layer of TPBi material as a second electron transport layer upon the organic light-emitting layer, at a deposition rate of 0.1nm/s, to get an evaporation coated film total thickness of 30nm.

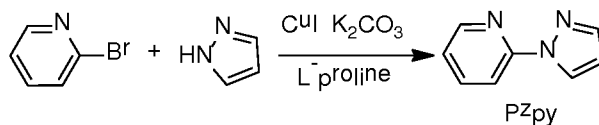
[0039] Finally, evaporation coating a Mg:Ag layer and a Ag layer in sequence as a cathode layer upon the electron transport layer, wherein the Mg:Ag layer is coated by using a double source co-evaporation method, and the mass percentages of Mg and Ag are controlled by using a film thickness monitor-controller to adjust the film coagulation speed, and the evaporation coated film thickness thereof is 150nm; the Ag layer is evaporation coated at a speed of 1.0nm/s, to get a thickness of 50nm.

Embodiment 1

[0040] The synthesis routes of the N^N ligand **Pzpy**, **Pyim**, **Ptop** and **Pop** in the complexes are as follows:

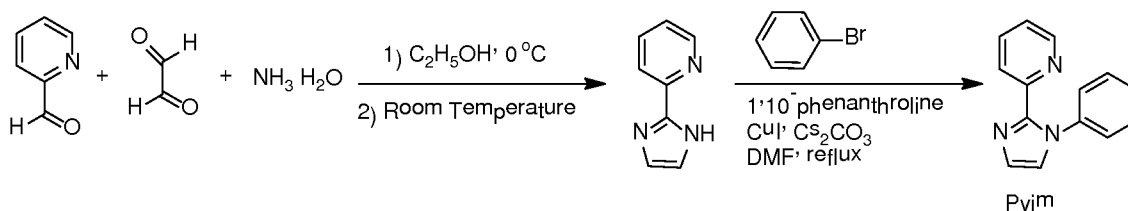
(1) synthesis process of **Pzpy**:

See details in He, L., et al., Adv. Funct. Mater. 18, 2123-2131 (2008).



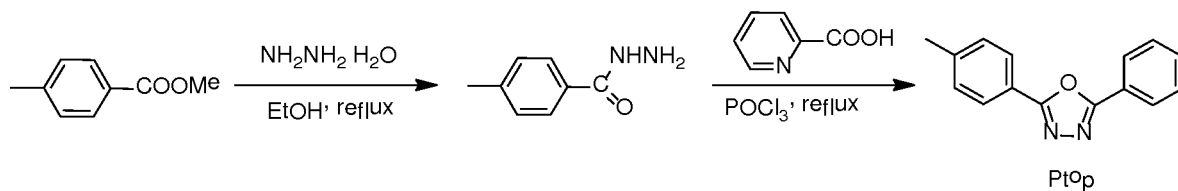
(2) synthesis process of **Pyim**:

See details in He, L., et al., Adv. Funct. Mater. 19, 2950-2960 (2009).

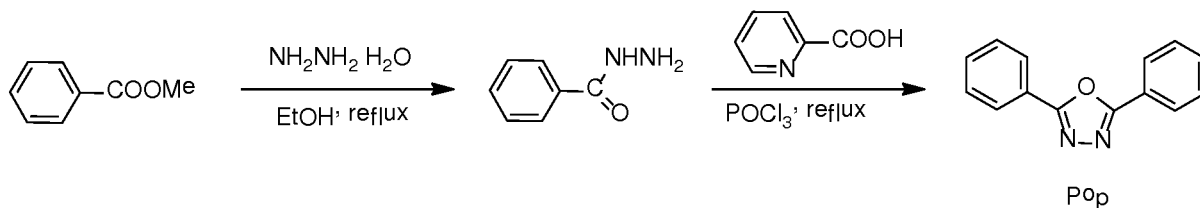


(3) synthesis process of **Ptop**:

See details in Zhang, J., et al. Adv. Funct. Mater. 23, 4667-4677 (2013).



(4) synthesis process of **Pop**:



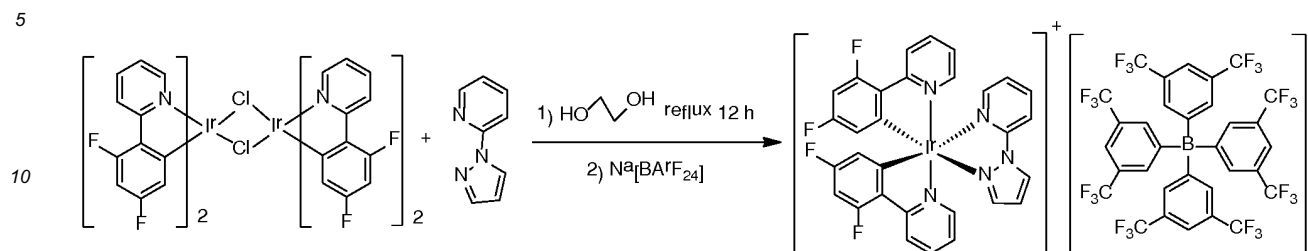
Embodiment 2

Synthesis process of $[\text{Ir}(\text{dfppy})_2(\text{pzpy})][\text{BARF}_{24}]$ shown in formula (11):

[0041] Di-chlorine bridged Iridium di-ligand $[\text{Ir}(\text{dfppy})_2\text{Cl}]_2$ (3.100g, 2.55mmol) and **pzpy** ligand (0.743g, 5.12mmol) is dissolved in 1,2-glycol (60mL). In nitrogen atmosphere, the solution system is refluxed for 12h at 140°C to get a clear bright yellow solution. After cooling to room temperature, $\text{Na}[\text{BARF}_{24}]$ (4.522g, 5.10mmol) is slowly added to the reaction system with stirring. The reaction product is suction filtrated, washed with CH_2Cl_2 , and then dried over a night in a 70°C vacuum drying oven. The crude product is subsequently passed through silica chromatographic column (200-300 mesh), with CH_2Cl_2 as the mobile phase, to get the clathrate compound $[\text{Ir}(\text{dfppy})_2(\text{pzpy})][\text{BARF}_{24}]$ shown in formula (11) as pale yellow powder (5.283g, 3.34mmol) at a yield of 66%.

$^1\text{H-NMR}$ (600 MHz, DMSO-d_6): δ 9.34 (d, $J = 3.1$ Hz, 1H), 8.55 (d, $J = 8.5$ Hz, 1H), 8.40-8.36 (m, 1H), 8.30 (d, $J = 7.3$ Hz, 2H), 8.07 (t, $J = 6.3$ Hz, 2H), 7.84 (d, $J = 5.1$ Hz, 1H), 7.78 (d, $J = 5.8$ Hz, 1H), 7.73 (s, 4H), 7.63 (s, 8H), 7.56 (t, $J = 5.4$ Hz, 2H), 7.32 (t, $J = 6.7$ Hz, 1H), 7.29 (t, $J = 6.7$ Hz, 1H), 7.01-6.91 (m, 2H), 5.65 (d, $J = 2.3$ Hz, 1H), 5.64 (d, $J =$

2.3 Hz, 1H), 5.62 (d, $J = 2.3$ Hz, 1H), 5.60 (d, $J = 2.3$ Hz, 1H); ^{19}F -NMR (600 MHz, DMSO-d_6): δ -61.68 (s, 24F), -106.51 (s, 1F), -107.12 (s, 1F), -108.67 (s, 1F), -109.29 (s, 1F); MS (ESI) $[m/z]$: $[\text{M-BArF}_{24}]^+$ calcd for $\text{C}_{30}\text{H}_{19}\text{F}_4\text{IrN}_5$, 718.12; found, 718.39; $[\text{M-Ir}(\text{dfppy})_2(\text{pzpy})]^-$ calcd for $\text{C}_{32}\text{H}_{12}\text{BF}_{24}$, 863.06; found, 863.35.

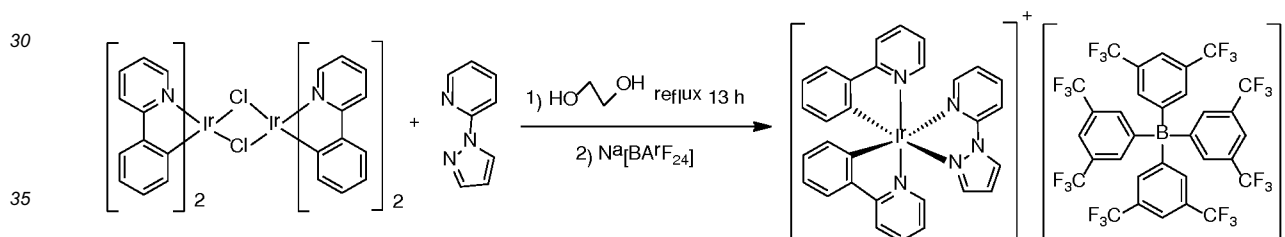


Embodiment 3

Synthesis process of $[\text{Ir}(\text{ppy})_2(\text{pzpy})][\text{BArF}_{24}]$ shown in formula (12):

[0042] The reactants are $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (1.662g, 1.55mmol) and **ppzy** ligand (0.468g, 3.22mmol), and by going through a synthesis method similar to that of Embodiment 2, the clathrate compound $[\text{Ir}(\text{ppy})_2(\text{pzpy})][\text{BArF}_{24}]$ shown in formula (12) is obtained as pale yellow powder (3.790g, 2.51mmol) at a yield of 81%.

^1H -NMR (600 MHz, DMSO-d_6): δ 9.30 (d, $J = 3.0$ Hz, 1H), 8.53 (d, $J = 8.5$ Hz, 1H), 8.35-8.30 (m, 1H), 8.26 (dd, $J = 8.0$ Hz, 3.9 Hz, 2H), 7.95 (ddd, $J = 7.7$ Hz, 3.2 Hz, 1.9 Hz, 2H), 7.89 (dd, $J = 12.6$ Hz, 7.8 Hz, 2H), 7.77 (d, $J = 5.7$ Hz, 1H), 7.71 (d, $J = 5.3$ Hz, 1H), 7.68 (s, 4H), 7.65 (d, $J = 5.6$ Hz, 1H), 7.61 (s, 8H), 7.55-7.51 (m, 1H), 7.28 (d, $J = 1.9$ Hz, 1H), 7.22 (t, $J = 6.7$ Hz, 1H), 7.18 (t, $J = 6.6$ Hz, 1H), 7.01 (t, $J = 8.0$ Hz, 1H), 6.98 (t, $J = 7.5$ Hz, 1H), 6.91-6.87 (m, 2H), 6.84 (t, $J = 7.4$ Hz, 1H), 6.19 (dd, $J = 9.6$ Hz, 7.9 Hz, 2H); ^{19}F -NMR (600 MHz, DMSO-d_6): δ -61.74 (s, 24F); MS (ESI) $[m/z]$: $[\text{M-BArF}_{24}]^+$ calcd for $\text{C}_{30}\text{H}_{23}\text{IrN}_5$, 646.16; found, 646.16; $[\text{M-Ir}(\text{ppy})_2(\text{pzpy})]^-$ calcd for $\text{C}_{32}\text{H}_{12}\text{BF}_{24}$, 863.06; found, 863.06.

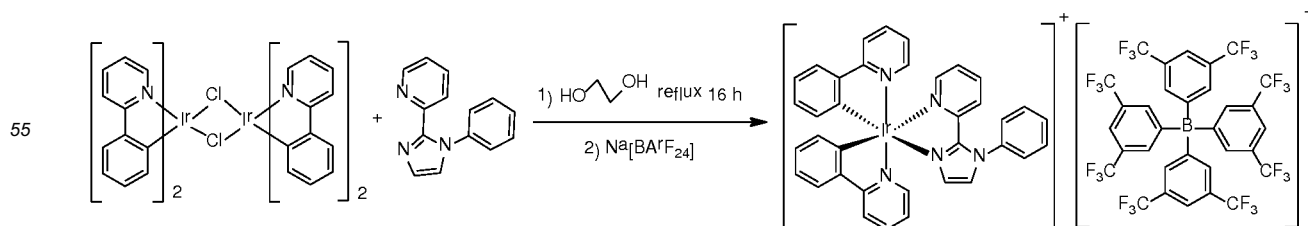


Embodiment 4

Synthesis process of $[\text{Ir}(\text{ppy})_2(\text{pyim})][\text{BArF}_{24}]$ shown in formula (13):

[0043] The reactants are $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (3.064g, 2.86mmol) and **pyim** ligand (1.255g, 5.67mmol), and by going through a synthesis method similar to that of Embodiment 2, the clathrate compound $[\text{Ir}(\text{ppy})_2(\text{pyim})][\text{BArF}_{24}]$ shown in formula (13) is obtained as yellow powder (1.024g, 0.77mmol) at a yield of 86%.

^1H -NMR (600 MHz, DMSO-d_6): δ 8.25 (t, $J = 8.6$ Hz, 2H), 7.98-7.87 (m, 8H), 7.86 (d, $J = 1.4$ Hz, 1H), 7.83 (d, $J = 5.4$ Hz, 1H), 7.73 (d, $J = 4.9$ Hz, 4H), 7.68 (s, 4H), 7.62 (s, 8H), 7.51-7.47 (m, 1H), 7.28-7.25 (m, 1H), 7.25-7.20 (m, 1H), 7.02-6.95 (m, 2H), 6.93 (d, $J = 8.3$ Hz, 1H), 6.91-6.84 (m, 2H), 6.64 (d, $J = 1.4$ Hz, 1H), 6.23 (dd, $J = 9.4, 8.2$ Hz, 2H); ^{19}F -NMR (600 MHz, DMSO-d_6): δ -61.12 (s, 24F); MS (ESI) $[m/z]$: $[\text{M-BArF}_{24}]^+$ calcd for $\text{C}_{36}\text{H}_{27}\text{IrN}_5$, 722.19; found, 722.19; $[\text{M-Ir}(\text{ppy})_2(\text{pyim})]^-$ calcd for $\text{C}_{32}\text{H}_{12}\text{BF}_{24}$, 863.06; found, 863.07.

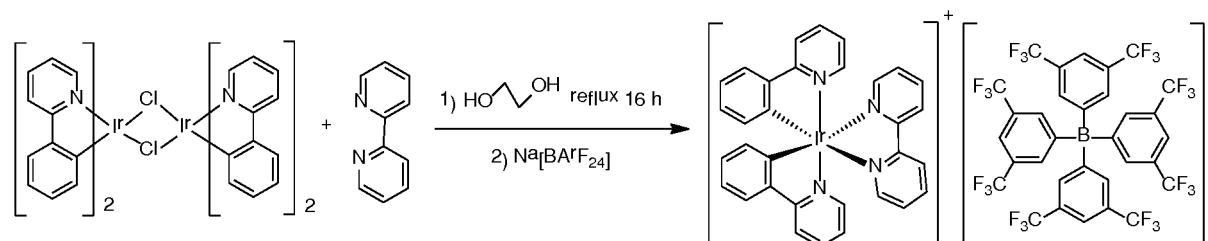


Embodiment 5

Synthesis process of $[\text{Ir}(\text{ppy})_2(\text{bpy})][\text{BArF}_{24}]$ shown in formula (14):

[0044] The reactants are $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (1.767g, 1.65mmol) and 2,2'-bipyridine (**bpy**) ligand (0.528g, 3.38mmol), and by going through a synthesis method similar to that of Embodiment 2, the clathrate compound $[\text{Ir}(\text{ppy})_2(\text{bpy})][\text{BArF}_{24}]$ shown in formula (14) is obtained as yellow powder (4.290g, 2.82mmol) at a yield of 86%.

$^1\text{H-NMR}$ (600 MHz, DMSO-d_6): δ 8.89 (d, $J = 8.2$ Hz, 2H), 8.27 (t, $J = 7.2$ Hz, 4H), 7.95-7.90 (m, 4H), 7.88 (d, $J = 4.7$ Hz, 2H), 7.71 (s, 4H), 7.69 (s, 2H), 7.63 (s, 2H), 7.62 (s, 8H), 7.16 (t, $J = 6.0$ Hz, 2H), 7.03 (dd, $J = 12.6$ Hz, 5.5 Hz, 2H), 6.90 (t, $J = 7.5$ Hz, 2H), 6.20 (d, $J = 7.2$ Hz, 2H); $^{19}\text{F-NMR}$ (600 MHz, DMSO-d_6): δ -61.74 (s, 24F); MS (ESI) $[m/z]$: $[\text{M-BArF}_{24}]^+$ calcd for $\text{C}_{32}\text{H}_{24}\text{IrN}_4$, 657.16; found, 657.16; $[\text{M-Ir}(\text{ppy})_2(\text{bpy})]^-$ calcd for $\text{C}_{32}\text{H}_{12}\text{BF}_{24}$, 863.06; found, 863.06.

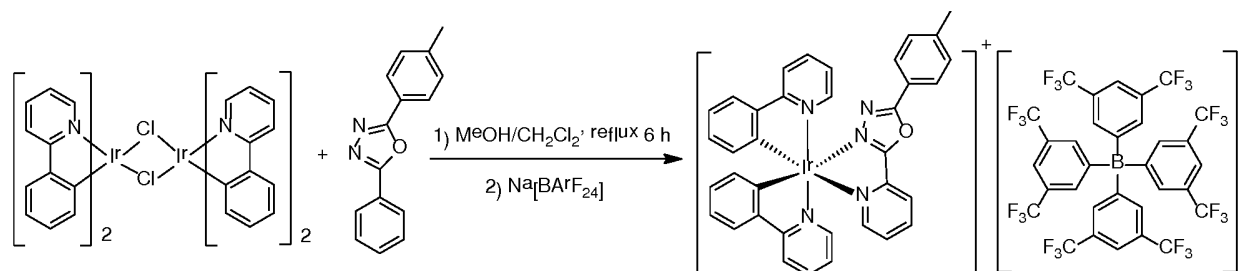


Embodiment 6

Synthesis process of $[\text{Ir}(\text{ppy})_2(\text{ptop})][\text{BArF}_{24}]$ shown in formula (15):

[0045] The reactants are $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (1.786g, 1.67mmol) and **ptop** ligand (0.798g, 3.36mmol), which are dissolved in methanol / CH_2Cl_2 (v/v = 60 : 60 mL), and the rest of the synthesis method is similar to that of Embodiment 2, thereby obtaining the clathrate compound $[\text{Ir}(\text{ppy})_2(\text{ptop})][\text{BArF}_{24}]$ shown in formula (15) as red powder (4.131g, 2.58mmol) at a yield of 77%.

$^1\text{H-NMR}$ (600 MHz, DMSO-d_6): δ 8.66 (d, $J = 7.8$ Hz, 1H), 8.37 (t, $J = 7.4$ Hz, 1H), 8.26 (d, $J = 6.0$ Hz, 1H), 8.22 (d, $J = 8.2$ Hz, 2H), 8.01 (d, $J = 8.1$ Hz, 2H), 7.93 (t, $J = 7.8$ Hz, 2H), 7.88 (d, $J = 7.6$ Hz, 1H), 7.82 (dd, $J = 5.9$ Hz, 1H), 7.69 (s, 4H), 7.63 (d, $J = 5.9$ Hz, 1H), 7.60 (s, 8H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.18 (t, $J = 6.6$ Hz, 2H), 7.01 (dd, $J = 9.8$ Hz, 4.9 Hz, 1H), 6.94 (t, $J = 7.4$ Hz, 1H), 6.89 (t, $J = 7.3$ Hz, 1H), 6.81 (t, $J = 7.1$ Hz, 1H), 6.11 (dd, $J = 13.1$ Hz, 7.6 Hz, 2H), 1.22 (s, 3H); $^{19}\text{F-NMR}$ (600 MHz, DMSO-d_6): δ -61.51 (s, 24F); MS (ESI) $[m/z]$: $[\text{M-BArF}_{24}]^+$ calcd for $\text{C}_{36}\text{H}_{27}\text{IrN}_5\text{O}$, 738.18; found, 738.18; $[\text{M-Ir}(\text{ppy})_2(\text{ptop})]^-$ calcd for $\text{C}_{32}\text{H}_{12}\text{BF}_{24}$, 863.06; found, 863.06.



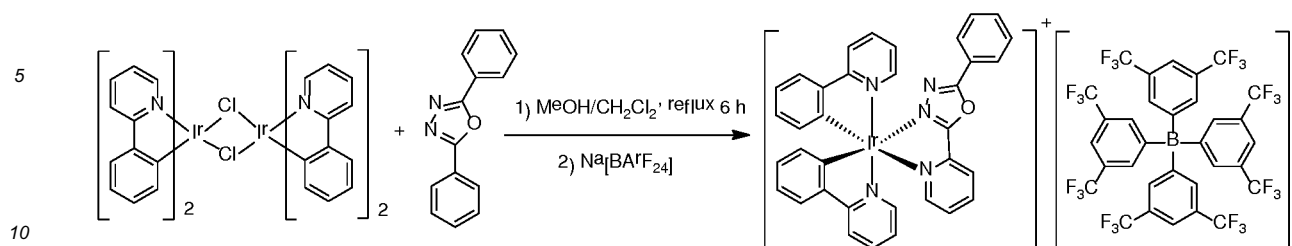
Embodiment 7

Synthesis process of $[\text{Ir}(\text{ppy})_2(\text{pop})][\text{BArF}_{24}]$ shown in formula (16):

[0046] The reactants are $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (1.775g, 1.66mmol) and **pop** ligand (0.740g, 3.32mmol), and by going through a synthesis method similar to that of Embodiment 2, the clathrate compound $[\text{Ir}(\text{ppy})_2(\text{pop})][\text{BArF}_{24}]$ shown in formula (16) is obtained as red powder (4.551g, 2.87mmol) at a yield of 87%.

$^1\text{H-NMR}$ (600 MHz, DMSO-d_6): δ 8.68 (d, $J = 7.7$ Hz, 1H), 8.38 (td, $J = 7.8$ Hz, 2.1 Hz, 1H), 8.26 (d, $J = 5.5$ Hz, 1H), 8.22 (d, $J = 8.5$ Hz, 2H), 8.14-8.10 (m, 2H), 7.94 (t, $J = 7.8$ Hz, 2H), 7.88 (d, $J = 8.7$ Hz, 1H), 7.86-7.81 (m, 3H), 7.72 (d, $J = 7.4$ Hz, 1H), 7.69 (s, 4H), 7.63 (dd, $J = 13.5$ Hz, 6.1 Hz, 3H), 7.60 (s, 8H), 7.18 (dt, $J = 6.0$ Hz, 4.7 Hz, 2H), 7.01 (t, $J = 7.6$ Hz, 1H), 6.94 (t, $J = 7.6$ Hz, 1H), 6.89 (dd, $J = 8.1$ Hz, 7.1 Hz, 1H), 6.81 (t, $J = 7.5$ Hz, 1H), 6.11 (dd, $J = 11.9$ Hz, 7.5 Hz, 2H); $^{19}\text{F-NMR}$ (600 MHz, DMSO-d_6): δ -61.60 (s, 24F); MS (ESI) $[m/z]$: $[\text{M-BArF}_{24}]^+$ calcd for $\text{C}_{35}\text{H}_{25}\text{IrN}_5\text{O}$,

724.17; found, 724.16; $[\text{M-Ir}(\text{ppy})_2(\text{pop})]^-$ calcd for $\text{C}_{32}\text{H}_{12}\text{BF}_{24}$, 863.06; found, 863.06.



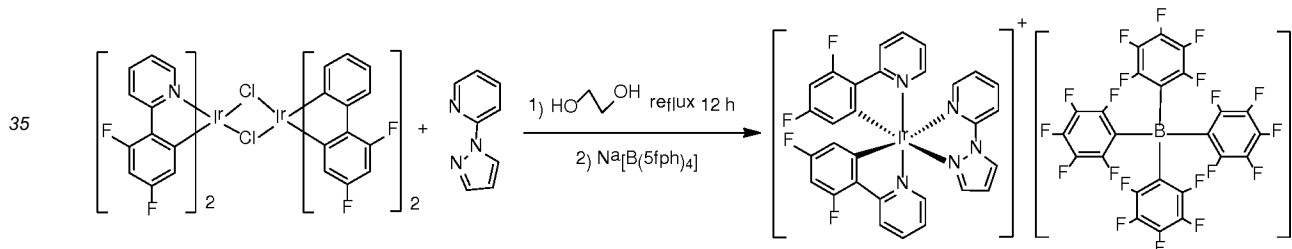
[0047] The clathrate compounds shown in formulas (11) to (16) prepared in Embodiments 2-7 undergo thermogravimetric analysis in N_2 atmosphere, as shown in Figure 1, it can be seen that the series of Iridium-containing depositable materials with $[\text{BArF}_{24}]^-$ as a counterion do not have notable mass loss until above 250°C , which indicates this type of materials have a high glass transition temperature and good thermal stability.

Embodiment 8

Synthesis process of $[\text{Ir}(\text{dfppy})_2(\text{pzpy})][\text{B}(\text{5fph})_4]$ shown in formula (21):

[0048] The reactants are $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (0.473g, 0.39mmol) and **dfpzpy** ligand (0.187g, 1.29mmol), and by going through a synthesis method similar to that of Embodiment 2, the clathrate compound $[\text{Ir}(\text{dfppy})_2(\text{pzpy})][\text{B}(\text{5fph})_4]$ shown in formula (21) is obtained as bright yellow powder (0.770g, 0.56mmol) at a yield of 71%.

^1H NMR (600 MHz, DMSO-d_6 , δ) 9.34 (dd, $J = 2.9$ Hz, 1.4 Hz, 1H), 8.55 (d, $J = 8.5$ Hz, 1H), 8.39-8.36 (m, 1H), 8.30 (d, $J = 6.3$ Hz, 2H), 8.09-8.04 (m, 2H), 7.84 (dd, $J = 6.8$ Hz, 6.4 Hz, 1H), 7.78 (d, $J = 5.8$ Hz, 1H), 7.75 (d, $J = 5.7$ Hz, 1H), 7.57-7.53 (m, 2H), 7.34-7.23 (m, 3H), 7.19-7.13 (m, 1H), 7.00-6.91 (m, 3H). ^{19}F NMR (600 MHz, DMSO-d_6 , δ) -106.45 (s, 1F), -107.10 (s, 1F), -108.60 (s, 1F), -109.25 (s, 1F), -132.23 (s, 8F), -161.17 (s, 4F), -165.71 (s, 8F). MS (ESI) $[m/z]$: 718.40 $[\text{M-B}(\text{5fph})_4]^+$, 679.28 $[\text{M-Ir}(\text{dfppy})_2(\text{pzpy})]^-$. Anal. Calcd. for $\text{C}_{54}\text{H}_{19}\text{BF}_{24}\text{IrN}_5$: C, 46.43; H, 1.37; N, 5.01. Found: C, 45.84; H, 1.50; N, 4.95.

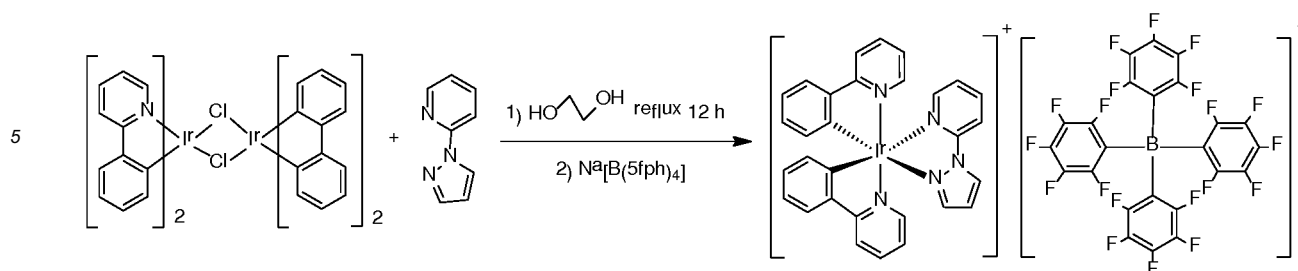


Embodiment 9

Synthesis process of $[\text{Ir}(\text{ppy})_2(\text{pzpy})][\text{B}(\text{5fph})_4]$ shown in formula (22):

[0049] The reactants are $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (0.578g, 0.54mmol) and **pzpy** ligand (0.231g, 1.59mmol), and by going through a synthesis method similar to that of Embodiment 2, the clathrate compound $[\text{Ir}(\text{ppy})_2(\text{pzpy})][\text{B}(\text{5fph})_4]$ shown in formula (22) is obtained as yellow powder (1.024g, 0.77mmol) at a yield of 72%.

^1H NMR (600 MHz, DMSO-d_6 , δ) 9.28 (d, $J = 2.8$ Hz, 1H), 8.51 (d, $J = 8.3$ Hz, 1H), 8.31 (t, $J = 8.0$ Hz, 1H), 8.28-8.21 (m, 2H), 7.94 (d, $J = 7.8$ Hz, 2H), 7.88 (dd, $J = 12.3$, 7.8 Hz, 2H), 7.75 (d, $J = 5.7$ Hz, 1H), 7.70 (d, $J = 5.6$ Hz, 1H), 7.64 (d, $J = 5.5$ Hz, 1H), 7.54-7.50 (m, 1H), 7.27 (s, 1H), 7.25-7.15 (m, 2H), 6.99 (dt, $J = 19.2$, 7.5 Hz, 2H), 6.93-6.80 (m, 3H), 6.22-6.15 (m, 2H). ^{19}F NMR (600 MHz, DMSO-d_6 , δ) -132.35 (s, 8F), -161.20 (s, 4F), -165.81 (s, 8F). MS (ESI) $[m/z]$: 646.40 $[\text{M-B}(\text{5fph})_4]^+$, 679.22 $[\text{M-Ir}(\text{ppy})_2(\text{pzpy})]^-$. Anal. Calcd. for $\text{C}_{54}\text{H}_{23}\text{BF}_{20}\text{IrN}_5$: C, 48.96; H, 1.75; N, 5.29. Found: C, 49.37; H, 2.00; N, 5.46.



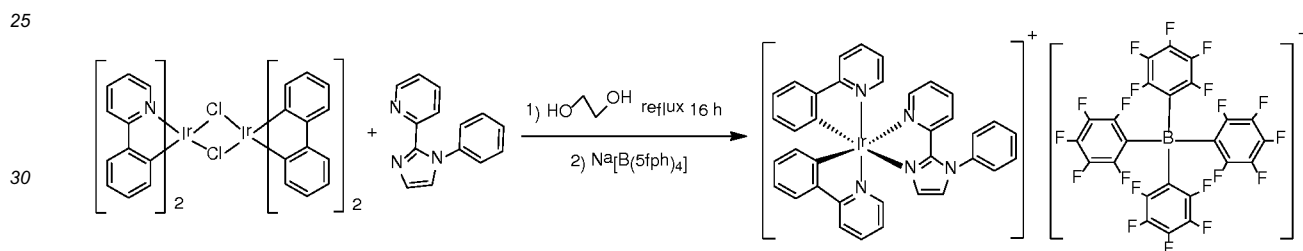
Embodiment 10

Synthesis process of $[\text{Ir}(\text{ppy})_2(\text{pyim})][\text{B}(\text{5fph})_4]$ shown in formula (23):

15 **[0050]** The reactants are $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (0.569g, 0.53mmol) and **pyim** ligand (0.233g, 1.05mmol), and by going through a synthesis method similar to that of Embodiment 2, the clathrate compound $[\text{Ir}(\text{ppy})_2(\text{pyim})][\text{B}(\text{5fph})_4]$ shown in formula (23) is obtained as yellow powder (1.024g, 0.77mmol) at a yield of 61%.

^1H NMR (600 MHz, DMSO- d_6 , δ) 8.24 (t, $J = 8.9$ Hz, 2H), 7.97-7.92 (m, 4H), 7.89 (dd, $J = 13.1, 6.8$ Hz, 4H), 7.85 (d, $J = 1.1$ Hz, 1H), 7.83 (d, $J = 5.3$ Hz, 1H), 7.74 (d, $J = 5.7$ Hz, 4H), 7.48 (dd, $J = 7.0, 6.2$ Hz, 1H), 7.26 (dd, $J = 9.7, 3.5$ Hz, 1H), 7.21 (t, $J = 6.6$ Hz, 1H), 7.01-6.92 (m, 3H), 6.88 (dd, $J = 12.5, 5.0$ Hz, 1H), 6.85 (t, $J = 7.4$ Hz, 1H), 6.64 (d, $J = 1.3$ Hz, 1H), 6.24 (dd, $J = 9.9, 7.8$ Hz, 2H). ^{19}F NMR (600 MHz, DMSO- d_6 , δ) -132.36 (s, 8F), -161.18 (s, 4F), -166.20 (s, 8F). MS (ESI) $[m/z]$: 722.19 $[\text{M}-\text{B}(\text{5fph})_4]^+$, 678.98 $[\text{M}-\text{Ir}(\text{ppy})_2(\text{pyim})]^-$. Anal. Calcd. for $\text{C}_{60}\text{H}_{27}\text{BF}_{20}\text{IrN}_5$: C, 51.44; H, 1.94; N, 5.00. Found: C, 51.79; H, 2.27; N, 4.87.

20



Embodiment 11

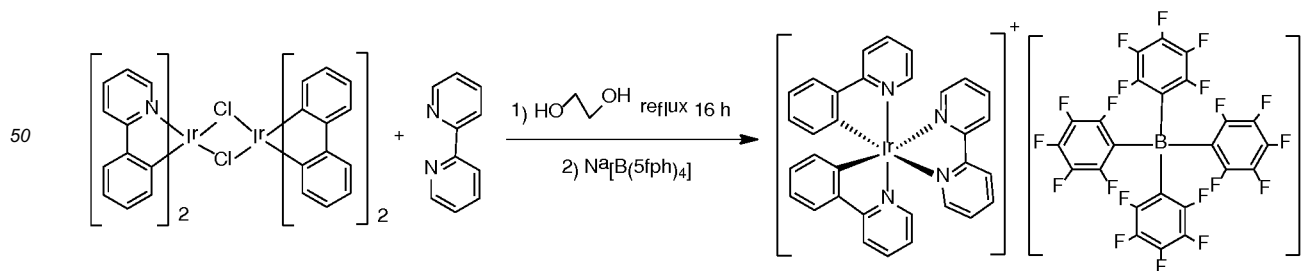
35 Synthesis process of $[\text{Ir}(\text{ppy})_2(\text{bpy})][\text{B}(\text{5fph})_4]$ shown in formula (24):

[0051] The reactants are $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (0.655g, 0.61mmol) and 2,2'-bipyridine (**bpy**) ligand (0.25g, 1.60mmol), and by going through a synthesis method similar to that of Embodiment 2, the clathrate compound $[\text{Ir}(\text{ppy})_2(\text{bpy})][\text{B}(\text{5fph})_4]$ shown in formula (24) is obtained as yellow powder (1.024g, 0.77mmol) at a yield of 65%.

40

^1H NMR (600 MHz, DMSO- d_6 , δ) 8.89 (d, $J = 8.4$ Hz, 2H), 8.28 (dd, $J = 11.0, 4.8$ Hz, 4H), 7.96-7.91 (m, 4H), 7.89-7.87 (m, 2H), 7.70 (ddd, $J = 7.6, 5.5, 1.1$ Hz, 2H), 7.62 (dd, $J = 5.8, 0.7$ Hz, 2H), 7.18-7.15 (m, 2H), 7.05-7.00 (m, 2H), 6.91 (td, $J = 7.5, 1.3$ Hz, 2H), 6.20 (dd, $J = 7.6, 0.6$ Hz, 2H). MS (ESI) $[m/z]$: 657.16 $[\text{M}-\text{B}(\text{5fph})_4]^+$, 678.98 $[\text{M}-\text{Ir}(\text{ppy})_2(\text{bpy})]^-$. Anal. Calcd. for $\text{C}_{56}\text{H}_{24}\text{BF}_{20}\text{IrN}_4$: C, 50.35; H, 1.81; N, 4.19. Found: C, 50.83; H, 2.24; N, 4.18.

45

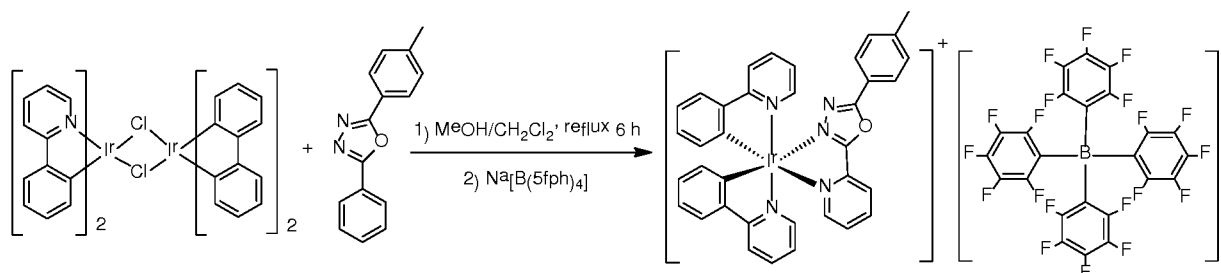


Embodiment 12

Synthesis process of $[\text{Ir}(\text{ppy})_2(\text{ptop})][\text{B}(\text{5fph})_4]$ shown in formula (25):

[0052] The reactants are $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (1.775g, 1.66mmol) and **ptop** ligand (0.341g, 1.44mmol), and by going through a synthesis method similar to that of Embodiment 2, the clathrate compound $[\text{Ir}(\text{ppy})_2(\text{ptop})][\text{B}(\text{5fph})_4]$ shown in formula (25) is obtained as red powder (1.65g, 1.16mmol) at a yield of 81%.

^1H NMR (600 MHz, DMSO- d_6 , δ) 8.71 (d, $J = 7.8$ Hz, 1H), 8.43 (td, $J = 7.8$ Hz, 1.9 Hz, 1H), 8.32-8.30 (m, 1H), 8.29-8.26 (m, 2H), 8.07 (d, $J = 8.2$ Hz, 2H), 8.01-7.97 (m, 2H), 7.93 (d, $J = 7.3$ Hz, 1H), 7.87 (ddd, $J = 6.8$ Hz, 5.5 Hz, 2.8 Hz, 3H), 7.69 (d, $J = 5.8$ Hz, 3H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.25-7.21 (m, 2H), 7.08-7.04 (m, 1H), 7.01-6.97 (m, 1H), 6.94 (td, $J = 7.5$ Hz, 1.2 Hz, 1H), 6.86 (td, $J = 7.5$ Hz, 1.2 Hz, 1H), 6.16 (dd, $J = 12.9$ Hz, 7.0 Hz, 1H), 2.53 (dt, $J = 3.6$ Hz, 1.8 Hz, 3H). ^{19}F NMR (600 MHz, DMSO- d_6 , δ) -133.28 (s, 8F), -161.68 (s, 4F), -165.84 (s, 8F). MS (ESI) $[m/z]$: 738.18 $[\text{M}-\text{B}(\text{5fph})_4]^+$, 678.97 $[\text{M}-\text{Ir}(\text{ppy})_2(\text{ptop})]^-$. Anal. Calcd. for $\text{C}_{60}\text{H}_{27}\text{BF}_{20}\text{IrN}_5\text{O}$: C, 50.86; H, 1.92; N, 4.94. Found: C, 51.93; H, 1.83; N, 4.98.

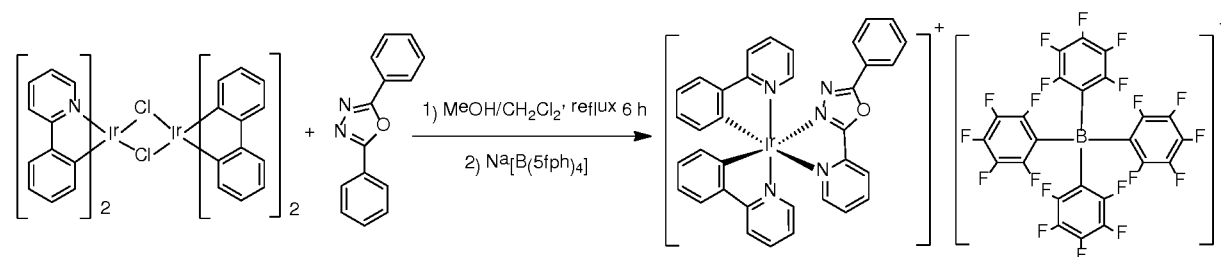


Embodiment 13

Synthesis process of $[\text{Ir}(\text{ppy})_2(\text{pop})][\text{BArF}_{24}]$ shown in formula (26):

[0053] The reactants are $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (0.576g, 0.54mmol) and **pop** ligand (0.243g, 1.09mmol), and by going through a synthesis method similar to that of Embodiment 2, the clathrate compound $[\text{Ir}(\text{ppy})_2(\text{pop})][\text{BArF}_{24}]$ shown in formula (26) is obtained as red powder (1.024g, 0.77mmol) at a yield of 74%.

^1H NMR (600 MHz, DMSO- d_6 , δ) 8.73 (d, $J = 7.7$ Hz, 1H), 8.43 (td, $J = 7.7$ Hz, 1.6 Hz, 1H), 8.32 (d, $J = 5.2$ Hz, 1H), 8.27 (d, $J = 8.0$ Hz, 2H), 8.18 (d, $J = 7.3$ Hz, 2H), 7.99 (t, $J = 7.8$ Hz, 2H), 7.93 (d, $J = 7.6$ Hz, 1H), 7.91-7.86 (m, 3H), 7.76 (t, $J = 7.5$ Hz, 1H), 7.69 (dd, $J = 15.8$ Hz, 7.5 Hz, 3H), 7.23 (ddd, $J = 6.0$ Hz, 4.5 Hz, 2.2 Hz, 2H), 7.06 (dd, $J = 9.7$ Hz, 5.3 Hz, 1H), 6.99 (t, $J = 7.5$ Hz, 1H), 6.94 (t, $J = 7.5$ Hz, 1H), 6.86 (t, $J = 7.4$ Hz, 1H), 6.17 (dd, $J = 12.0$ Hz, 7.6 Hz, 2H). ^{19}F NMR (600 MHz, DMSO- d_6 , δ) -133.30 (s, 8F), -161.68 (s, 4F), -166.65 (s, 8F). MS (ESI) $[m/z]$: 724.17 $[\text{M}-\text{B}(\text{5fph})_4]^+$, 678.97 $[\text{M}-\text{Ir}(\text{ppy})_2(\text{pop})]^-$. Anal. Calcd. for $\text{C}_{59}\text{H}_{25}\text{BF}_{20}\text{IrN}_5\text{O}$: C, 50.51; H, 1.80; N, 4.99. Found: C, 51.88; H, 1.92; N, 4.98.



[0054] The clathrate compounds shown in formulas (21) to (26) prepared in Embodiments 8-13 undergo thermogravimetric analysis in N_2 atmosphere, as shown in Figure 5, it can be seen that the series of Iridium-containing depositable materials with $[\text{B}(\text{5fph})_4]^-$ as a counterion do not have notable mass loss until above 320°C , which indicates this type of materials have a high glass transition temperature and good thermal stability.

Embodiment 14

[0055] Devices 1-6 of this embodiment have the following structure:

ITO / NPB (40nm) / host material : x% dye (20nm) / TPBi (30nm) / Mg : Ag (150nm) / Ag (50nm)

The "x%" before the dye of the devices 1-6 represents a doping concentration of the dye in the organic light-emitting layer. In this embodiment and hereinafter, the doping concentration is measured in wt%.

Table 1 Performance of OLED devices made with clathrate compounds 11-16

Structure of the organic light-emitting layer	PL wavelength	Current efficiency	Luminance	EL wavelength	CIE
	λ [nm] ^b	$\eta_{\max}$ [cd A ⁻¹]	$B_{\max}$ [cd m ⁻²]	λ [nm] ^b	(x,y) ^d
CzPO ₂ : 2% clathrate compound 11	452, 481	1.3	6.0×10^3	446	(0.16, 0.12)
26DCzPPy : 8% clathrate compound 12	473, 502	3.0	11.9×10^3	476, 501	(0.20, 0.37)
DIC-TRZ : 4% clathrate compound 13	527	16.3	$>27.1 \times 10^3$	532	(0.36, 0.57)
DIC-TRZ : 2% clathrate compound 14	554	22.6	$>27.1 \times 10^3$	551	(0.42, 0.54)
DIC-TRZ : 10% clathrate compound 15	597	7.1	16.3×10^3	588	(0.51, 0.46)
DIC-TRZ : 6% clathrate compound 16	597	5.1	11.1×10^3	594	(0.52, 0.46)
In table 1: The clathrate compound 11 refers to [Ir(dfppy)₂(pzpy)][BArF₂₄] shown in formula (11), and the corresponding device serial number is 1; The clathrate compound 12 refers to [Ir(ppy)₂(pzpy)][BArF₂₄] shown in formula (12), and the corresponding device serial number is 2; The clathrate compound 13 refers to [Ir(ppy)₂(pyim)][BArF₂₄] shown in formula (13), and the corresponding device serial number is 3; The clathrate compound 14 refers to [Ir(ppy)₂(bpy)][BArF₂₄] shown in formula (14), and the corresponding device serial number is 4; The clathrate compound 15 refers to [Ir(ppy)₂(ptop)][BArF₂₄] shown in formula (15), and the corresponding device serial number is 5; The clathrate compound 16 refers to [Ir(ppy)₂(pop)][BArF₂₄] shown in formula (16), and the corresponding device serial number is 6.					

[0056] The current density-voltage spectrogram of the devices 1-6 is shown in Figure 2, their luminance-voltage spectrogram is shown in Figure 3, their electroluminescence spectrogram is shown in Figure 4. As seen from Figures 2-4, the devices begin to illuminate at a drive voltage of 4V, the maximum luminance is as high as $27.1 \times 10^3 \text{ cd/m}^2$, and as seen from the electroluminescence spectrogram, they can realize light-emitting colors from blue to red. The "11, 12, 13, 14, 15, 16" in Figures 2-4 respectively represent the devices corresponding to the compounds shown in formula (11), formula (12), formula (13), formula (14), formula (15), formula (16).

Embodiment 15

[0057] Devices 7-12 of this embodiment have the following structure:

ITO / NPB (40nm) / host material : x% dye (20nm) / TPBi (30nm) / Mg : Ag (150nm) / Ag (50nm)

The "x%" before the dye of the devices 7-12 represents a doping concentration of the dye in the organic light-emitting layer. In this embodiment and hereinafter, the doping concentration is measured in wt%.

Table 2 Performance of OLED devices made with clathrate compounds 21-26

Structure of the organic light-emitting layer	PL wavelength	Current efficiency	Luminance	EL wavelength	CIE
	λ [nm] ^b	$\eta_{\max}$ [cd A ⁻¹]	$B_{\max}$ [cd m ⁻²]	λ [nm] ^b	(x, y) ^d
CzPO ₂ : 8% clathrate compound 21	452, 480	1.5	5.7×10^3	452	(0.18, 0.19)
26DCzPPy : 6% clathrate compound 22	476, 503	6.7	8.2×10^3	506	(0.25, 0.47)
DIC-TRZ : 6% clathrate compound 23	531	15.3	$>27.1 \times 10^3$	532	(0.35, 0.57)
DIC-TRZ : 8% clathrate compound 24	555	24.3	$>27.1 \times 10^3$	550	(0.42, 0.54)
DIC-TRZ : 4% clathrate compound 25	599	4.5	22.1×10^3	588	(0.51, 0.47)
DIC-TRZ : 6% clathrate compound 26	599	4.5	19.4×10^3	596	(0.52, 0.46)
In table 2: The clathrate compound 21 refers to [Ir(dfppy)₂(pzpy)][B(5fph)₄] shown in formula (21), and the corresponding device serial number is 7; The clathrate compound 22 refers to [Ir(ppy)₂(pzpy)][B(5fph)₄] shown in formula (22), and the corresponding device serial number is 8; The clathrate compound 23 refers to [Ir(ppy)₂(pyim)][B(5fph)₄] shown in formula (23), and the corresponding device serial number is 9; The clathrate compound 24 refers to [Ir(ppy)₂(bpy)][B(5fph)₄] shown in formula (24), and the corresponding device serial number is 10; The clathrate compound 25 refers to [Ir(ppy)₂(ptop)][B(5fph)₄] shown in formula (25), and the corresponding device serial number is 11; The clathrate compound 26 refers to [Ir(ppy)₂(pop)][BArF₂₄] shown in formula (26), and the corresponding device serial number is 12.					

[0058] "CzPO₂ : 2% clathrate compound 21" of the structure of the organic light-emitting layer in the first column of the Tables above refers to that the host material CzPO₂ of the organic light-emitting layer is doped with 2wt% of dye, and the dye is **[Ir(dfppy)₂(pzpy)][B(5fph)₄]** shown in formula (21). And so on for the second to sixth lines.

[0059] The current density-voltage spectrogram of devices 7-12 is shown in Figure 6, their luminance-voltage spectrogram is shown in Figure 7, their electroluminescence spectrogram is shown in Figure 8. As seen from Figures 6-8, the devices begin to illuminate at a drive voltage of 4V, the maximum luminance is as high as $27.1 \times 10^3 \text{ cd/m}^2$, and as seen from the electroluminescence spectrogram, they can realize light-emitting colors from blue to red. The "21, 22, 23, 24, 25, 26" in Figures 6-8 respectively represent the devices corresponding to the compounds shown in formula (21), formula (22), formula (23), formula (24), formula (25), formula (26).

Embodiment 16

[0060] A device 13 of this embodiment has the following structure:

ITO / NPB (40nm) / host material : 4% dye (50nm) / TPBi (30nm) / Mg : Ag (150nm) / Ag (50nm)

The host material and dye of the device 13 is the same as the device 1.

Embodiment 17

[0061] A device 14 of this embodiment has the following structure:

ITO / NPB (40nm) / host material : 6% dye (30nm) / TPBi (30nm) / Mg : Ag (150nm) / Ag (50nm)

The host material and dye of the device 14 is the same as the device 1.

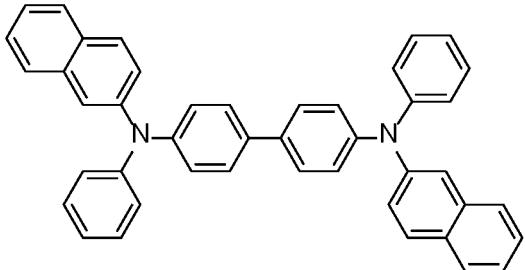
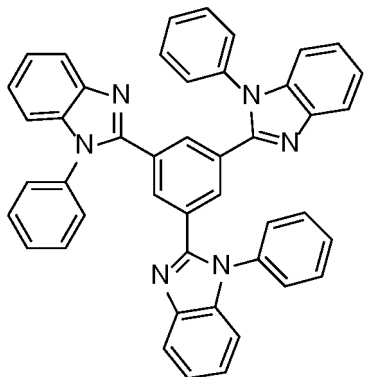
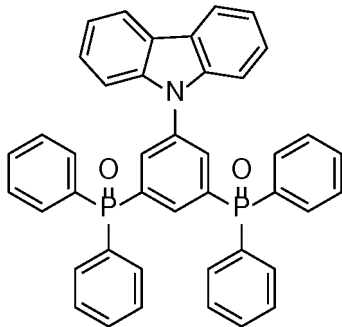
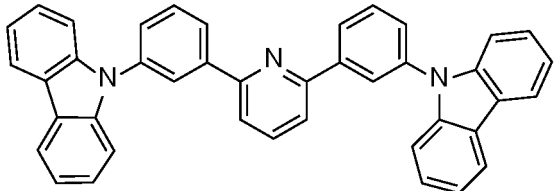
Embodiment 18

[0062] A device 15 of this embodiment has the following structure:

ITO / NPB (40nm) / host material : 7% dye (10nm) / TPBi (30nm) / Mg : Ag (150nm) / Ag (50nm)

The host material and dye of the device 15 is the same as the device 1.

[0063] The molecular formulas of the materials involved in the present invention are as follows:

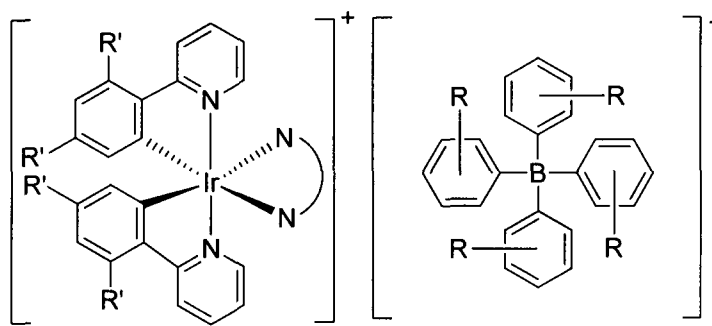
Abbreviation	Full name	Structural formula
NPB	N,N' -di-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4, 4'-diamine	 NPB
TPBi	1,3,5-tri-(1-phenyl-1H-benzimidazole-2-yl)-benzene	
CzPO ₂	9-(3,5-di-(diphenyl-phosphoryl) -phenyl)-9H-carbazole	
26DCzPPy	2,6-di-(3-(9H-carbazole-9-yl)-phenyl)-pyridine	

(continued)

Abbreviation	Full name	Structural formula
DIC-PIZ	2-[9-phenyl]-indolo[2,3-A]carbazole-4,6-diphenyl-1,3,5-triazine	

Claims

1. A depositable ionic organic functional material, **characterized in** having a structure shown in the following formula (1):

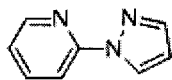


formula (1)

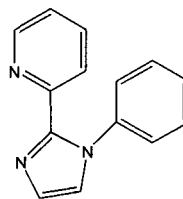
wherein, R is a hydrogen atom, a halogen atom or -CF₃;

R' is a hydrogen atom or a halogen atom;

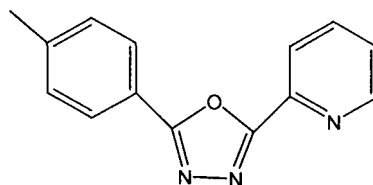
the N^N ligand is selected from **Pzpy** shown in the following formula (31), **Pyim** shown in the following formula (32), **Ptop** shown in the following formula (33), **Pop** shown in the following formula (34), and **Bpy** shown in the following formula (35):



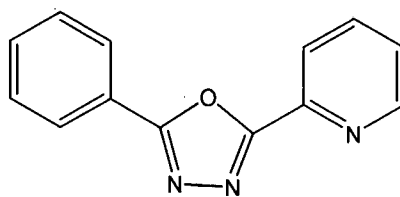
formula (31)



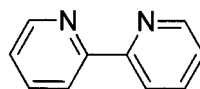
formula (32)



formula (33)

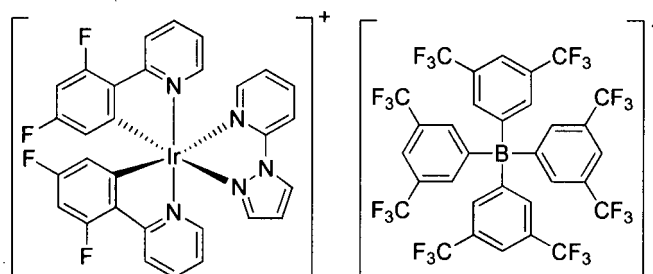


formula (34)

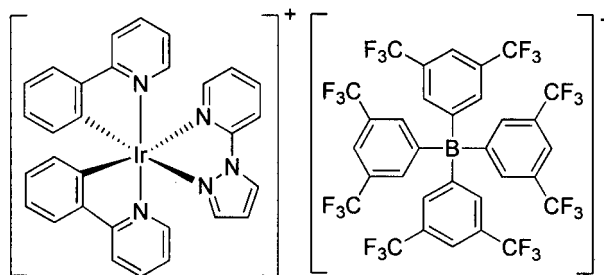


formula (35)

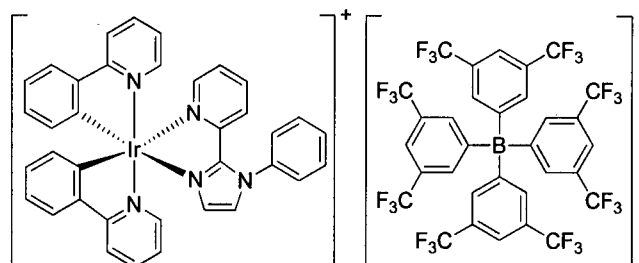
2. The depositable ionic organic functional material according to Claim 1, **characterized in that**, the depositable ionic complex has a structure shown in the following formulas (11) to (16) and formulas (21) to (26):



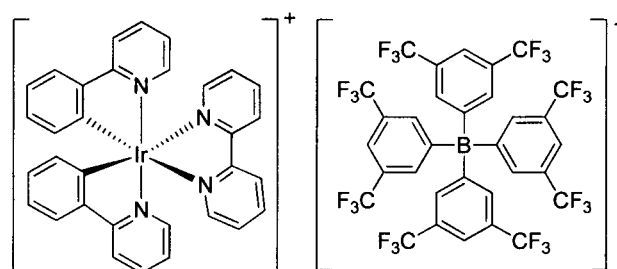
formula (11)



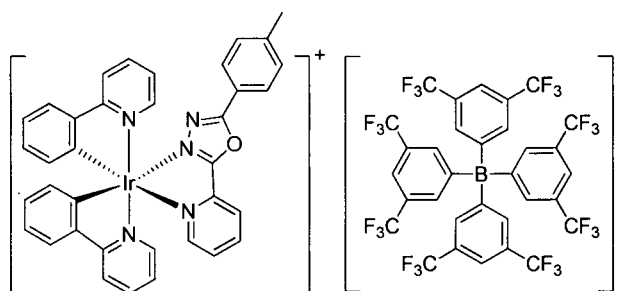
formula (12)



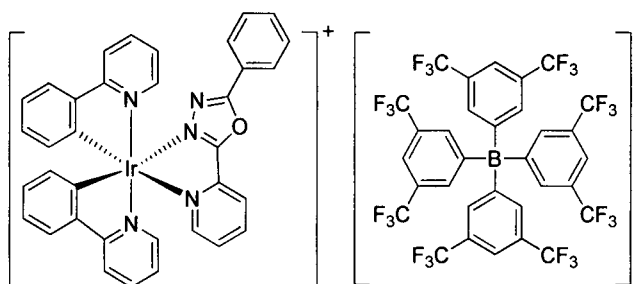
formula (13)



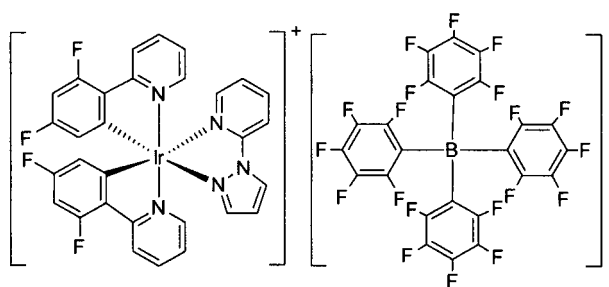
formula (14)



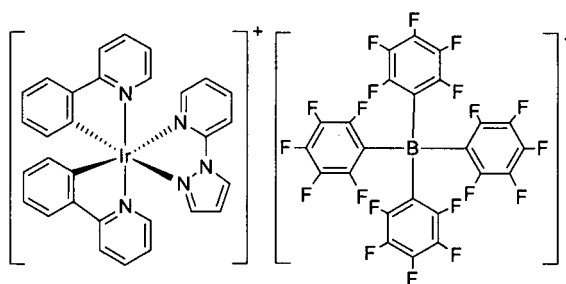
formula (15)



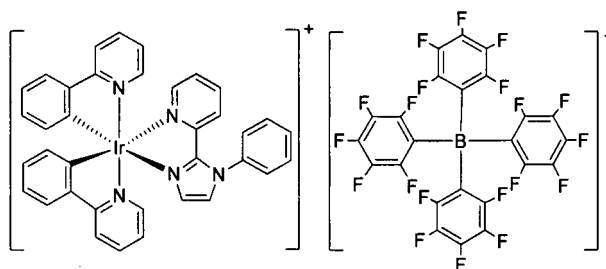
formula (16)



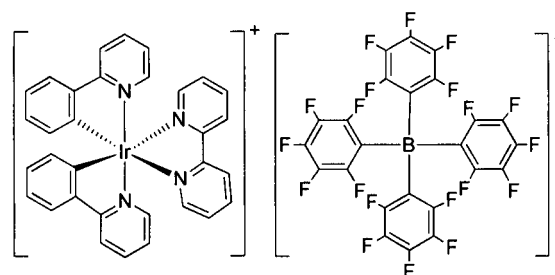
formula (21)



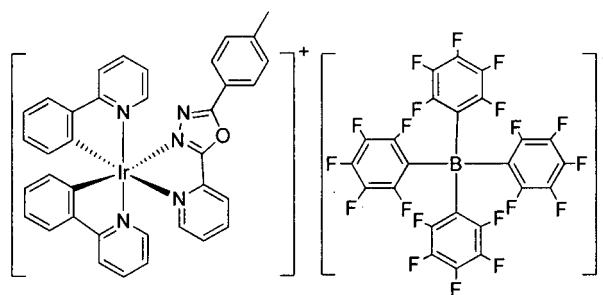
formula (22)



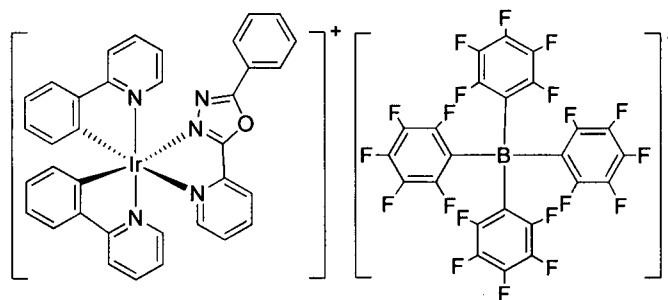
formula (23)



formula (24)



formula (25)



formula (26).

3. A use of the depositable ionic organic functional material according to Claim 1 or 2 in an organic electroluminescent device, wherein, the depositable ionic organic functional material is used as a dye in an organic light-emitting layer of the organic electroluminescent device.

4. An organic electroluminescent device, comprising a substrate, and an anode layer, an organic light-emitting functional layer, a cathode layer formed in sequence upon the substrate, wherein the organic light-emitting functional layer comprises a hole transport layer, an organic light-emitting layer and an electron transport layer,

characterized in that,

a host material of the organic light-emitting layer is doped with the depositable ionic organic functional material according to Claim 1 or 2.

5. The organic electroluminescent device according to Claim 4, **characterized in that,** doping concentration of the depositable ionic organic functional material is 2wt%-10wt%.

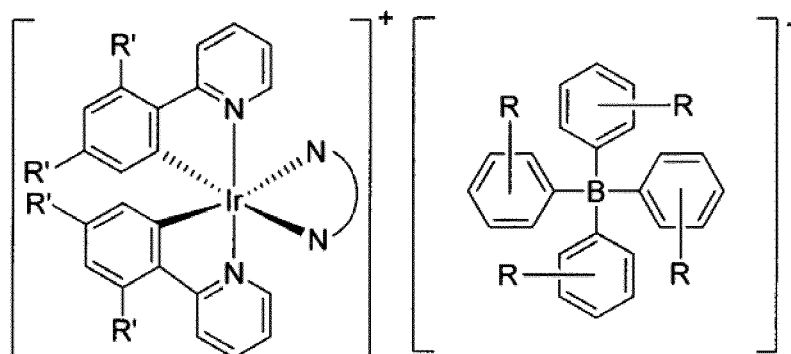
6. The organic electroluminescent device according to Claim 4, **characterized in that,** the depositable ionic organic functional material is red, yellow, green or blue light emitting material.

7. The organic electroluminescent device according to Claim 4, **characterized in that,** the organic light-emitting layer has a thickness of 10nm-50nm.

8. The organic electroluminescent device according to Claim 7, **characterized in that,** the organic light-emitting layer has a thickness of 10nm-30nm.

Patentansprüche

1. Abscheidbares organisches Ionenfunktionsmaterial, **dadurch gekennzeichnet, dass** es eine in der nachfolgenden Formel (1) gezeigte Struktur besitzt:

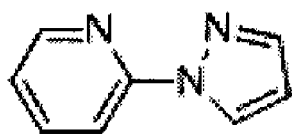


Formel (1)

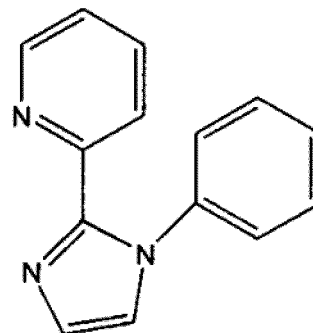
wobei R ein Wasserstoffatom, ein Halogenatom, oder $-\text{CF}_3$ ist;

R' ein Wasserstoffatom oder ein Halogenatom ist;

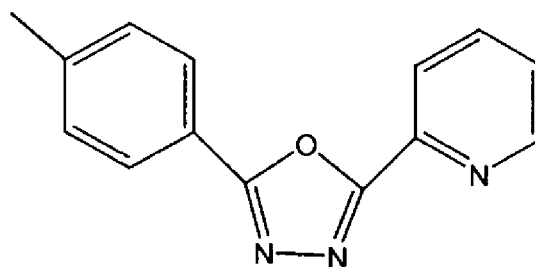
der N^N-Ligand ausgewählt ist aus **Pzpy**, gezeigt in der nachstehenden Formel (31), **Pyim**, gezeigt in der nachstehenden Formel (32), **Ptop**, gezeigt in der nachstehenden Formel (33), **Pop**, gezeigt in der nachstehenden Formel (34), und **Bpy**, gezeigt in der nachstehenden Formel (35);



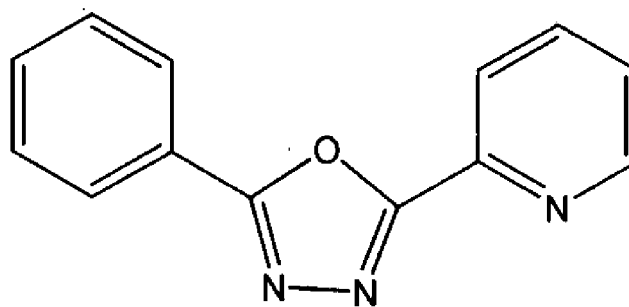
Formel (31)



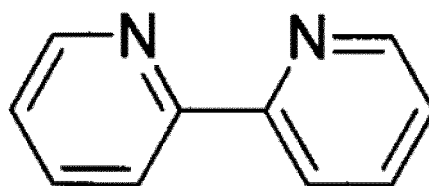
Formel (32)



Formel (33)

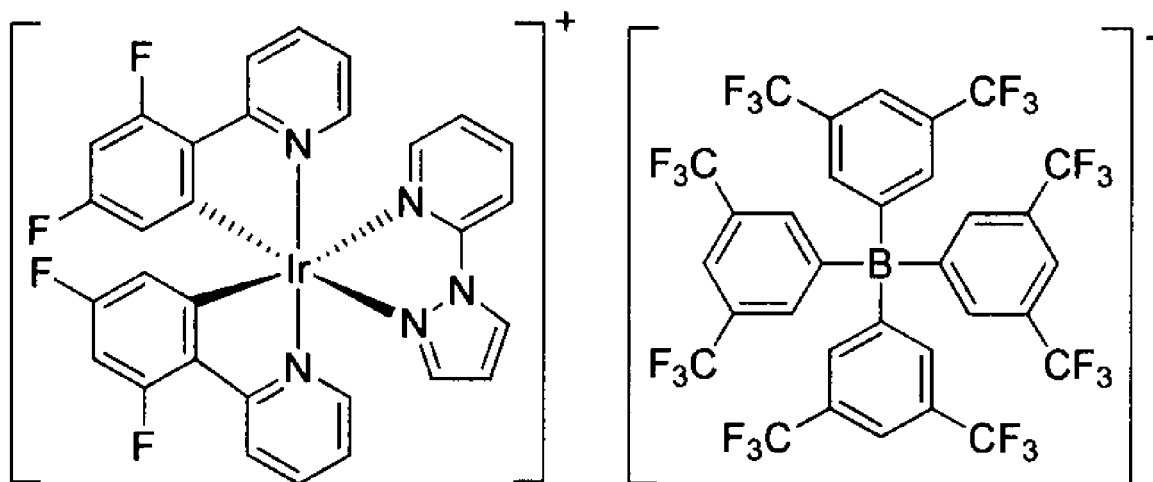


Formel (34)

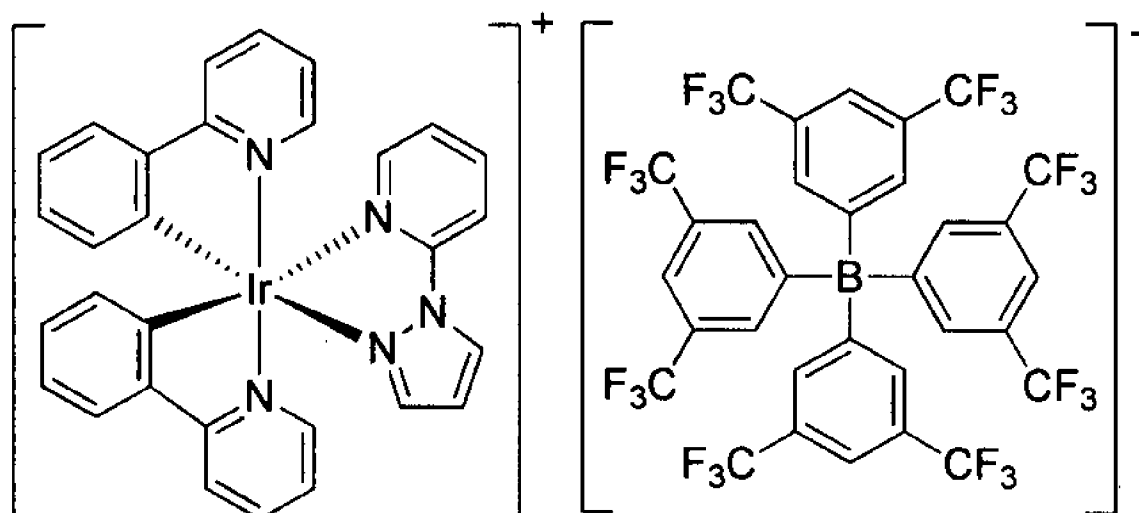


Formel (35)

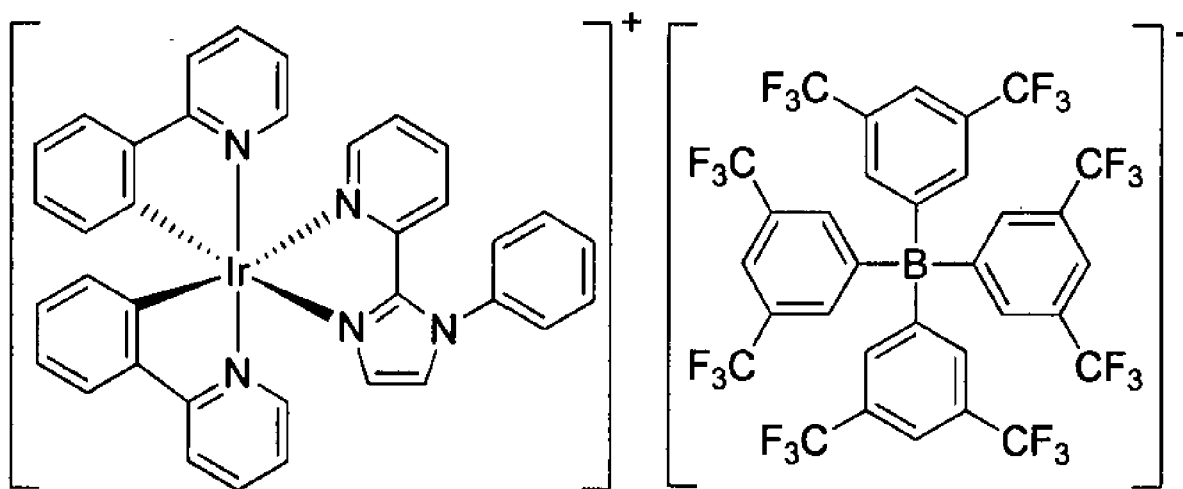
2. Abscheidbares organisches Ionenfunktionsmaterial nach Anspruch 1, **dadurch gekennzeichnet, dass** der abscheidbare Ionenkomplex eine Struktur hat, die in der nachfolgenden Formeln (11) bis (16) und Formeln (21) bis (26) gezeigt ist:



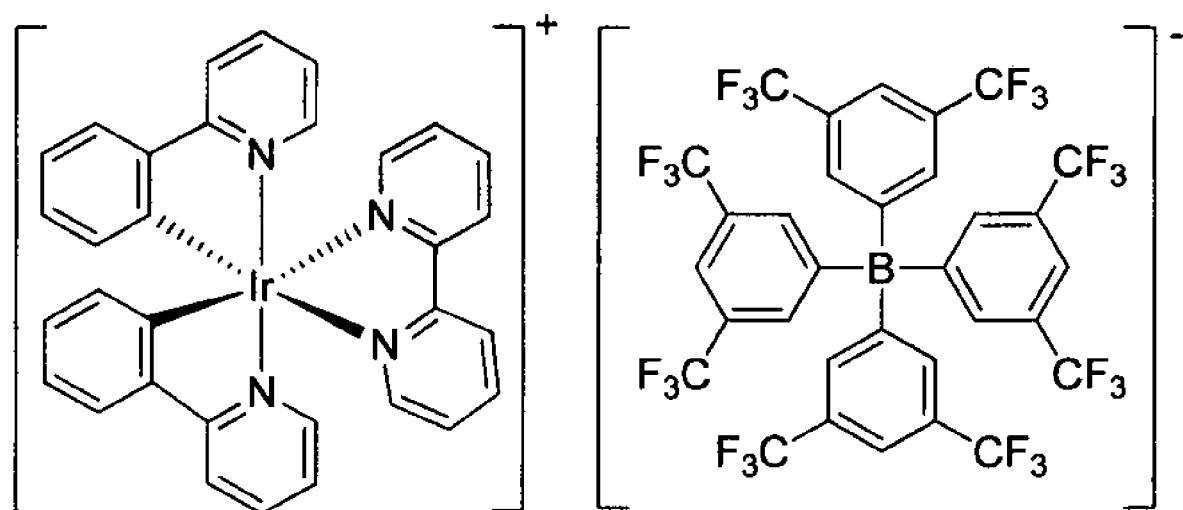
Formel (11)



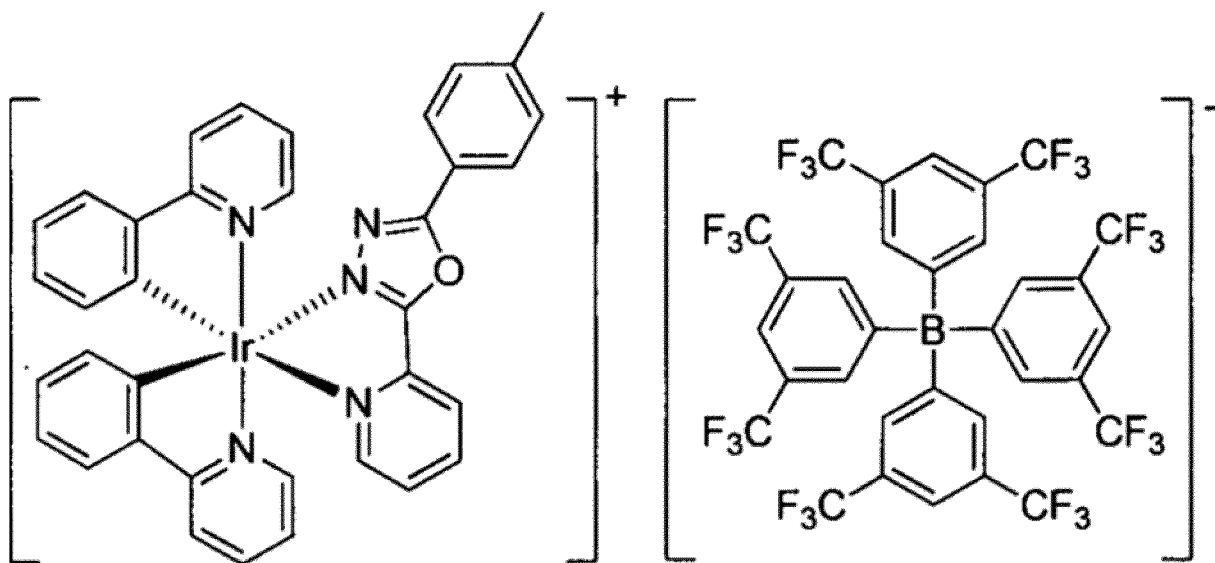
Formel (12)



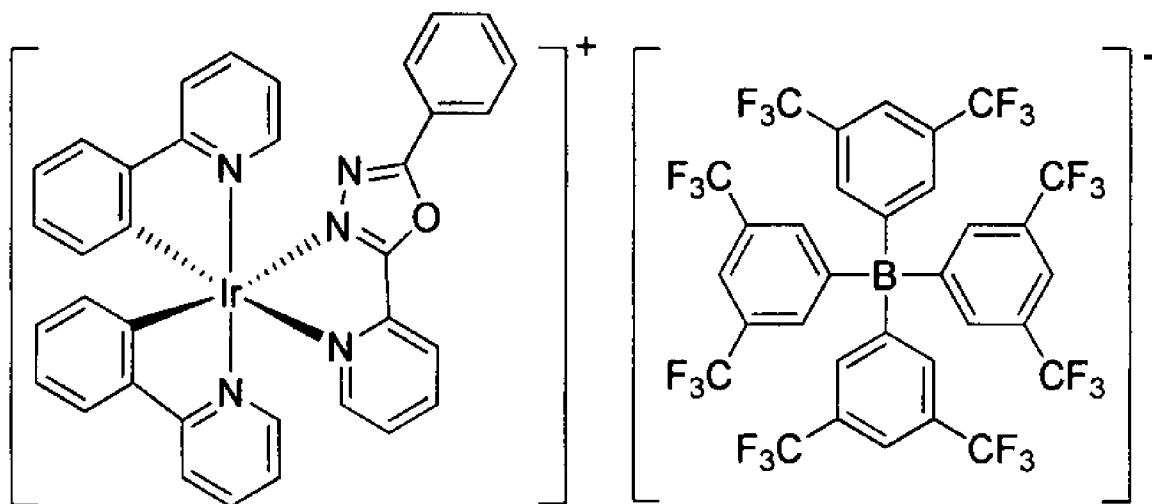
Formel (13)



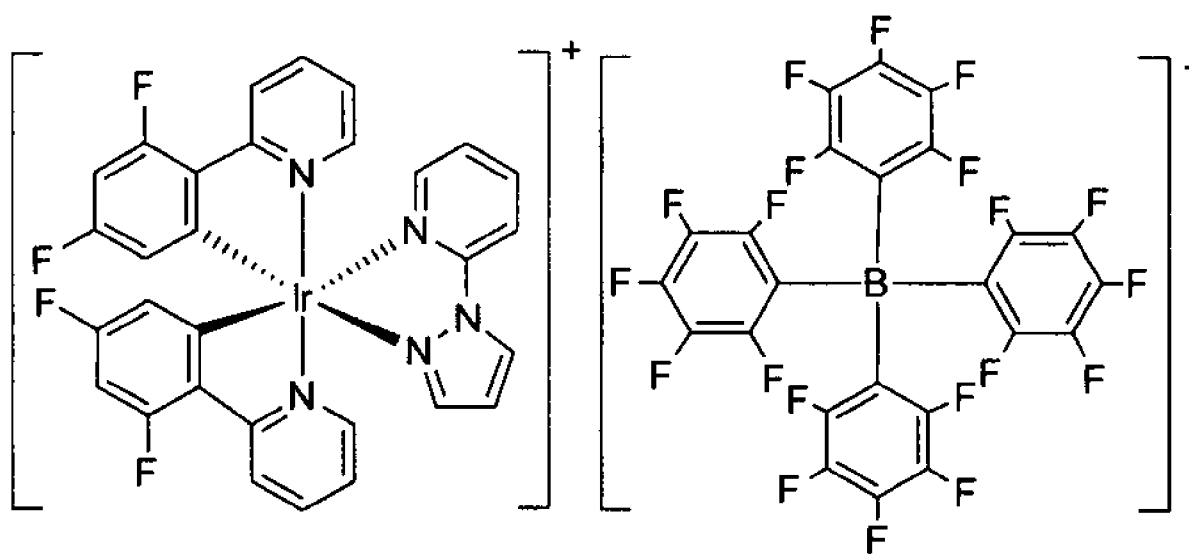
Formel (14)



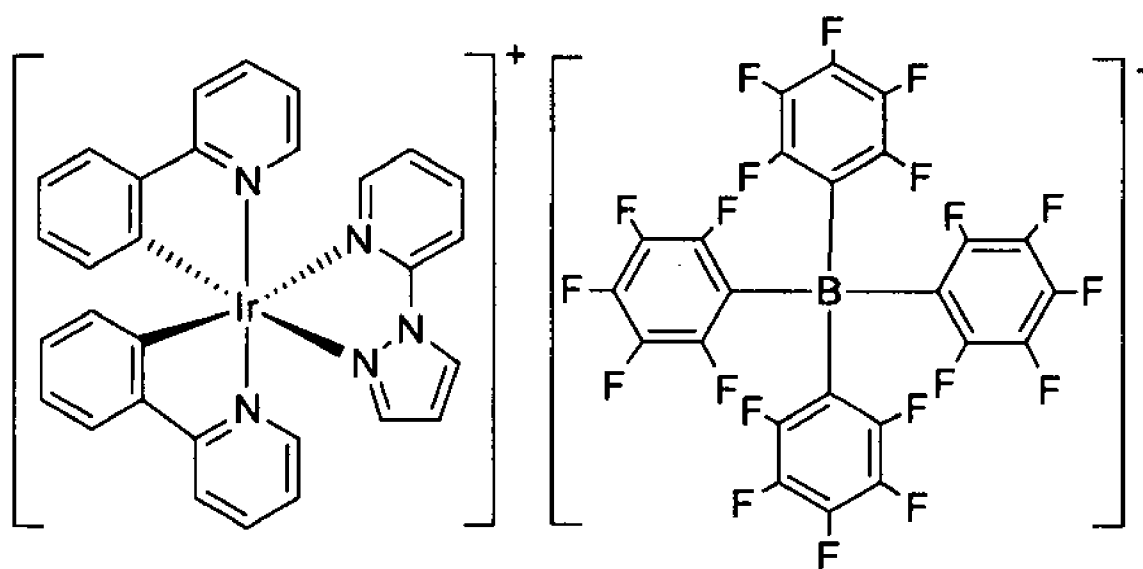
Formel (15)



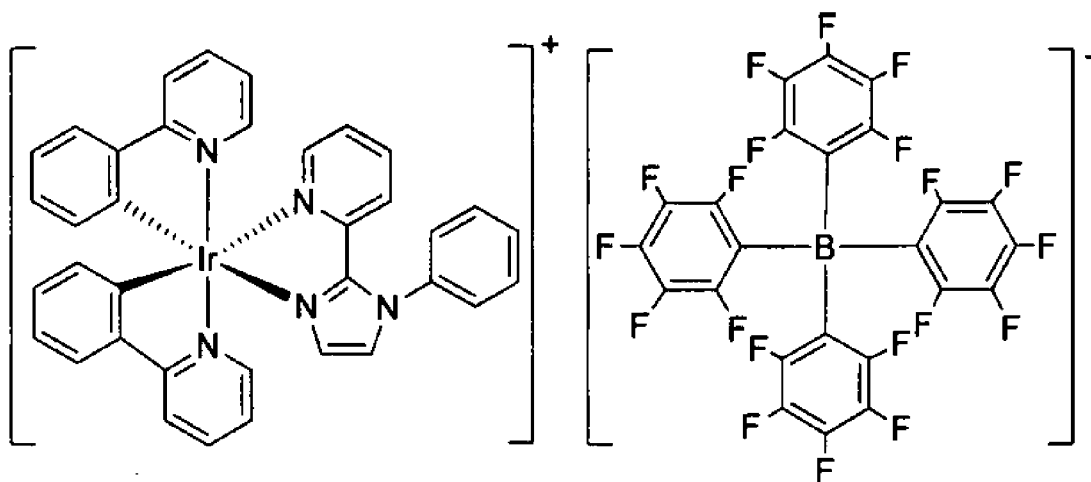
Formel (16)



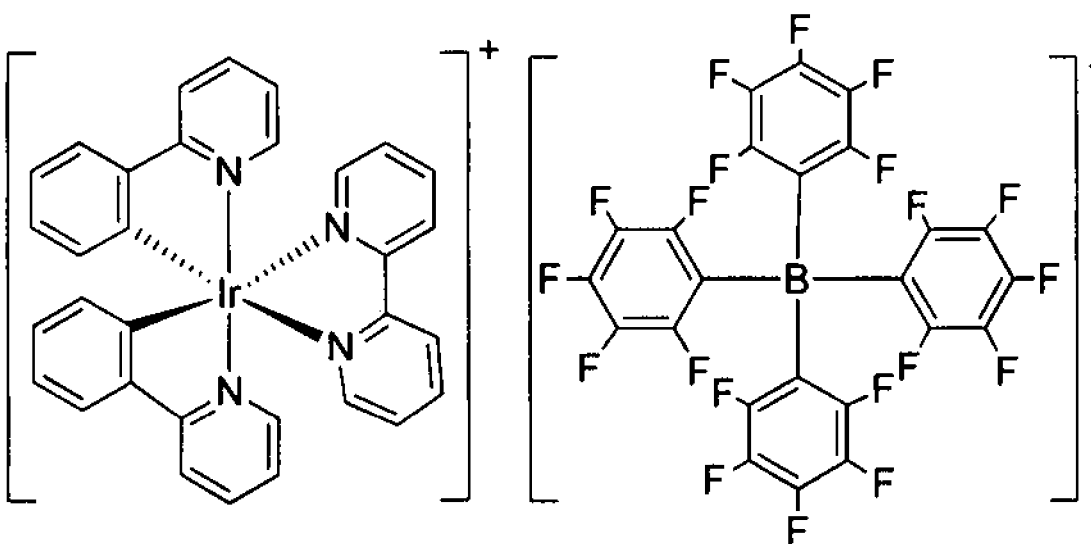
Formel (21)



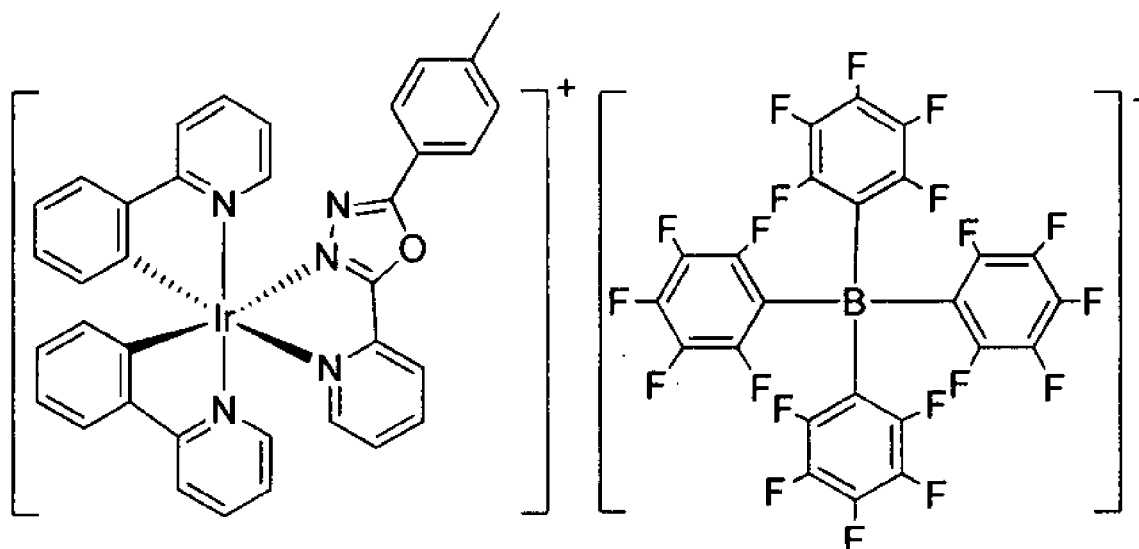
Formel (22)



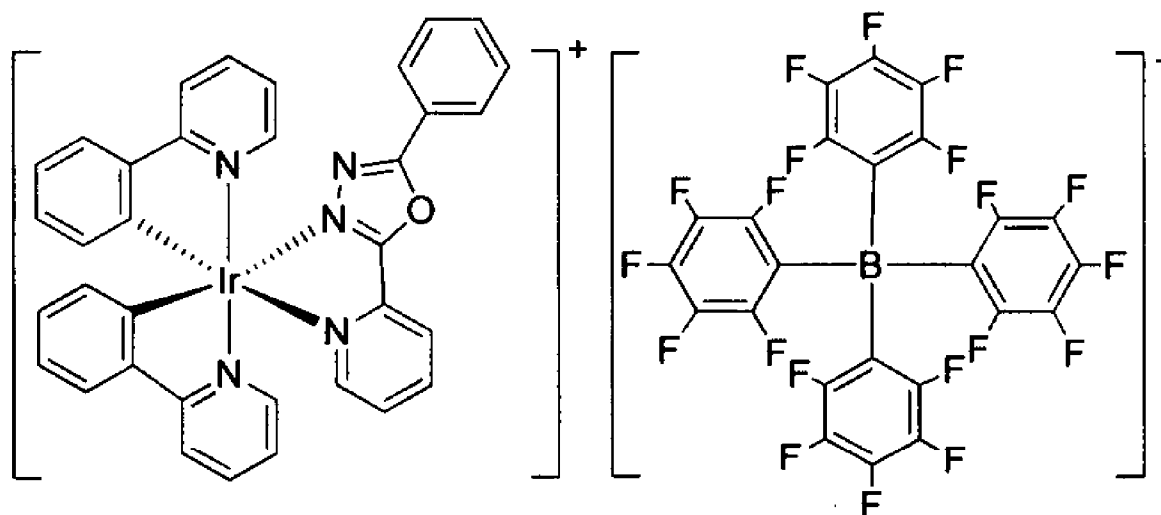
Formel (23)



Formel (24)



Formel (25)



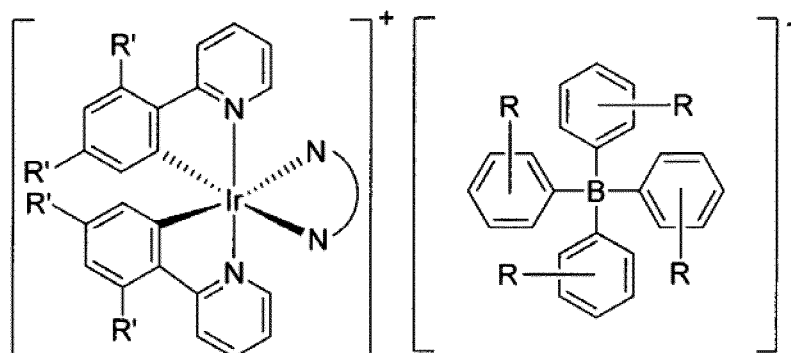
Formel (26).

3. Verwendung eines abscheidbaren Ionenfunktionsmaterials nach Anspruch 1 oder 2 in einer organischen Leucht-
vorrichtung, wobei das abscheidbare Ionenfunktionsmaterial als Farbstoff in einer organischen Licht-emittierenden
Schicht der organischen Leuchtvorrichtung verwendet wird.
4. Organische Leuchtvorrichtung, aufweisend ein Substrat und eine Anodenschicht, eine organische Licht-emittierende
funktionale Schicht, eine Kathoden Schicht, die nacheinander auf dem Substrat gebildet sind, wobei die organische,
Licht-emittierende funktionale Schicht eine Löchertransportschicht, eine organische Licht-emittierende Schicht und
eine Elektronentransportschicht aufweist,
dadurch gekennzeichnet, dass
das Lochmaterial der organischen Licht-emittierenden Schicht mit dem abscheidbaren organischen Ionenfunktions-
material nach Anspruch 2 oder 3 dotiert ist.
5. Organische Leuchtvorrichtung nach Anspruch 4, **dadurch gekennzeichnet, dass** die Dotierkonzentration des ab-
scheidbaren organischen Ionenfunktionsmaterial 2 Gew.-% bis 10 Gew.-% beträgt.
6. Organische Leuchtvorrichtung nach Anspruch 4, **dadurch gekennzeichnet, dass** das abscheidbare organische
Ionenfunktionsmaterial ein rotes Licht, gelbes Licht, grünes Licht oder blaues Licht emittierendes Material ist.

7. Organische Leuchtvorrichtung nach Anspruch 4, **dadurch gekennzeichnet, dass** die organische Licht-emittierende Schicht eine Dicke von 10 nm bis 50 nm aufweist.
8. Organische Leuchtvorrichtung nach Anspruch 7, **dadurch gekennzeichnet, dass** die organische, Licht-emittierende Schicht eine Dicke von 10 nm bis 30 nm hat.

Revendications

1. Matériau fonctionnel organique ionique pouvant être déposé, **caractérisé en ce qu'il** présente une structure représentée dans la formule suivante (1) :



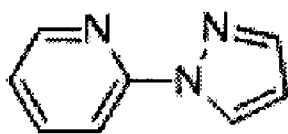
formule (1)

où

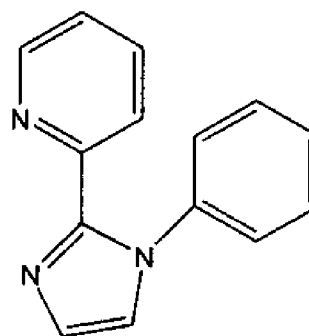
R est un atome d'hydrogène, un atome d'halogène, ou $-CF_3$;

R' est un atome d'hydrogène ou un atome d'halogène ;

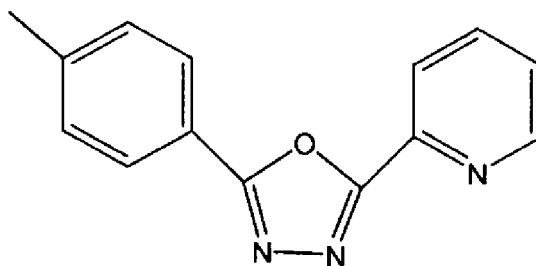
le ligand N^N est sélectionné parmi **Pzpy** représenté dans la formule suivante (31), **Pyim** représenté dans la formule suivante (32), **Ptop** représenté dans la formule suivante (33), **Pop** représenté dans la formule suivante (34), et **Bpy** représenté dans la formule suivante (35) ;



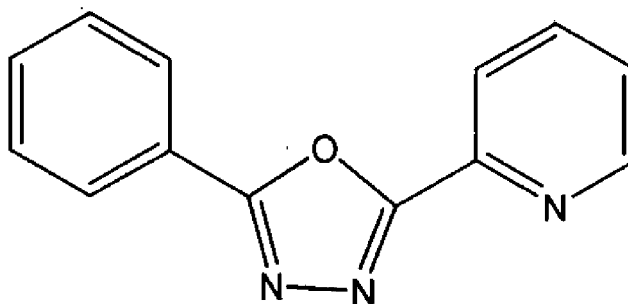
Formule (31)



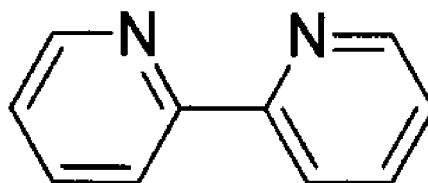
formule (32)



formule (33)

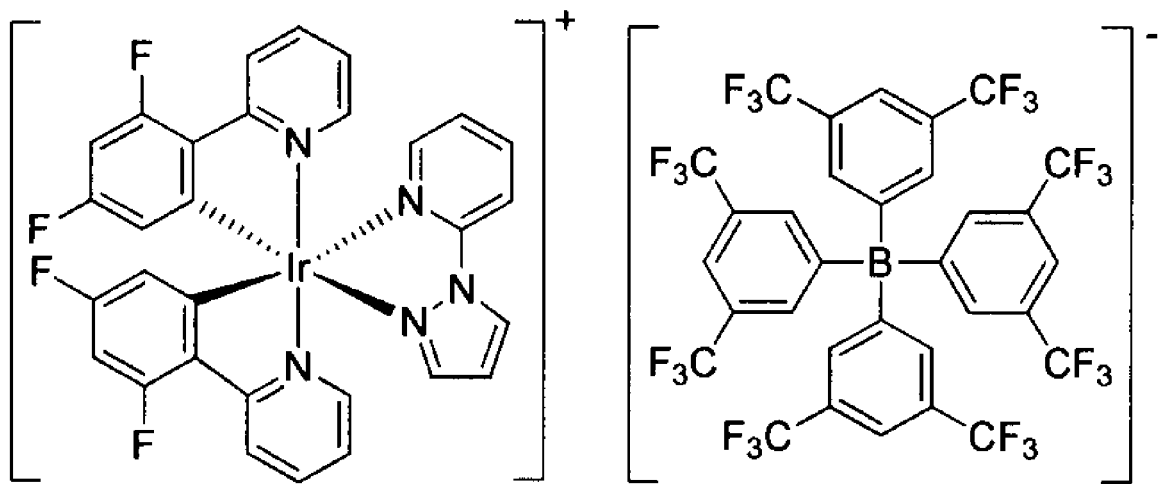


formule (34)

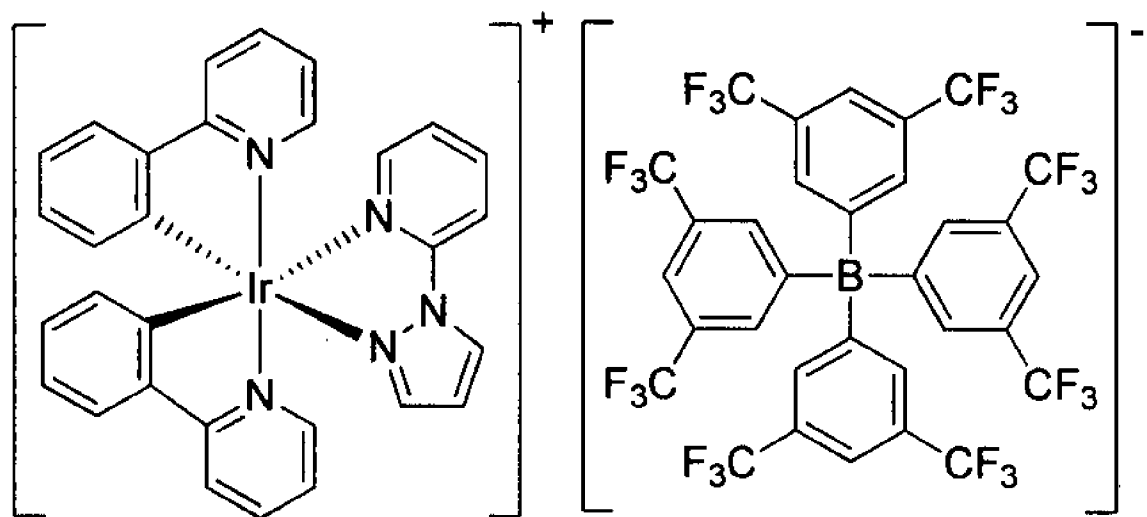


formule (35).

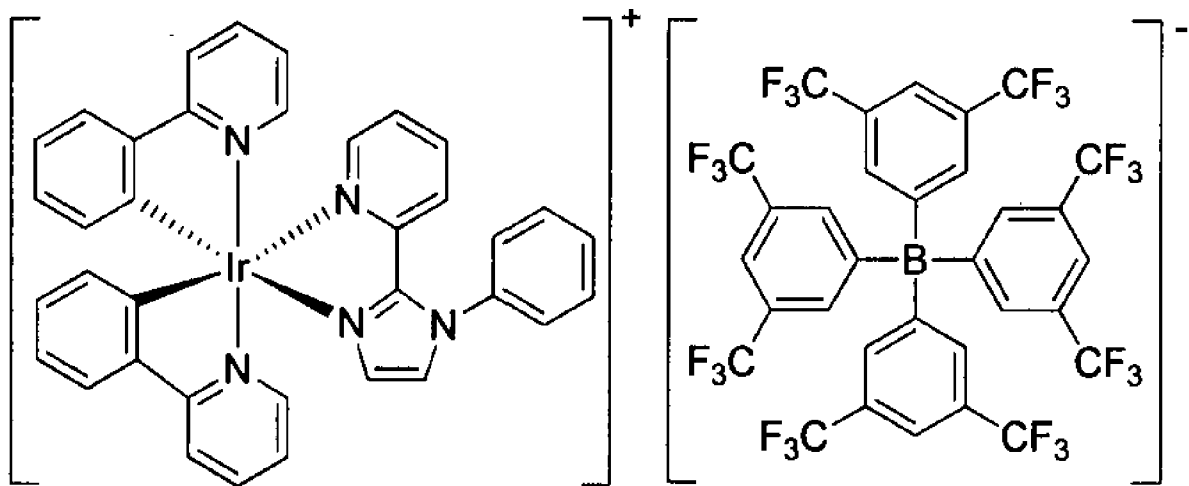
2. Matériau fonctionnel organique ionique pouvant être déposé selon la revendication 1, **caractérisé en ce que** le complexe ionique pouvant être déposé présente une structure représentée dans les formules suivantes (11) à (16) et les formules (21) à (26) :



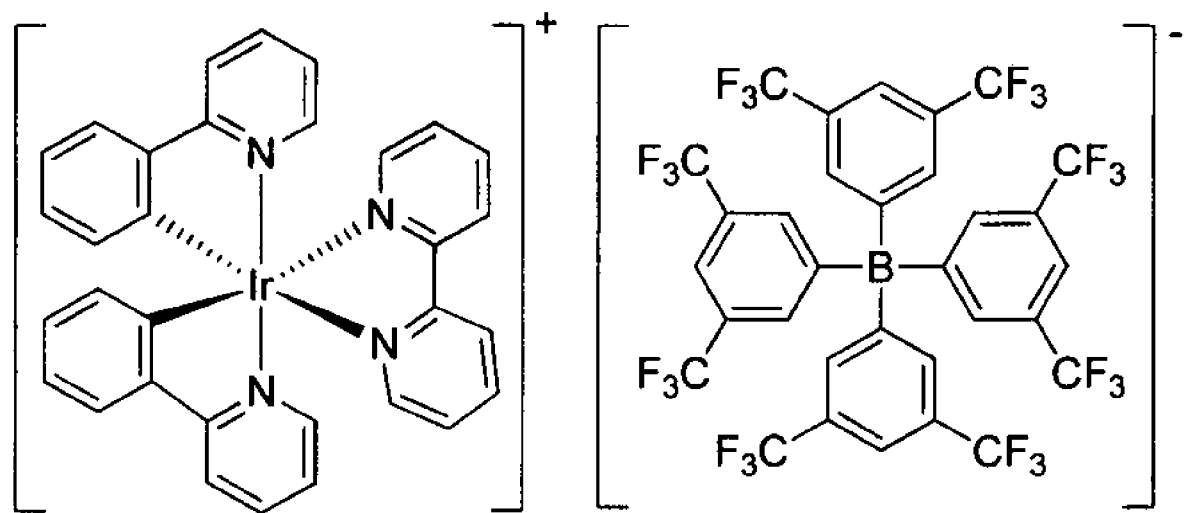
formule (11)



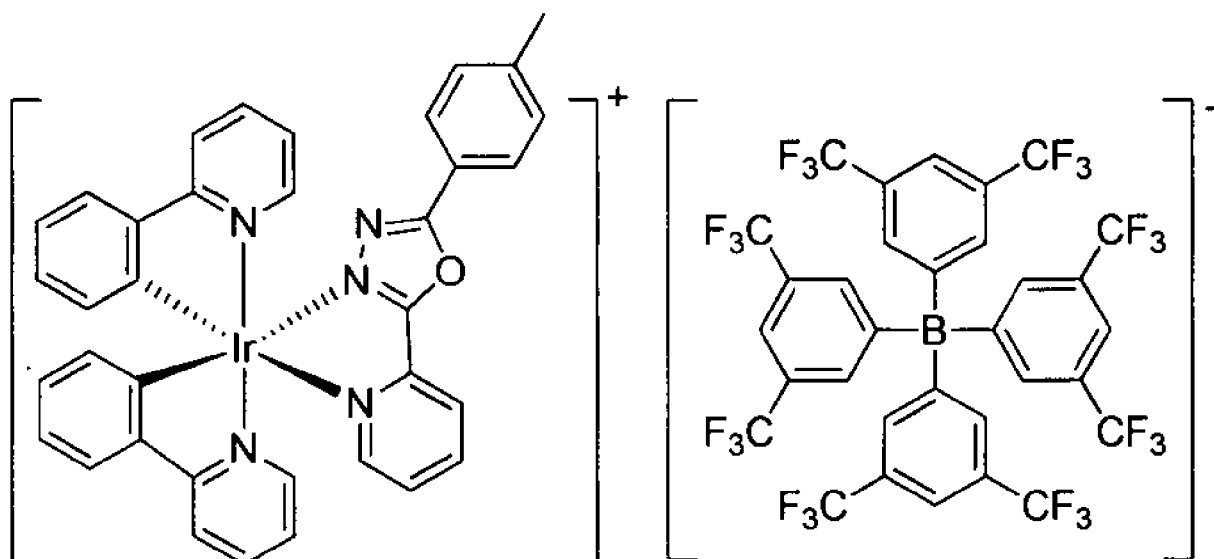
formule (12)



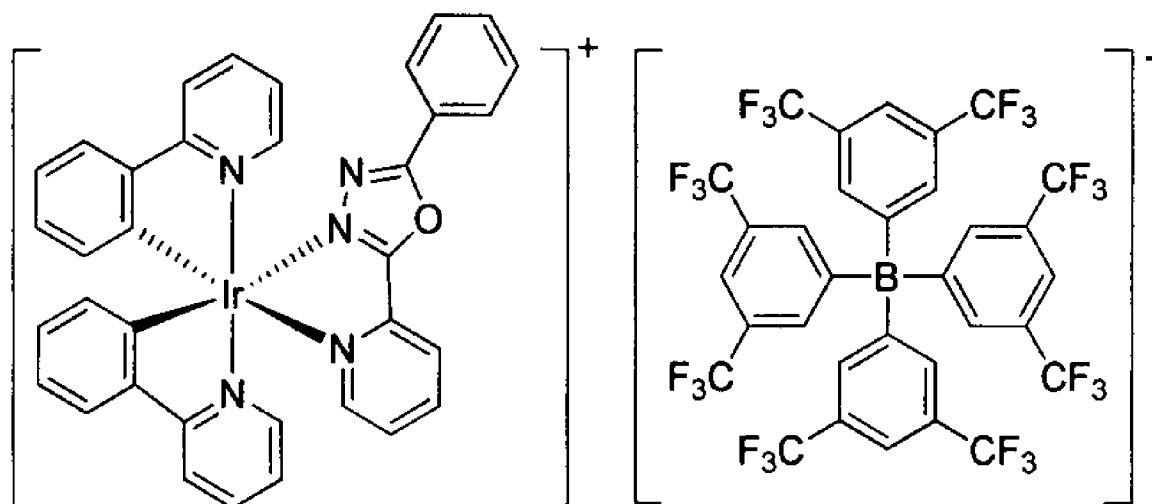
formule (13)



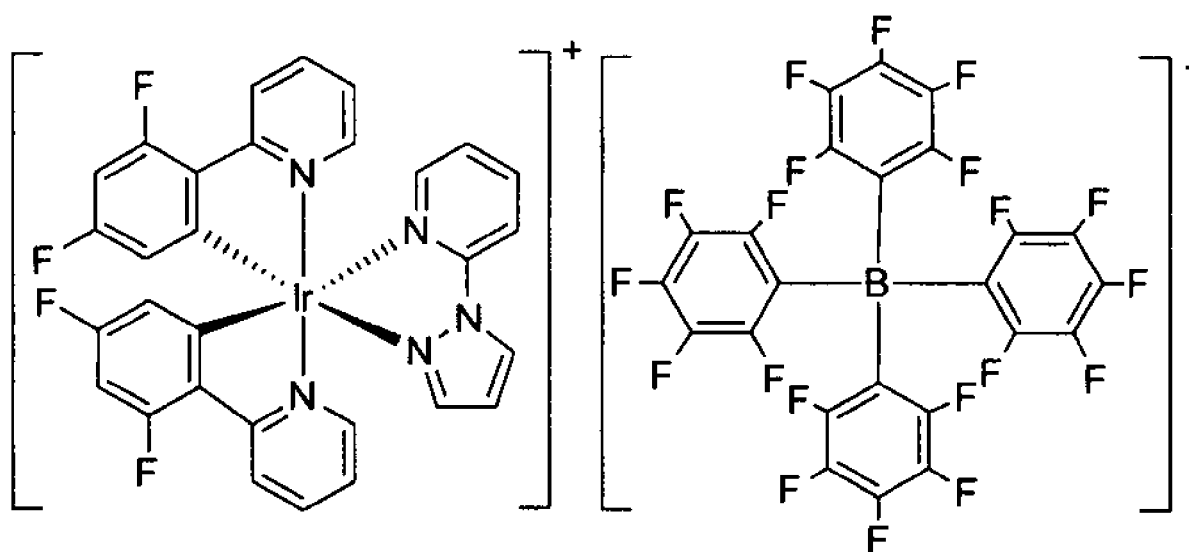
formule (14)



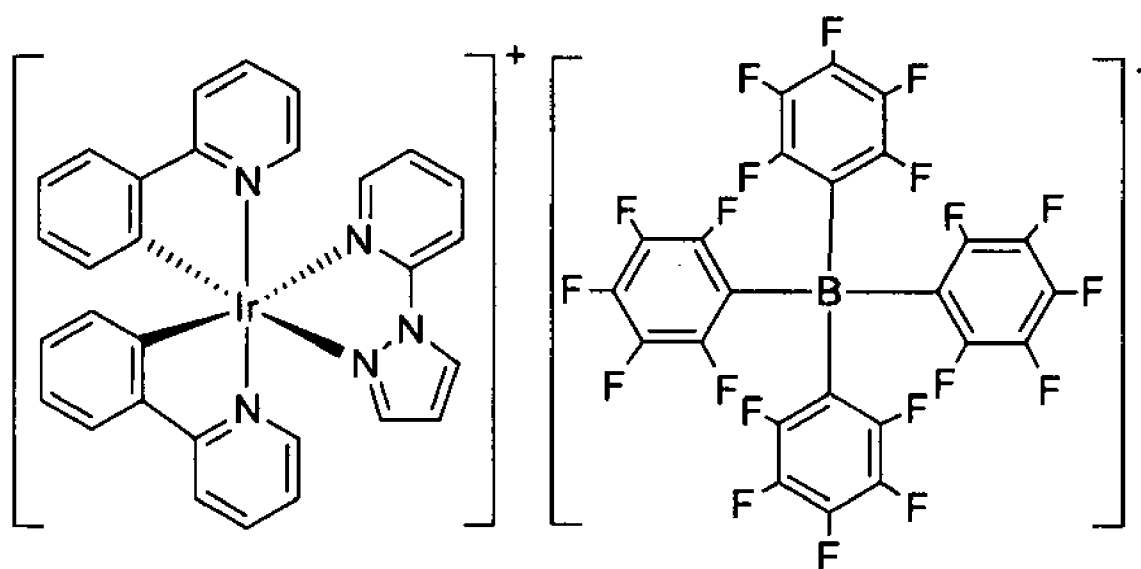
formule (15)



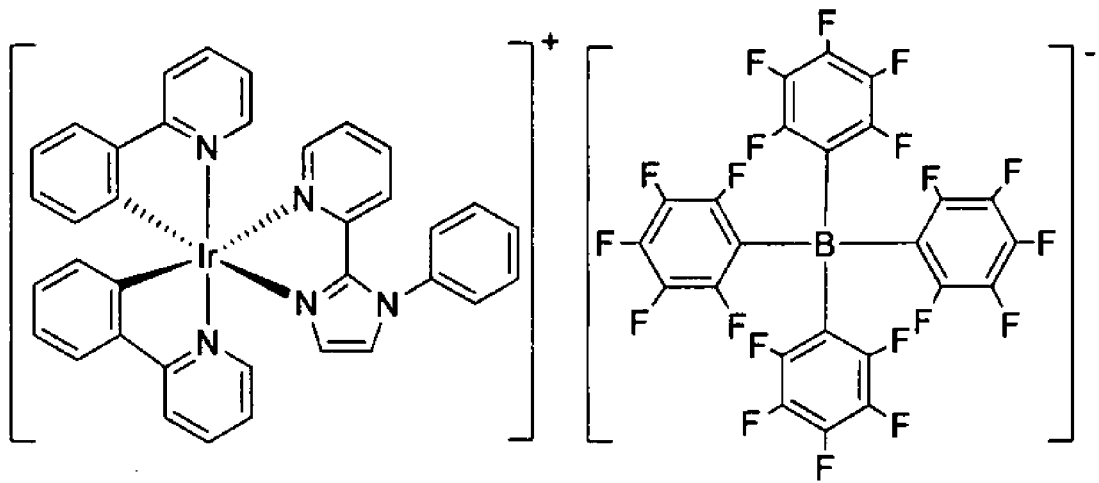
formule (16)



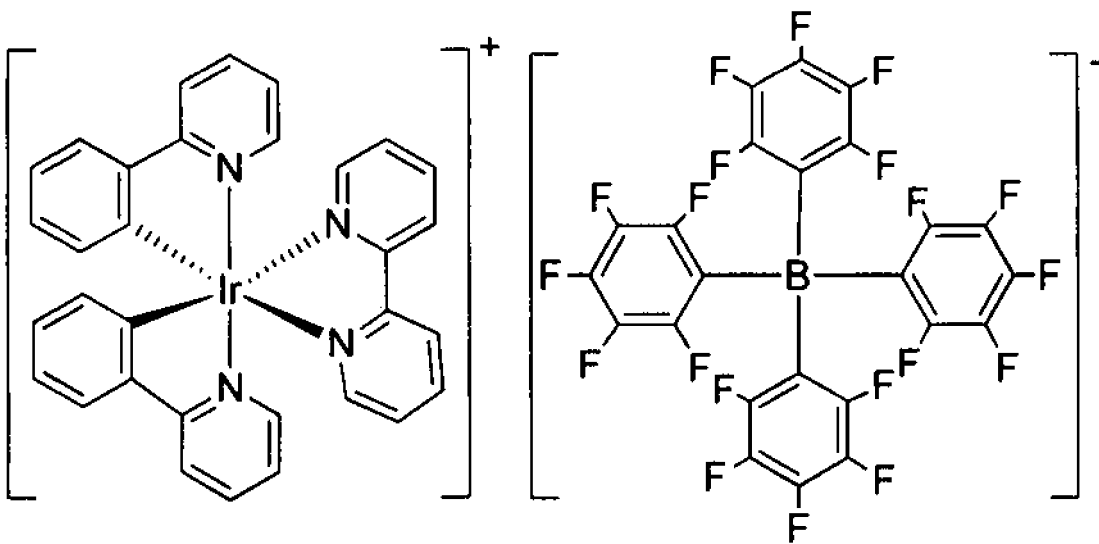
formule (21)



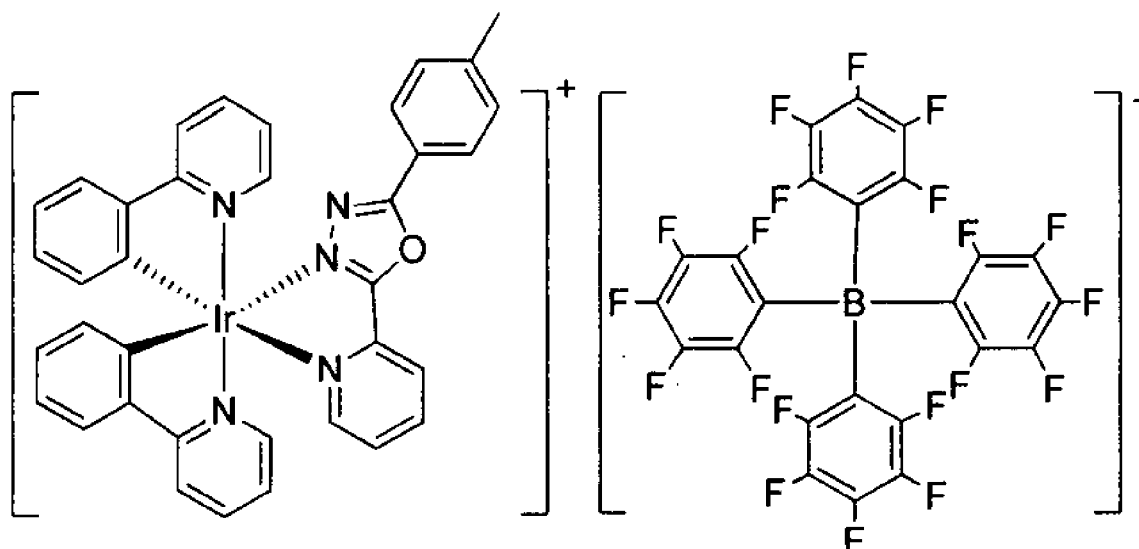
formule (22)



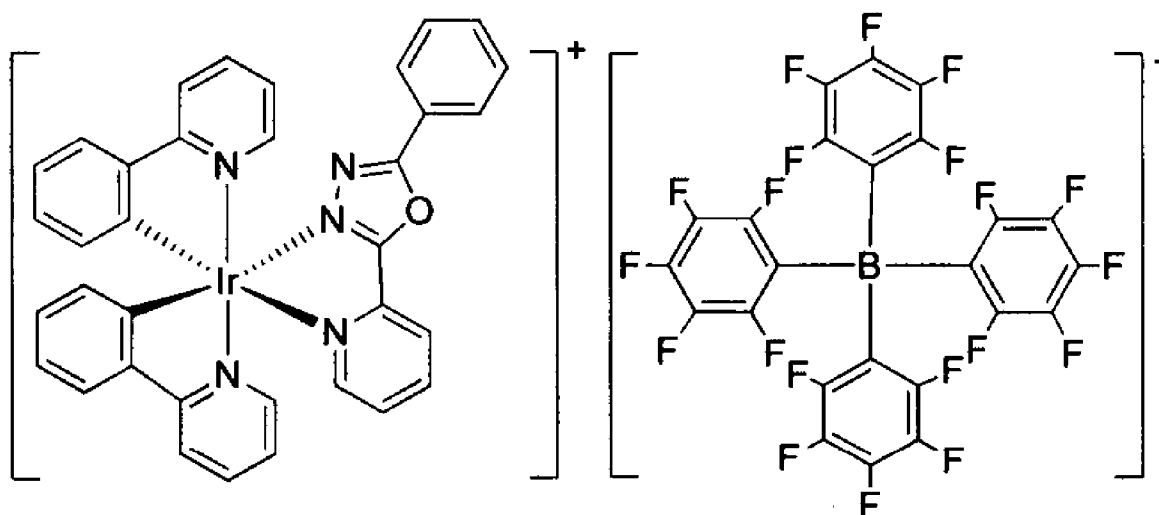
formule (23)



formule (24)



formule (25)



formule (26).

3. Utilisation du matériau fonctionnel organique ionique pouvant être déposé selon la revendication 1 ou 2 dans un dispositif électroluminescent organique, dans laquelle le matériau fonctionnel organique ionique pouvant être déposé est utilisé comme colorant dans une couche luminescente organique du dispositif électroluminescent organique.
4. Dispositif électroluminescent organique, comprenant un substrat, et une couche anodique, une couche fonctionnelle luminescente organique, une couche cathodique, formés dans l'ordre sur le substrat, dans lequel la couche fonctionnelle luminescente organique comprend une couche de transport de trous, une couche luminescente organique, et une couche de transport d'électrons,
caractérisé en ce que
 un matériau hôte de la couche luminescente organique est dopé avec le matériau fonctionnel organique ionique pouvant être déposé selon la revendication 1 ou 2.
5. Dispositif électroluminescent organique selon la revendication 4, **caractérisé en ce que** la concentration de dopage du matériau fonctionnel organique ionique pouvant être déposé est égale à 2 % en poids à 10 % en poids.
6. Dispositif électroluminescent organique selon la revendication 4, **caractérisé en ce que** le matériau fonctionnel organique ionique pouvant être déposé est un matériau émettant une lumière rouge, jaune, verte, ou bleue.

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7. Dispositif électroluminescent organique selon la revendication 4, **caractérisé en ce que** la couche luminescente organique présente une épaisseur de 10 nm à 50 nm.
8. Dispositif électroluminescent organique selon la revendication 7, **caractérisé en ce que** la couche luminescente organique présente une épaisseur de 10 nm à 30 nm.

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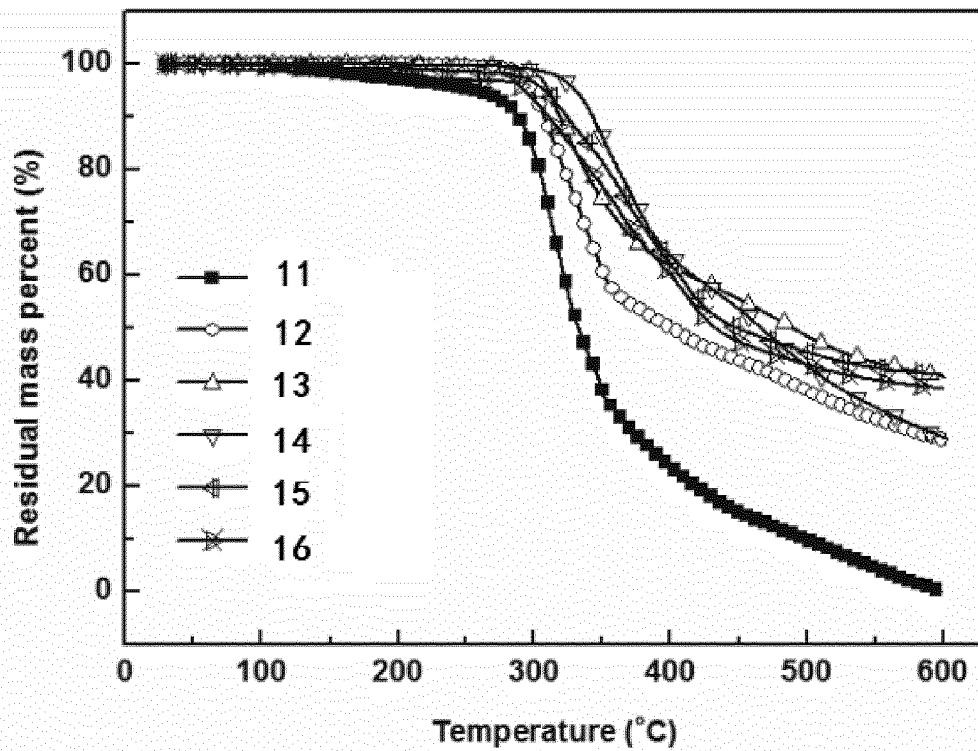


Figure 1

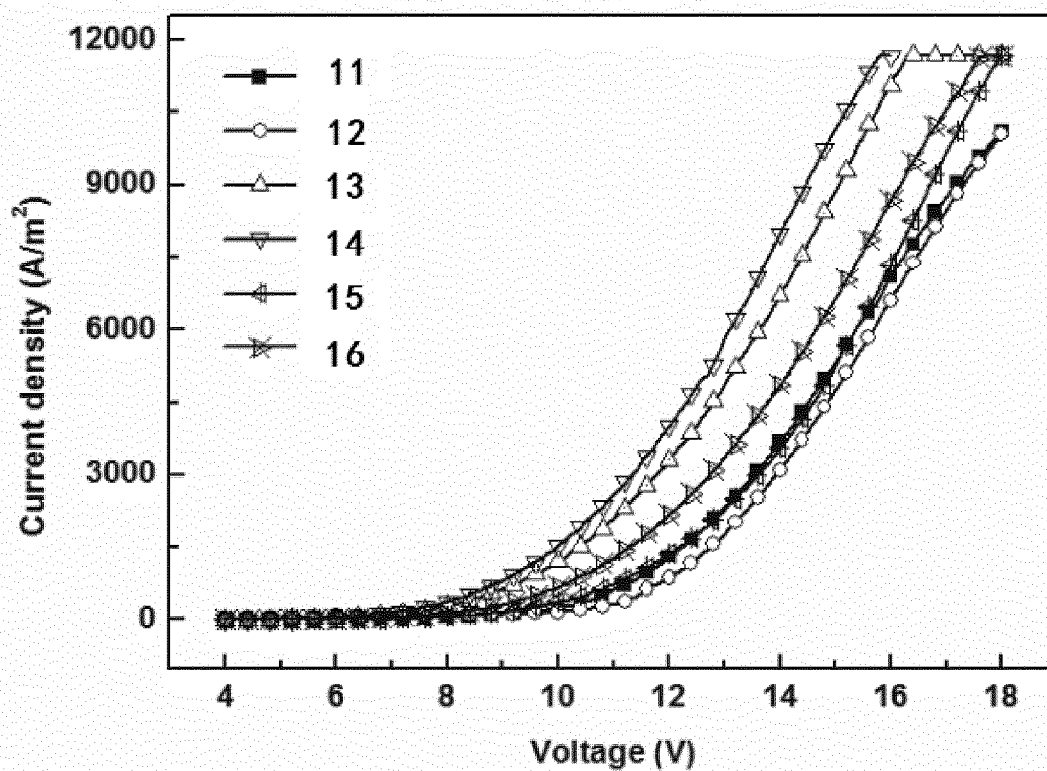


Figure 2

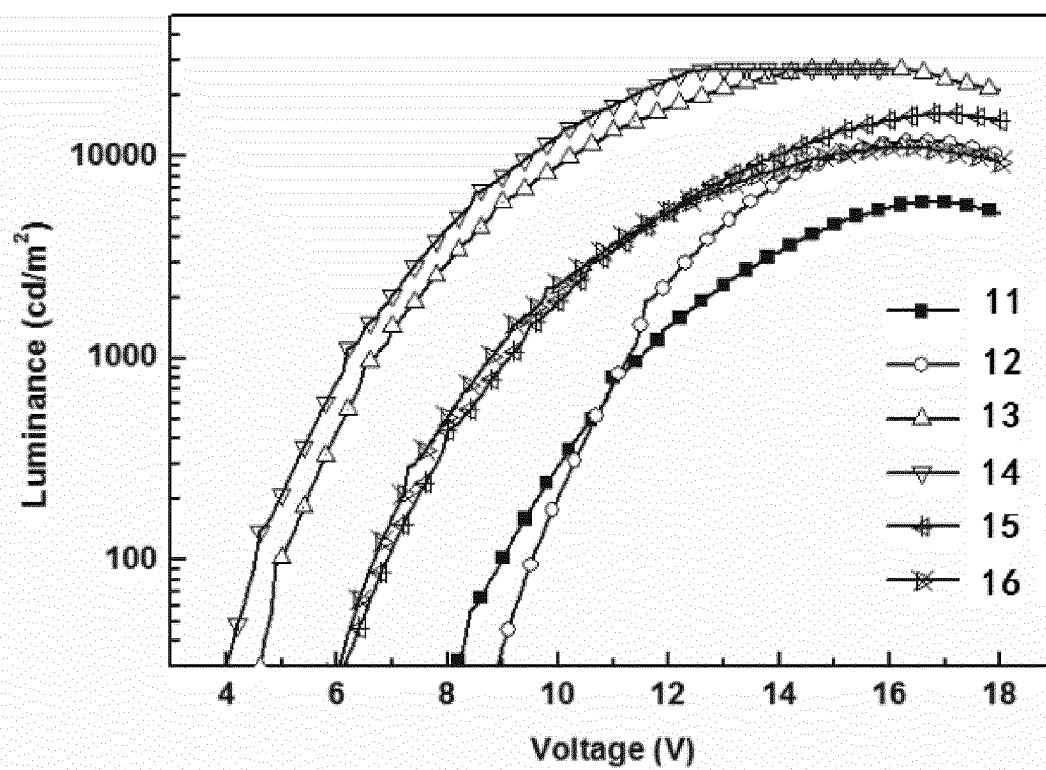


Figure 3

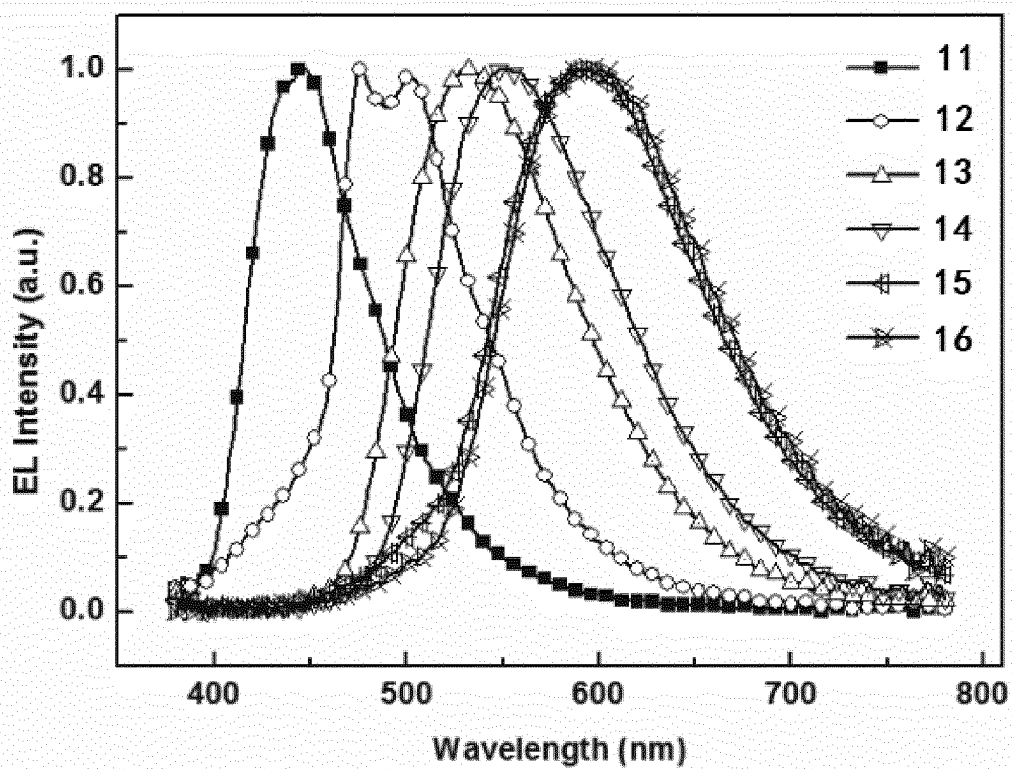


Figure 4

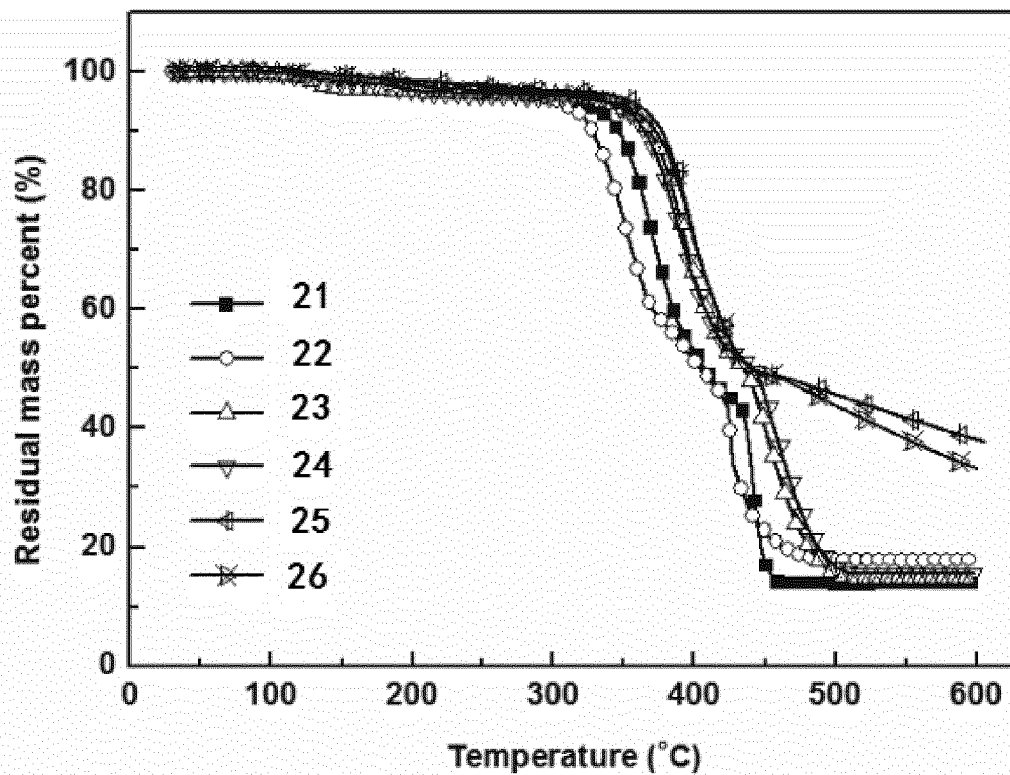


Figure 5

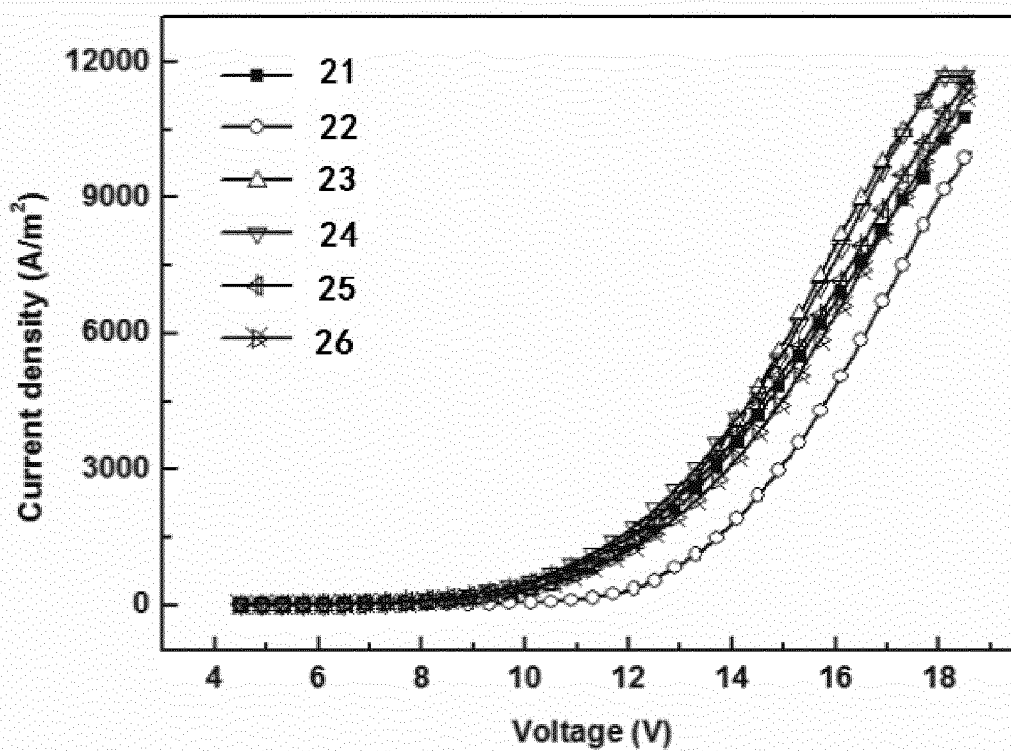


Figure 6

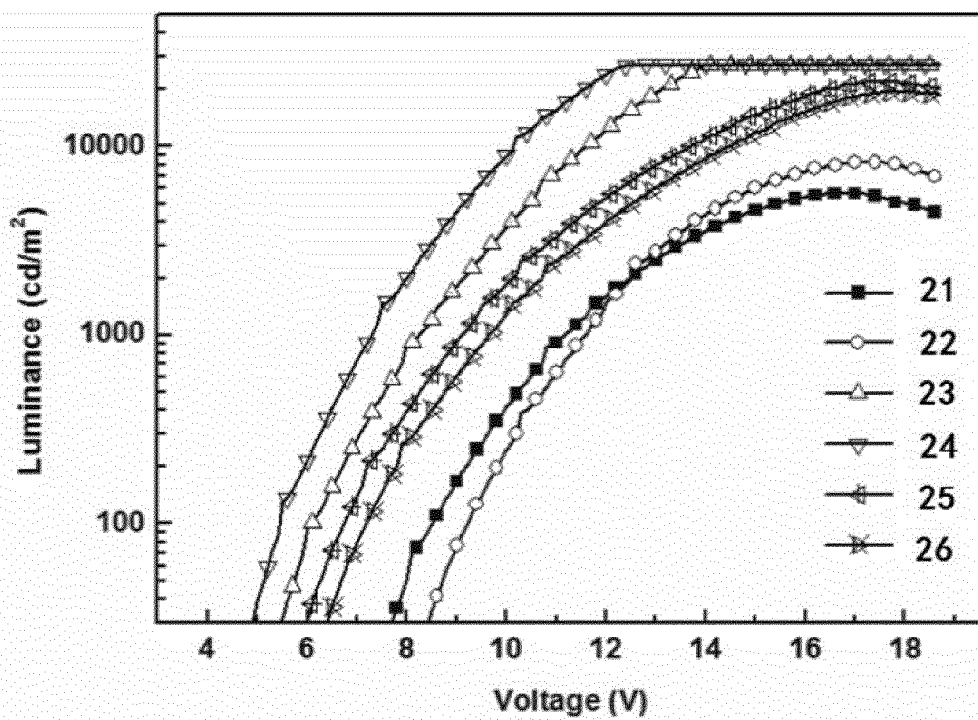


Figure 7

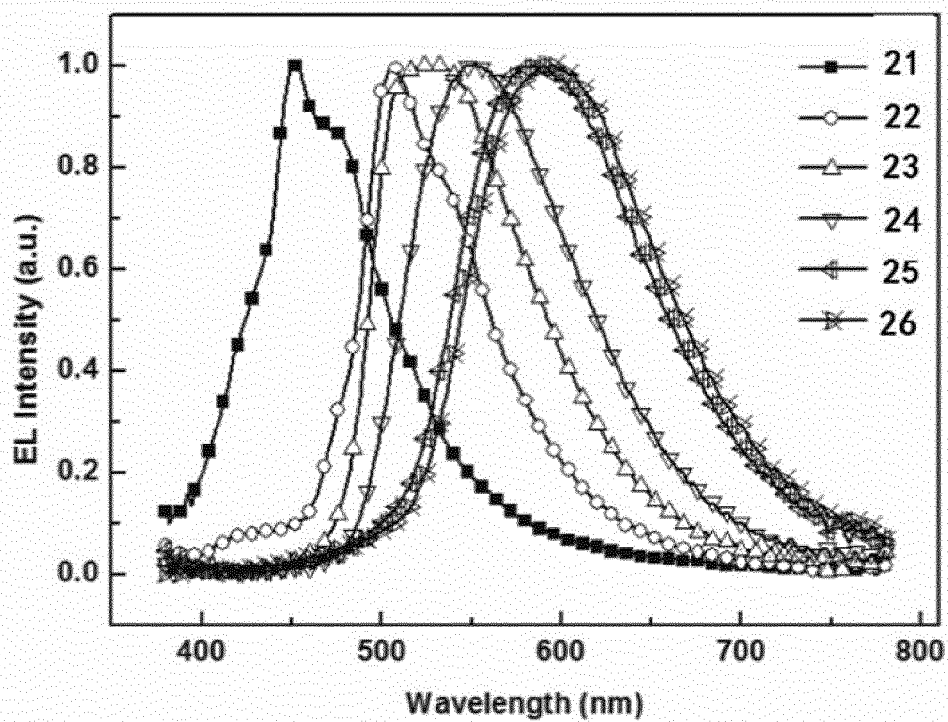


Figure 8

03
07
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Figure 9

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 20060177695 A1 [0003]

Non-patent literature cited in the description

- *Advanced Functional Materials*, 2007, vol. 17, 315 [0003]
- **HE, L. et al.** *Adv. Funct. Mater.*, 2008, vol. 18, 2123-2131 [0040]
- **HE, L. et al.** *Adv. Funct. Mater.*, 2009, vol. 19, 2950-2960 [0040]
- **ZHANG, J. et al.** *Adv. Funct. Mater.*, 2013, vol. 23, 4667-4677 [0040]

专利名称(译)	可沉积的离子有机功能材料及其在有机电致发光器件中的用途		
公开(公告)号	EP3318617B1	公开(公告)日	2019-08-14
申请号	EP2016817142	申请日	2016-06-15
[标]申请(专利权)人(译)	昆山国显光电有限公司 清华大学		
申请(专利权)人(译)	昆山GO-维信诺光电科技有限公司. 清华大学		
当前申请(专利权)人(译)	昆山GO-维信诺光电科技有限公司. 清华大学		
[标]发明人	DUAN LIAN MA DONGXIN LIU SONG XIE JING ZHAO FEI		
发明人	DUAN, LIAN MA, DONGXIN LIU, SONG XIE, JING ZHAO, FEI		
IPC分类号	C09K11/06 C07F15/00 H01L51/54		
CPC分类号	C07F15/00 C09K11/06 C07F15/0033 C09K2211/185 H01L51/0002 H01L51/0085 H01L51/5024 H01L51/5036 H01L51/5056 H01L51/5072 H01L51/5088 H01L51/5206 H01L51/5221		
代理机构(译)	HERRMANN , UWE		
优先权	201510382459.7 2015-07-02 CN		
其他公开文献	EP3318617A4 EP3318617A1		
外部链接	Espacenet		

摘要(译)

本发明涉及具有下式(1)所示结构的可沉积离子有机功能材料：其中，R是氢原子，卤原子或-CF₃；R'是氢原子或卤原子；N⁺配体选自下式(31)所示的Pzpy及其衍生物，下式(32)所示的Pyim，下式(33)所示的Ptop，下式(34)所示的Pop和下式(35)所示的Bpy：当功能性材料用作发光染料时，合成条件温和且易于进行，产率高，产品易于纯化。功能材料可用于高效蓝色至红色OLED。

