The present invention relates to light emitting materials including a novel Ir complex having a pyridyl triazole ligand substituted with at least one substituent on its pyridyl ring. Such light emitting materials were found to have a significantly enhanced photophorescence quantum yield and hypsochromic blue shifted photophorescence emission over other Ir complexes with a pyridyl triazole ligand having no substituent in its pyridine ring. The present invention further relates to the use of such light emitting materials and an organic light emitting device including the same.

Figure 1
PHOSPHORESCENT LIGHT-EMITTING IRIDIUM COMPLEX
CONTAINING PYRIDYLTRIAZOLE LIGAND

TECHNICAL FIELD

The present invention relates to a light-emitting material and its use, as well as a light-emitting device capable of converting electrical energy into light.

BACKGROUND ART

Recently, various display devices have been actively researched and developed, particularly those based on electroluminescence from organic materials.

Although many organic materials exhibit fluorescence (i.e., luminescence from a symmetry-allowed process) from singlet excitons, there is only few materials exhibit phosphorescence efficiently at room temperature. If phosphorescent materials are successfully utilized, then they can produce enormous benefits for organic electroluminescent devices especially in efficiencies. For example, the advantage of utilizing phosphorescent materials is that all singlet and triplet excitons (formed by combining holes and electrons in an EL), which are, in part, triplet-based in phosphorescent devices, may participate in the energy transfer and luminescence. This can be achieved by phosphorescence emission itself. Alternatively, it can be accomplished by using phosphorescent materials to improve the efficiency of 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.

As a candidate for blue emissive material, there has been reported a light-emitting device utilizing the emission from an iridium complex having a phenylpyridine and picolinic acid ligands (e.g., iridium(III) bis[(4,6-difluorophenyl)pyridinato-N,C2']picolinate), which are standard complexes for blue-light emission. Further, other types of heterocycles containing nitrogen have been also studied.

U.S. Patent No. US 7329898 B2 discloses various Ir complexes having phenylpyridine and heterocyclic ligands, which can emit a light of blue, white, etc. with high luminance and light-emitting efficiency as well as low minimum driving voltage and excel durability. Japanese Patent Publication No. 2008 143826 A discloses Pt complexes having nitrogen-containing cycloplatinated ligands, e.g., dimethylbis(2-phenylpyridine)Pt(IV) and organic electroluminescent devices having emitter layers containing the complexes, which emit blue light with high
luminescence efficiency and long service life. A OLED device manufactured using one Pt complex, dimethylbis(2-phenylpyridine)Pt(IV), exhibits luminescence peaks at 449, 478 and 507 nm, as well as luminescence quantum yield of 0.16 (in CH₂Cl₂).


DISCLOSURE

TECHNICAL PROBLEM

However, the above light-emitting materials do not exhibit sufficient luminescent efficiency at the blue region. Thus, there is a need to develop iridium complexes exhibiting high external quantum efficiencies and luminance compared to the standard complexes used while emitting blue light.

TECHNICAL SOLUTION

It is thus an object of the present invention to provide an Ir complex represented by formula (I):

![Diagram](image-url)

(I)
wherein:

$E_1$ represents an 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 a ring comprising

$E_2$, said ring coordinating to the metal $M$ via a $sp^2$ hybridized carbon;

$E_2$ represents a N-containing aromatic 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 $E_i$, said ring coordinating to the metal $M$ via a $sp^2$ hybridized nitrogen;

$R_i$ is an electron-donating group, which is same or different at each occurrence and is independently selected from $-F$, $-Cl$, $-Br$, a straight or branched $C_{1-20}$ alkyl, a $C_{3-20}$ cyclic alkyl, a straight or branched $C_{1-20}$ alkoxy, a $C_{1-20}$ dialkylamino, a $C_{4-14}$ aryl, a $C_{4-14}$ heteroaryl which may be substituted by one or more non-aromatic radicals; and a plurality of substituents $R_i$ either on the same ring or on two different rings forming a further mono- or polycyclic ring system which is optionally aromatic;

$R_2$ is an electron-withdrawing group, which is selected from $-F$, $-CN$, $-NO_2$, (per)fluoroalkyl, (per)fluoroaryl, (per)fluororalkylaryl, alkylcarbonyl, (per)fluororalkylcarbonyl, (per)fluoroalkylarylcarbonyl, and (per)fluoroalkylheteroarylcarbonyl each of which may be substituted by at least one substituent; and

$n$ is same or different at each occurrence and is an integer from 1 to 4.

Another object of the present invention relates to the use of the above light emitting material and to provide an organic light emitting device including the above light emitting material.

Thus, the present invention provides a light emitting material, in which

![Diagram]

the ligand is selected from phenylpyridine ligands substituted by at least one fluorine atom in the phenyl ring.

In some embodiments of the present invention, the phenylpyridine ligand is selected from the group consisting of:
In other embodiments of the present invention, \( R_i \) is independently selected from alkyl, dialkylamino and alkoxy groups. Specifically, \( R_i \) is methyl or methoxy group. In such embodiments, \( n \) is 1.

In some embodiments of the present invention, \( R_2 \) is trifluoroalkyl, and more specifically trifluoromethyl group.

In specific embodiments of the present invention, the Ir complex has a formula selected from the group consisting of:

\[
\text{(2),}
\]
Surprisingly, it has been found that when an Ir complex has a pyridyl triazole ligand substituted with at least one substituent, the photoluminescence quantum yield (PQY) of the emitting material for specifically improving the efficiency of a device is significantly enhanced over other Ir complexes with a phenyl pyridine ligand having no substituent in its pyridine ring.

Generally, according to the first embodiment of the present invention, the Ir complexes having Formulae (2), (3) and (5) to (7) are prepared by reacting a dimer ([C₄N]₂Ir(μ-X°)₂Ir[C₄N]₂) comprising two Ir atoms, two phenyl pyridine ligands(C₄N) and two halogen ligands (X°) in the presence of a base compound with a substituted pyridyl triazole. The phenyl pyridine and substituted pyridyl triazole ligands are commercially available or can be easily synthesized by using well-known organic synthetic methods.

In particular, phenyl pyridine ligands can be prepared with good to excellent yields by Suzuki coupling the substituted pyridine compound with corresponding arylboronic acids in the presence of alkali metallic base such as potassium bicarbonate, as described in Lohse et al, "The Palladium Catalyzed Suzuki Coupling of 2- and 4-Chloropyridines," Syn. Lett., 1:15-18 (1999) and U.S. Patent No. 6,670,645 assigned
to Dupont de Nemours.

\[ \text{[C} \text{A} \text{N}]_2 \text{Ir(µ-} \text{X}^\circ) \text{2Ir[C} \text{A} \text{N}]_2 \text{ complexes, wherein } \text{X}^\circ \text{ is halogen (e.g., Cl), can be} \]

prepared by using procedures already described in, for example, the following

In some embodiments, the reaction is carried out by using an excess of the
neutral form of the orthometalated ligand (H-C\text{A}N) and high-boiling temperature
solvents. The term "high-boiling temperature solvent" is intended to denote a
solvent having a boiling point of at least 80°C, at least 85°C or at least 90°C. For
example, suitable solvents may be methoxyethanol, ethoxyethanol, glycerol,
dimethylformamide (DMF), N-methylpyrrolidone (NMP), dimethylsulfoxide
(DMSO) and the like, wherein the solvents can be used as is or in admixture with
water.

Optionally, the reaction can be carried out in the presence of a suitable
Brønsted base such as metal carbonates (e.g., potassium carbonate (K_2CO_3)), metal
hydrides (e.g., sodium hydride (NaH)), metal ethoxide or metal methoxide (e.g.,
NaOCH_3 and NaOC_2H_5), alkylammonium hydroxides (e.g., tetramethylammonium
hydroxide) or imidazolium hydroxides.

A nucleophilic substitution at the metal atom with a pyridyl triazole ligand
may be carried out in the presence of a base compound by more or less contacting a
stoichiometric amount of the pyridyl triazole ligand with a bridged intermediate in a
suitable solvent.

The present invention is also directed to the use of a light emitting material in
the emitting layer of an organic light emitting device (OLED).

Furthermore, the present invention relates to using the light emitting material
including the Ir complexes, as described above, as a dopant in a host layer under
conditions effective to function as an emissive layer in an organic light emitting
device.

The present invention also relates to an OLED including an emissive layer.
The emissive layer includes the light emitting material, as described above, optionally
with a host material (wherein the light emitting material is specifically present as a
dopant). The host material is notably adapted to luminesce when a voltage is applied
across the device structure.

As depicted in Figure 1, the OLED devices of the present invention
comprises: a substrate(1); an anode(2); optionally a hole transporting layer (HTL, 3);
an emissive layer (EML, 4); optionally a hole blocking layer (HBL, 5) and/or an
electron transporting layer (ETL, 6); and a cathode(7). Such devices can be prepared
by any method known in the art, e.g., U.S. Patent No. 7,329,898 B1 assigned to
Fujifilm Corp. and WO/2008/043815 assigned to Solvay (Societe Anonyme).

Another aspect of the present invention relates to a display device including
the above OLED.

DESCRIPTION OF DRAWINGS
Figure 1 is a cross-sectional view of a display device having an organic light
emitting device of the present invention.
Figures 2-8 show absorption and phosphorescence spectra of the complexes
of Formulae (1) to (7).
Figures 9a-9f show cyclic voltammograms of the complexes of Formulae (1)
to (5) and (7).

BEST MODE
The Ir complex of the present invention is represented by formula (I) of:

\[
\begin{align*}
&\text{(I)} \\
&\text{wherein:} \\
&E_1, E_2, R_1, R_2, \text{ and } n \text{ are as previously defined herein.}
\end{align*}
\]

MODE FOR INVENTION
Examples
Hereinafter, the present invention will be explained in detail with reference to
examples and comparative examples. These examples, however, should not in any
sense be interpreted as limiting the scope of the present invention. Further, units are
expressed by weight unless otherwise described.

Example 1 - Experimental Section
Chemical reagents have been purchased from Aldrich Chemical Co. and were
used without further purification. Tetrahydrofuran (THF) was distilled over sodium in the presence of benzophenone. \(^1\)H-NMR and \(^{13}\)C-NMR spectra were taken on the Variant Mercury 300 MHz spectrometer on CDCl\(_3\) or CD\(_2\)OD solutions. All chemical shifts are reported in parts per million (d) relative to residual CHCl\(_3\) at 7.26 ppm (for \(^1\)H-NMR) and 77.0 ppm (for \(^{13}\)C-NMR) or CH\(_3\)OH at 4.78(s), 3.30(q) ppm (for \(^1\)H-NMR) and 49.0(septet) ppm (for \(^{13}\)C-NMR). The following abbreviations are used to denote signal patterns: s=singlet; d=doublet; t=triplet; q=quintet; br=broad; and m=multiplet. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25mm silica gel 60F precoated aluminium plates with fluorescent indicator UV254.

Example 2. Synthesis of Pyridyltriazole Ancillary Ligands (21,22 and 23)

The pyridyl triazole-based ligand (i.e., compounds 21, 22 and 23) can be prepared by the following reaction scheme.
2-1. Preparation of 4-Methylpyridine IV-Oxide (16)

4-Methylpyridine (3.0 ml, 30.0 mmol) was dissolved in glacial acetic acid (20.0 ml), 30% hydrogen peroxide (2.9 ml, 30.0 mmol) was added, and the reaction mixture was refluxed for 24 h. The reaction mixture was concentrated \textit{in vacuo} and the resulting bright red solid, 16 (3.0 g, 27.0 mmol, 90%), was used without purification.
2-2. Preparation of 4-Methoxypyridine N-Oxide (17)

4-Methoxylpyridine(1 0.0ml, 85.9mmol) was dissolved in glacial acetic acid (50.0ml), 30% hydrogen peroxide (8.4ml, 85.9mmol) was added, and the reaction mixture was refluxed for 24h. The reaction mixture was concentrated in vacuo and the resulting red gummy liquid, 17 (9.6g, 76.5mmol, 89%), was used without further purification.

2-3. Preparation of 2-Cyano-4-methylpyridine (18)

4-Methylpyridine N-Oxide, 16 (1.32g, 12.1mmol), was dissolved in distilled dichloromethane (10.7ml) and added to trimethylsilyl cyanide (1.8ml, 13.6mmol) at room temperature. Dimethylcarbamyl chloride (1.2ml, 13.6mmol) in dichloromethane (5.8ml) was added dropwise with stirring to the reaction mixture. The reaction mixture was stirred at room temperature for 24h. A solution of 10% aqueous potassium carbonate (20ml) was added and stirring was continued for 30min. The organic layer was separated and aqueous layer was extracted with dichloromethane. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (solvent; dichloromethane). The desired 2-cyano-4-methylpyridine, 18 (1.4g, 11.6mmol, 96%), was obtained as a white solid.

2-4. Preparation of 2-Cyano-4-methoxylpyridine (19)

4-Methoxylpyridine N-Oxide, 17 (12.8g, 0.1mol), was dissolved in distilled dichloromethane (130ml) and added to trimethylsilyl cyanide (16.0ml, 0.1mmol) at room temperature. Dimethylcarbamyl chloride (11.0ml, 0.1mmol) in dichloromethane (20.0ml) was added dropwise with stirring to the reaction mixture. The reaction mixture was stirred at room temperature for 24h. A solution of 10% aqueous potassium carbonate (100.0ml) was added and stirring was continued for 30min. The organic layer was separated and aqueous layer was extracted with dichloromethane. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (ethyl acetate:«-hexane=1:6). The desired 2-cyano-4-methoxylpyridine, 19 (10.7g, 801.1mmol, 80%), was obtained as a white solid.

2-5. Preparation of Trifluoroacetyl hydrazide (20)
Ethyl trifluoroacetate (9.0ml, 80.0mmol) in methanol (8.0mL) was stirred at 0°C while hydrazine (90.0ml, 0.1mol, LOM solution in THF) was added. After 13h, dichloromethane (100.0ml) was added at room temperature and concentrated in vacuo. After evaporating the solvent, dichloromethane (60.0ml) was added and the mixture was stirred at room temperature to produce an insoluble white solid. The solid was removed and the solution was concentrated in vacuo and white gummy liquid, 20 (6.83g, 53.3mmol, 67%), was obtained.

2-6. Preparation of 3-Trifluoromethyl-5-(4-methyl-2-pyridyl)-1,2,4-triazole (21)

2-Cyano-4-methylpyridine, 18 (1.3g, 9.3mmol), in N,N-dimethyl formamide (60.0ml) was added to 20 (2.2g, 17.2mmol) and stirred at room temperature. After 30min, 28% NaOCH₃ solution in methanol (0.2g) was added to the reaction mixture and refluxed at 153°C for 2 days. The solution was evaporated in vacuo and water (50ml) was added to the residue. This solution was extracted with ethyl acetate (50ml x 2). The organic solution was dried over sodium sulfate and the filtrate was evaporated in vacuo. The crude product was subjected to column chromatography on silica (solvent: ethyl acetate/chloroform=l/5) and white solid, 21 (0.6g, 2.5mmol, 27%), was obtained.

¹H-NMR (CDCl₃) δ 8.70(d, IH, J=5.4Hz), 8.21(s, IH), 7.36(s, IH, J=5.4Hz), 2.51(s, 3H), ¹³C-NMR (CDCl₃) 521.1, 117.2, 120.8, 123.6, 126.9, 149.1, 150.6, 155.1, HRMS(M⁺, 229.0703, Calcd, 229.0623).

2-7. Preparation of 3-Trifluoromethyl-5-(4-methoxy-2-pyridyl)-1,2,4-triazole (22)

2-Cyano-4-methoxypyridine, 19 (2.0g, 15.0mmol), in N,N-dimethyl formamide (50.0ml) was added to 20 (2.5g, 19.5mmol) and stirred at room temperature. After 30min, 28% NaOCH₃ solution in methanol (L4g) was added to reaction mixture and refluxed at 153°C for 3 days. The solution was evaporated in vacuo and water (40ml) was added to the residue. This solution was extracted with ethyl acetate (40ml x 2). The organic solution was dried over sodium sulfate and the filtrate was evaporated in vacuo. The crude product was subjected to column chromatography on silica (solvent: ethyl acetate/chloroform=l/5) and colorless liquid, 22 (0.7g, 3.0mmol, 20%), was obtained.

¹H-NMR (CDCl₃) 58.18(d, IH, J=6.3Hz), 7.32(s, IH), 6.78(s, IH, J=6.3Hz), 4.24(s, 3H), ¹³C-NMR (CDCl₃) 39.0, 113.4, 113.8, 114.7, 117.0, 120.6, 124.1, 143.2,
2-8. Preparation of 3-Trifluoromethyl-5-(2-pyridyl)-1,2,4-triazole (23)

2-Cyanopyridine (0.93 ml, 9.6 mmol), purchased from Aldrich, in ethanol (30.0 ml) was added to 20 (2.5 g, 19.5 mmol) and stirred at room temperature. After 30 min, 28% NaOCH$_3$ solution in methanol (1.4 g) was added to reaction mixture and refluxed. After 2 h, ethanol was removed in vacuo and the remaining yellow gummy liquid was heated at 130 °C overnight. Water was added to the reaction mixture and the mixture was extracted with chloroform. The organic layer was dried over sodium sulfate and the filtrate was evaporated in vacuo. The crude product was subjected to column chromatography on silica (solvent: ethyl acetate/chloroform=1/5) and yellow solid, 23 (1.06 g, 5.0 mmol, 52%), was obtained.

$^1$H-NMR (CDCl$_3$) $\delta$ 8.84 (d, $J=5.1$ Hz, 1H), 8.35 (d, $J=8.1$ Hz, 1H), 8.01-7.95 (m, 1H), 7.57-7.52 (m, 1H)

Example 3. Synthesis of Main Ligand, 2-Phenylpyridines (24, 26 and 28)
3-1. Synthesis of 2-(2',4'-Difluorophenyl)-4-picoline (24)

2,4-Difluorophenyl boronic acid (1.1g, 7.0mmol), Ba(OH)₂·8H₂O (6.2g, 19.5mmol) and Pd(PPh₃)₄ (0.2g, 0.3mmol) were placed in a 100mL one-neck round bottom flask equipped with a condenser. The flask was evacuated and filled with N₂ gas. 1,4-Dioxane (20.0ml), H₂O (7.0ml) and 2-bromo-4-picoline (1.2g, 7.0mmol)
were added. The reaction mixture was refluxed for 3Oh under N₂ gas and cooled to room temperature. The solvent dioxane was removed by evaporation and the contents were poured into a dichloromethane (30ml). The precipitate was removed through filter paper and the organic layer washed with 1M NaOH (30ml x 2) and saturated aqueous NaCl (30ml). It was then dried over sodium sulfate. After evaporation of the solvent, purification of the product by column chromatography (solvent: ethyl acetate/hexane=1/6) provided 2-(2',4'-difluorophenyl)-4-picoline, 24 (1.0g, 4.9mmol, 70%), as the oil.

\[ ^1 \mathrm{H}-\text{NMR (CDCl}_3) \delta 8.56(\text{d}, J=4.8\text{Hz}, \text{IH}), 7.92-8.00(\text{m}, \text{IH}), 7.53-7.59(\text{m}, \text{IH}), 7.08(\text{d}, J=5.3\text{Hz}, \text{IH}), 6.96-7.02(\text{m}, \text{IH}), 6.87-6.95(\text{m}, \text{IH}), 2.41(\text{s}, 3\text{H}) \]

3-2. Synthesis of 2-(2',4'-difluoro-3'-iodophenyl)-4-picoline (25)

2.0M Solution (12.5ml, 25.0mmol) of lithium diisopropyl amide in heptane/THF/ethylbenzene was added dropwise to the THF (43.0ml) solution of 24 (3.5g, 10.8mmol) at -78 °C and stirred for 1h. Then, iodine (6.1g, 24mmol) dissolved in THF (35ml) was added to the solution. The mixture was stirred for 3h at -78 °C and warmed to room temperature. Then, water (300ml) was added and the solution was extracted with diethyl ether twice (100ml x 2). The ether solution was washed with water (100ml), a saturated aqueous solution of NaCl (100ml) and a saturated aqueous solution of NaOH (100ml). The solution was dried over sodium sulfate and the filtrate was evaporated in vacuo. The residue was subjected to column chromatography on silica gel (solvent: ethyl acetate/hexane=1/6). The desired 2-(2',4'-difluoro-3'-iodophenyl)-4-picoline, 25 (5.4g, 16.3mmol, 65%), was obtained as a beige solid.

3-3. Synthesis of 2-(2',4'-Difluoro-3'-(trifluoromethyl)phenyl)-4-picoline (26)

A mixture of copper (I) iodide (1.7g, 9.1mmol) and spray-dried anhydrous potassium fluoride (0.5g, 9.1g) was heated with a heat gun under reduced pressure while being gently shaken until the color changed into yellow. After the addition of 25 (2.0g, 6.0mmol), a vessel was Ar-purged and N-methylpyrrolidinone (10ml) and (trifluoromethyl)trimethylsilane (1.8ml, 12.1mmol) were added to the mixture. Then, the suspension was vigorously stirred for 24h at room temperature. The mixture was poured into 28% aqueous ammonia (66ml) and extracted with dichloromethane. The organic layer was washed with water, brine and dried over sodium sulfate. The filtrate was evaporated in vacuo. The residue was subjected to column chromatography on silica gel (solvent: ethyl acetate/hexane=1/6). The desired 2-(2',4'-Difluoro-3'-(trifluoromethyl)phenyl)-4-picoline, 26 (0.9g, 1.2mmol, 57%), was obtained as a beige solid.
chromatography on silica gel (solvent: ethyl acetate/hexane=l/6). The desired 2-[2',4'-
difluoro-3'-(trifluoromethyl)phenyl]-4-picoline, (26, 0.3g, 1.2mmol, 20%), was
obtained as a white solid.

3-4. Synthesis of 2-Bromo-4-(dimethylamino)pyridine (27)

A solution of 2-(dimethylamino)ethanol (1.6ml, 16mmol) in hexane (10ml)
was cooled at 0°C. n-BuLi (20ml, 32mmol, 1.6M solution in hexane) was added
dropwise under a nitrogen atmosphere. After 30min at 0°C, 4-(dimethylamino)pyridine
(1.0g, 8.0mmol) was added at once as a solid. After 1h of
stirring at 0°C, the reaction medium was cooled at -78°C and a solution of CBr₄ (6.7g,
20.2mmol) in hexane (20ml) was added dropwise (20min). The temperature was then
allowed to rise to 0°C (1.5h). Hydrolysis was performed at this temperature with H₂O
(20ml). The aqueous phase was first extracted with diethyl ether and then with
dichloromethane. After drying (Na₂SO₄), filtration and evaporation of solvents, the
crude product was purified by column chromatography (solvent: ethyl
acetate/hexane=l/2) and brown gummy solid, 27 (0.9g, 4.3mmol, 54%) was obtained.

3-5. Synthesis of 2-(2',4'-Difluorophenyl)-4-(dimethylamino)pyridine (28)

2,4-Difluorophenyl boronic acid (1.1g, 6.9mmol), Ba(OH)₂·8H₂O (6.5g,
20.6mmol) and Pd(PPh₃)₄ (0.4g, 0.3mmol) were placed in a 100mL one-neck round
bottom flask equipped with a condenser. The flask was evacuated and filled with N₂
gas. 1,4-Dioxane/H₂O=l/3 (34.3ml) and 2-bromo-4-(dimethylamino)pyridine (1.2g,
6.9mmol) were added. The reaction mixture was refluxed for 30h under N₂ gas and
cooled to room temperature. The dioxane was removed by evaporation and the
contents were poured into dichloromethane(30ml), the precipitate was removed
through filter paper, and the organic layer washed with saturated aqueous NaCl(30ml),
and dried over sodium sulfate. After evaporation of the solvent, purification of the
product by column chromatography (solvent: ethyl acetate/hexane=l/2) provided 2-(2',4'-
difluorophenyl)-4-(dimethylamino)-pyridine (28,1.2g, 5.0mmol, 72%), as the
yellow oil.

Example 4. Synthesis of Ir(III)-m-chloro-bridged Dimer Complexes
(29-31)

A mixture of iridium(III) chloride trihydrate (83.0mg, 0.2mmol) and 2-(2'4'-
difluorophenyl)-4-picoline, 24 (0.12g, 0.6mmol) in 2-ethoxyethanol/water (4ml; 3/1)
was refluxed under nitrogen for 18h at 120°C. After cooling to room temperature,
the mixture was evaporated _in vacuo_ and water was added to residue. The mixture was extracted with dichloromethane and the organic layer was washed with water and brine, and dried over sodium sulfate. The filtrate was evaporated _in vacuo_ to provide the crude Ir(III)-m-chloro-bridged dimer complex, 29. Other new complexes 30, 31 were also prepared from the corresponding 2-phenylpyridine ligands 26, 28 by the similar procedure.

Example 5. Synthesis of Iridium(III) Complexes (1)~(7).

A mixture of the resulting dimer complex 29 (0.13g, 0.1 lmmol), 2-(4-methylpyridyl)triazole (19, 0.06g, 0.26mmol) as an ancillary ligand and sodium carbonate (160mg) was heated at 135 °C in 2-ethoxyethanol(7ml) for 24h under nitrogen. After cooling to room temperature, the solution was evaporated _in vacuo_ and water was added to the residue. The mixture was extracted with dichloromethane and the dichloromethane solution was dried over sodium sulfate. The filtrate was evaporated _in vacuo_. The crude product was subjected to column chromatography on silica gel (solvent: dichloromethane/hexane=1/10) and finally purified by recrystallization from dichloromethane/hexane to provide complex 2 as a yellow solid. Other new Iridium (III) complexes 1 and 3~7 were also prepared from the corresponding ancillary ligands 5-(2-pyridyl)triazoles 21 and 23 by the similar procedure with the corresponding iridium chloro-bridged dimer 30-3 1.

5-1. Synthesis of Iridium (III) Complex (1) (38%)

$^1$H-NMR (CDCl$_3$) δ 8.29(d, J=5.4Hz, IH), 8.06(s, IH), 8.04(s, IH), 7.57-7.73(m, IH) 7.56(d, J=5.4Hz, IH), 6.81(d, J=4.8Hz, IH), 6.72(d, J=4.8Hz, IH), 6.55-6.40(m, 2Hz), 5.79(dd, J=8.4Hz, 2.4Hz, IH), 5.69(dd, J=8.4Hz, 2.4Hz, IH), 2.5 l(s, 6H)

5-2. Synthesis of Iridium (III) Complex (2) (45%)

$^1$H-NMR (CDCl$_3$) δ 8.12(s, IH), 8.07(s, IH), 8.025(s, IH) 7.55(d, J=5.4Hz, IH), 7.53(d, J=5.4Hz, IH), 7.00(d, J=5.4Hz, IH), 6.79(d, J=5.4Hz, IH), 6.70(d, J=5.4Hz, IH), 6.52-6.36(m, 2H), 5.78(dd, J=8.4Hz, 2.4Hz, IH), 5.70(dd, J=8.4Hz, 2.4Hz, IH), 2.48(m, 9H), $^{13}$C-NMR (CDCl$_3$) δ21.2, 21.4, 21.5, 53.4, 97.9, 98.2, 114.0, 122.7, 123.2, 123.6, 124.0, 124.1, 126.2, 147.4, 148.8, 149.3, 149.6, 149.9, 150.3, 151.1, 152.2, 163.4, 163.8, 164.7 HRMS (M+, 828.15, Calcd, 828.14)

5-3. Synthesis of Iridium (III) Complex (3) (48%)


$^1$H-NMR (CDCl$_3$) $\delta$ 8.04(s, 1H), 8.00(s, 1H), 7.72(d, $J=2.4$Hz, 1H), 7.52(d, $J=6$Hz, 1H), 7.45(d, $J=6$Hz, 1H), 7.23(d, $J=6$Hz, 1H), 6.77?d, $J=6$Hz, 1H), 6.70( d, $J=8GHZ$, 1H ), 6.69(d, $J=6$Hz, 1H), 6.49-6.33(m, 2H), 5.75(dd, $J=8.4$Hz, 2.7Hz, 1H), 5.68(dd, $J=8.4$Hz, 2.7Hz, 1H), 3.92(s, 3H), 2.46(s, 6H), HRMS (M+, 844.13, Calcd, 844.14)

5-4. Synthesis of Iridium (III) Complex (4) (30%)
$^1$H-NMR (CDCl$_3$) $\delta$ 8.88(d, $J=5.4$Hz, 1H), 8.63(s, 1H), 8.58(s, 1H), 8.01-7.96(m, 1H), 7.91-7.82(m, 1H), 7.60(d, $J=5.4$Hz, 1H), 6.66(d, $J=4.8$Hz, 1H), 6.62(d, $J=4.8$Hz, 1H), 5.75-5.62(m, 2Hz), 2.47(s, 6H)

5-5. Synthesis of Iridium (III) Complex (5) (51%)
$^1$H-NMR (CDCl$_3$) $\delta$ 8.14(s, 2H), 8.10(s, 1H), 7.53(d, $J=5.7$Hz, 2H), 7.28(d, $J=5.7$Hz, 1H), 7.08(d, $J=5.7$Hz, 1H), 6.90(d, $J=5.7$Hz, 1H), 6.82(d, $J=5.7$Hz, 1H), 5.89(d, $J=10.5$Hz, 1H), 5.79(d, $J=10.5$Hz, 1H), 2.52(s, 6H), 2.49(s, 3H), HRMS(M+, 964.12, Calcd, 964.12)

5-6. Synthesis of Iridium (III) Complex (7) (49%)
$^1$H-NMR (CDCl$_3$) $\delta$ 8.08(s, 1H), 7.58(d, $J=5.7$Hz, 1H), 7.44(s, 1H), 7.38(s, 1H), 7.21(d, $J=6.9$Hz, 1H), 6.96(d, $J=5.7$Hz, 1H), 6.92(d, $J=6.9$Hz, 1H), 6.4-6.32(m, 2), 6.16(d, $J=6.9$Hz, 2.7Hz, 1H), 6.08(d, $J=6.9$Hz, 2.7Hz, 1H), 5.91(d, $J=8.5$Hz, 2.7Hz, 1H), 5.86(d, $J=8.5$Hz, 2.7Hz, 1H), 3.06(d, 12H), 2.43(s, 3H), HRMS(M+, 886.1960, Calcd, 886.1954)

Example 6. Measurement of Absorbance and Photoluminescence
The absorption and photoluminescence (PL) spectra were measured using the JASCO V-570 UV-vis spectrometer and the Hitach F-4550 fluorescence spectrometer in dichloromethane, respectively, at room temperature. Phosphorescence quantum yields ($\Phi_p$) were estimated by using a chloroform solution of tris-2-tolylpyridyl iridium complex Ir(tpy)$_3$ as a standard with a known value of $\Phi_p = 0.45$. Mass spectra were recorded by using electron impact ionization (EI) or fast atomic bombardment (FAB) techniques.

As shown in Figs. 2-8 and Table 1, the Ir complexes of the present invention, i.e., compounds 2, 3, 5, and 7, exhibit higher quantum efficiency than compounds 1 and 4 having no substituent on the pyridyl ring of 5-pyridyltriazole ancillary ligand, as well as deeper blue emissions (more hypsochromic shift of the phosphorescent
emission).

TABLE 1

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<tr>
<th>Compound</th>
<th>MLCT (nm)&lt;sup&gt;a)&lt;/sup&gt;</th>
<th>MLCT (nm)&lt;sup&gt;a)&lt;/sup&gt;</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt; (nm)&lt;sup&gt;a)&lt;/sup&gt;</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt; (nm)&lt;sup&gt;b)&lt;/sup&gt;</th>
<th>Stokes shift (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>E&lt;sub&gt;g&lt;/sub&gt; (eV)&lt;sup&gt;c)&lt;/sup&gt;</th>
<th>E&lt;sub&gt;g&lt;/sub&gt; (eV)&lt;sup&gt;f)&lt;/sup&gt;</th>
<th>Φ&lt;sub&gt;p&lt;/sub&gt;&lt;sup&gt;c)&lt;/sup&gt;</th>
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<tr>
<td>1 (Ir-1)</td>
<td>366</td>
<td>426</td>
<td>464, 489</td>
<td>462, 489</td>
<td>1923</td>
<td>2.97</td>
<td>2.72</td>
<td>0.22</td>
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<tr>
<td>2 (Ir-2)</td>
<td>370</td>
<td>424</td>
<td>456, 483</td>
<td>456, 483</td>
<td>1655</td>
<td>3.00</td>
<td>2.73</td>
<td>0.39</td>
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<tr>
<td>3 (Ir-3)</td>
<td>368</td>
<td>424</td>
<td>456, 484</td>
<td>456, 483</td>
<td>1655</td>
<td>3.00</td>
<td>2.73</td>
<td>0.25</td>
</tr>
<tr>
<td>4 (Ir-4)</td>
<td>352</td>
<td>422</td>
<td>456, 482</td>
<td>454, 481</td>
<td>1768</td>
<td>3.02</td>
<td>2.74</td>
<td>0.20</td>
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<tr>
<td>5 (Ir-5)</td>
<td>364</td>
<td>416</td>
<td>448, 475</td>
<td>448, 475</td>
<td>1717</td>
<td>3.07</td>
<td>2.78</td>
<td>0.42</td>
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<tr>
<td>6 (Ir-6)</td>
<td>372</td>
<td>n.m.&lt;sup&gt;d)&lt;/sup&gt;</td>
<td>459, 489, 521</td>
<td>458, 488</td>
<td>n.m.</td>
<td>2.91</td>
<td>(d)</td>
<td>n.m.</td>
</tr>
<tr>
<td>7 (Ir-7)</td>
<td>364</td>
<td>426</td>
<td>469</td>
<td>449,464</td>
<td>2153</td>
<td>3.07</td>
<td>2.72</td>
<td>0.06</td>
</tr>
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</table>

(a) 2.7x10<sup>-4</sup>-1.3x10<sup>-3</sup> M in dichloromethane; (b) A film state prepared by spin coating from dichloromethane solution with PMMA (5% w.t); (c) Phosphorescence quantum yields measured in dichloromethane solution using Ir(tpy)<sub>3</sub> (Φ<sub>p</sub>=0.45) as a reference; and (d) not measured, (e) Singlet optical band gap was calculated from singlet absorption edge (f) Triplet optical band gap was calculated from triplet absorption edge.

Example 7 - Determination of HOMO and LUMO Levels

Electrochemical measurements were performed by using CHI600C (CH Instruments Inc., USA) with an electrochemical cell consisting of a platinum electrode (2 mm diameter), a Pt wire counter electrode and an Ag/AgCl reference electrode at RT. 0.1 M Tetrabutylammonium perchlorate (Bu<sub>4</sub>NClO<sub>4</sub>, TBAP) in dichloromethane (Aldrich, HPLC grade) was used as a supporting electrolyte (scan rate 50mVs<sup>-1</sup>). Figures 9a-9f show cyclic voltammograms of the Ir complexes of the present invention. The HOMO levels of Ir complexes (1) to (5) and (7) were determined as -5.63 eV, -5.65 eV, -5.66 eV, -5.65 eV, -5.84 eV and -5.48 eV, respectively, while the LUMO levels were -2.66 eV, -2.65 eV, -2.66 eV, -2.63 eV, -2.77 eV and -2.41 eV, respectively. An incorporation of methyl group at 4-position of pyridyl ring in 5-(2-pyridyl)triazole ancillary ligand, particularly for complex (5), resulted in a slight increase in band gap between the HOMO and LUMO levels.
INDUSTRIAL APPLICABILITY

As described above, the iridium complexes of the present invention show the blue emission at 448 nm at the shortest and a great applicability for efficient blue OLED phosphorescent compound, while exhibiting very high phosphorescent quantum efficiencies. Such improved performance makes them promising compounds as emissive materials for blue emission.

It will be apparent to those skilled in the art that various modifications and variations can be made to the present invention without departing from the spirit and scope of the invention. Thus, it is intended that the present disclosure covers the modifications and variations of this invention, provided they come within the scope of the appended claims and their equivalents.
1. An Ir complex represented by formula (I):

wherein:

E₁ represents an 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 a ring comprising E₂, said ring coordinating to the metal M via a sp² hybridized carbon;

E₂ represents a N-containing aromatic 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;

R₁ is an electron-donating group which is same or different at each occurrence and is independently selected from -F, -Cl, -Br, a straight or branched C₃₋₂₀ alkyl, a C₃₋₂₀ cyclic alkyl, a straight or branched C₁₋₂₀ alkoxy, a C₁₋₂₀ dialkylamino, a C₄₋₁₄ aryl, a C₄₋₁₄ heteroaryl which may be substituted by one or more non-aromatic radicals; and a plurality of substituents R₁ either on the same ring or on two different rings forming a further mono- or polycyclic ring system which is optionally aromatic;

R₂ is an electron-withdrawing group which is selected from -F, -CN, NO₂, (per)fluoroalkyl, (per)fluoroaryl, (per)fluoralkylaryl, alkylcarboyl, (per)fluoralkylcarbonyl, (per)fluoroalkylarylcarbonyl, and (per)fluoroalkylheteroarylcarbonyl each of which may be substituted by at least one substituent; and

n is same or different at each occurrence and is an integer from 1 to 4.
2. The Ir complex according to Claim 1, wherein the ligand is selected from phenylpyridine ligands substituted by at least one fluorine atom in the phenyl ring.

3. The Ir complex according to Claim 2, wherein the phenylpyridine ligand is selected from the group consisting of

\[
\begin{align*}
&\text{H}_3\text{C} - \text{Ph} - \text{N} - \text{Ph} - \text{F} - \text{F} ,
&\text{H}_3\text{C} - \text{Ph} - \text{N} - \text{Ph} - \text{F} - \text{F} - \text{F}_3\text{C} ,
&\text{H}_3\text{C} - \text{Ph} - \text{N} - \text{Ph} - \text{F} - \text{NC} - \text{F} ,
&\text{H}_3\text{C} - \text{Ph} - \text{N} - \text{Ph} - \text{F} - \text{O}_2\text{N} - \text{F} \\
&\text{H}_3\text{C} - \text{Ph} - \text{N} - \text{Ph} - \text{O}_3\text{C} - \text{CF}_3 - \text{F} ,
&\text{H}_3\text{C} - \text{Ph} - \text{N} - \text{Ph} - \text{F} - \text{F}_3\text{C} ,
&\text{H}_3\text{C} - \text{Ph} - \text{N} - \text{Ph} - \text{F} .
\end{align*}
\]
4. The Ir complex according to any one of Claims 1-3, wherein \( R_i \) is independently selected from alkyl, dialkylamino, and alkoxy groups.

5. The Ir complex according to any one of Claims 1-4, wherein \( R_i \) is methyl and \( n \) is 1.

6. The Ir complex according to any one of Claim 1-4, wherein \( R_1 \) is dialkylamino and \( n \) is 1.

7. The Ir complex according to any one of Claims 1-4, wherein \( R_1 \) is methoxy and \( n \) is 1.

8. The Ir complex according to any one of Claims 1-7, wherein \( R_2 \) is trifluoromethyl.

9. The Ir complex according to any one of Claims 1-8, wherein said Ir complex has a formula selected from the group consisting of:
10. A light emitting material comprising the Ir complex according to any one of Claims 1 to 9.

11. A use of the light emitting material according to Claim 10 in an emissive layer of an organic light emitting device.

12. A use of the light emitting material according to Claim 10 as a dopant in a host layer under conditions effective to function as an emissive layer in an organic light emitting device.

13. An organic light emitting device comprising an emissive layer, wherein said emissive layer comprises the light emitting material according to Claim 10 and optionally a host material.

Figure 2

\[ \Phi = 0.22 \]
\[ \Delta \nu = 1923 \]
Figure 3

\( \Phi = 0.39 \)
\( \Delta \nu = 1655 \)
Figure 4

- Abs.
- Wavelength (nm)
- PL Intensity

- UV
- PL

$\Phi = 0.25$

$\Delta\nu = 1655$

Ir-3

- Wavelength (nm)

Solution

Film
Figure 5

$\Phi = 0.20$

$\Delta \nu = 1768$

Abs.

PL Intensity

Wavelength (nm)

Intensity

Wavelength (nm)

Ir-4

Solution

Film

456

482

352

422
Figure 6

Distribution of a certain compound across different wavelengths. The graph shows the absorption (Abs.) and emission (PL Intensity) levels for wavelengths ranging from 300 to 600 nm.

**Ir-5**

- **Absorption**
  - Wavelengths: 364, 448, 475 nm
- **Emission**
  - Wavelengths: 448, 475 nm

**Parameters**

- **Φ** = 0.42
- **Δν** = 1717
Figure 8

Ir-7

\[ \Phi = 0.06 \]
\[ \Delta \nu = 2153 \]

Abs. vs Wavelength (nm)

Ir-7

Solution

Film

Intensity vs Wavelength (nm)
Figure 9

(a) Ir-1

\[ E_{\text{HOMO}} = -5.63 \text{ eV} \]
\[ E_{\text{LUMO}} = -2.66 \text{ eV} \]

(b) Ir-2

\[ E_{\text{HOMO}} = -5.65 \text{ eV} \]
\[ E_{\text{LUMO}} = -2.65 \text{ eV} \]

(c) Ir-3

\[ E_{\text{HOMO}} = -5.66 \text{ eV} \]
\[ E_{\text{LUMO}} = -2.66 \text{ eV} \]

(d) Ir-4

\[ E_{\text{HOMO}} = -5.65 \text{ eV} \]
\[ E_{\text{LUMO}} = -2.63 \text{ eV} \]

(e) Ir-5

\[ E_{\text{HOMO}} = -5.84 \text{ eV} \]
\[ E_{\text{LUMO}} = -2.77 \text{ eV} \]

(f) Ir-7

\[ E_{\text{HOMO}} = -5.48 \text{ eV} \]
\[ E_{\text{LUMO}} = -2.41 \text{ eV} \]
A. CLASSIFICATION OF SUBJECT MATTER

C07F 15/00(2006.01)1, C09K 11/06(2006.01)1, H05B 33/00(2006.01)1

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC8 C07F, C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Utility models and applications for Utility models since 1975
Japanese Utility models and applications for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) "Ir" "phenyl pyridine" "hquand" "pyrazole" "OLED"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No</th>
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<td>US 2006/0286404 A1 (AU OTRONICS CORP ) 21 December 2006 see the abstract and claims 7-8</td>
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<td>A</td>
<td>EP 1772 507 A1 (SOLVAY) 11 April 2007 see the abstract and claim 1</td>
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<td>KR 10-2008-0057377 A (PUSAN NATIONAL UNIVERSITY INDUSTRY-UNIVERSITY COOPERATION FOUNDATION) 25 June 2008 see the abstract and claim 2</td>
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<td>US 2008/0194821 A1 (Techmsche Umsivschaft Braunschweig) 14 August 2008 see the abstract</td>
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Further documents are listed in the continuation of Box C

See patent family annex

* Special categories of cited documents
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "E" earlier application or patent but published on or after the international filing date
  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
  "O" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search

22 OCTOBER 2009 (22 10 2009)

Date of mailing of the international search report

22 OCTOBER 2009 (22.10.2009)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
Government Complex-Daejeon, 139 Seonsa-ro, Seo-gu, Daejeon 302-701, Republic of Korea

Facsimile No 82-42-472-7140

Authorized officer

LEE, SI GEUN

Telephone No 82-42-481-8491

Form PCT/ISA/210 (second sheet) (July 2008)
INTERNATIONAL SEARCH REPORT

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

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

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

2 [ ] Claims Nos 11-14
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically

The subject-matter of claims 11-14 is not considered to be clear, since said claims 11-14 are referring to one of the claims 10 or 13, respectively, which are not drafted in accordance with Rule 6.4(a)

3 [ ] Claims Nos 5 - 10
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

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

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

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

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

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

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

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee

[ ] The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation

[ ] No protest accompanied the payment of additional search fees

Form PCT/ISA/210 (continuation of first sheet (2)) (July 2008)
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