(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(54) **Title:** LIGAND MEDIATED LUMINESCENCE ENHANCEMENT IN CYCLOMETALATED RHODIUM(III) COMPLEXES AND THEIR APPLICATIONS IN HIGHLY EFFICIENT ORGANIC LIGHT-EMITTING DEVICES

(57) **Abstract:** A series of highly luminescent cyclometalated rhodium (III) complexes, with photoluminescence quantum yields up to 0.65 in thin films, have been designed and prepared. The strong luminescence property is realized by the judicious choice of a strong σ-donor cyclometalating ligand with lower-lying intraligand state and the ability to raise the d-d excited state. This is the first report to demonstrate the capability of rhodium(III) complexes as high efficient light-emitting materials for organic light-emitting devices. Compelling external quantum efficiencies of up to 12.2% and operational half-lifetime of over 3, 000 hours have been achieved.

Ligand Mediated Luminescence Enhancement in Cyclometalated Rhodium(III) Complexes and Their Applications in Highly Efficient Organic Light-Emitting Devices

TECHNICAL FIELD

The invention relates to fluorescent sensing field. More particularly, a non-fullerene acceptor, which was formed by introduction of chlorine atoms onto the terminal groups of acceptor-donor-acceptor type small molecule electron acceptors, and a polymer derived therefrom.

BACKGROUND ART

Excited state properties of octahedral d^6 transition metal complexes, including ruthenium(II),[1,2] rhenium(I), [1,3] osmium(II),[1,2,4] iridium(III) [1,5-7] and rhodium(III),[1,8-10], have aroused tremendous interests due to their attractive photophysical and photochemical behaviors. From the last two decades, the establishment of the predominant role of luminescent cyclometalated iridium(III) system[5-7] as photo-functional materials has stemmed from their overwhelming properties for the potential biological and energy related applications.[6,7] Since the pioneering work of Thompson, Forrest and coworkers[7a] in employing cyclometalated iridium(III) complexes first reported by Watts[5a,b] as phosphorescent emitters in organic light-emitting devices (OLEDs), promising applications[7,11] have been realized as demonstrated by their rapid adoption in smartphones and displays everywhere.

Being the most important components in OLEDs, there has been a rapid surge of interest in the studies of phosphorescent emitters with heavy metal centers because of their capability to achieve 100% internal quantum efficiency from harvesting the accessible triplet excited state associated with strong spin-orbit coupling (SOC).[11] While most of the related works have been placed with particular emphasis on the use of iridium(III)[7,11] and platinum(II)[11,12] complexes, the use of metal complexes of other transition metals[11,13-15] as emitters has remained a relatively niche topic in order to provide a diversity of OLED materials. Recently, Che[16a,b] and Li[16c] have independently developed different classes of palladium(II) complexes, coordinated to tetradentate ligands with C-deprotonated donor atoms, which have also been demonstrated to be strongly luminescent for the application in OLEDs. This strategy by using not only the strong field ligand but also the rigid

scaffold with four coordination sites are anticipated to disfavor the non-radiative deactivation pathway in order to boost up the luminescence properties. Another interesting class is cyclometalated gold(III) complexes, which is isoelectronic and isostructural to the platinum(II) system. Through the choice of strong σ-donating ligand, the gold(III) complexes exhibit strong luminescence properties, as proven by the demonstration of highly efficient OLEDs based on such gold(III) complexes.[11,17] Yam and co-workers have recently pioneered a unique concept of thermally stimulated delayed phosphorescence (TSDP), from which triplet excitons are up-converted from a lower-lying triplet state to a higher-lying triplet state through spin-allowed reverse internal conversion (RIC). This up-conversion process was found to significantly enhance the luminescence quantum yields (Φ_{lum}) by over 20-folds.[17e] Similarly, high Φ_{lum} could also be obtained through the process of thermally activated delayed fluorescence (TADF) or metal assisted delayed fluorescence (MADF) arising from the reversed intersystem crossing (RISC).[18] In such case, very small energy gap between the lowest singlet state (S_1) and the lowest triplet excited state (T_1) as well as the spatially well-separated frontier orbitals, i.e. highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), are required There has recently been a fast-growing interest in the use of TADF/MADF light material for the fabrication of high-efficient OLEDs.[15,16c,18]

Rhodium(III) and iridium(III) are considered as very close congeners in the family of platinum group metals (PGMs) sharing similar synthetic methodology, structural characteristics, and some physical and chemical properties.[1,5-10] On the contrary, the luminescence studies of polypyridyl and cyclometalated rhodium(III) system have been much less explored,[8c,9a-c,10] based on the fact that most of them are only luminescent at low temperature. The related photo-functional application of luminescent rhodium(III) system is also very rare.[10c] This is mainly suffered from the lack of luminescence at room temperature owing to the presence of thermally accessible non-luminescent d-d ligand field (LF) excited state. The presence of LF state at comparable energy to those of the luminescence excited states of ligand-centered (LC) and/or metal-to-ligand charge transfer (MLCT) characters, as revealed by temperature-dependent luminescence lifetime measurements,[9d] remains challenging to be overcome. Through the incorporation of a cyclometalating 1,3-bis(1-isoquinolyl)benzene pincer ligand having the advantages of strong ligand field as well as rigid structural motif, Williams and co-workers have recently synthesized luminescent rhodium(III) complexes with the highest Φ_{lum} of up to 10% in solution state at room temperature.[10e]

Although tremendous efforts have been put in to tackle the shortcomings of the luminescence performance of rhodium(III) system, the reported Φ_{lum} still could not satisfactorily meet the requirement for OLED application. To the best of our knowledge, rhodium(III) system is up to now the only remaining family member of PGMs for not being utilized as light-emitting material in OLEDs.

SUMMARY OF THE INVENTION

The inventors develop a series of strongly luminescent cyclometalated rhodium(III) complexes, which satisfactorily meet the requirement for OLED application.

The invention provides a highly luminescent cyclometalated rhodium(III) complex having the formula (a):

,
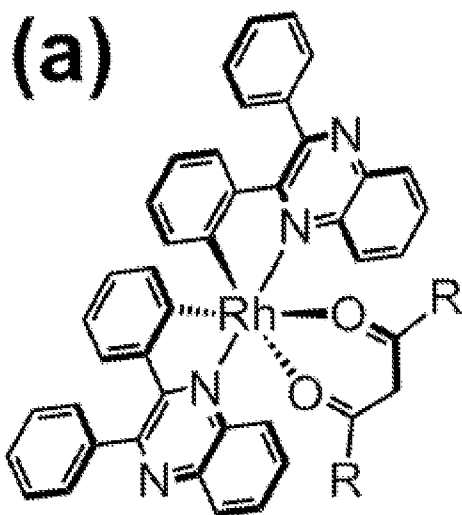
wherein R is an unsubstituted or substituted C_{1-6} alkyl.

In a preferred embodiment, R is a halogen substituted C_{1-6} alkyl.

In a more preferred embodiment, R is a fluorine substituted C_{1-6} alkyl.

In a most preferred embodiment, R is selected from CH_3, CF_3 and C_6F_5.

The invention further provides use of the highly luminescent cyclometalated rhodium(III) complex of the invention as a light-emitting material in OLEDs.

DESCRIPTION OF FIGURES

Figure 1 shows (a) molecular structures of 1–3. (b) X-Ray crystal structure of 1. The solvent molecules and hydrogen atoms are omitted, and only the Δ form is shown for clarity.

Figure 2 shows (a) UV-Vis absorption and emission spectra of complexes 1–3 in dichloromethane solution at 298 K. (b) Normalized PL spectra and PLQY of complexes 1–3 at different excitation wavelengths in solid-state thin film (2 wt% in MCP). Insert shows the photo of thin-film PL of 3 under UV irradiation.

Figure 3 shows plots of spin density (isovalue = 0.002) of the T_1 states of 1–3.

Figure 4 shows Characteristics of vacuum-deposited OLEDs based on 3. (a) EL spectra with different dopant concentrations. (b) EQEs with different hole-transporting layers. (c) Operational lifetime of the vacuum-deposited OLED made with 5 v/v% 3.

SPECIFIC EMBODIMENTS

The strongly luminescent cyclometalated rhodium(III) complexes of the invention was demonstrated to be a breakthrough as the first example of a highly efficient rhodium(III) emitter for OLED application. Through the judicious choice of a strong σ-donor cyclometalating ligand with lower-lying intraligand (IL) state, the enhanced luminescence properties of rhodium(III) system from the integration of two strategies, i.e. raising d-d excited state and introduction of lower-lying emissive IL excited state, have been anticipated. The neutral formal charge, high thermal stability and superior Φlum of over 60 % in solid-state thin films render these complexes possible for device fabrication by vapor deposition or solution processing technique. Notably, compelling external quantum efficiencies (EQEs) up to 12.2% and fairly respectable operational half-lifetime of over 3,000 hours at 100 cd m–2 in the optimized OLEDs have been achieved from this rhodium(III) system.

For the introduction of a lower-lying IL state and the maintenance of neutral formal charge in the target complexes **1–3**, the cyclometalating ligand of 2,3-diphenylquinoxaline (dpqx) and anionic acetylacetonate (acac) were chosen, respectively. Experimental details of their synthesis and characterizations (^{1}H, ^{13}C{^{1}H} NMR, HR-MS and elemental analysis) were provided in the

Supporting Information. All complexes **1–3** are thermally stable with high decomposition temperatures as revealed by the TGA experiment (Figure S1). The X-ray crystal structure exhibits an octahedral geometry about the rhodium(III) metal center (Figure 1b and Figure S2) and all the bond lengths and bond angles (See Supporting Information) are within normal ranges.[10c,e]

The photophysical data of **1–3** have been determined and the data are summarized in Table 1. Their UV-vis absorption spectra in fluid solution at 298 K (Figure 2a) show intense high-energy absorption bands at 335–410 nm and less intense low-energy absorption bands at 420–530 nm. The high-energy absorption bands, which are commonly observed in the related iridium(III) analouges,[7d] are assignable to the spin-allowed singlet intraligand (^{1}IL) π-π* transitions of the dpqx ligand. The low-energy absorption bands are attributed to the MLCT dπ(Rh)$\rightarrow\pi$*(dpqx) transition, mixed with some IL charge transfer transition from the phenyl moiety to the quinoxaline unit on the dpqx ligand. Unlike most of the rhodium(III) complexes which are essentially non-luminescent, it is noteworthy that the present cyclometalated rhodium(III) complexes show intense orange-red photoluminescence (PL) with peak maxima at 598–612 nm in dichloromethane solutions at 298 K (Figure 2a). This luminescence is suggested to originated from a triplet parentage, taking into consideration the large Stokes shift and the relatively long luminescence lifetimes (0.79–1.64 μs). In light of the excitation peaks that are resemble the corresponding low-energy absorption bands, the luminescence origin is reasonably assigned as the triplet excited state of MLCT dπ(Rh)$\rightarrow\pi$*(dpqx) origin, with some mixing of intraligand charge transfer (ILCT) character. Nanosecond transient absorption (TA) spectroscopy in dichloromethane solution at 298 K was investigated in order to study the nature of the excited states. From the TA difference spectra of **1–3**, two positive absorption bands at 375 nm and 415 nm, assignable to the radical anion absorptions of the cyclometalating ligand, are observed (Figure S3). The TA spectra also showed an additional broad absorption band ranging from 550–775 nm, with the similar lifetimes (0.9–1.7 μs) as their respective PL. These absorption bands are tentatively assigned as absorption from the triplet excited state of MLCT dπ(Rh)$\rightarrow\pi$*(dpqx) origin, with some mixing of ILCT character.

Table 1. Photophysical and electrochemical data of **1–3**.

Complex	Absorption		Emission		Oxidation[c]	Reduction[c]	E_{HOMO}[f] [eV]	E_{LUMO}[f] [eV]
	In CH$_2$Cl$_2$ λ_{abs} [nm] (ε [dm^3 mol^{-1} cm^{-1}])		In CH$_2$Cl$_2$ λ_{em} [nm] (Φ_{sol} [%][a]; τ[μs]; k_r [10^5 s^{-1}])	2 wt% doped in MCP thin film λ_{em} [nm] (Φ_{film} [%][b]; τ[μs]; k_r [10^5 s^{-1}])	E_{pa}[d] [V] vs. SCE	$E_{1/2}$[e] [V] vs. SCE		

1	240 (45535), 285 (27280), 326 (15130), 375 (13865), 455 (5005)	612 (0.11; 0.79; 0.014)	603 (49.10; 23; 0.21)	+1.32, +1.69	−1.36, −1.62	−6.12	−3.44
2	240 (64940), 259 (51030), 283 (41085), 383 (22540), 441 (7615)	598 (0.98; 1.64; 0.060)	597 (44.80; 32; 0.14)	+1.63, +2.38	−1.28, −1.50	−6.43	−3.52
3	243 (63715), 262 (52860), 284 (41315), 370 (24355), 455 (5725)	603 (0.31; 0.81; 0.038)	602 (65.40; 25; 0.26)	+1.38, +1.67	−1.38, −1.67	−6.14	−3.42

[a] Luminescence quantum yield Φ_{sol}, measured at room temperature using [Ru(bpy)$_3$]Cl$_2$ in degassed aqueous solution as the reference (λ_{ex} = 436 nm, Φ_{lum}= 0.042). [b] Absolute emission quantum yields Φ_{film} in solid-state thin film. [c] In dichloromethane solution with $^nBu_4NPF_6$ (0.1 M) as the supporting electrolyte at room temperature; scan rate 100 mV s^{-1}. [d] E_{pa} refers to the anodic peak potential for the irreversible oxidation waves. [e] $E_{1/2}$=(E_{pa}+E_{pc})/2; E_{pa} and E_{pc} are anodic peak and cathodic peak potentials, respectively. [f] E_{HOMO} and E_{LUMO} levels were calculated from electrochemical potentials, i.e., E_{HOMO} = −e(4.8 V+E^{ox}_{pa}); E_{LUMO} = −e(4.8 V+$E^{red}_{1/2}$).

Figure 2b depicts the PL spectra of 1–3 in doped N,N-dicarbazolyl-3,5-benzene (MCP) thin films, in which intense orange luminescence of 1–3 at 597–603 nm has been observed (Figure 2a). In contrast to common square-planar metal complexes which will suffer from triplet-triplet annihilation and π-π interaction between the molecules at high doping concentration, no observable luminescence quenching as well as luminescence peak maxima shift are found in 1–3, upon increasing the doping concentration from 2 to 10 wt% (Figures S4–S6). It is noteworthy that remarkably high Φlum of 0.44–0.65 has been obtained in the doped thin films (Figure 2b). Nevertheless, to the best of our knowledge, these are the highest Φlum values among all reported rhodium(III) complexes, demonstrating the successful luminescence enhancement by employing a strong σ-donor cyclometalating ligand with lower-lying IL state in metal complexes with octahedral geometry. Variable-temperature PL measurement of 3 was also carried out in thin film from 298 K to 78 K. Upon cooling, the emission peaks remain unchanged except that the vibronic-structured features are becoming more apparent (Figure S7a). In addition, it is found that the emission intensity has been increased by more than two-folds with elongation of lifetimes (Figure S7b). One may argue that the emission in this system may originate from TADF or MADF. The large energy difference between the singlet and triplet states $\Delta E(S1–T1)$, from the computational studies (vide infra), indicates that the occurrence of such delayed fluorescence is unlikely.

The electrochemical properties of 1–3 were investigated by cyclic voltammetry and the potentials, together with the estimated HOMO and LUMO energy levels, are tabulated in Table 1. Upon cathodic scan, two quasi-reversible reduction couples are featured at −1.28 to −1.38 V and at −1.50 to −1.67 V (vs. SCE) (Figure S8a), attributed to the successive dqpx ligand-centered reductions. Anodic shifts of the first reduction by about 0.08 V are observed in 2, relative to those in 1 and 3, resulting from the indirect influence upon coordination of the more electron-deficient

hexafluoroacetylacetone (hfac) ligand with -CF3 groups. For the anodic scan, the first irreversible anodic peak at +1.32 to +1.63 V (Figure S8b) is attributed to a mixed metal-/ligand-centered oxidation of the rhodium(III) metal center and ligated phenyl ring on dqpx ligand. Similarly, the more positive potential for this oxidation in 2 is due to the lower electron-richness of the rhodium(III) metal center, upon the attachment of the hfac ligand.

In order to gain more insight into the electronic structures as well as the nature of the absorption and emission origins of these rhodium(III) complexes, density functional theory (DFT) and time-dependent DFT (TDDFT) calculations have been performed on 1–3. Summarized in Table S1 are the first fifteen singlet–singlet transitions of 1–3 computed by the TDDFT/CPCM (CH_2Cl_2) method, and some of the molecular orbitals involved in the transitions are shown in Figures S9–S11. The S0→S1 transitions of 1–3 computed at 467, 455 and 466 nm, respectively, correspond to the HOMO→LUMO excitation. The HOMO is the π orbital localized on the phenyl ring, which is ligated to the rhodium(III) metal center, of the dpqx ligand, with mixing of the dπ(Rh) orbital. The LUMO is mainly the π* orbital on the quinoxaline unit of the dpqx ligand. Therefore, the S0→S1 transition can be assigned as MLCT [dπ(Rh)→π*(dpqx)] transition with mixing of an ILCT [π→π*] transition from the phenyl moiety to the quinoxaline unit of the dpqx ligand, which is in agreement with the experimental energy trend of the low-energy absorption bands and their spectral assignments.

To investigate the nature of the emissive states, geometry optimization on the lowest triplet excited states (T_1) of **1–3** has been performed with the unrestricted method (UPBE0-D3/CPCM). As shown in Figure 3, the spin density is localized on the metal center, the quinoxaline unit and the ligated phenyl ring of the dpqx ligand, supporting the assignment of emissive states of ^{3}MLCT [dπ(Rh)→π*(dpqx)]/^{3}ILCT [π→π*] character. The computed emission energies of **1–3** (Table S2) are generally over-estimated, yet the trend is well in agreement with the corresponding experimental results, i.e. **1** ≈ **3** > **2**. The energy differences between the geometry optimized S_1 and T_1 states of **1–3**, ΔE(S_1–T_1), given in Table S3 range from 0.20 to 0.38 eV, indicating a relatively low possibility for TADF to occur.

Solution-processed OLEDs based on **1–3** were prepared for the investigation of the electroluminescence (EL) properties of these rhodium(III) complexes. As shown in Figure S12, all devices display the vibronic-structured EL spectra and are almost identical to their PL spectra in solid-state thin films in the absence of undesired emission from adjacent carrier-transporting or

host materials. Similar to the corresponding PL studies, only small changes of ±0.01 in the CIE x and y values for all the devices are observed with increasing dopant concentration from 2 to 10 wt%. Remarkably, satisfactory performance with high maximum current efficiency of 9.4 cd A^{-1} and EQE of 6.4 % is achieved for the optimized device made with 8 wt% **2** (Figure S13). Table S13 summarizes the key parameters for solution-processed devices based on **1–3**.

Using **3** with the highest Φ_{lum} in solid-state thin film and the highest decomposition temperature, vacuum-deposited OLEDs were also fabricated, in which **3** was doped into MCP at different concentrations (i.e. x = 2, 5, 8, 11, and 14 v/v%). Almost identical EL spectra were featured (Figure 4a) as in the corresponding solution-processed OLEDs. High maximum current efficiency of 9.9 cd A^{-1} and EQE of 7.0 % were achieved for the 5 v/v% doped device (Figure S14). In order to improve the efficiencies, various host materials, including TCTA, m-CBP and Bebq$_2$, were employed. Remarkably, device efficiencies could be improved to 11.9 cd A^{-1} and 8.1 % when mCBP was used as the host (Figure S15). Further enhancement could be done by either removing the hole-injecting MoO$_x$ or using a hole-transporting material (HTM) with lower hole mobility (i.e. α-NPD or TCTA). Apparently, the current efficiencies and EQEs could be significantly boosted up to ~17.5 cd A^{-1} and ~12.2 %, respectively (Figure 4b). While TCTA is an excellent electron-blocking material, the insertion of a thin TCTA layer (i.e. 5 nm) at the HTM/emissive interface can effectively accumulate electrons within the emissive layer for exciton formation and light emission. The reduced hole-transport can result in a better balance in the hole and electron currents in the emissive layer and thus improved device efficiency. Tables S14–S16 summarize the key parameters for vacuum-deposited devices based on **3**. The operational stability for the vacuum-deposited device based on **3** was also explored. Particularly, the vacuum-deposited device was measured by accelerated testing at a constant driving current density of 20 mA cm^{-2}. Impressively, the device exhibits an operational half-lifetime (i.e. the time required for the luminance to drop to 50 % of its initial value) of ~52.7 hours at an initial brightness of 1,084 cd m^{-2} (Figure 5c). This corresponds to ~946 hours at 1,000 cd m^{-2} and over 3,000 hours at 100 cd m^{-2}. The high EQE values and satisfactory operational stability clearly demonstrate the capability of such cyclometalated rhodium(III) complexes serving as promising phosphorescent dopants, and more importantly, this work represents the first successful demonstration of application studies of rhodium(III) complexes in OLEDs.

In summary, we have developed a new class of highly luminescent rhodium(III) complexes in which the luminescence quenching problem from the lowest-lying d–d state is overcome by the

incorporation of a strong σ-donor cyclometalating ligand with lower-lying intraligand (IL) state. These complexes exhibit high thermal stability and excellent Φ_{lum} as high as up to 0.65 in thin film offering themselves as promising light-emitting materials in OLEDs. Notably, efficient solution-processed and vacuum-deposited OLEDs based on these rhodium(III) complexes with compelling EQEs of 6.4 % and 12.2 %, respectively, and fairly respectable operational half-lifetime of over 3,000 hours have been realized. This work represents for the first time the application studies of rhodium(III) complexes in OLEDs and opens up a new avenue for diversifying the development of OLED materials, and filling the gap of PGMs with rhodium metal being utilized as phosphors. Apart from the main application of rhodium in catalysis for nitrogen oxides reduction in exhaust gases in catalytic converters for cars, the breakthrough of another potential application of rhodium in OLEDs is demonstrated. Modification of the cyclometalating ligand as well as the ancillary ligand is in progress in order to tune the luminescence color and further improve the EL performance.

In summary, the inventors have developed a new class of highly luminescent rhodium(III) complexes in which the luminescence quenching problem from the lowest-lying d–d state is overcome by the incorporation of a strong σ-donor cyclometalating ligand with lower-lying intraligand (IL) state. These complexes exhibit high thermal stability and excellent Φ_{lum} as high as up to 0.65 in thin film offering themselves as promising light-emitting materials in OLEDs. Notably, efficient solution-processed and vacuum-deposited OLEDs based on these rhodium(III) complexes with compelling EQEs of 6.4 % and 12.2 %, respectively, and fairly respectable operational half-lifetime of over 3,000 hours have been realized. This work represents for the first time the application studies of rhodium(III) complexes in OLEDs and opens up a new avenue for diversifying the development of OLED materials, and filling the gap of PGMs with rhodium metal being utilized as phosphors. Apart from the main application of rhodium in catalysis for nitrogen oxides reduction in exhaust gases in catalytic converters for cars, the breakthrough of another potential application of rhodium in OLEDs is demonstrated. Modification of the cyclometalating ligand as well as the ancillary ligand is in progress in order to tune the luminescence color and further improve the EL performance.

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C L A I M S

1. A highly luminescent cyclometalated rhodium(III) complex having the formula (a):
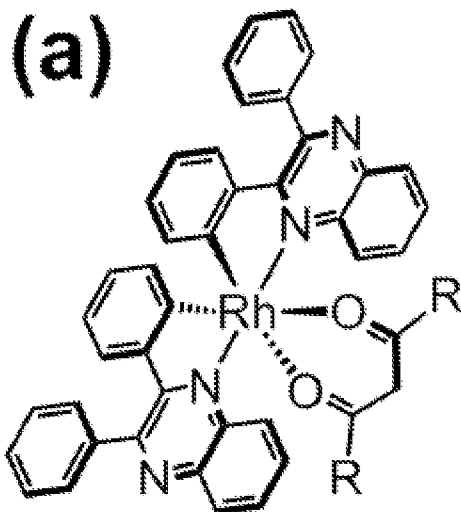
wherein R is an unsubstituted or substituted C1-6 alkyl.

2. The highly luminescent cyclometalated rhodium(III) complex according to claim 1, wherein R is a halogen substituted C1-6 alkyl.

3. The highly luminescent cyclometalated rhodium(III) complex according to claim 1, wherein R is a fluorine substituted C1-6 alkyl.

4. The highly luminescent cyclometalated rhodium(III) complex according to claim 1, wherein R is selected from CH_3, CF_3 and C_6F_5.

5. Use of the highly luminescent cyclometalated rhodium(III) complex according to any of claims 1-4 as a light-emitting material in OLEDs.
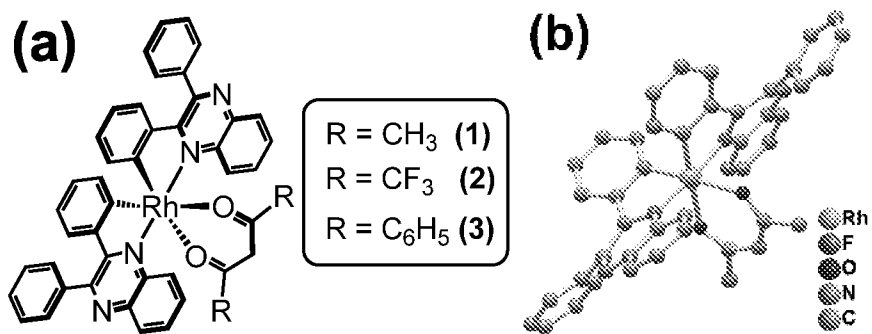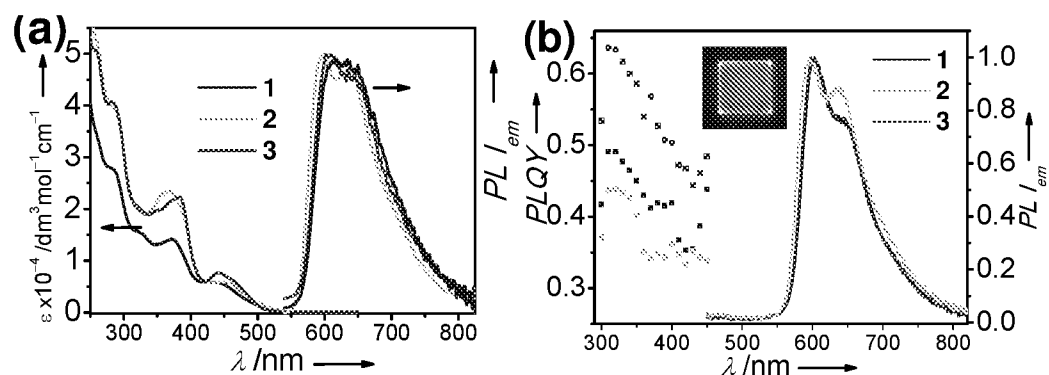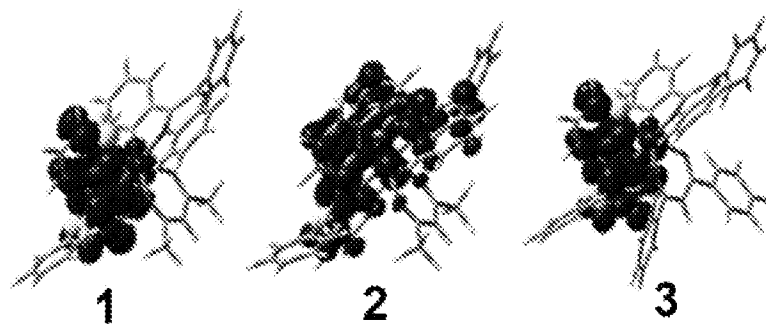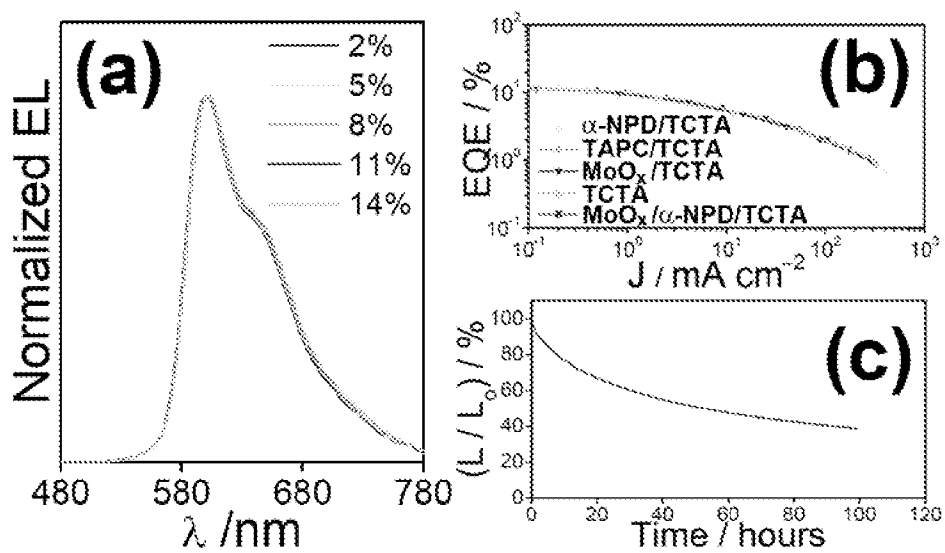
Fig.1

Fig.2

Fig.3

Fig.4

A.   CLASSIFICATION OF SUBJECT MATTER

C07F 15/00(2006.01)i; C09K 11/06(2006.01)i; H01L 51/54(2006.01)i

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

B.   FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07F,C09K,H01L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT,EPODOC,WPI,USTXT,CNTXT,CNKI,STN, Rh, rhodium, light emitting, luminescent, cyclometal? , metal, complex, OLED, structure search

C.   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 108409793 A (AAC MICROTECH CHANGZHOU CO. LTD.et al.) 17 August 2018 (2018-08-17) paragraphs [0007]-[0037], [0038]-[0040], [0055]	1-5
X	CN 108409792 A (AAC MICROTECH CHANGZHOU CO. LTD.et al.) 17 August 2018 (2018-08-17) claims 1-2, 9	1-5
X	WO 2005115061 A1 (SEMICONDUCTOR ENERGY LABORATORY CO. LTD. et al.) 01 December 2005 (2005-12-01) paragraphs [0039]-[0041], [0060]-[0062], [0079]-[0082]	1-5
X	US 2005191527 A1 (Fujii et al.) 01 September 2005 (2005-09-01) paragraphs [0010]-[0016], [0051], [0074], [0095], [00116]	1-5

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

* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
01 March 2020	26 March 2020

Name and mailing address of the ISA/CN	Authorized officer
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Form PCT/ISA/210 (second sheet) (January 2015)

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	108409793	A	17 August 2018	None			
CN	108409792	A	17 August 2018	None			
WO	2005115061	A1	01 December 2005	US	2011024732	A1	03 February 2011
				JP	2008235874	A	02 October 2008
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				KR	101187399	B1	02 October 2012
				EP	1749424	A1	07 February 2007
				JP	5047239	B2	10 October 2012
				JP	2009298794	A	24 December 2009
				US	8637167	B2	28 January 2014
				EP	1749424	A4	22 April 2009
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