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(12) **United States Patent**
Che et al.(10) **Patent No.:** US 7,595,119 B2(45) **Date of Patent:** *Sep. 29, 2009(54) **ORGANOMETALLIC LIGHT-EMITTING MATERIAL**(76) Inventors: **Chi-Ming Che**, Flat 5, 5/F, Block A, Parkway Court, 4 Park Road, Hong Kong (CN); **Wei Lu**, 7/F, Room B, 41 Western Street, Hong Kong (CN); **Michael Chi-Wang Chan**, 9B Fairview Court, 75 Pokfulan Road, Hong Kong (CN)

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This patent is subject to a terminal disclaimer.

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Related U.S. Application Data

(63) Continuation of application No. 11/401,537, filed on Apr. 10, 2006, which is a continuation of application No. 10/094,384, filed on Mar. 8, 2002, now Pat. No. 7,026,480.

(60) Provisional application No. 60/274,142, filed on Mar. 8, 2001.

(51) **Int. Cl.**
H01L 51/54 (2006.01)(52) **U.S. Cl.** 428/690; 428/917; 313/504; 313/506; 257/E51.044(58) **Field of Classification Search** None
See application file for complete search history.(56) **References Cited**

U.S. PATENT DOCUMENTS

5,698,048	A *	12/1997	Friend et al.	136/263
6,048,630	A	4/2000	Burrows et al.	
6,120,586	A	9/2000	Harada et al.	
6,150,545	A	11/2000	Harada et al.	
6,252,028	B1	6/2001	Fehn et al.	
7,026,480	B2 *	4/2006	Che et al.	546/4
2004/0091738	A1	5/2004	Psai et al.	

FOREIGN PATENT DOCUMENTS

WO	WO 00/57676	9/2000
WO	WO 01/41512 A1	6/2001

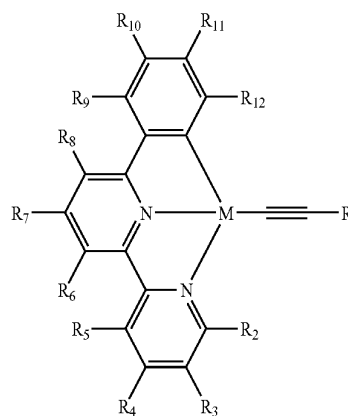
OTHER PUBLICATIONS

Bunten et al., "Synthesis, Optical Absorption, Fluorescence . . . Pt(II) . . . Acetylide Monomers and Polymers", *Macromolecules*, vol. 29, No. 8, pp. 2885-2893 (1996).*

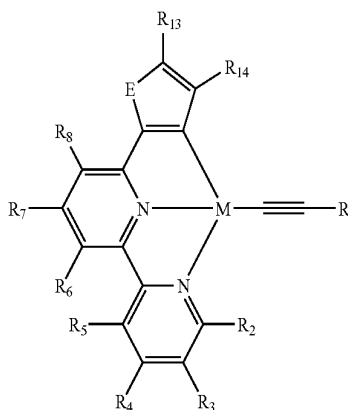
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Primary Examiner—Marie R. Yamnitzky(74) *Attorney, Agent, or Firm*—McDonnell Boehnen Hulbert & Berghoff LLP(57) **ABSTRACT**

Disclosed herein are novel light-emitting materials of Formula I and II below. These new complexes are synthesized and found to be sufficiently stable to allow sublimation and vacuum deposition. These new emitters are electrophosphorescent and can be used in organic light-emitting devices (OLEDs) for device elements capable of emitting light of color ranging from orange to red with high-efficiency and high-brightness.



I



II

wherein E=Group 16 elements (including sulphur); M=Group 10 metal (including platinum); R₁-R₁₄ are each independently selected from the group consisting of hydrogen; halogen; alkyl; substituted alkyl; aryl; substituted aryl, with substituents selected from the group consisting of halogen, lower alkyl and recognized donor and acceptor groups. R₁ can also be selected from (C≡C)_nR₁₅, where (C≡C) represents a carbon-carbon triple bond (acetylide group), n is selected from 1 to 10, and R₁₅ is selected from alkyl, aryl, substituted aryl, and tri(alkyl)silyl.

13 Claims, 10 Drawing Sheets

OTHER PUBLICATIONS

- Wong et al., "Synthesis, Redox and Optical Properties of Low-Bandgap Platinum(II) Polyynes . . .", *Macromol. Rapid Commun.*, 22, pp. 461-465 (Mar. 2001).*
- O'Brien et al., "Improved energy transfer in electrophosphorescent devices", *Appl. Phys. Lett.* 74(3), pp. 442-444 (Jan. 18, 1999).*
- Siu-Wai Lai, et al, *Inorganic Chem* 38(18) pp. 4046-4055, 1999.
- Siu-Wai Lai, *Organometallics* pp. 3327-3336, 1999.
- Raffaello Romeo, *Inorganica Chimica Acta*, vol. 265, Issues 1-2, Nov. 1997, pp. 225-233.
- Yungdong Jahng, *Inorganica Chimica Acta*, vol. 267, Issue 2, Jan. 1998, pp. 265-270.
- Chin Wing Chan, *JACS*, pp. 11245-11253, 1993.
- Minghetti, *Inorganic Chemistry* 29(26) pp. 5137-5138 (1990).
- Malcolm H. Chisholm *Inorg. Chem* 16(9), 1977, pp. 2177-2182.
- R. A. Bell, *Inorg Chem* 16(3), 1977, pp. 677-686.
- Robert A. Bell *Inorg Chem* 16(3), 1977, pp. 687-697.
- C. W. Tang and S. A. VanSlyke, "Organic electroluminescent diodes", *Appl. Phys. Lett.* 51 (12), Sep. 1987, pp. 913-915.
- David E. Mentley, "The Market Potential for Organic Light-Emitting Diode Displays", *Commercial Report*, Stanford Resources, 5 pages, (publication date not given).
- M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson & S. R. Forrest, "Highly efficient phosphorescent emission from organic electroluminescent devices", *Nature*, vol. 395, Sep. 1998, pp. 151-154.
- Yuguang Ma, Houyu Zhang, Jiacong Shen, Chiming Che, "Electroluminescence from triplet metal-ligand charge-transfer excited state of transition metal complexes", *Synthetic Metals* 94 (1998), pp. 245-248.
- Chihaya Adachi, Marc A. Baldo and Stephen R. Forrest, "High-efficiency organic electrophosphorescent devices with tris (2-phenylpyridine)iridium doped into electron-transporting materials", *Applied Physics Letters*, vol. 77, No. 6, Aug. 2000, pp. 904-906.
- Siu-Wai Lai, Michael Chi-Wang Chan, Tsr-Chun Cheung, Shie-Ming Peng and Chi-Ming Che, "Probing d⁸-d⁸ Interactions in Luminescent Mono- and Binuclear Cyclometalated Platinum(II) Complexes of 6-Phenyl-2,2'-bipyridines", *Inorg. Chem.* 1999,38, pp. 4046-4055.
- Tsz-Chun Cheung, Kung-Kai Cheung, Shie-Ming Peng and Chi-Ming Che, "Photoluminescent cyclometalated diplatinum(II,II) complexes: photophysical properties and crystal structures of [PtL(PPh₃)ClO₄] and [Pt₂L₂(p-dppm)][ClO₄]₂ (HL = 6-phenyl-2,2'-bipyridine, dppm = Ph₂PCH₂PPh₂)", *J. Chem. Soc., Dalton Trans.* 1996, p. 1645-1651.
- Siu-Wai Lai, Michael Chi-Wang Chan, Kung-Kai Cheung and Chi-Ming Che, "Carbene and Isocyanide Ligation at Luminescent Cyclometalated 6-Phenyl-2,2'-bipyridyl Platinum(II) Complexes: Structural and Spectroscopic Studies", *Organometallics* 1999, 18, pp. 3327-3336.
- John H. K. Yip, Suwarno and Jagadese J. Vittal, "Syntheses and Electronic Spectroscopy of [PtL(L1)] [ClO₄] Complexes (H₂L = 6-Phenyl-2,2'-bipyridine; L' = Pyridine, 4-Aminopyridine, 2-Aminopyridine, and 2,6-Diaminopyridine)", *Inorgan. Chem.* 2000, 39, pp. 3537-3543.
- Francesco Neve and Alessandra Crispini, Sebastiano Campagna, "Anisometric Cyclometalated Palladium(II) and Platinum(II) Complexes. Structural and Photophysical Studies", *Inorg. Chem.* 1997,36, pp. 6150-6156.
- Fritz-Krohnke. "The Specific Synthesis of Pyridines and Oligopyridines", *Synthesis*, Jan. 1976, pp. 1-24.
- Edwin C. Constable, Roland P. G. Henney, Paul R. Raithby and Lynn R. Sousa, "Cyclometallation Reactions of 6-(2-Thienyl)-2,2'-bipyridine with d⁸ Transition Metal Ions", *J. Chem. Soc. Dalton Trans.* 1992, pp. 225 1-2258.
- Edwin C. Constable, Roland P. G. Henney and Troy A. Leese, Derek A. Tocher, "Cyclometallation Reactions of 6-Phenyl-2,2'-bipyridine; a Potential C,N,N- Donor Analogue of 2,2':6',2"-Terpyridine, Crystal and Molecular Structure of Dichlorobis(6-phenyl-2,2'-bipyridine)ruthenium(II)", *J. Chem. Soc. Dalton Tras.* 1990, pp. 443-449.
- Wei Lu, Boa-Xiu Mi, Michael C. W. Chan, Zheng Hui, Nianyong Zhu, Shuit-Tong Lee and Chi-Ming Che, "[C^{^N^N}Pt(C=C)_nR] (HC^{^N^N} = 6-aryl-2,2'-bipyridine, n = 1-4, R = aryl, SiMe₃) as a new class of light-emitting materials and their applications in electrophosphorescent devices", *Chemical Communications*, DOI: 10.1039/b108793b, 4 pages, (first published on Web Jan. 7, 2002).
- Vladimir V. Grushin, Norman Herron, Daniel D. LeCloux, William J. Marshall, Viacheslav A. Petrov and Ying Wang, "New, efficient electroluminescent materials based on organometallic Ir complexes", *Chem. Commun.*, 2001, pp. 1494-1495.
- Hong Zhi Xie, Man Wah Liu, Oi Yan Wang, Xiao Hong Zhang, Chun Sing Lee, Liang Sun Hung, Shuit Tong Lee, Pang Fei Teng, Hoi Lun Kwong, Hui Zheng and Chi Min Che, "Reduction of Self-Quenching Effect in Organic Electrophosphorescence Emitting Devices via the Use of Sterically Hindered Spacers in Phosphorescence Molecules", *Advanced Materials* 2001, 13, No. 16, Aug. 16, pp. 1425-1248.
- Sergey Lamansky, Peter Djurovich, Drew Murphy, Feras Abdel-Razzaq, Hae-Eun Lee, Chihaya Adachi, Paul E. Burrows, Stephen R. Forrest and Mark E. Thompson, "Highly Phosphorescent Bis-Cyclometalated Iridium Complexes: Synthesis, Photophysical Characterization, and Use in Organic Light Emitting Diodes", *J. Am. Chem. Soc.* 2001 vol. 123, No. 18, pp. 4304-4312.
- Chihaya Adachi, Marc A. Baldo, Mark E. Thompson and Stephen R. Forrest, "Nearly 100% internal phosphorescence efficiency in an organic light emitting device", *Journal of Applied Physics*, vol. 90, No. 10, Nov. 15, 2001, pp. 5048-5051.
- Chihaya Adachi, Raymond C. Kwong, Peter Djurovich, Vadim Adamovich, Marc A. Baldo, Mark E. Thompson and Stephen R. Forrest, "Endothermic energy transfer: A mechanism for generating very efficient high-energy phosphorescent emission in organic materials", *Applied Physics Letters*, vol. 79, No. 13, Sep. 24, 2001, pp. 2082-2084.
- Chihaya Adachi, Marc A. Baldo and Stephen R. Forrest, "High-efficiency red electrophosphorescence devices", *Applied Physics Letters*, vol. 78, No. 11, Mar. 12, 2001, pp. 1622-1624.

* cited by examiner

Figure 1

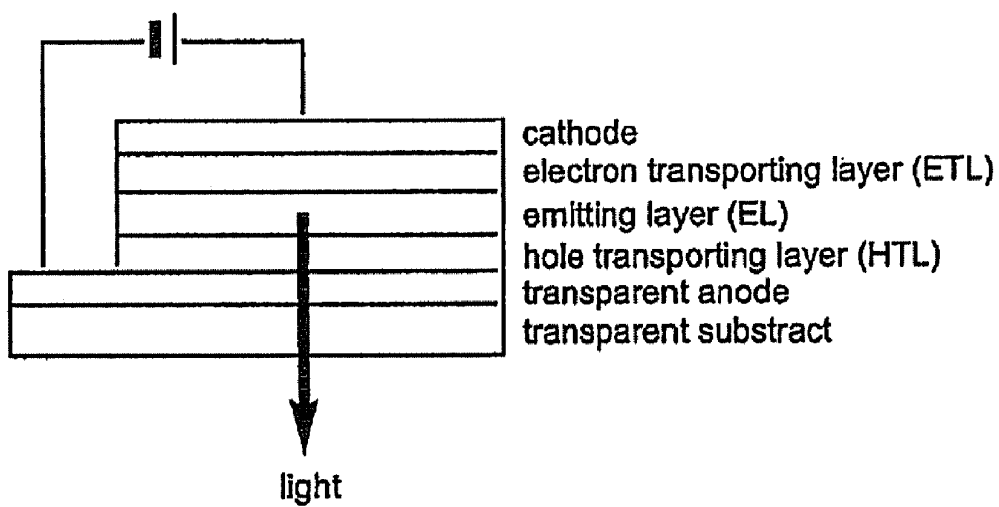


Figure 2

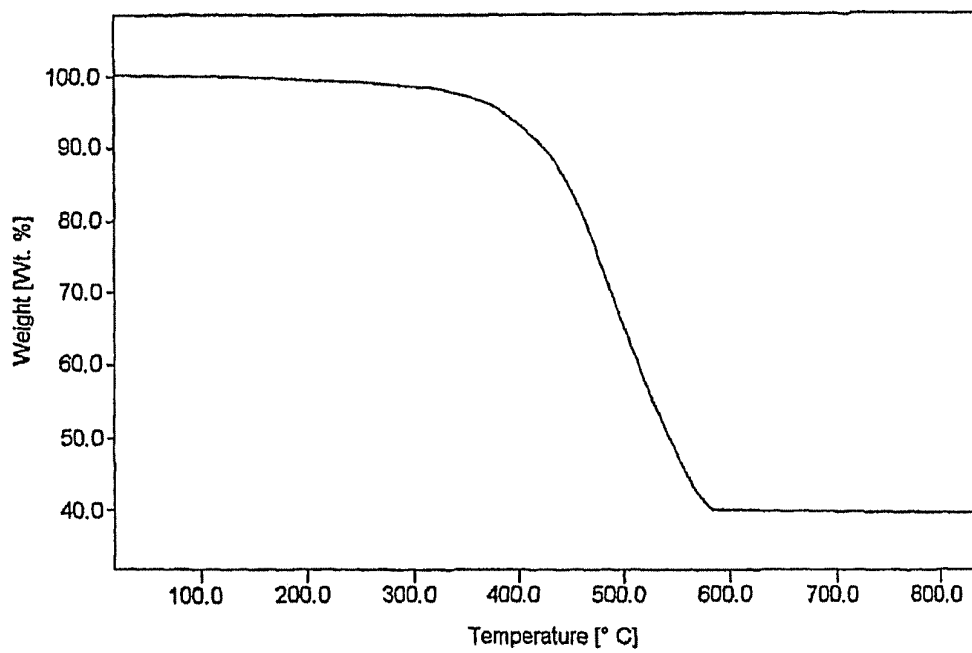


Figure 3

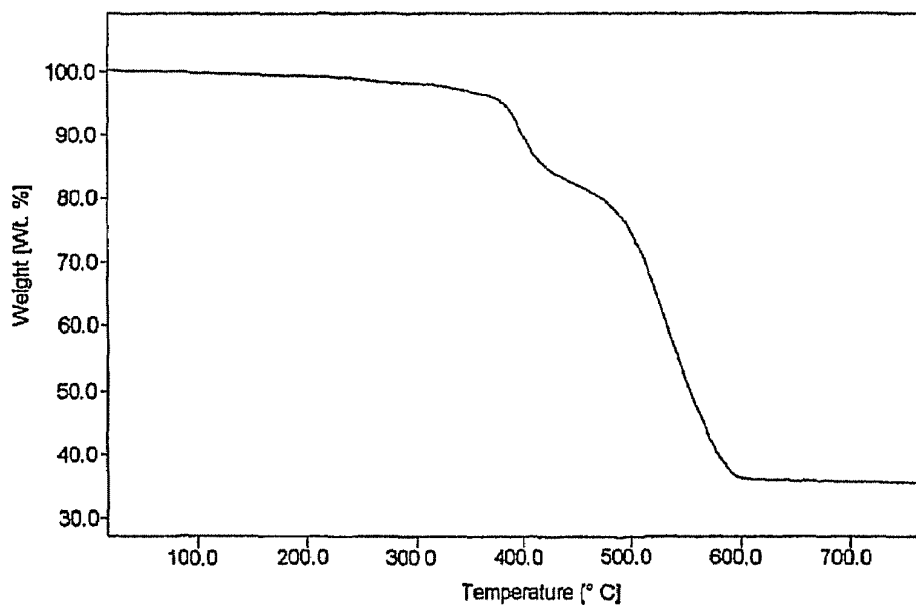


Figure 4

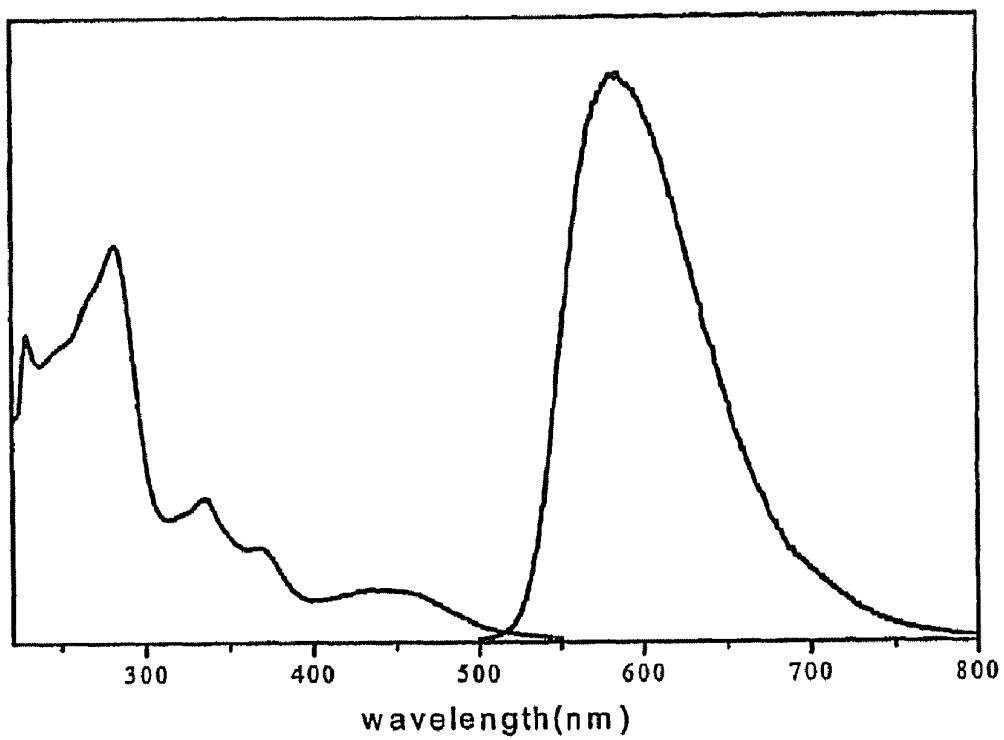


Figure 5

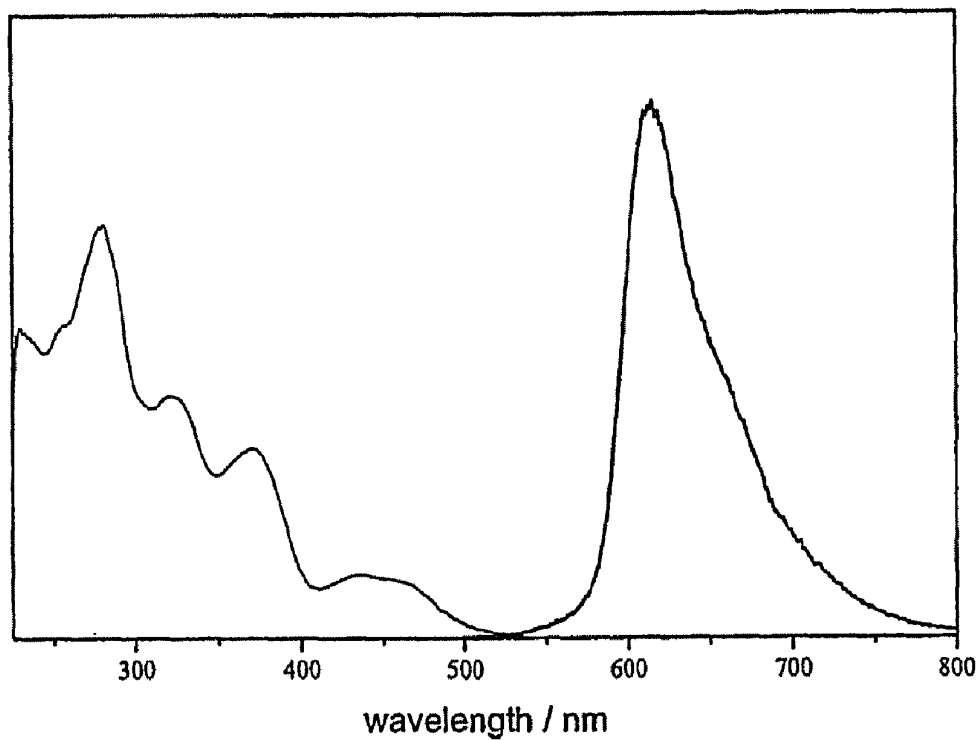


Figure 6

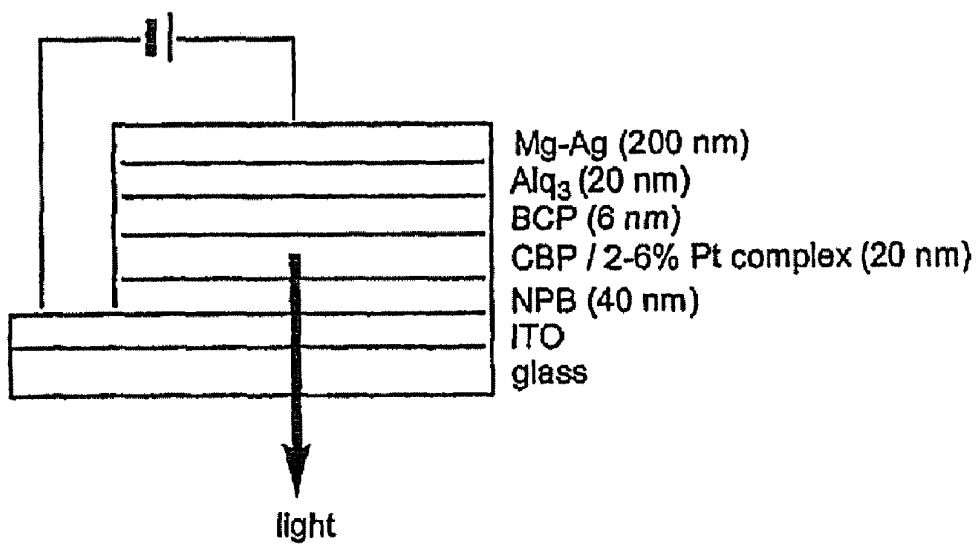


Figure 7

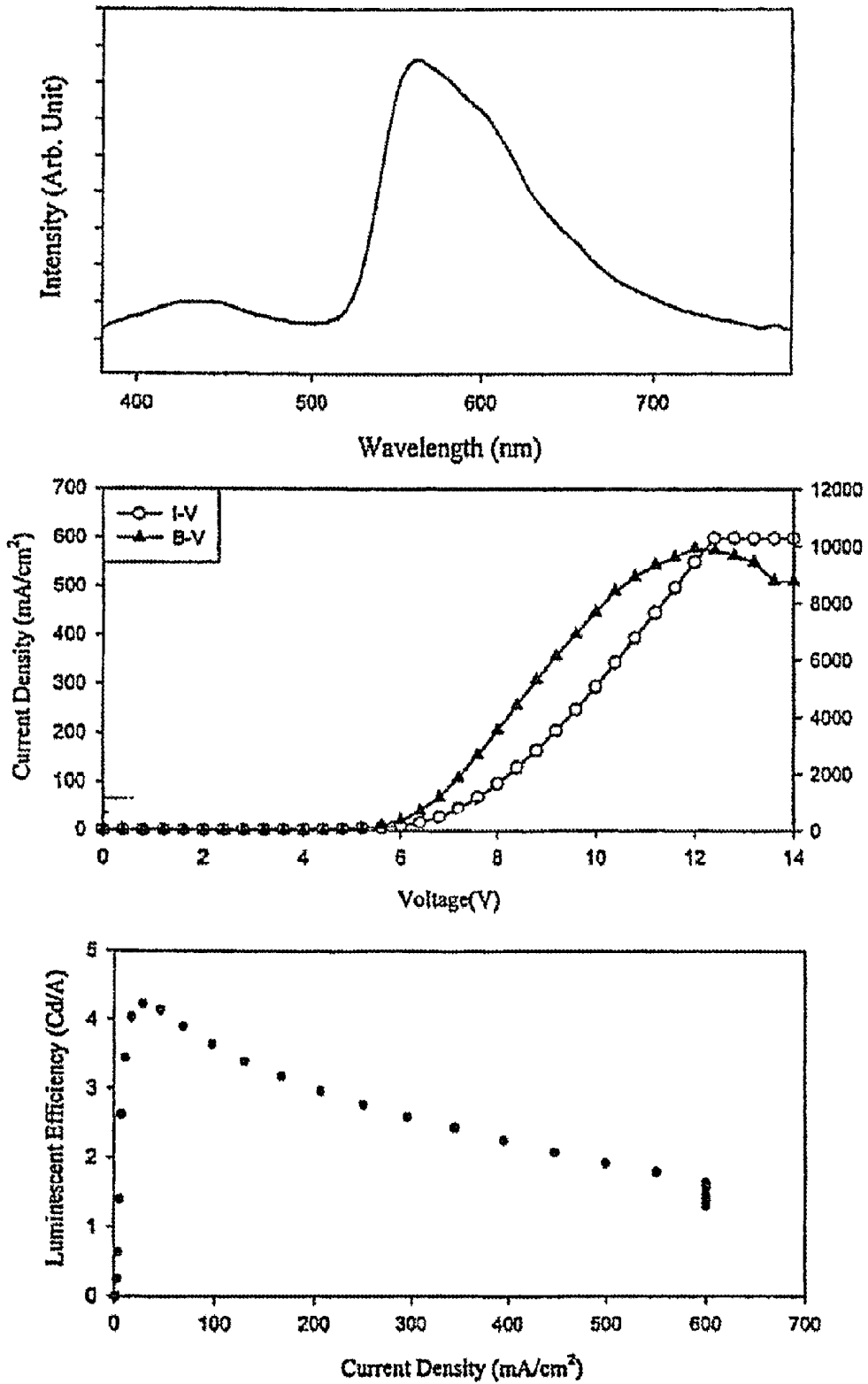


Figure 8

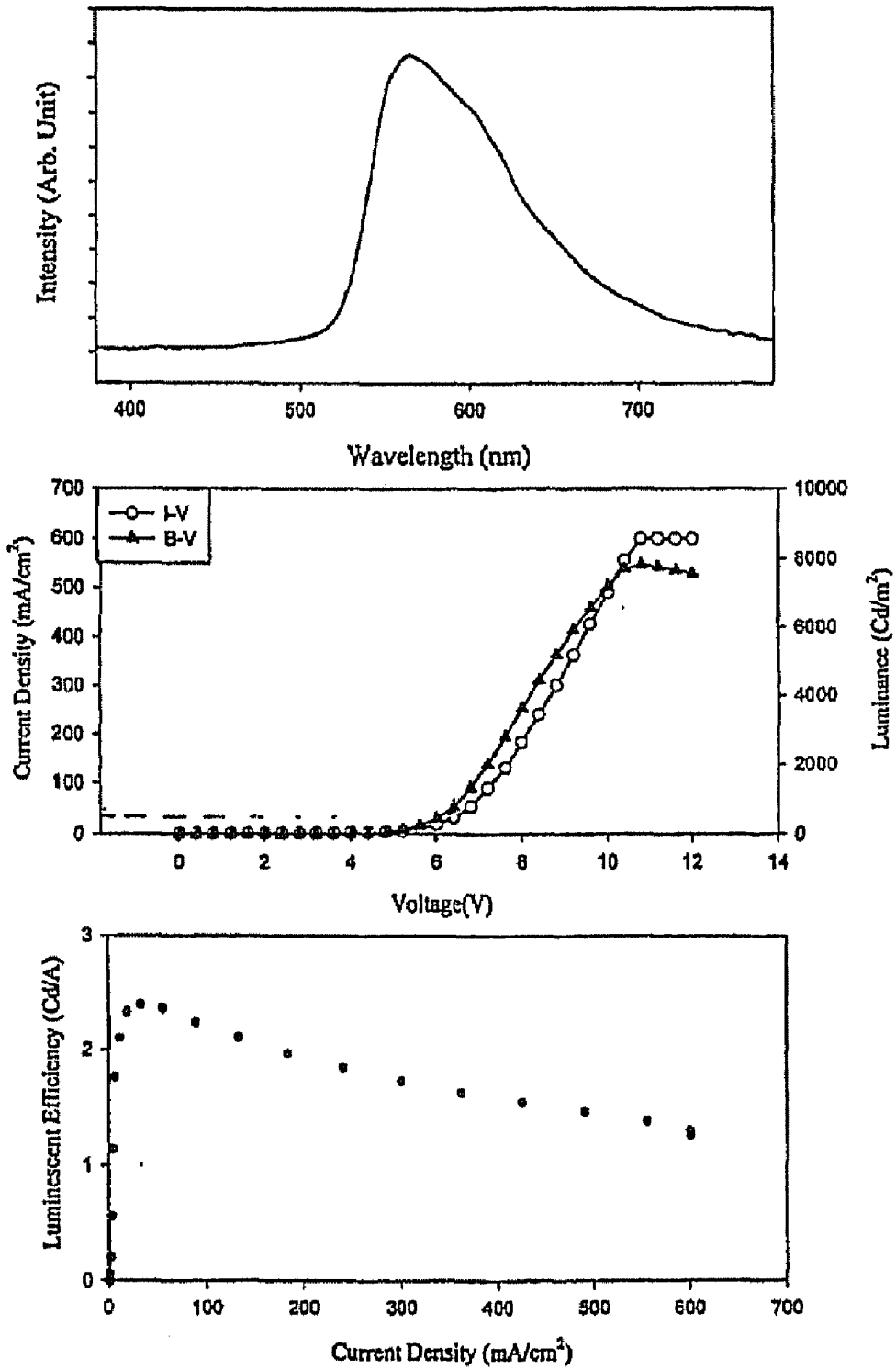


Figure 9

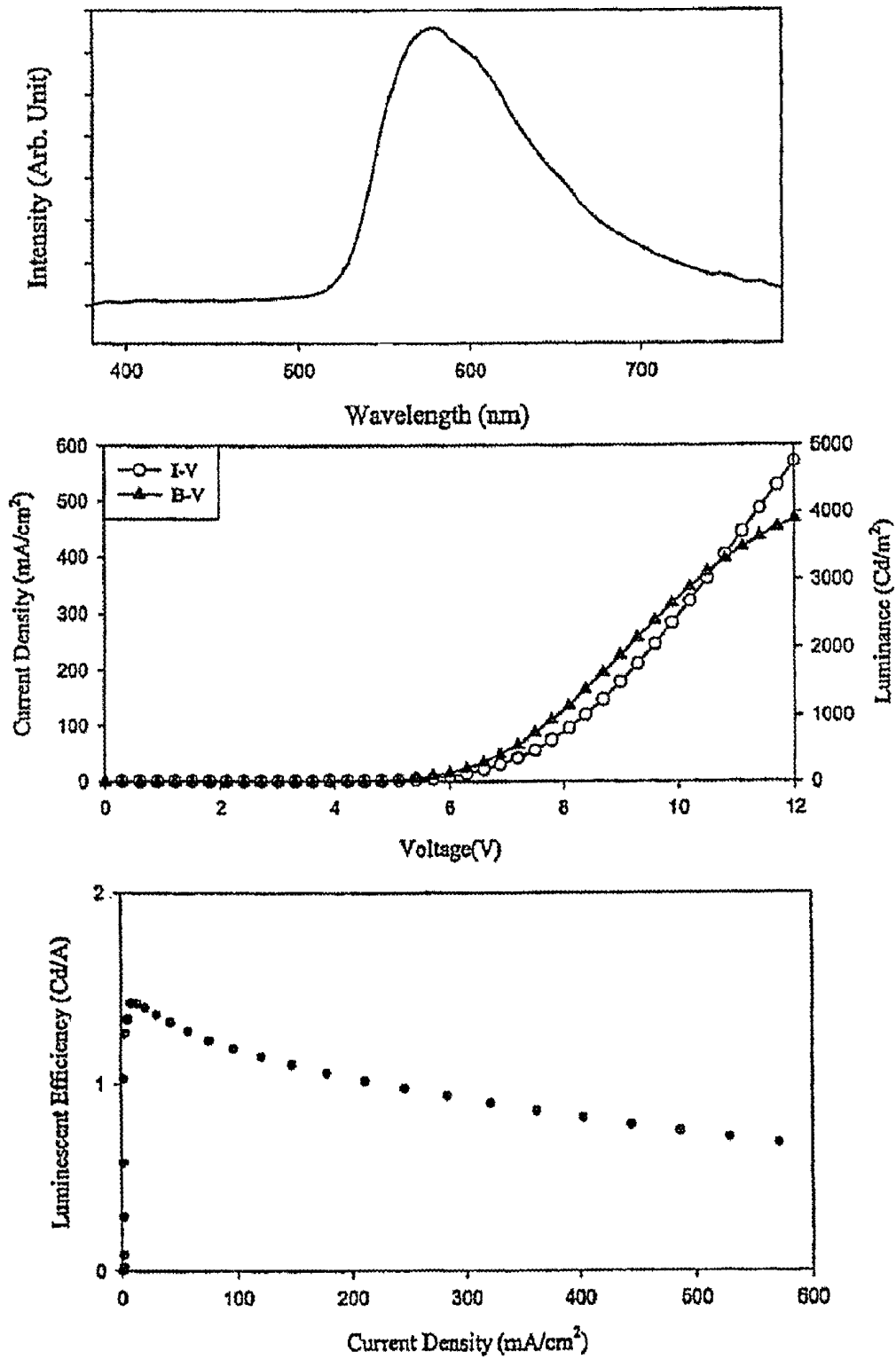
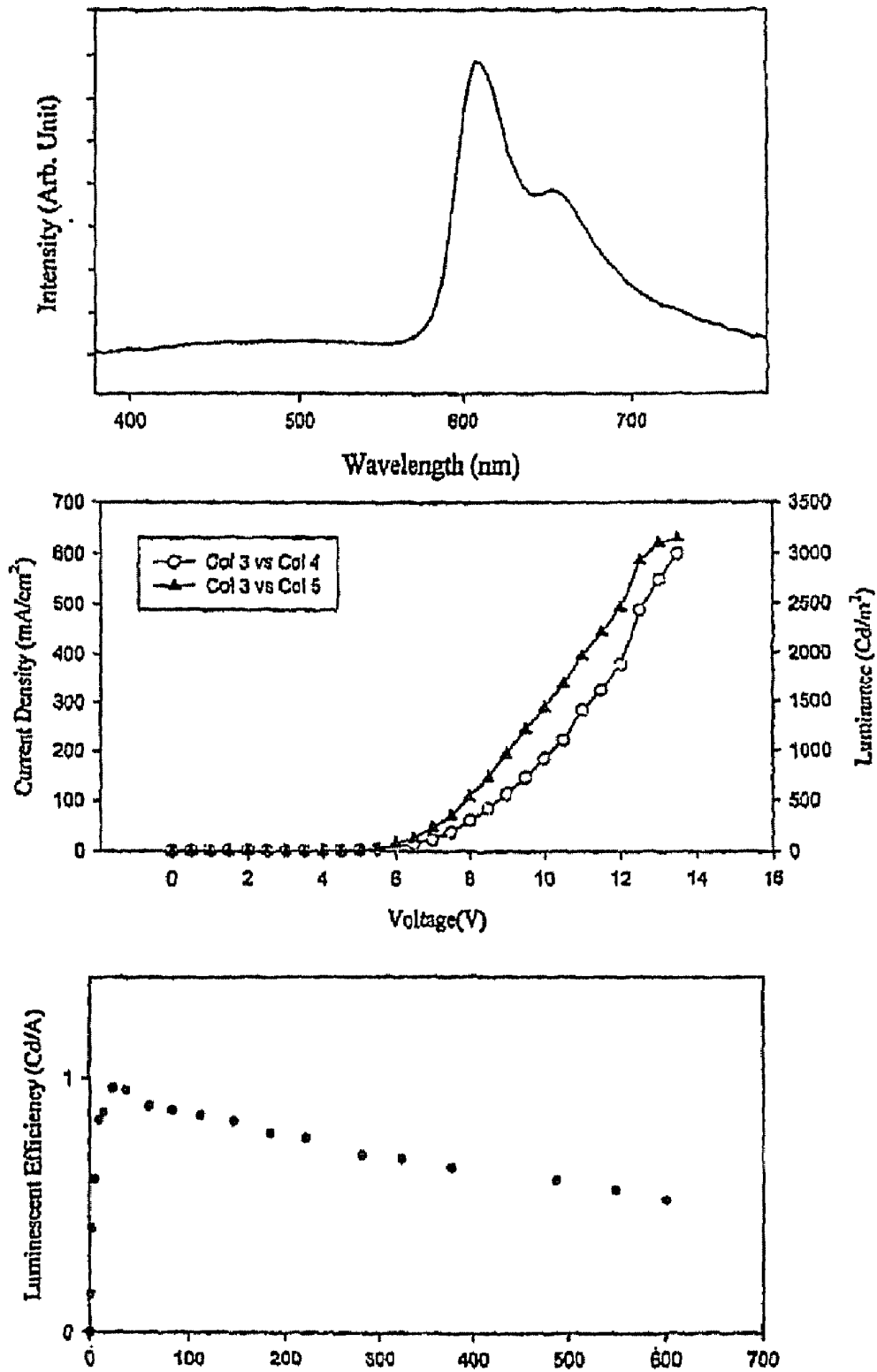


Figure 10



ORGANOMETALLIC LIGHT-EMITTING MATERIAL

RELATED APPLICATIONS

The present application is a continuation of U.S. application Ser. No. 11/401,537, titled "Organometallic Light-Emitting Material," filed Apr. 10, 2006 by Che et al., which is a continuation of U.S. application Ser. No. 10/094,384 titled "Organometallic Light-Emitting Material," filed Mar. 8, 2002 by Che et al., now U.S. Pat. No. 7,026,480, which claims priority to U. S. Provisional Application Ser. No. 60/274,142, titled "Organometallic Light-Emitting Material," filed Mar. 8, 2001, by Che et al.

FIELD OF THE INVENTION

This invention relates to light-emitting materials which are discrete organometallic molecules in nature, which can be deposited as a thin layer by vacuum deposition, and which can act as electrophosphorescent emitters in high-efficiency and high-brightness organic light-emitting devices (OLEDs).

BACKGROUND OF THE INVENTION

Tang and coworkers first reported on high-performance organic light-emitting devices (OLEDs) in 1987 (Tang, C. W.; et al. *Appl. Phys. Lett.* 51, 913 (1987)). Their discovery was based on employing a multilayer structure containing an emitting layer and a hole transport layer of a suitable organic substrate. Alq₃(q =deprotonated 8-hydroxyquinoliny) was chosen as the emitting material and proven to be of high performance because (1) it can form uniform thin films under 1000 Å using vacuum deposition, (2) it is a good charge carrier and (3) it exhibits strong fluorescence. Since then, there has been a flourish of research on OLEDs and materials used in these devices. Indeed, nearly every large chemical company in the world with optoelectronic interests has demonstrated some level of interest in OLEDs. Clearly, OLED technology is heading directly and rapidly into the marketplace, as suggested in a commercial report by Stanford Resources (by David E. Mentley, "The Market Potential for Organic Light-Emitting Diode Displays," *Commercial Report*. The attractiveness of OLEDs as it challenges traditional technologies such as cathode ray tubes (CRTs), liquid crystal displays (LCDs) and plasma displays is based on many features and advantages, including:

- Low operating voltage,
- Thin, monolithic structure,
- Emits, rather than modulates light,
- Good luminous efficiency,
- Full color potential, and
- High contrast and resolution.

OLED is a device built with organic semiconductors from which visible light can be emitted upon electrical stimulation. The basic heterostructure of an OLED is described in FIG. 1.

The layers may be formed by evaporation, spin-casting or chemical self-assembly. The thickness ranges from a few monolayers (self-assembled films) to about 1000 to 2000 Å. Such devices whose structure is based on the use of layers of organic optoelectronic materials generally rely on a common mechanism leading to optical emission, namely, the radiative recombination of a trapped charge. Under a DC bias, electrons are injected from a cathode (usually Ca, Al, Mg—Ag) and holes are injected from an anode (usually transparent indium tin oxide (ITO)) into the organic materials, where they travel in the applied field across the electron transporting

layer (ETL) and the hole transporting layer (HTL) respectively until they meet, preferably on molecules in the emitting layer, and form a luminescent excited state (Frenkel exciton) which, under certain conditions, experiences radiative decay to give visible light. The electroluminescent material may be present in a separate emitting layer between the ETL and the HTL in what is referred as a multi-layer heterostructure. In some cases, buffer layers and/or other functional layers are also incorporated to improve the performance of the device. Alternatively, those OLEDs in which the electroluminescent emitters are the same materials that function either as the ETL or HTL are referred to as single-layer heterostructures.

In addition to emissive materials that are present as the predominant component in the charge carrier layers (HTL or ETL), other efficient luminescent material(s) may be present in relatively low concentrations as a dopant in these layers to realize color tuning and efficiency improvement. Whenever a dopant is present, the predominant material in the charge carrier layer may be referred to as a host. Ideally, materials that are present as hosts and dopant are matched so as to have a high level of energy transfer from the host to the dopant, and to yield emission with a relatively narrow band centered near selected spectral region with high-efficiency and high-brightness.

While fluorescent emitters with high luminescence efficiencies have been extensively applied as dopant in OLEDs, phosphorescent emitters have been neglected in this domain. However, the quantum efficiency of an electrofluorescence device is limited by the low theoretical ratio of singlet exciton (25%) compared to triplet exciton (75%) upon electron-hole recombination from electrical excitation. In contrast, when phosphorescent emitters are employed, the potentially high energy/electron transfer from the hosts to the phosphorescent emitters may result in significantly superior electroluminescent efficiency (Baldo, M. A.; et al. *Nature* 395, 151 (1998) and Ma, Y. G.; et al. *Synth. Met.* 94, 245 (1998)). Several phosphorescent OLED systems have been fabricated and have indeed proven to be of relative high-efficiency and high-brightness.

It is desirable for OLEDs to be fabricated using materials that provide electrophosphorescent emission corresponding to one of the three primary colors, i.e., red, green and blue so that they may be used as a component layer in full-color display devices. It is also desirable that such materials are capable of being deposited as thin films using vacuum deposition techniques, which has been prove to be a common method for high-performance OLED fabrication, so that the thickness of the emitting layer can be precisely controlled.

Presently, the highest efficiencies and brightness have been obtained with green electrophosphorescent devices (15.4±0.2% for external quantum efficiency and almost 100% for internal efficiency, 10⁵ Cd/m² for maximum luminance) using Ir(ppy)₃ (ppy=deprotonated 2-phenylpyridine) as emitter (Adachi, C.; et al. *Appl Phys. Lett.* 77, 904 (2000)). An OLED emitting saturated red light based on the electrophosphorescent dopant Pt(OEP) (H₂OEP=octaethylporphyrin) has also been published and patented (Burrows, P.; et al. U.S. Pat. No. 6,048,630) but the maximum luminance is only around 500 Cd m⁻². A relevant patent is the use of the cyclometalated platinum(II) complex Pt(thpy)₂ (thpy=deprotonated 2-(2-thienyl)pyridine) as dopant and PVK (poly(N-vinyl)carbazole) as host in a orange OLED (Lamansky, S.; et al. WO Pat. No. 00/57676). However, the Pt(ID) complex used by the inventors was not stable for sublimation or vacuum deposition, thus a spin-casting

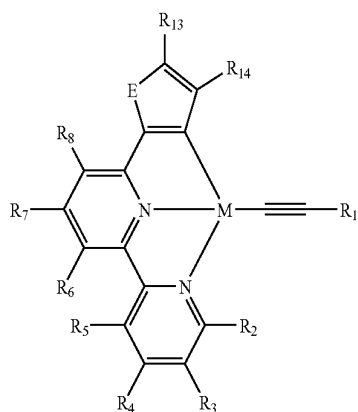
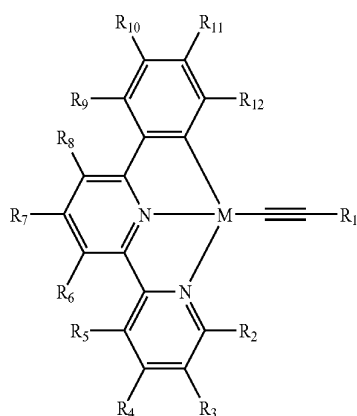
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method was applied, which led to higher driving voltages, quantum efficiency of 0.11% and luminance of 100 Cd/m² were obtained at 22 V.

SUMMARY OF THE INVENTION

The present invention is directed to novel organometallic light-emitting materials which may be used as electrophosphorescent emitters or dopants in high-performance OLEDs. In particular, the present invention is directed to the design, synthesis, properties and applications of a family of phosphorescent emitters which, when added in effective amounts to suitable host material, including emissive compounds, electron transporting compounds and hole transporting compounds, tune the color of emission in the near-red range and enhance the device efficiency and brightness. Furthermore, the thermal stability of these phosphorescent emitters in the present invention are sufficient to allow sublimation, so that they may be readily incorporated into devices using vacuum deposition techniques, and hence high-performance electrophosphorescent devices prepared entirely from vacuum-deposited materials may be realized.

The family of electrophosphorescent emitters for use in the present invention are acetylide (alkynyl) complexes of the Group 10 metals, including platinum, with chemical structures of either Formula I or II:



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wherein E=Group 16 elements (including sulphur); M=Group 10 metal (including platinum); R₁-R₁₄ are each independently selected from the group consisting of hydrogen; halogen; alkyl; substituted alkyl; aryl; substituted aryl, with substituents selected from the group consisting of halogen, lower alkyl and recognized donor and acceptor groups. R₁ can also be selected from (C≡C)_nR₁₅, where (C≡C) represents a carbon-carbon triple bond (acetylide group), n is selected from 1 to 10, and R₁₅ is selected from alkyl, aryl, substituted aryl, and tri(alkyl)silyl. Group 16 elements are also known as the Group VIA elements. Group 10 elements also belong to Group VIII B.

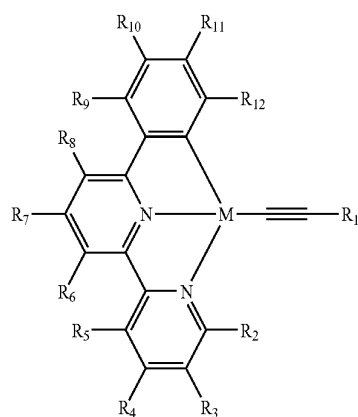
As established by thermogravimetric analysis, some of these complexes are thermally stable up to ~400° C. These complexes are good phosphorescent emitters and give strong orange to red emissions (λ_{max} 550-630 nm) in fluid solutions by photo excitation and in OLEDs by electrical stimulation.

Generally, the present invention is directed to the syntheses and OLED applications of the family of electrophosphorescent emitters defined by Formula I and II. Our claims include the synthetic method for these novel complexes as well as their use as light-emitting material. These OLED applications include OLEDs wherein these complexes are incorporated as components either by vacuum deposition, spin-casting or other device fabrication methods.

In the present invention, the light-emitting material for use as an emitter or dopant in an OLED can comprise one or more metal-acetylide (metal-alkynyl) groups. In alternative, the light-emitting material for use as an emitter or dopant in an OLED comprises one or more platinum-acetylide (platinum-alkynyl) groups. In one embodiment, the light-emitting material for use as an emitter or dopant in an OLED can comprise a platinum atom coordinated by a tridentate ligand using one carbon and two nitrogen atoms. In another embodiment, the light-emitting material for use as an emitter or dopant in an OLED comprising a platinum atom coordinated by a tridentate ligand bearing a deprotonated phenyl carbonion and 2,2'-bipyridine.

In an exemplary embodiment, the light-emitting material for use as an emitter or dopant in an OLED can have a chemical structure represented by either Formula I or II:

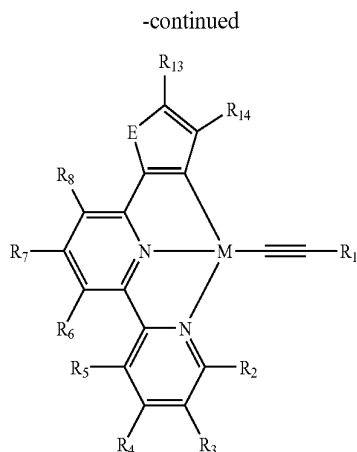
II



I

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wherein E=Group 16 elements (including sulphur); M=Group 10 metal (including platinum); R_1 - R_{14} are each independently selected from the group consisting of hydrogen; halogen; alkyl; substituted alkyl; aryl; substituted aryl, with substituents selected from the group consisting of halogen, lower alkyl and recognized donor and acceptor groups. R_1 can also be selected from $(C\equiv C)_n R_{15}$, where $(C\equiv C)$ represents a carbon-carbon triple bond (acetylide group), n is selected from 1 to 10, and R_{15} is selected from alkyl, aryl, substituted aryl, and tri(alkyl)silyl.

In one embodiment, the light-emitting material can be deposited as a thin layer by sublimation or vacuum deposition. In another embodiment, the light-emitting material can be fabricated into OLEDs using spin-coating or other methods.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1. General heterostructure of OLEDs.

FIG. 2. TGA curve of complex 2.

FIG. 3. TGA curve of complex 15.

FIG. 4. UV-vis absorption and emission spectra of complex 2 in CH_2Cl_2 at 298 K.

FIG. 5. UV-vis absorption and emission spectra of complex 15 in CH_2Cl_2 at 298 K.

FIG. 6. The heterostructure of OLEDs in present invention.

FIG. 7. Electroluminescent spectrum, current-voltage (I-V) and luminance-voltage (B-V) curves and luminescent efficiency-current density curve of the device using complex 2 as emitter with a doping level of 2%.

FIG. 8. Electroluminescent spectrum, current-voltage (I-V) and luminance-voltage (B-V) curves and luminescent efficiency-current density curve of the device using complex 2 as emitter with a doping level of 4%.

FIG. 9. Electroluminescent spectrum, current-voltage (I-V) and luminance-voltage (B-V) curves and luminescent efficiency-current density curve of the device using complex 3 as emitter with a doping level of 4%.

FIG. 10. Electroluminescent spectrum, current-voltage (I-V) and luminance-voltage (B-V) curves and luminescent efficiency-current density curve of the device using complex 16 as emitter with a doping level of 4%.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is generally directed to syntheses and properties of a family of organometallic light-emitting

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materials and their applications in high-performance OLEDs. These novel complexes possess several chemical and structural characteristics as follows:

II

5 Cyclometalated diimine complexes of Group 10 metals, including platinum,

Neutral molecules,

Square planar coordination environment around metal,

10 Tridentate ligands defined as (CANAN) occupy three of the coordination sites, and

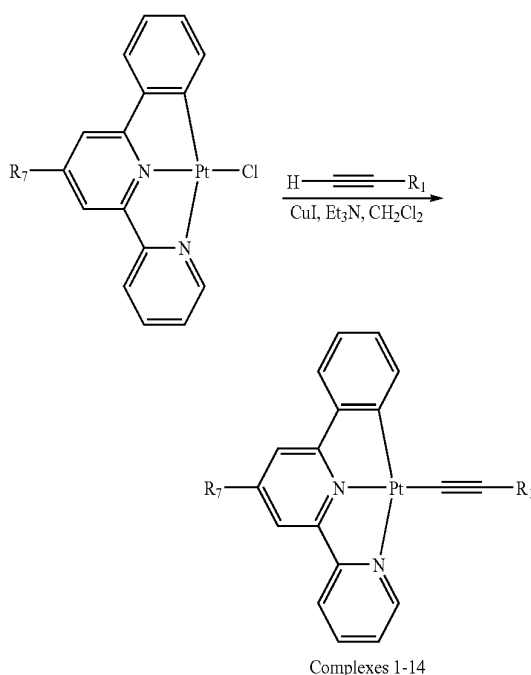
Acetylide (alkynyl) group occupies the fourth coordination site.

The type of $[(C^*N^*N)Pt(II)]$ complexes which combine the 15 structural and spectroscopic characteristics of both diimine and cyclometalated Pt(II) complexes have been reported ((a) Lai, S. W.; et al. *Inorg. Chem.* 38, 4046 (1999). (b) Cheung, T. C.; et al. *J. Chem. Soc., Dalton Trans.* 1645 (1996). (c) Lai, S. W.; et al. *Organometallics* 18, 3327 (1999). (d) Yip, J. H. K.; et al. *Inorg. Chem.* 39, 3537 (2000). (e) Neve, F.; et al. *Inorg. Chem.* 36, 6150 (1997)). The results demonstrated that these complexes are good room-temperature phosphorescent emitters both in solid state and in fluid solution. The relatively long-lived emissions occurring in the range of λ_{max} 530-800 25 nm have been assigned to triplet metal-to-ligand charge transfer (3MLCT) or metal-metal-to-ligand charge transfer (3MMLCT) excited states.

The present invention will now be described in detail for 30 specific preferred embodiment of the invention, it being understood that these embodiments are intended only as illustrative examples and the invention is not to be limited thereto.

Syntheses of the Complexes

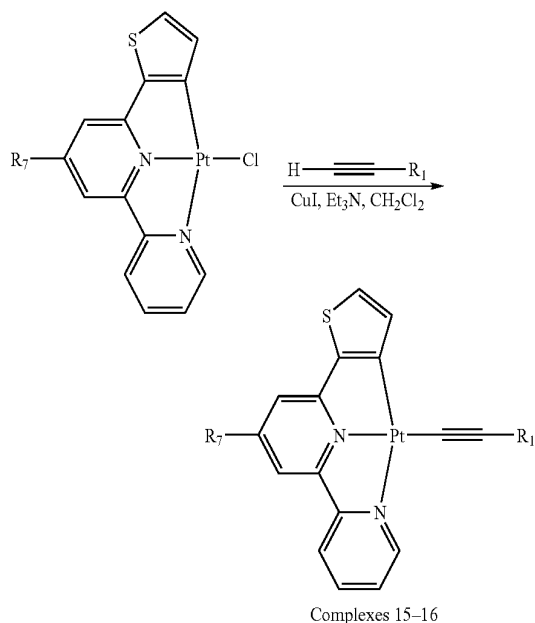
35 We have synthesized a number of the tridentate cyclometalated Pt(II) arylacetylides



65 with different substituents on the aryl rings which are depicted in either Formula I or II. The synthetic methods are shown in Scheme 1:

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Scheme 1



8

The tridentate (C[∞]N[∞]N) ligands were prepared according to Kröhnke's method (Kröhnke, F. *Synthesis* 1 (1976)). The various acetylenes were prepared with Sonogashira's method (Takahashi, S. et al. *Synthesis* 627 (1980)). The Cl-ligated precursors [(C[∞]N[∞]N)PtCl] were prepared under Constable's condition (Constable, E. C.; et al. *J. Chem. Soc., Dalton Trans.* 2251 (1992) and 443 (1990)). The desired complexes were synthesized by Cu(I)-organic amine-catalyzed reactions. For example, to a mixture of [(C[∞]N[∞]N)PtCl] (0.33 mmol), terminal acetylene (1 mmol) and Et₃N (3 mL) in degassed CH₂Cl₂ (30 mL) solution was added CuI (5 mg). The suspension was stirred for 12 h under a nitrogen atmosphere at room temperature and in the absence of light. The resultant mixture was rotatory-evaporated to dryness. The crude product was purified by flash chromatography (neutral Al₂O₃, CH₂Cl₂ as eluent) and/or recrystallization from dichloromethane/diethyl ether. Examples are listed in Table I but not limited by them:

TABLE I

Complex	Chemical Structure	Characterization Data
1		orange crystalline powder. FAB MS: 524 (M ⁺ + H), 523 (M ⁺); ¹ H NMR (300 MHz, CDCl ₃ , 22° C., TMS): δ = 9.02 (d, 1H, J=5.3 Hz), 7.94 (t, 1H, J=7.8 Hz), 7.87 (d, 1H, J=7.4 Hz), 7.82 (d, 1H, J=8.0 Hz), 7.68 (t, 1H, J=8.0 Hz), 7.51 (d, 1H, J=7.7 Hz), 7.45 (t, 1H, J=7.5 Hz), 7.41 (d, 1H, J=8.1 Hz), 7.21 (d, 1H, J=7.2 Hz), 7.15 (t, 1H, J=7.4 Hz), 7.02 (t, 1H, J=7.5 Hz), 0.27 (s, 9H).
2		orange crystalline powder. FAB MS: 528 (M ⁺ + H), 527 (M ⁺); ¹ H NMR (300 MHz, CDCl ₃ , 22° C., TMS): δ = 9.15 (d, 1H, J=4.3 Hz), 7.97 (m, 2H), 7.85 (d, 1H, J=8.1 Hz), 7.75 (t, 1H, J=8.0 Hz), 7.55 (m, 3H), 7.48 (m, 2H), 7.31 (m, 3H), 7.17 (t, 2H, J=7.0 Hz), 7.05 (t, 1H, J=7.4 Hz).

TABLE I-continued

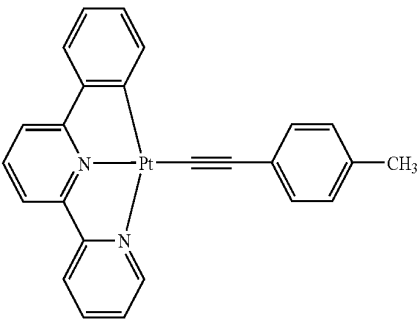
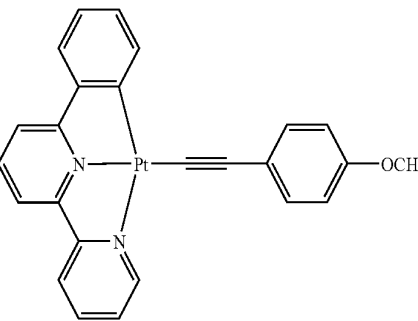
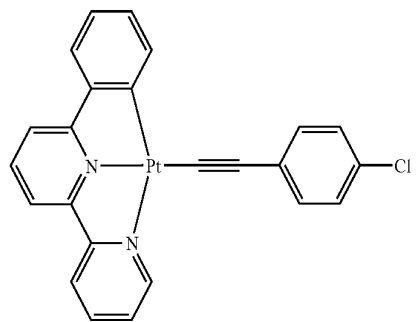
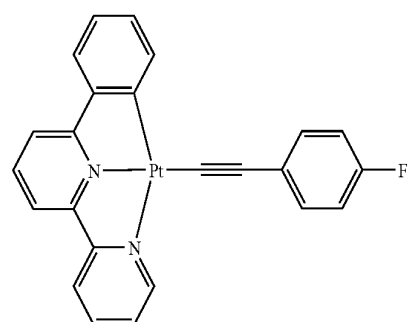
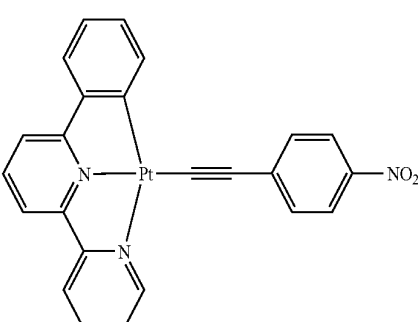
Complex	Chemical Structure	Characterization Data
3		<p>orange-red crystalline powder. FAB MS: 542 ($M^+ + H$), 541 (M^+); 1H NMR (300 MHz, $CDCl_3$, 22° C., TMS): δ = 9.07 (d, 1H, $J=4.3$ Hz), 7.92 (m, 2H), 7.82 (d, 1H, $J=7.8$ Hz), 7.69 (t, 1H, $J=8.0$ Hz), 7.53 (d, 1H, $J=7.3$ Hz), 7.43 (m, 4H), 7.27 (d, 1H, $J=6.3$ Hz), 7.15 (t, 1H, $J=7.3$ Hz), 7.10 (d, 2H, $J=7.9$ Hz), 7.02 (t, 1H, $J=7.5$ Hz), 2.35 (s, 3H).</p>
4		<p>red crystalline powder. FAB MS: 558 ($M^+ + H$), 557 (M^+); 1H NMR (300 MHz, $CDCl_3$, 22° C., TMS): δ = 9.12 (d, 1H, $J=5.2$ Hz), 7.95 (m, 2H), 7.83 (d, 1H, $J=7.9$ Hz), 7.72 (t, 1H, $J=8.0$ Hz), 7.50 (m, 3H), 7.49 (d, 2H, $J=8.8$ Hz), 7.30 (d, 1H, $J=6.6$ Hz), 7.16 (t, 1H, $J=7.4$ Hz), 7.03 (t, 2H, $J=7.4$ Hz), 6.84 (d, 2H, $J=8.8$ Hz), 3.82 (s, 3H).</p>
5		<p>orange-red crystalline powder. FAB MS: 562 (M^+); 1H NMR (300 MHz, $CDCl_3$, 22° C., TMS): δ = 9.05 (d, 1H, $J=5.1$ Hz), 7.94 (t, 1H, $J=7.8$ Hz), 7.87 (d, 1H, $J=7.5$ Hz), 7.81 (d, 1H, $J=7.9$ Hz), 7.71 (t, 1H, $J=8.0$ Hz), 7.52 (d, 1H, $J=7.7$ Hz), 7.46 (m, 2H), 7.45 (d, 1H, $J=8.5$ Hz), 7.27 (d, 1H, $J=4.2$ Hz), 7.23 (d, 2H, $J=8.8$ Hz), 7.15 (t, 1H, $J=7.4$ Hz), 7.03 (t, 1H, $J=7.4$ Hz).</p>
6		<p>black-red crystals. FAB MS: 546 ($M^+ + H$), 545 (M^+); 1H NMR (300 MHz, $CDCl_3$, 22° C., TMS): δ = 9.12 (d, 1H, $J=5.2$ Hz), 7.97 (t, 1H, $J=7.9$ Hz), 7.92 (d, 1H, $J=7.6$ Hz), 7.84 (d, 1H, $J=8.0$ Hz), 7.74 (t, 1H, $J=8.0$ Hz), 7.56–7.47 (m, 5H), 7.32 (d, 1H, $J=7.6$ Hz), 7.17 (t, 1H, $J=7.4$ Hz), 7.05 (t, 1H, $J=7.5$ Hz), 6.98 (pseudo-t, 2H, $J=7.7$ Hz).</p>
7		<p>orange crystalline powder. FAB MS: 573 ($M^+ + H$), 572 (M^+); 1H NMR (300 MHz, d_6-DMSO, 22° C., TMS): δ = 8.98 (d, 1H, $J=4.5$ Hz), 8.48 (d, 1H, $J=8.0$ Hz), 8.32 (t, 1H, $J=8.0$ Hz), 8.20 (d, 1H, $J=7.4$ Hz), 8.14 (d, 2H, $J=8.8$ Hz), 8.11 (t, 1H, $J=8.0$ Hz), 7.99 (d, 1H, $J=7.8$ Hz), 7.83 (t, 1H, $J=7.5$ Hz), 7.68 (d, 1H, $J=7.3$ Hz), 7.62 (d, 1H, $J=7.4$ Hz), 7.58 (d, 2H, $J=8.9$ Hz), 7.11 (t, 1H, $J=7.3$ Hz), 7.05 (t, 1H, $J=7.3$ Hz).</p>

TABLE I-continued

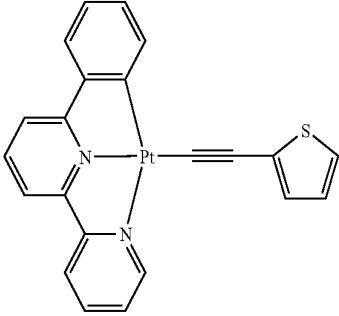
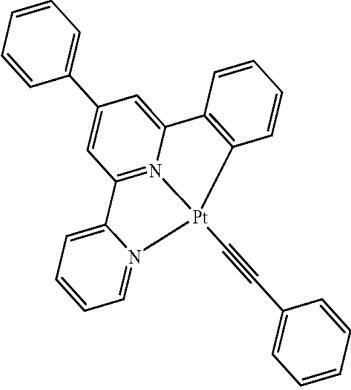
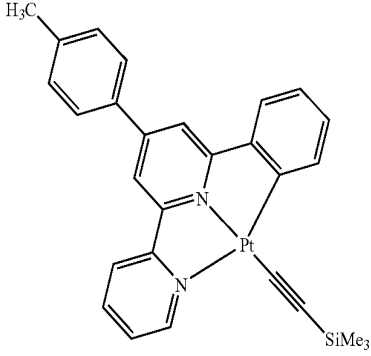
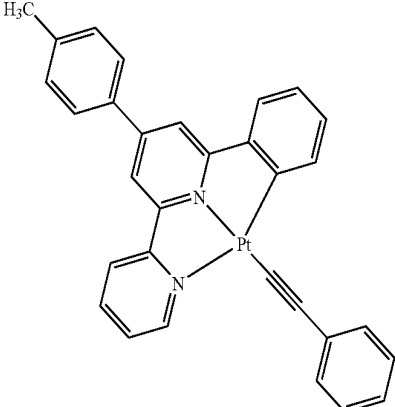
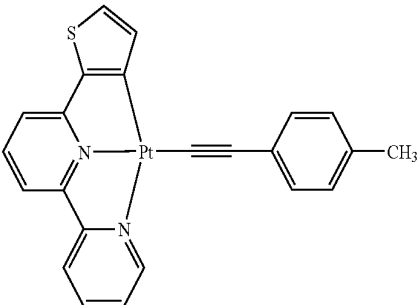
Complex	Chemical Structure	Characterization Data
8		brown crystals. FAB MS: 534 ($M^+ + H$), 533 (M^+); 1H NMR (300 MHz, d_6 -DMSO, 22° C., TMS): δ = 8.94 (d, 1H, J =5.1 Hz), 8.46 (d, 1H, J =7.9 Hz), 8.30 (t, 1H, J =7.8 Hz), 8.17 (d, 1H, J =7.6 Hz), 8.08 (t, 2H, J =7.9 Hz), 7.96 (d, 1H, J =7.9 Hz), 7.84 (t, 1H, J =6.4 Hz), 7.66 (d, 1H, J =6.2 Hz), 7.59 (d, 1H, J =7.4 Hz), 7.21 (d, 1H, J =4.9 Hz), 7.10 (t, 1H, J =7.3 Hz), 7.03 (t, 1H, J =7.3 Hz), 6.97–6.92 (m, 2H).
9		orange crystalline powder. FAB MS: 604 ($M^+ + H$), 603 (M^+); 1H NMR (300 MHz, d_6 -DMSO, 22° C., TMS): δ = 8.99 (d, 1H, J =4.8 Hz), 8.68 (d, 1H, J =8.0 Hz), 8.50 (s, 1H), 8.32 (t, 1H, J =7.7 Hz), 8.24 (s, 1H), 8.08–8.05 (m, 2H), 7.84–7.78 (m, 2H), 7.70 (d, 1H, J =7.9 Hz), 7.61–7.55 (m, 3H), 7.36 (d, 1H, J =7.2 Hz), 7.26 (t, 1H, J =7.6 Hz), 7.17–7.01 (m, 3H).
10		orange crystalline powder. FAB MS: 614 ($M^+ + H$), 613 (M^+); 1H NMR (300 MHz, $CDCl_3$, 22° C., TMS): δ = 8.90 (d, 1H, J =5.4 Hz), 7.99 (t, 1H, J =7.5 Hz), 7.90 (d, 1H, J =8.0 Hz), 7.76 (d, 1H, J =6.2 Hz), 7.60–7.57 (m, 3H), 7.40–7.31 (m, 4H), 7.26 (d, 1H, J =6.1 Hz), 7.03–6.98 (m, 2H), 2.48 (s, 3H), 0.33 (s, 9H).
11		orange crystalline powder. FAB MS: 618 ($M^+ + H$), 617 (M^+); 1H NMR (300 MHz, d_6 -DMSO, 22° C., TMS): δ = 9.04 (d, 1H, J =5.0 Hz), 8.69 (d, 1H, J =7.9 Hz), 8.50 (s, 1H), 8.34 (t, 1H, J =7.7 Hz), 8.24 (s, 1H), 8.01 (d, 2H, J =7.5 Hz), 7.84–7.74 (m, 3H), 7.40–7.30 (m, 4H), 7.30 (t, 2H, J =7.5 Hz), 7.18–7.06 (m, 3H), 2.40 (s, 3H).

TABLE I-continued

Complex	Chemical Structure	Characterization Data
12		red crystals. FAB MS: 632 ($M^+ + H$), 631 (M^+); 1H NMR (300 MHz, d_6 -DMSO, 22° C., TMS): δ = 9.05 (d, 1H, $J=4.9$ Hz), 8.56 (d, 1H, $J=8.0$ Hz), 8.34 (s, 1H), 8.20 (t, 1H, $J=7.9$ Hz), 8.00 (s, 1H), 7.85 (d, 2H, $J=8.1$ Hz), 7.76–7.68 (m, 2H), 7.62 (d, 1H, $J=8.2$ Hz), 7.31 (d, 2H, $J=8.1$ Hz), 7.25 (d, 2H, $J=8.0$ Hz), 7.07–6.97 (m, 4H), 2.39 (s, 3H), 2.28 (s, 3H).
13		orange crystalline powder. FAB MS: 634 ($M^+ + H$), 633 (M^+); 1H NMR (300 MHz, d_6 -DMSO, 22° C., TMS): δ = 9.00 (d, 1H, $J=4.9$ Hz), 8.69 (d, 1H, $J=8.1$ Hz), 8.48 (s, 1H), 8.32 (t, 1H, $J=7.9$ Hz), 8.26 (s, 1H), 8.08 (d, 2H, $J=8.8$ Hz), 8.06–7.81 (m, 2H), 7.72 (d, 1H, $J=7.1$ Hz), 7.35 (d, 2H, $J=7.1$ Hz), 7.26 (t, 2H, $J=7.6$ Hz), 7.16–7.04 (m, 5H), 3.84 (s, 3H).
14		brown crystalline powder. FAB MS: 638 (M^+); 1H NMR (300 MHz, d_6 -DMSO, 22° C., TMS): δ = 8.99 (broad, 1H), 8.64 (d, 1H, $J=7.7$ Hz), 8.47 (s, 1H), 8.31 (t, 1H, $J=7.6$ Hz), 8.21 (s, 1H), 8.09 (d, 2H, $J=8.1$ Hz), 7.82–7.68 (m, 3H), 7.62 (d, 2H, $J=8.2$ Hz), 7.38 (d, 2H, $J=7.2$ Hz), 7.28 (t, 2H, $J=7.3$ Hz), 7.18 (t, 1H, $J=7.0$ Hz), 7.08–7.03 (m, 2H).
15		brown needles. FAB MS: 534 ($M^+ + H$), 533 (M^+); 1H NMR (300 MHz, d_6 -DMSO, 22° C., TMS): δ = 9.01 (d, 1H, $J=5.0$ Hz), 8.46 (d, 1H, $J=8.2$ Hz), 8.35 (t, 1H, $J=7.9$ Hz), 8.02 (d, 1H, $J=7.6$ Hz), 7.96 (t, 1H, $J=7.8$ Hz), 7.85 (t, 1H, $J=6.4$ Hz), 7.72 (d, 1H, $J=4.9$ Hz), 7.56 (d, 1H, $J=7.3$ Hz), 7.38 (d, 2H, $J=7.0$ Hz), 7.29 (t, 2H, $J=7.6$ Hz), 7.17 (t, 1H, $J=7.3$ Hz), 7.11 (d, 1H, $J=4.6$ Hz).

TABLE I-continued

Complex	Chemical Structure	Characterization Data
16		brown needles. FAB MS: 548 ($M^+ + H$), 547 (M^+); 1H NMR (300 MHz, d_6 -DMSO, 22° C., TMS): δ = 9.03 (d, 1H, $J=5.2$ Hz), 8.47 (d, 1H, $J=8.2$ Hz), 8.34 (t, 1H, $J=7.2$ Hz), 8.02 (d, 1H, $J=7.9$ Hz), 7.96 (t, 1H, $J=7.7$ Hz), 7.86 (t, 1H, $J=6.3$ Hz), 7.73 (d, 1H, $J=4.9$ Hz), 7.56 (d, 1H, $J=7.6$ Hz), 7.26 (d, 2H, $J=7.9$ Hz), 7.13 (d, 1H, $J=4.6$ Hz), 7.11 (d, 2H, $J=7.9$ Hz), 2.30 (s, 3H).

Thermal-Stability of the Complexes

Ideally, a low molecular weight component to be used in OLEDs should be sublimable and stable at standard deposition conditions. Importantly, many of the complexes in the present invention are thermally stable up to ~400° C. and decompose to give metallic platinum only at temperature above 420° C. (see TGA curves for complexes **2** and **15** in FIGS. **2** and **3** respectively).

The observed thermal stability of these complexes described in the present invention which contain a tridentate cyclometalating ligand, contrasts sharply with the bidentate Pt(thpy)₂ emitter described by Lamasky, et al. which are unstable upon sublimation.

Spectroscopic Properties of the Complexes

In present invention, the ligation of an acetylide group to the (C[^]N[^]N)Pt(II) moiety neutralizes the positive charge centered on Pt(II), enhances the stability of these complexes, and moreover, shifts the ³MLCT emission bathochromically. The family of complexes depicted by Formula I and II display strong orange to red photoluminescence in fluid solution. Examples of characteristic absorption and emission band of these emitters in present invention are summarized in Table II:

TABLE II

Complex (see Table I)	Absorption MLCT Band/nm ($\epsilon/mol\ dm^{-1}\ cm^{-1}$)	Emission λ_{max}/nm ($\tau_0/\mu s; \Phi_0$)
1	427 (5490), 450 (sh, 4920), 505 (sh, 430)	570 (0.31; 0.041)
2	434 (5180), 455 (4940), 510 (sh, 470)	582 (0.39; 0.037)
3	440 (5090), 465 (sh, 4950), 515 (sh, 1190)	600 (0.17; 0.019)
4	440 (4200), 460 (sh, 4220), 520 (sh, 1570)	630
5	432 (8670), 455 (sh, 8310), 515 (sh, 720)	598 (0.53; 0.076)
6	433 (4880), 453 (sh, 4760), 515 (sh, 640)	585 (0.33; 0.033)
7	415 (sh, 12930), 510 (sh, 540)	560 (0.93; 0.077)
15	436 (4970), 460 (sh, 4490), 515 (sh, 460)	615 (1.02; 0.029), 660 (sh)
16	442 (5010), 465 (sh, 4800), 520 (sh, 670)	616 (0.91; 0.025), 660 (sh)

Notice that all the data were collected with degassed CH₂Cl₂ solution at 298 K. Exemplified absorption and emission spectra for complexes **2** and **15** are shown in FIGS. **4** and **5** respectively. The intense orange to red phosphorescence of the complexes in the present invention together with their stability towards sublimation means that these materials can be used as emitters or dopants in high-performance OLEDs.

Organic Light-Emitting Devices

The devices using the complexes in present invention, as fabricated by Prof. S. T. Lee of City University of Hong Kong, possess the multi-layer heterostructure shown in FIG. **6**.

All the organic layers including the Pt complexes described above and cathodes were vacuum-deposited onto the ITO substrate. NPB (N,N'-di-1-naphthyl-N,N'-diphenyl-benzidine) and Alq₃ (q=8-hydroxyquinolyl) were used as the hole transporting and electron transporting layer, respectively. BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, bathocuproine) was used to confine excitons within the luminescent zone. Magnesium silver alloy was applied as the cathode. The selected Pt complex was doped into the conductive host material CBP (4,4'-N,N'-dicarbazole-biphenyl) as phosphorescent emitter. The optimal doping levels were adjusted at 2, 4 and 6% and electroluminescence from the Pt complexes were observed.

EXAMPLES

A number of examples are listed below to further illustrate the invention

Example 1

Complex **2** was used as the emitter. Typical electroluminescent spectrum, current-voltage (I-V) and luminance-volt-

age (B-V) curves and luminescent efficiency-current density curve of the device with a doping level of 2% are shown in FIG. **7**. Turn-on voltage: ~5 V; maximum luminance: 9600 Cd/m² at 12 V; maximum efficiency: 4.2 Cd/A at 25 mA/cm². In the electroluminescent spectrum, a peak at 430 nm besides the band at 560-630 nm is observed, indicating insufficient energy transfer between the host and the dopant.

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Example 2

The performance of the device using complex **2** as emitter with a doping level of 4% are shown in FIG. **8**. Turn-on voltage: ~5 V; maximum luminance: 7900 Cd/m² at 10 V; maximum efficiency: 2.4 Cd/A at 30 mA/cm². At this doping level, energy transfer between the host and the dopant is saturated, thus emission from the host is avoided.

Example 3

Complex **3** was used as the emitter. The performance of the device with a doping level of 4% are shown in FIG. **9**. A bathochromic electroluminescence is observed (λ_{max} 580 nm), which is coinciding with the trend of the photoluminescence shown by these complexes in room-temperature CH₂Cl₂ solutions. Turn-on voltage: ~5 V; maximum luminance: 4000 Cd/m² at 12 V; maximum efficiency: 1.4 Cd/A at 20 mA/cm².

Example 4

Complex **16** was used as the emitter. The performance of the device with a doping level of 4% are shown in FIG. **10**. The electroluminescence is red with vibronically structured emission spectrum (λ_{max} 610 nm, 660 nm). Turn-on voltage: ~5 V; maximum luminance: 3200 Cd/m² at 13 V; maximum efficiency: 1.0 Cd/A at 30 mA/cm².

Generally, the organometallic light-emitting materials as depicted in FIGS. I and II in present invention are demonstrated to be novel electrophosphorescent emitters applicable to high-efficiency and -brightness orange to red light OLEDs.

While it is apparent that the embodiments of the invention herein disclosed are well suited to fulfill the objectives stated above, it will be appreciated that numerous modifications and other embodiments may be implemented by those skilled in the art, and it is intended that the appended claims cover all such modifications and embodiments that fall within the true spirit and scope of the present invention.

A number of references have been cited and the entire disclosures of which are incorporated herein by reference.

What is claimed is:

1. An apparatus, comprising:
an electron transporting layer;

a hole transporting layer; and

a light emitting layer comprising one or more light emitting compounds, wherein the light emitting compounds include an acetylide group and a tridentate (C⁻N⁻N) ligand coordinated to a Group 10 metal; wherein the light emitting layer is disposed between the electron transporting layer and the hole transporting layer.

2. The apparatus of claim 1, wherein the light emitting compounds further comprise one or more platinum-acetylide groups.

3. The apparatus of claim 1, wherein the Group 10 metal is platinum and the tridentate ligand comprises a deprotonated phenyl carbanion and 2,2'-bipyridine.

4. The apparatus of claim 1, wherein the light emitting layer is configured to emit light comprising a wavelength in the range of 550-630 nm.

5. The apparatus of claim 1, wherein the light emitting compounds are thermally stable up to about 400 degrees C.

6. A process, comprising:

disposing a hole transporting layer on an anode layer;

disposing a host material doped with one or more light emitting compounds on the hole transporting layer,

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wherein the light emitting compounds include an acetylide group and a tridentate (C⁻N⁻N) ligand coordinated to a Group 10 metal;

disposing a bathocuproine buffer layer on the light emitting layer; and

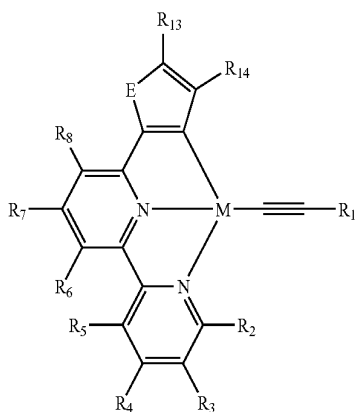
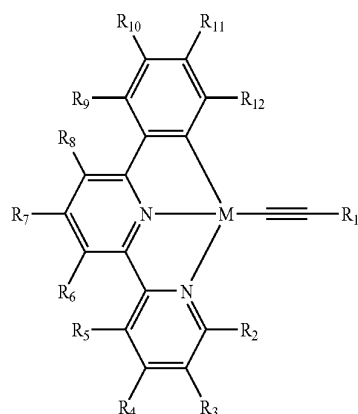
disposing an electron transporting layer on the bathocuproine layer.

7. The process of claim 6, wherein the light emitting compounds comprise one or more platinum-acetylide groups.

8. The process of claim 6, wherein the Group 10 metal is platinum and the tridentate ligand comprises a deprotonated phenyl carbanion and 2,2'-bipyridine.

9. The process of claim 6, wherein disposing is carried out via vacuum deposition or spin-casting.

10. The apparatus of claim 1, wherein the one or more light emitting compounds are according to formula I or II,



wherein:

E is a Group 16 element;

M is a Group 10 metal;

R₁ is selected from the group consisting of hydrogen, halogen, alkyl, substituted alkyl, aryl, and substituted aryl; or R₁ is (C≡C)_nR₁₅, wherein:

(C≡C) is a carbon-carbon triple bond;

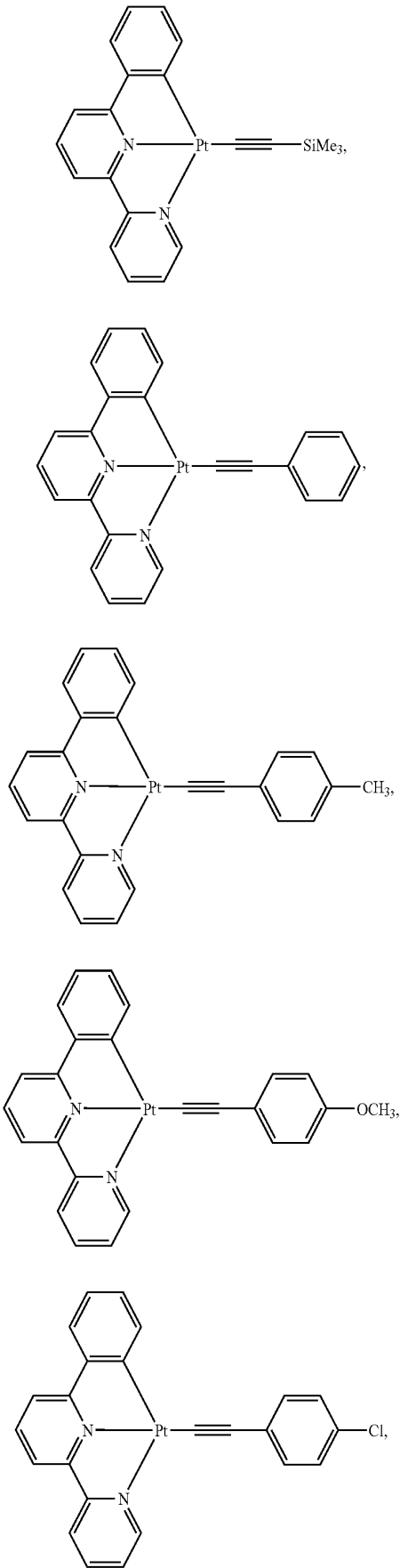
n is selected from 1 to 10; and

R₁₅ is selected from alkyl, aryl, substituted aryl, and tri(alkyl)silyl; and

R₂-R₁₄ are each independently selected from the group consisting of hydrogen, halogen, alkyl, substituted alkyl, aryl, and substituted aryl.

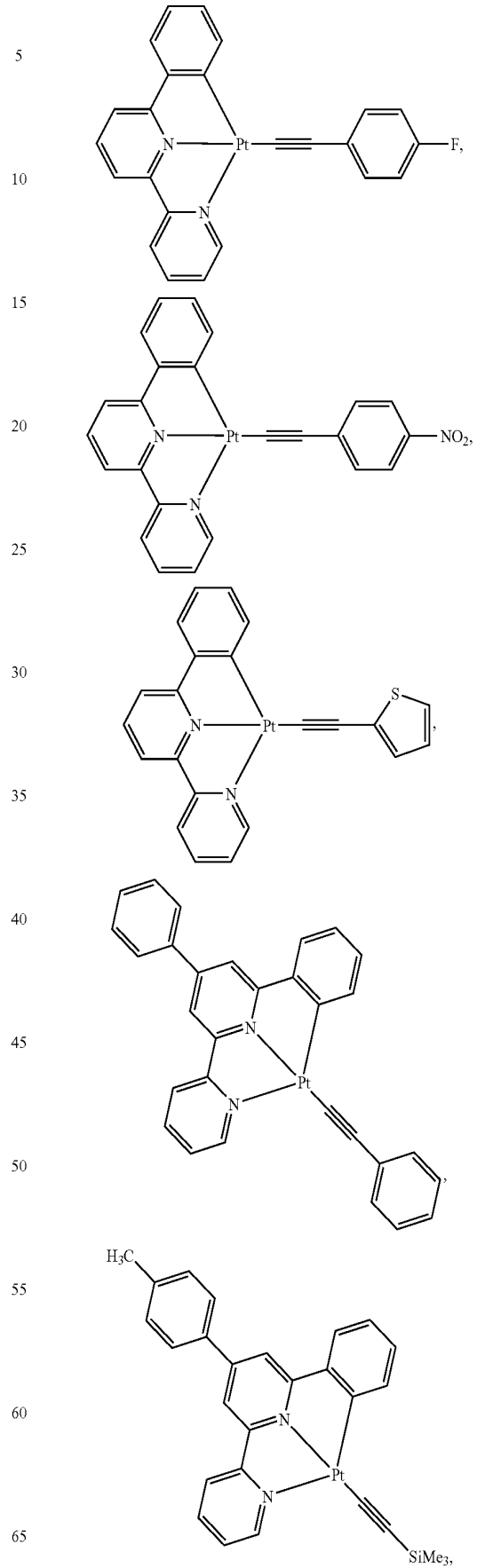
11. The apparatus of claim 1, wherein the one or more light emitting compounds are selected from the group consisting of,

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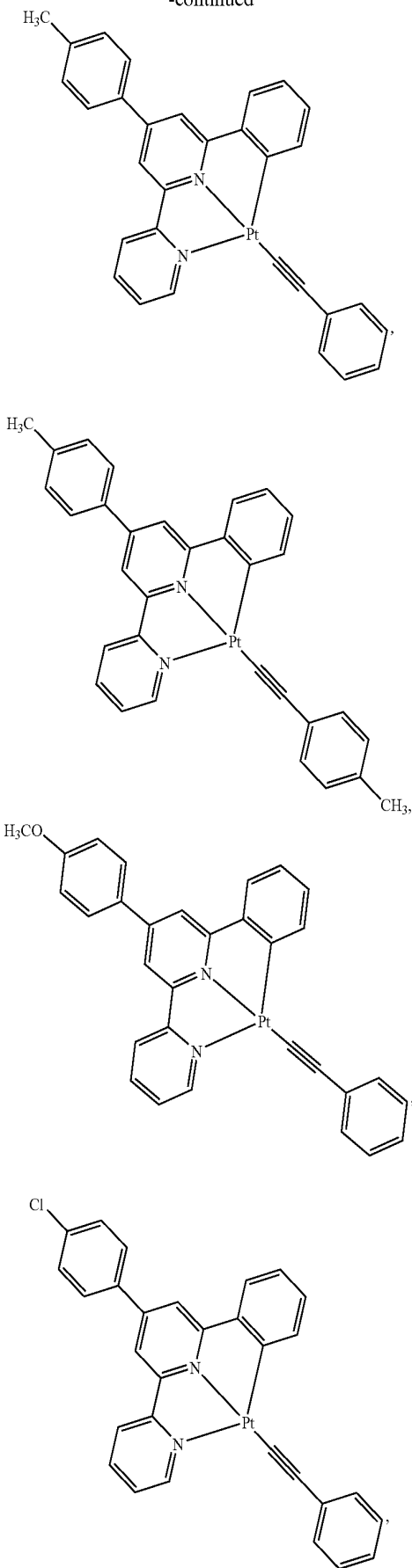
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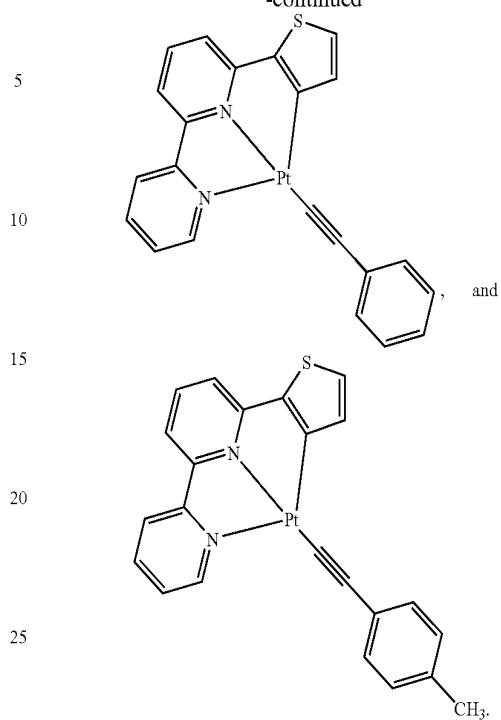
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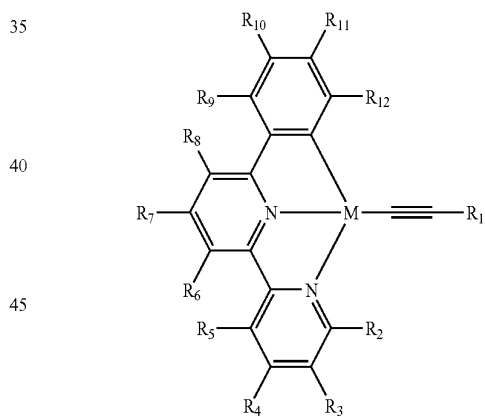
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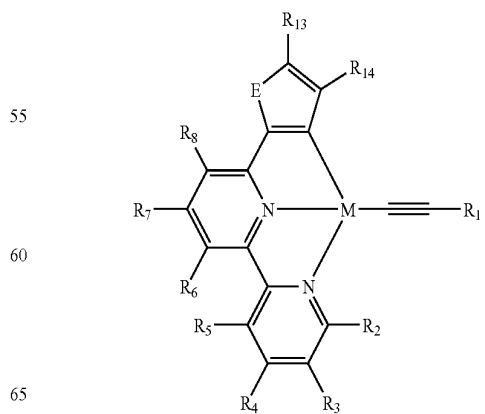


12. The process of claim 6, wherein the one or more light emitting compounds are according to formula I or II,

I



II



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wherein:

E is a Group 16 element;

M is a Group 10 metal;

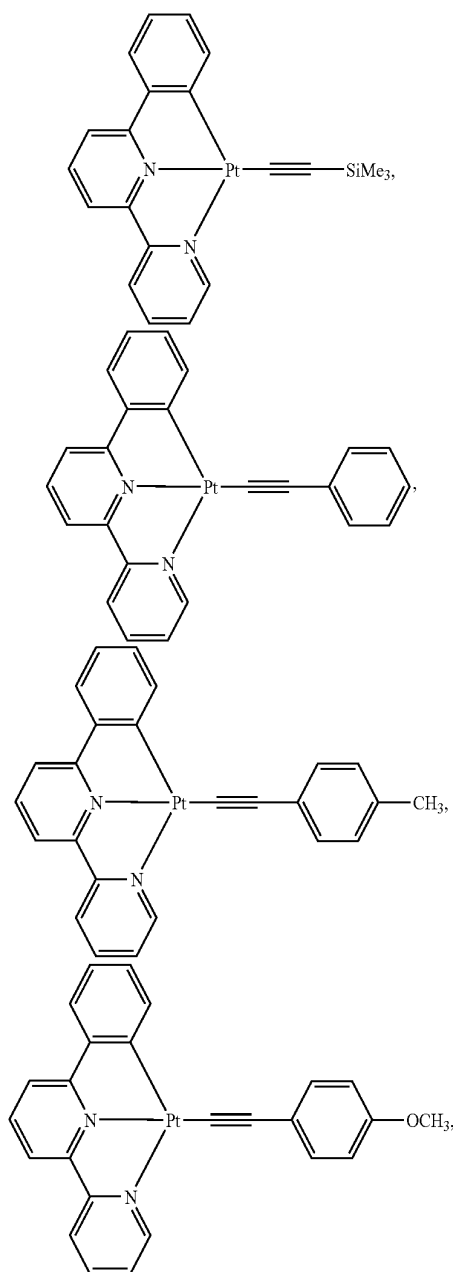
R₁ is selected from the group consisting of hydrogen, halogen, alkyl, substituted alkyl, aryl, and substituted aryl; orR₁ is (C≡C)_nR₁₅, wherein:

(C≡C) is a carbon-carbon triple bond;

n is selected from 1 to 10; and

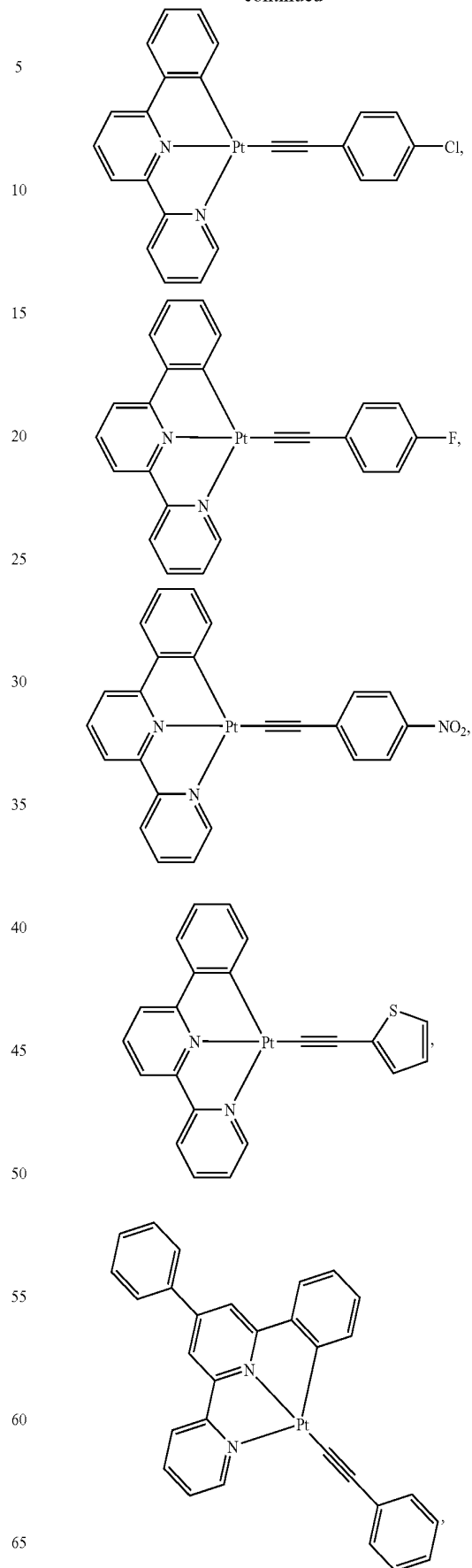
R₁₅ is selected from alkyl, aryl, substituted aryl, and tri(alkyl)silyl; andR₂-R₁₄ are each independently selected from the group consisting of hydrogen, halogen, alkyl, substituted alkyl, aryl, and substituted aryl.

13. The process of claim 6, wherein the one or more light emitting compounds are selected from the group consisting of,



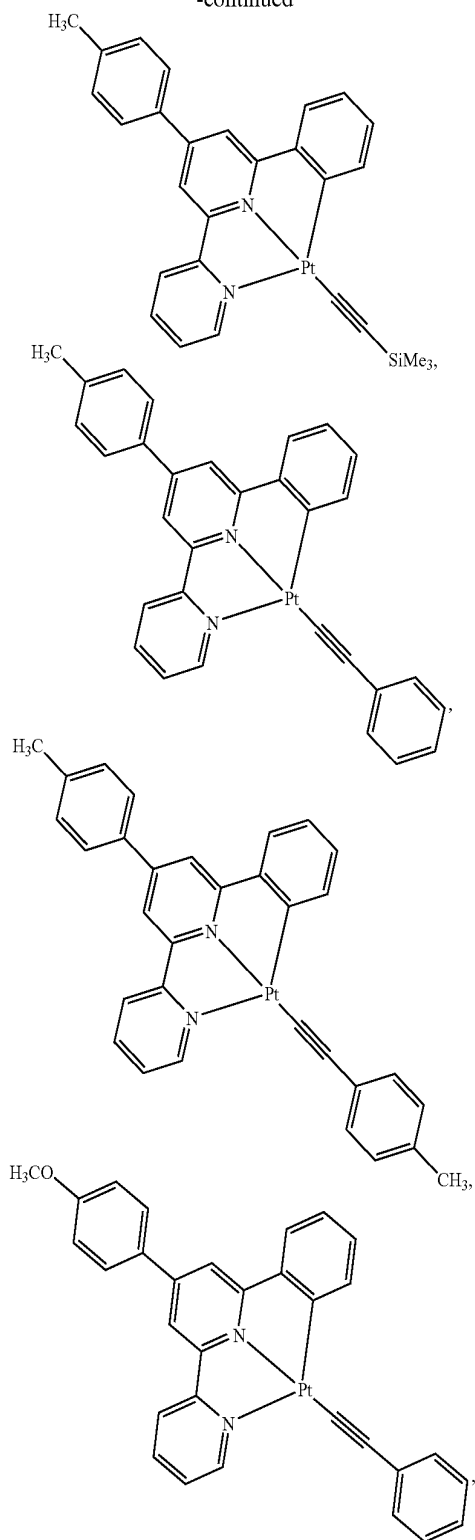
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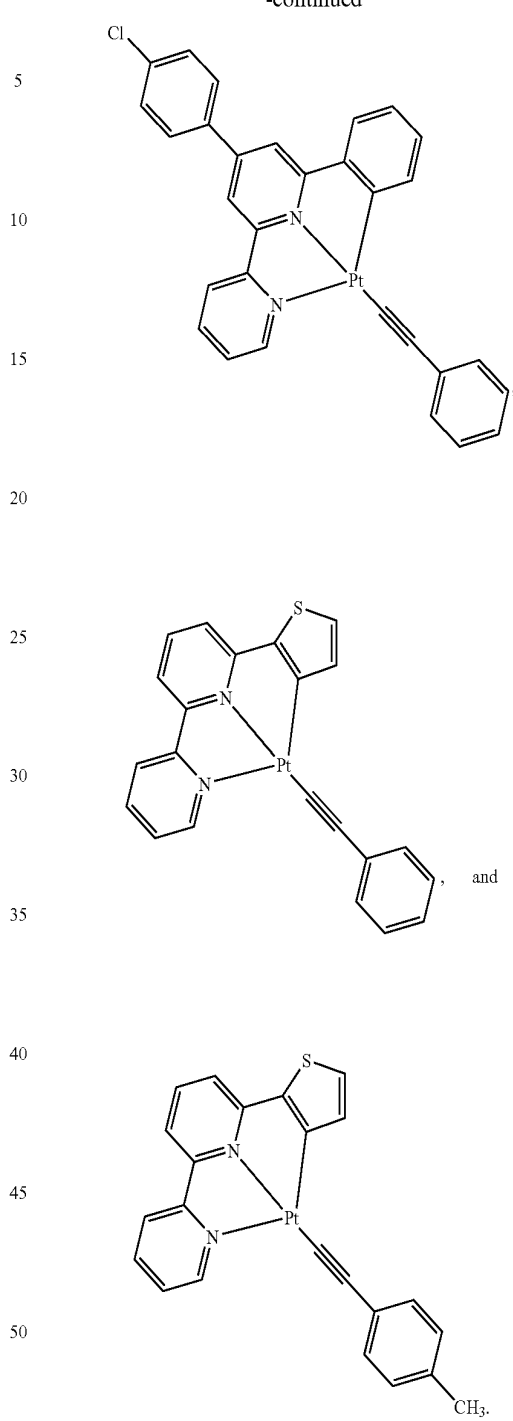
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