

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

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
6 January 2011 (06.01.2011)

(10) International Publication Number
WO 2011/000873 A1

PCT

(51) International Patent Classification:

C07F 15/00 (2006.01) **H05B 33/14** (2006.01)
C08F 230/04 (2006.01) **H01L 51/00** (2006.01)
C09K 11/06 (2006.01)

(21) International Application Number:

PCT/EP2010/059289

(22) International Filing Date:

30 June 2010 (30.06.2010)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/222,275 1 July 2009 (01.07.2009) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: PHOSPHORESCENT PLATINUM COMPLEXES, THEIR MONOMERS AND COPOLYMERS, AND USES IN ORGANIC ELECTRONIC DEVICES

(57) Abstract: The inventions disclosed and described herein relate to phosphorescent platinum complexes that can be optionally substituted and/or optionally bonded to polymerizable groups, including styrene, acrylate, or norbornene groups, the phosphorescent polynorbornene copolymers made therefrom, and electronic devices comprising the platinum complexes and their copolymers, including organic light emitting diodes. Methods of making the Platinum complexes and the related copolymers and/or devices are also described.



WO 2011/000873 A1

Phosphorescent platinum complexes, their monomers and copolymers, and
uses in organic electronic devices

STATEMENT OF GOVERNMENT LICENSE RIGHTS

The inventors received partial funding support through the STC Program of the National Science Foundation under Agreement Number DMR-020967 and the Office of Naval Research through a MURI program, Contract Award
5 Number 68A-1060806. The Federal Government may retain certain license rights in this invention.

RELATED APPLICATIONS

This application claims the priority of U.S. Provisional Application No. 61/222,275 filed 01 July 2009. The entire disclosure of the predecessor
10 application is hereby incorporated herein by reference in its entirety.

TECHNICAL FIELD OF THE INVENTION

The various inventions disclosed, described, and/or claimed herein relate to the field of platinum complexes and their uses, including uses of those platinum complexes in connection with the manufacture of organic electronic devices,
15 electro-optical materials, and organic light-emitting diodes (OLEDs).\

BACKGROUND OF THE INVENTION

Luminescent metal complexes have been investigated for use as a light emitting component of organic light-emitting diodes (OLEDs) and related organic electronic devices. Such OLEDs can contain a light emissive layer
20 comprising the luminescent metal complex guest dispersed or dissolved in a host/carrier material capable of conducting holes, electrons, and/or excitons into contact with the metal complex guest. The light emissive layer is often disposed between additional layers of the OLED devices, such as anodic layers comprising a hole transport material and cathodic layers comprising an electron
25 transport material. Upon application of voltage/current across the OLED, holes and electrons are conducted into the emissive layer, where they can combine to form excitons and/or stimulate the formation of excited states of the metal complexes.

Upon excitation of the metal complexes, singlet excited states of the metal
30 complexes are often initially formed, which can in some cases fluoresce (relatively inefficiently). However, the strong spin-orbit coupling of third row

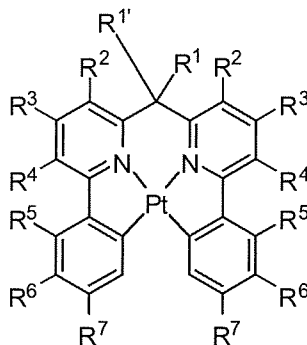
transition metal complexes can induce efficient intersystem crossing from the singlet to the triplet excited states of the excited metal complexes, which can phosphoresce, typically more efficiently. Although not being bound by theory, it is believed that using such 3d row phosphorescent transition metal complexes as
5 the emission centers in OLEDs can allow for the efficient collection of and phosphorescent emission from a much higher percentage of the singlet and triplet excitons initially generated upon electrical excitation of an OLED device than would typically be obtained with fluorescent emitters.

In much of the prior art relating to the manufacture of such OLEDs,
10 relatively low molecular weight “monomeric” transition metal complexes are applied and/or dispersed into hole, electron, and/or exciton carrying host materials via vacuum deposition processes to form the emissive layers. Unfortunately, such vacuum deposition processes can be difficult and/or expensive, and in some cases the emissive metal complexes can be thermally
15 degraded during deposition, or undesirably migrate within the device and/or crystallize in the device in response to device heating, which can lead to quenching of the desired emissions. Accordingly, there is still a need in the art for improved and/or more thermally stable luminescent materials for the manufacture of OLEDs.

20 Recently, alternative approaches for incorporation of phosphorescent metal complexes into OLEDs have also been explored. For example, covalent anchoring of phosphorescent metal complexes onto polymer backbones can provide solution processable polymeric phosphorescent materials that can potentially be photo-patterned and can resist migration and/or crystallization of
25 the luminescent materials, or phase separations from the host materials. In practice however, devices based on currently known polymeric luminescent materials have often only yielded lower initial performance than OLED devices based on related vacuum-deposited low molecular weight luminescent materials. Accordingly, there remains a need in the art for new and improved polymeric
30 and/or co polymeric luminescent materials and/or compositions that can provide improved processability, performance, cost, and stability in use in organic electronic devices. It is to that end that the various embodiments of the inventions described below are directed.

SUMMARY OF THE INVENTION

The various inventions and/or their embodiments disclosed herein relate to and include the Platinum complexes having polycyclic ligands as shown by Formula (I) below, and their various uses:



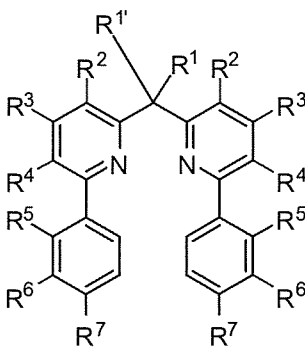
(I)

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wherein various selections of the R^x peripheral substituents shown in the drawing are further described and defined below.

In some embodiments, the inventions disclosed herein relate to the corresponding free ligands (II) that can be used to prepare luminescent complexes of Platinum and other similar transition metals, and methods for their preparation.

10



(II)

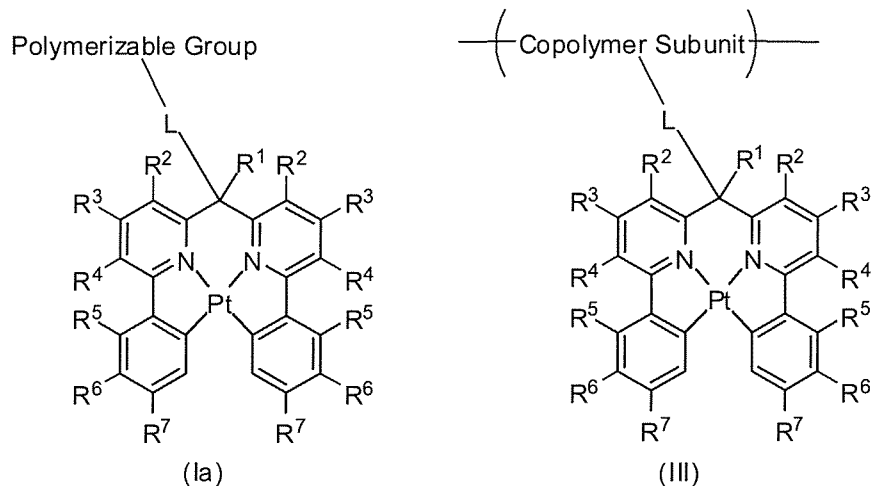
If the R^x peripheral substituents of compounds of classes (I) and (II) are suitably chosen, low molecular weight metallic complexes with desirable emission properties and also high thermal and chemical stability result, and can be used in either vacuum deposition or solution processes for forming OLEDs.

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In many embodiments of the inventions, one or more of the R^x groups, including the R^1 and $R^{1'}$ groups provide a link to a polymerizable group and/or a polymer or copolymer, to form the polymerizable monomers(Ia) or copolymers

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comprising at least one polymerized subunit having structure (III) as shown below



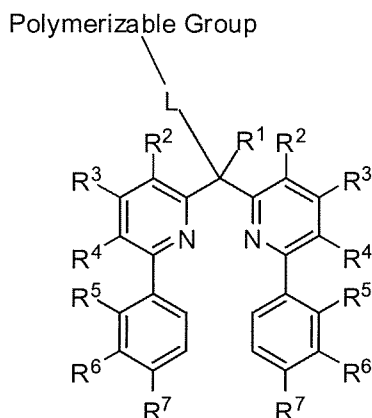
wherein

- 5 a) the polymerizable group comprises a functional group that can be copolymerized with other comonomers, to form copolymers comprising in their backbone at least one of the copolymer subunits;
- b) L links the polymerizable group or copolymer subunit to the platinum complex;
- 10 c) R¹ is fluoride, or a C₁-C₁₂ organic group;
- d) R², R³, and R⁴ are independently selected from hydrogen and inorganic or organic substituent groups;
- e) R⁵, R⁶, and R⁷ are independently selected from hydrogen, inorganic, and organic substituent groups, or together two of R⁵, R⁶, and R⁷ form a benzene ring that can be optionally substituted by one or two independently selected
- 15 inorganic or organic groups.

The inventions described herein also relate to free ligand compounds of class (II) used to prepare transition metal complexes, and methods for the preparation of such free ligand compounds. For example, in some embodiments

20 the inventions described herein relate to a compound comprising a polymerizable group linked to a potentially multi-dentate ligand for transition metals, having the formula:

- 5 -



wherein

- a) the polymerizable group comprises from 2 to 20 carbon atoms, and a functional group that can be copolymerized with other comonomers,
 - a. L is a C₁-C₂₀ organic group linking the polymerizable group to the platinum complex;
- b) R¹ is fluoride, or a C₁-C₁₂ alkyl, alkoxy, hydroxyalkyl, aryloxy, or arylalkyloxy group;
- c) R², R³, and R⁴ are independently selected from hydrogen and a C₁-C₁₂ organic substituent group;
- d) R⁵, R⁶, and R⁷ are independently selected from hydrogen, fluoride, and a C₁-C₁₂ organic substituent group, or together two of R⁵, R⁶, and R⁷ form a benzene ring that can be optionally substituted by one or two substituent groups independently selected fluoride, C₁-C₁₂ alkyl, alkoxy, hydroxyalkyl, cyano, aryloxy, and arylalkyloxy groups.

The R¹-R⁷ optional substituent groups for the polycyclic ligand of the Platinum complexes of class (I) and their precursor ligands of class (II) are further described hereinbelow. Either the Pt complexes (I) or the resulting emissive copolymers (III) can be used to manufacture OLEDs, via solution processes.

The Pt complexes of formula (I) have been discovered to be unexpectedly efficient phosphorescent emitters. In some embodiments, the Pt complexes of Formula (I) have relatively low molecular weights and high solubilities in organic solvents, and therefore are useful for the manufacture of OLEDs via either solution processing or vacuum deposition of the Pt complexes into host materials. Furthermore, the physical and emissive properties of these relatively low molecular weight Pt complexes can be rationally manipulated by variations in the structure and/or positions of the substituents of the ligands.

OLEDs comprising the low molecular weight Pt complexes shown above can emit light in high quantum efficiencies and can exhibit unexpectedly superior processability and can have excellent thermal stability during OLED operation.

5 The various copolymers comprising phosphorescent Pt complexes disclosed and described herein can often be readily solution processed and spin coated onto appropriate anodic or cathodic substrates, optionally in the presence of crosslinking agents so as to permit photo-patterning of the resulting emissive layer, as part of the process of making OLEDs comprising the Pt metal
10 complexes described herein. Such OLEDs have been discovered to have the highly unexpected and highly useful property that the wavelength and/or color of the emitted radiation can be tuned by simply varying the loading of the Pt complexes within the emissive layers.

15 Further detailed description of preferred embodiments of the various inventions broadly outlined above will be provided below in the Detailed Description section provided below.

BRIEF DESCRIPTION OF THE FIGURES

20 **Figure 1** discloses a generic scheme for the synthesis of optionally substituted polyheterocyclic organic ligands and platinum complexes **5** and **8** derived therefrom.

Figure 2 discloses a generic scheme for the synthesis of optionally substituted polymerizable norbornene-polyheterocyclic organic ligands, and platinum complexes **13** and **16** derived therefrom.

25 **Figure 3** discloses the specific synthesis of platinum complexes **5a** and **8a** and their organic ligand precursors, as further described in Example 1.

Figure 4 discloses the specific synthesis of polymerizable norbornene-linked platinum complexes **13a** and **16a**, and their organic ligand precursors, as further described in Example 2.

30 **Figure 5** discloses a method of synthesis of a genus of monomeric acrylate compounds linked to a Pt Complex.

Figure 6 discloses a method of synthesis of a genus of monomeric styrene compounds linked to a Pt Complex.

Figure 7 graphically discloses the specific synthesis of a polymerizable norbornene linked carbazole compound **22**, as further described in Example 3.

35 **Figure 8** graphically discloses both the ROMP homopolymerization of the norbornene linked carbazole compound **22** to form the hole carrying

polycarbazole polymer **23**, and also the ROMP co-polymerization of polymerizable norbornene/carbazole **22** with the norbornene linked Pt Complexes **13a** or **16a**, to form the phosphorescent copolymers **24** and **25**.

5 **Figure 9a** illustrates a plot of M_n vs. monomer to catalyst ratio for the ROMP polymerization of norbornene/carbazole monomer **22** to produce the polynorbornene/carbazole polymer **23**. Numbers in parentheses are the polydispersity indices of the polymer **23**. **Figure 9b** shows the carbene ^1H -NMR signals for the 3rd-generation Grubbs' initiator (top), and similar ^1H -NMR signals observed during the polymerizations of **22** (bottom).

10 **Figure 10a** illustrates the UV/visible absorption and also the photoluminescence spectra of Pt complexes **5a** and **13a** in CH_2Cl_2 . **Figure 10b** illustrates the solid-state photoluminescence spectra of monomeric Pt complex **5a** dispersed in mixture of PVK, and the solid-state photoluminescence spectrum of norbornene/carbazole/Pt complex copolymer **24**.

15 **Figure 11a** illustrates the UV/visible absorption spectra and also the photoluminescence spectra of the polymerizable norbornene linked Pt complexes **8a** and **16a** in CH_2Cl_2 . **Figure 11b** illustrates the solid-state photoluminescence spectra of Pt complex **8a** dispersed in PVK, and the solid-state photoluminescence spectrum of norbornene/carbazole/Pt complex copolymer **25**.

20 Figures **12a** and **12b** show plots of current density, luminescence, and external quantum efficiency versus voltage for an OLED device comprising an emissive layer comprising PVK, PBD, and Pt complex **5a**. **Figure 12c** shows the electroluminescence spectrum of the device, as a function of the concentration of Pt complex **5a** in the emissive layer. See **Example 6**.

25 **Figure 13a** shows the luminescence and external quantum efficiency versus voltage performance of an OLED device having an emissive layer comprising PVK, PBD, and Pt Complex **8a** as a phosphorescent emitter (see **Example 5**). **Figure 13b** shows the electroluminescence spectrum of the device, as a function of the concentration of Pt complex **5a** in the emissive layer. See **Example 6**.

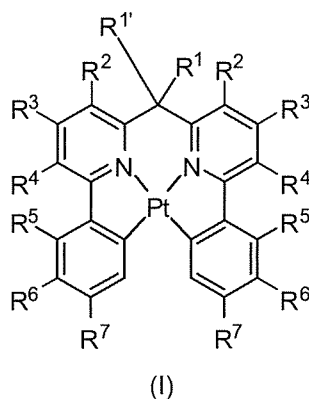
30 **Figure 14** shows the luminescence and external quantum efficiency versus voltage performance of OLED devices having emissive layers comprising copolymers **24** or **25** as a phosphorescent emitter. See **Example 6**.

35 **Figure 15** shows chromaticity diagrams for OLED devices comprising varying percentages of Pt complex **5a** in their emissive layers, as described in **Example 6**.

Figure 16 shows chromaticity diagrams for OLED devices comprising varying percentages of Pt complex **8a** in their emissive layers, as described in **Example 6**.

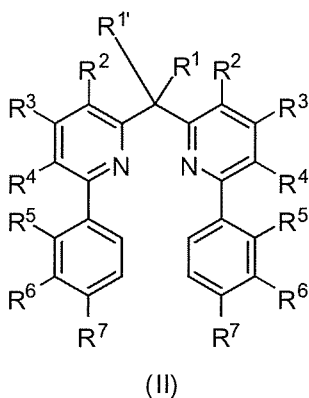
DETAILED DESCRIPTION OF THE INVENTION

5 The various inventions and/or their embodiments disclosed herein relate to Platinum complexes having polycyclic ligands as shown by Formula (I) below, and their uses:



10 Such platinum complexes can typically phosphoresce from their lowest triplet excited states, and as a result are useful as a phosphor for the manufacture of organic electronic devices, such as organic light emitting diodes (OLEDs), as will be further described below, and various other uses as well.

The inventions also relate to the platinum free organic ligands having Formula (II)



15

which can be used to form metal complexes of other metals, such as for example nickel, palladium, cobalt, rhodium, iridium, manganese, rhenium, and the like, which complexes may also be useful as phosphors, or for other uses.

20 In general, the various peripheral substituents of the organic ligands of (I) and/or (II) (R^x , where x is 1-7, i.e. R^1 , $R^{1'}$, R^2 , R^3 , R^4 , R^5 , R^6 , and R^7) can be any

inorganic or organic substituent group that is chemically and electrochemically stable and desired for the intended end use applications. Typical suitable inorganic R^x substituents include halides (fluoride, chloride, bromide, iodide), amino ($-NH_2$) groups and their protonated salts, hydroxyl ($-OH$) groups, nitro groups, sulfate groups and their salts, (hydrosulfide ($-SH$), and the like. In some
5 embodiments, fluoride is a preferred inorganic R^x substituent.

Typical organic R^x substituent groups often comprise from 1 to 20 carbon atoms, along with associated hydrogen atoms, and may comprise either normal or branched chain hydrocarbon groups such as alkyls, cycloalkyls, alkenyls, alkynyls, aryls, heteroaryl and the like. The aryls or heteroaryl may optionally
10 be fused to one of the phenyl rings of the ligands bonded directly to the platinum atom. The organic R^x substituents may optionally also comprise one or more heteroatom substituents, including halides, O, N, S, or P atoms, as exemplified by alkoxyalkyls, perfluoroalkyls, alkoxides, perfluoroalkoxides, cyano groups, phenoxy groups, heteroaryl groups, mercaptoalkyl groups, alkyl phosphate
15 groups, and the like. In some embodiments the organic R^x substituents can comprise between 1 to 12 or 1 to 6 carbon atoms.

In many electronic applications, especially in OLED device end use applications, it is desirable that the various R^1 , $R^{1'}$, R^2 , R^3 , R^4 , R^5 , R^6 , and R^7 peripheral substituents of the organic ligands of (I) and/or (II) be resistant to
20 degradation by oxidation (by holes) or reduction (by electrons) that come into contact with the ligands and/or Pt complexes during operation of the electronic devices. Alkyl, perfluoroalkyl, alkylene, alkynyl, aryl, alkoxy, perfluoroalkoxy, cyano, aryloxy, arylalkyloxy, alkylether, alkoxyalkyl, alkylamide, alkyylimide, alkylester and similar R^x substituent groups can provide the requisite degree of
25 chemical resistance. Fluoride, cyano, and alkyls such as methyl or t-butyl, perfluoroalkyls such as trifluoromethyl, alkoxides such as methoxy, and perfluoroalkyls such as trifluoromethyl typically provide the desired high degrees of degradative resistance.

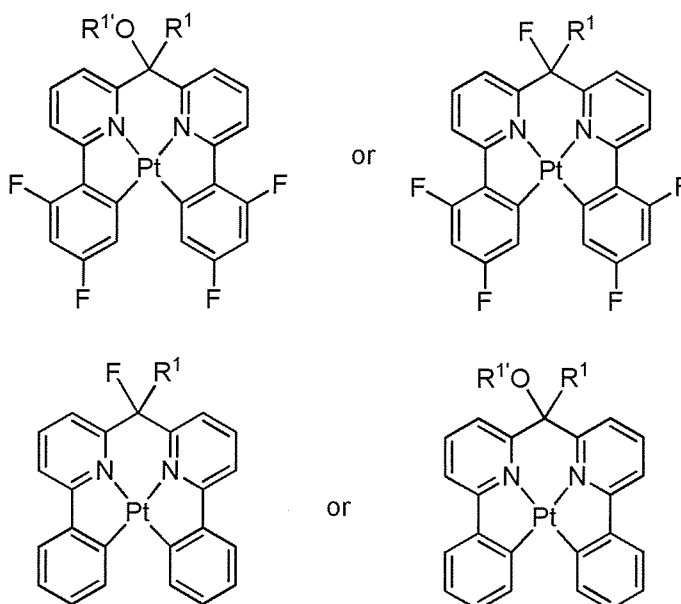
Also, by varying the identity of the R^1 , $R^{1'}$, R^2 , R^3 , R^4 , R^5 , R^6 , and R^7 peripheral substituents of complex (I) and ligand (II), the electronic and physical properties of the metal complexes and their precursor ligands can be rationally
30 "tuned" so as to optimize the energy of the phosphorescent emissions and/or the physical properties of the Pt complexes and/or the precursor ligands. In order to "tune" the Pt complexes of the invention so as to produce shorter wavelength
35 "blue" light, or white light, it can be desirable to employ one or more electron

donating substituents (such as alkyls or alkoxides) at R^2 , R^3 , and R^4 , and electron withdrawing substituents (fluorides, cyano, perfluoroalkyls, etc) at R^5 , R^6 , and R^7 . Preferably, at least one of R^1 and $R^{1'}$ is not an alkyl, and preferably, at least one of R^1 and $R^{1'}$ is either fluoride or an alkoxide.

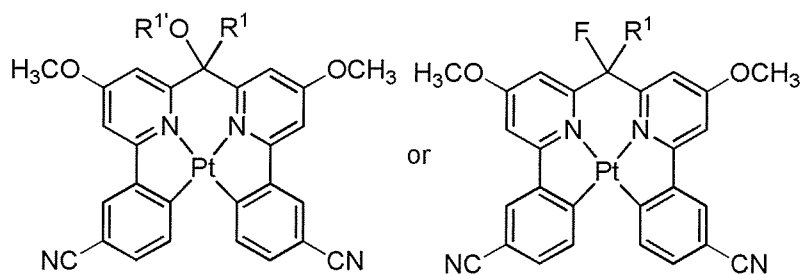
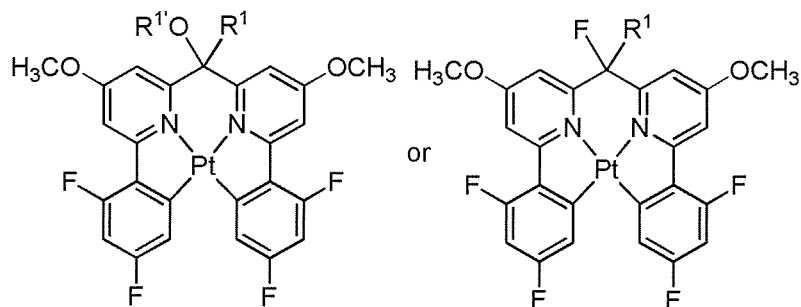
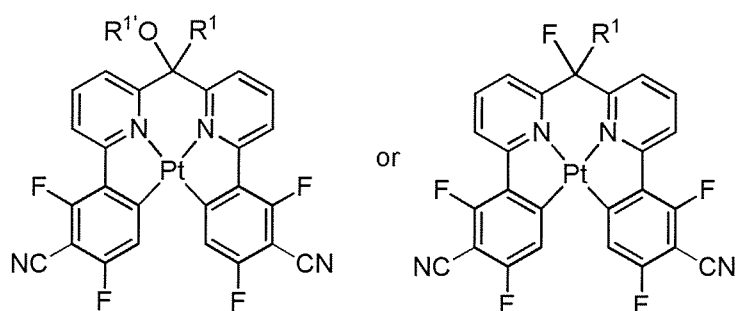
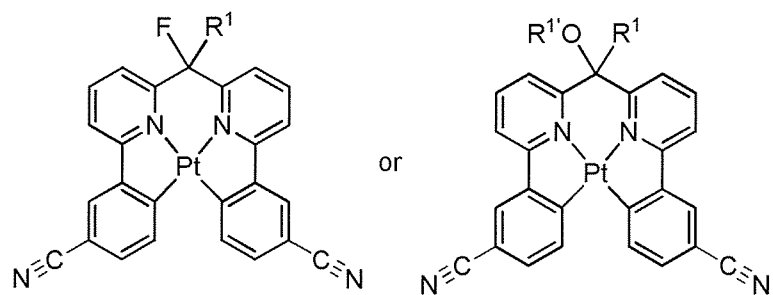
- 5 In some embodiments of the Pt complexes of the Formula (I), R^1 and $R^{1'}$ are independently selected from fluoride or a C_1 - C_{12} alkyl, alkoxy, alkoxyalkyl, aryloxy, or arylalkyloxy group; R^2 , R^3 , and R^4 are independently selected from hydrogen and a C_1 - C_{12} organic substituent group; and R^5 , R^6 , and R^7 are independently selected from hydrogen, fluoride, cyano, and a C_1 - C_{12}
- 10 perfluoroalkyls group. In some embodiments of the Pt complexes of the Formula (I), at least one of R^1 and $R^{1'}$ are fluoride or a C_1 - C_{12} alkoxy group.

- In related embodiments of the Pt complexes of the Formula (I), R^1 and $R^{1'}$ are independently selected from fluoride or a methyl or methoxy group; R^2 , R^3 , and R^4 are hydrogen; and R^5 , R^6 , and R^7 are independently selected from
- 15 hydrogen, fluoride, cyano, or together two of R^5 , R^6 , and R^7 form an additional fused benzene ring that can be optionally substituted by 1 or two fluorides, or C_1 - C_{12} alkyl, alkoxy, hydroxyalkyl, aryloxy, or arylalkyloxy groups.

The Pt complexes of formula (I) include "small molecule" complexes having the formulas:



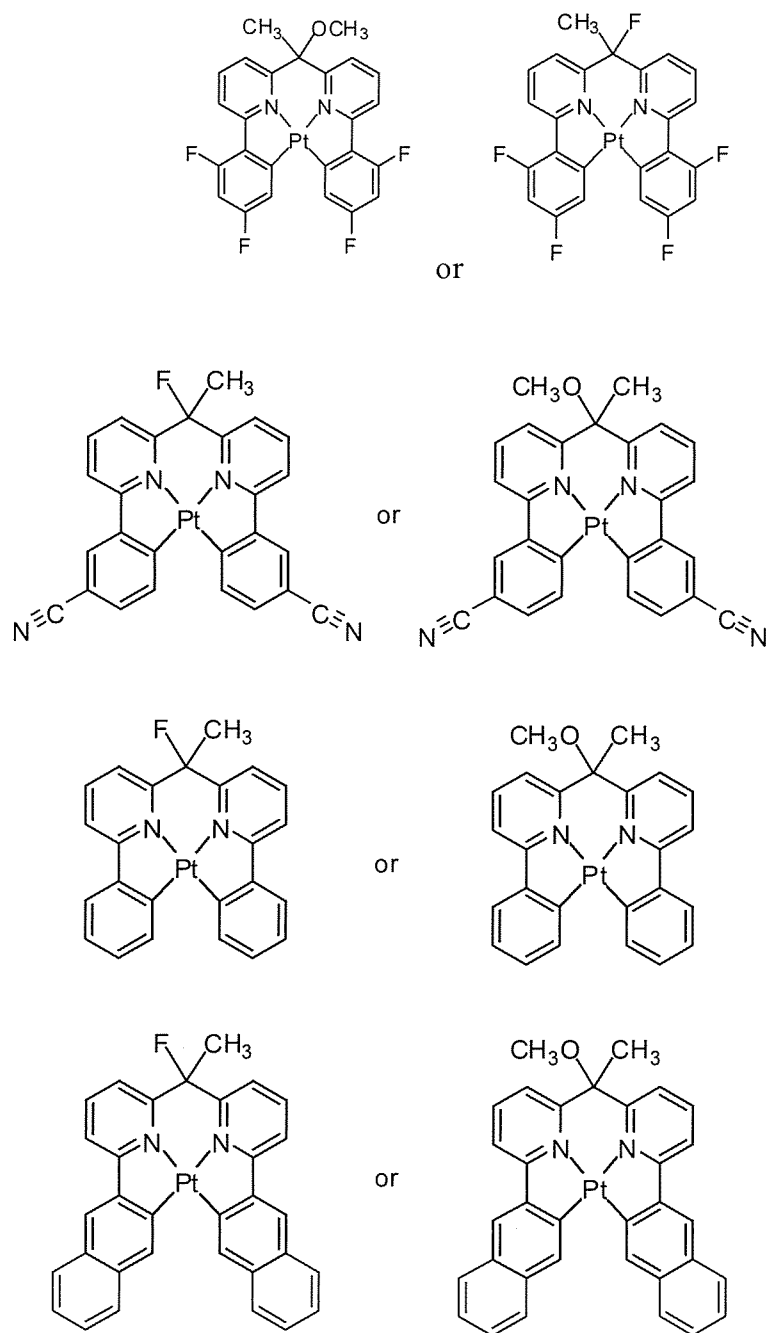
- 11 -



wherein R¹ and R^{1'} are independently selected from hydrogen and C₁-C₁₂ alkyl groups.

- 5 Especially useful low molecular weight complexes that can be used to make electronic OLED devices by vacuum sublimation include the following complexes.

- 12 -



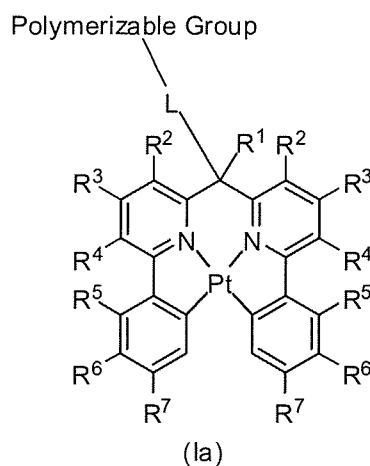
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Methods for synthesizing such Pt complexes are disclosed below, see for example **Figure 1**.

Polymerizable Norbornenes Linked To A Phosphorescent Pt Complex

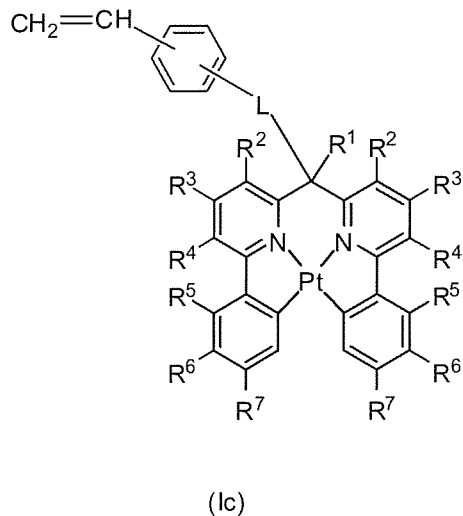
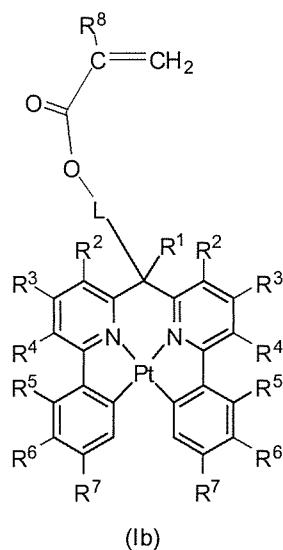
10 In many embodiments of the Pt complexes of formula (I), one of the R^x groups, especially one of the R^1 or $\text{R}^{1'}$ substituents can be modified to be a C_1 - C_{20} organic "L" organic linking group, to structurally link the ligand of the platinum complex to a polymerizable group, so as to form a polymerizable

monomeric compound. Some embodiments of such complexes are illustrated in the drawing below:



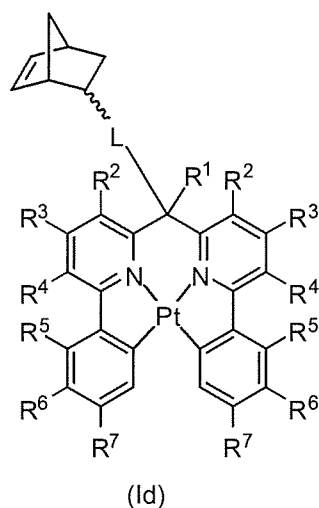
- 5 wherein
- a) the polymerizable group comprises a functional group that can be copolymerized with other comonomers,
 - b) L links the polymerizable group to the platinum complex;
 - c) R¹ is fluoride, or an organic group;
 - 10 d) R², R³, and R⁴ are independently selected from hydrogen and inorganic or organic substituent groups;
 - e) R⁵, R⁶, and R⁷ are independently selected from hydrogen, inorganic, and organic substituent groups, or together two of R⁵, R⁶, and R⁷ form a benzene ring that can be optionally substituted by 1 or two independently selected
 - 15 inorganic or organic groups.

Non-limiting examples of such polymerizable monomeric Pt complex compounds can comprise a polymerizable acrylate, methacrylate, styrene, or norborne group as shown below:



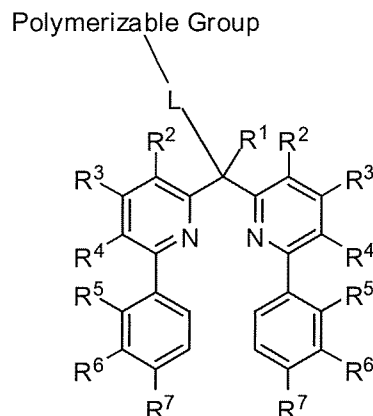
or

or



5 wherein L and the R¹-R⁷ substituents can be the same as described above for the complexes of Formula I.

The inventions described herein also relate to the corresponding novel free ligand compounds of class (II) that can be used to prepare the metal complexes of class (I), and methods for the preparation of such free ligand compounds. For example, in some embodiments the inventions described herein relate to a compound comprising a polymerizable group linked to a potentially multi-
 10 dentate ligand for transition metals, having the formula:



wherein

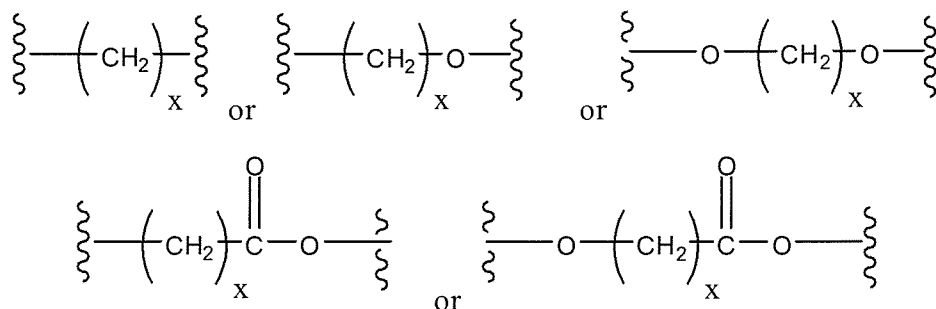
- a. the polymerizable group comprises from 2 to 20 carbon atoms, and a functional group that can be copolymerized with other comonomers,
- 5 b. L is a C₁-C₂₀ organic group linking the polymerizable group to the platinum complex;
- c. R¹ is fluoride, or a C₁-C₁₂ alkyl, alkoxy, hydroxyalkyl, aryloxy, or arylalkyloxy group;
- d. R², R³, and R⁴ are independently selected from hydrogen and a C₁-C₁₂ organic substituent group;
- 10 e. R⁵, R⁶, and R⁷ are independently selected from hydrogen, fluoride, and a C₁-C₁₂ organic substituent group, or together two of R⁵, R⁶, and R⁷ form a benzene ring that can be optionally substituted by one or two substituent groups independently selected fluoride, C₁-C₁₂ alkyl, alkoxy, hydroxyalkyl, cyano, aryloxy, and arylalkyloxy groups.
- 15

The L group of the metal complexes of class (I), their free ligand precursors (II), and derivative polymers (III) and (IV) can be any organic group comprising 1 to 20, 1 to 12, or 2 to 6 carbon atoms, as well as associated hydrogen atoms, and may also comprise optional heteroatoms or heteroatomic groups such as halide, or O, N or P atoms bound within known functional groups, and are preferably resistant to oxidative, reductive, or thermal destruction under the normal operating conditions of OLED devices. In many embodiments, L may contain alkylene, alkoxy, alkylether, alkyl or alkylester, alkylamide, alkylimide, arylene, or arylalkylene, and arylalkyloxy groups that may themselves be optionally substituted.

20

25

In some embodiments, L is an alkylene group having the formula



wherein x is an integer from 1 to 20. In such embodiments, X may also be an integer from 2 to 18, 2 to 12, or 1 to 6. In some embodiments, oxygen atoms
 5 may be inserted into or onto such methylene chains, to form ether or ester linking groups.

For the polymerizable compounds of formulas (Ib), (Ic), or (Id), the optional R¹, R², R³, R⁴, R⁵, R⁶, and R⁷ peripheral substituents can be any of the R^x groups described above in connection with the Pt complexes of formula (I),
 10 but in many embodiments R¹ is fluoride, or a C₁-C₁₂ alkyl, alkoxy, alkoxyalkyl, aryloxy, or arylalkyloxy group; R², R³, and R⁴ can be independently selected from hydrogen and an C₁-C₁₂ organic substituent groups, such as for example electron donating alkyl alkoxy, amino, alkylamino, or dialkylamino groups. R⁵, R⁶, and R⁷ are independently selected from hydrogen, fluoride, and a C₁-C₁₂
 15 organic substituent group, including electron withdrawing fluoride, cyano, or perfluoroalkyl groups.

In some embodiments of the compounds of formula (I b), (Ic), or (Id), R², R³, and R⁴ are independently selected from hydrogen and a C₁-C₁₂ alkyl alkoxy, or dialkylamino group.

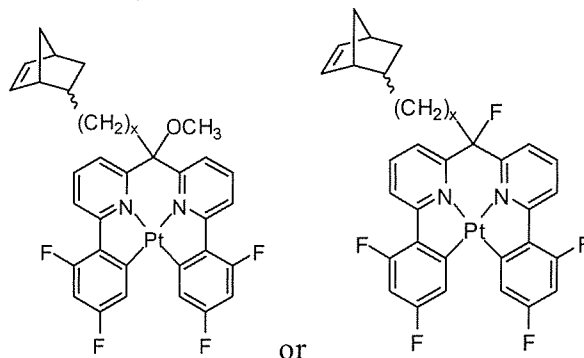
20 In some embodiments of the compounds of formula (Ic), R², R³, and R⁴ are all hydrogen.

In related embodiments of the Pt complexes of formula (I b), (Ic), or (Id), R⁵, R⁶, and R⁷ can be independently selected from hydrogen, fluoride, cyano, and a C₁-C₁₂ perfluoroalkyl or perfluoroalkoxy group. In other related
 25 embodiments, R⁵, R⁶, and R⁷ are independently selected from hydrogen, cyano, and fluoride. In some embodiments, the inclusion of electron donating groups at R², R³, and/or R⁴, and electron withdrawing groups at R⁵, R⁶, and/or R⁷ tends to shorten the wavelength of emission from the platinum complexes.

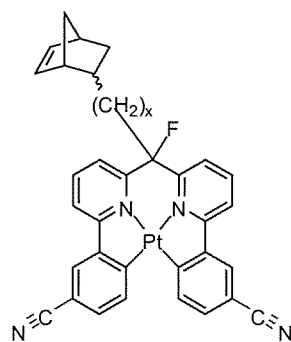
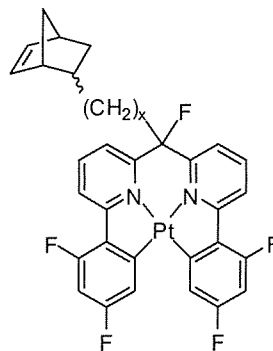
In related embodiments of the Pt complexes of formula (I b), (Ic), or (Id),
 30 R¹ is selected from fluoride or a methyl or methoxy group; R², R³, and R⁴ are

hydrogen; and R^5 , R^6 , and R^7 are independently selected from hydrogen and fluoride.

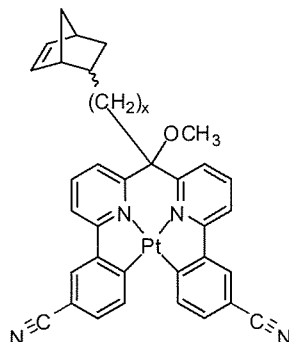
Some exemplary compounds of formula (Ic) have the formula:



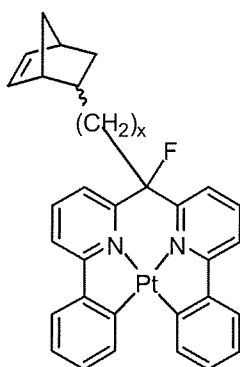
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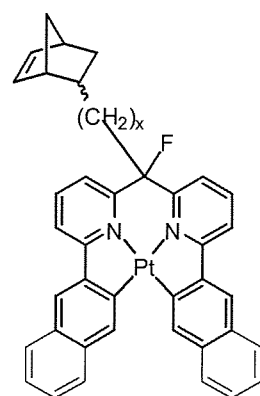
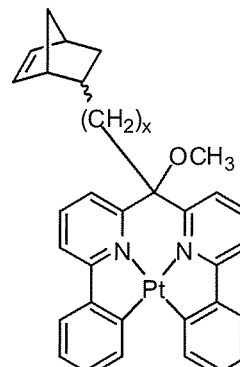
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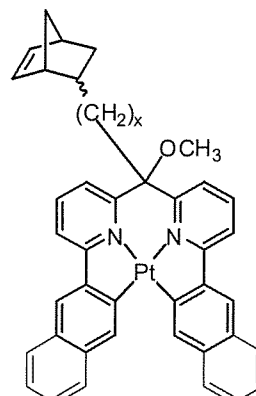
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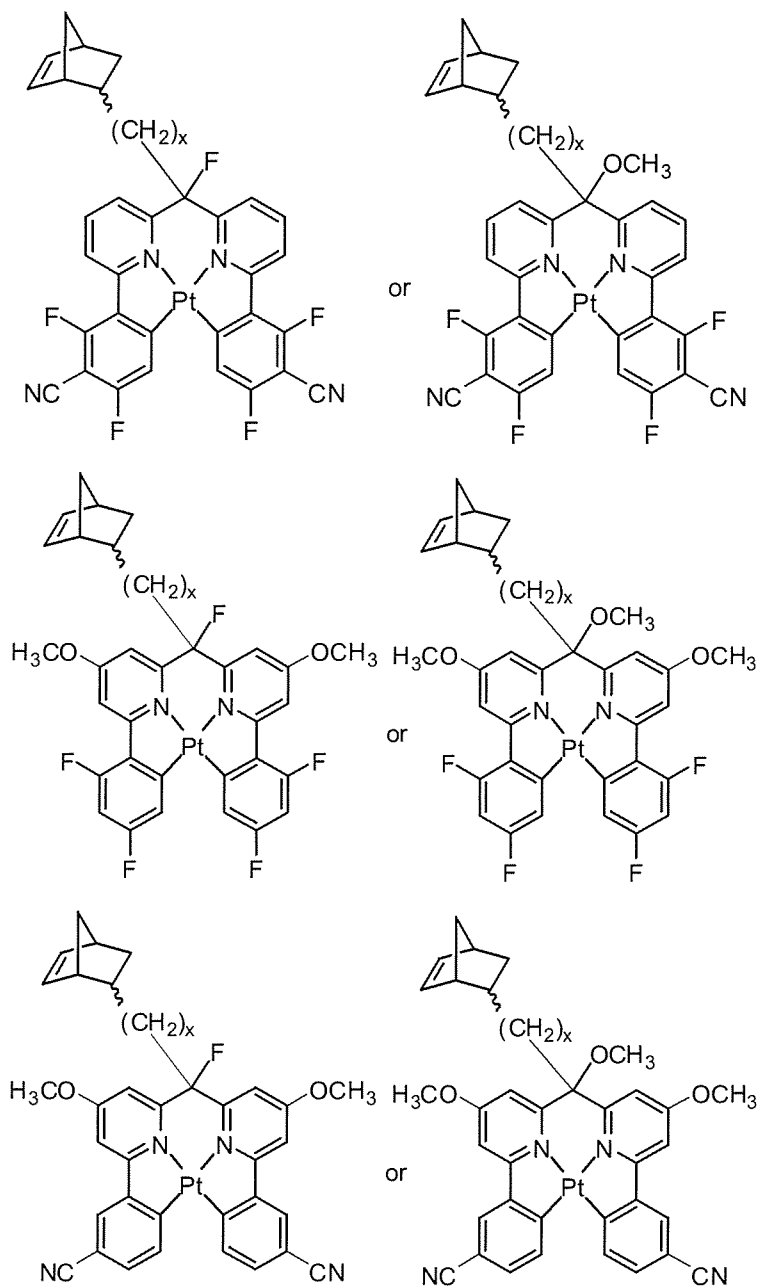


or



or



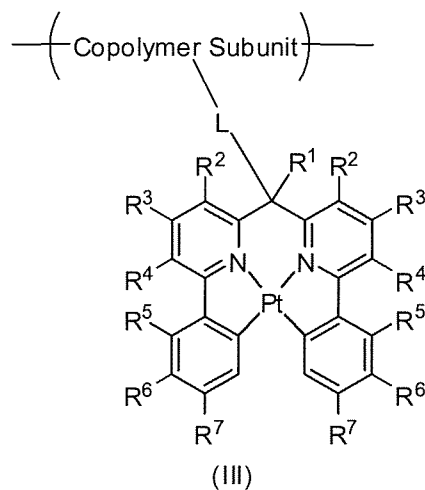


wherein x is an integer from 2 to 18.

- 5 Methods for synthesizing such Pt complexes are disclosed below, see for example **Figure 2**.

Copolymers Linked To A Phosphorescent Pt Complex

- In some aspects, the inventions relate to copolymers linked to Pt complexes described above, which can be formed by the polymerization or
- 10 copolymerization of monomers of formula (Ib), (Ic), or (Id) with one or more additional comonomers, copolymers comprising at least one polymerized subunit having structure (III) as shown below



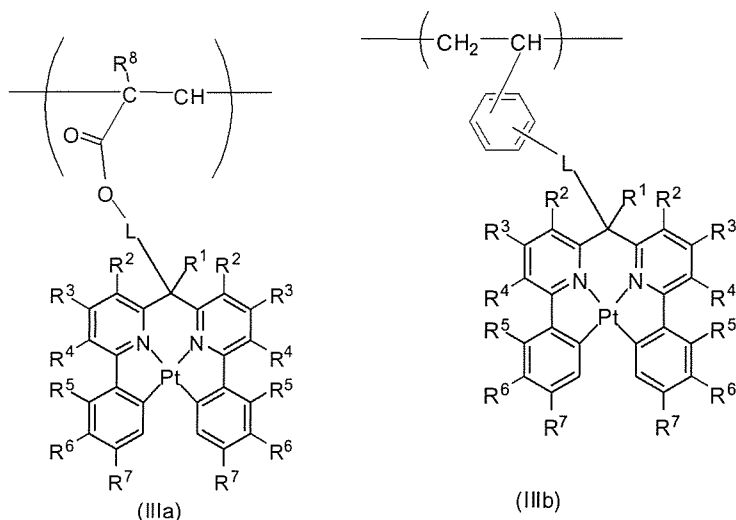
wherein

- a. the copolymer subunit comprises from 2 to 20 carbon atoms,
- b. L is a C₁-C₂₀ organic group linking the copolymer subunit to the platinum complex;
- c. R¹ is fluoride, or a C₁-C₁₂ alkyl, alkoxy, hydroxyalkyl, aryloxy, or arylalkyloxy group;
- d. R², R³, and R⁴ are independently selected from hydrogen and a C₁-C₁₂ organic substituent group;
- e. R⁵, R⁶, and R⁷ are independently selected from hydrogen, fluoride, and a C₁-C₁₂ organic substituent group, or together two of R⁵, R⁶, and R⁷ form a benzene ring that can be optionally substituted by one or two substituent groups independently selected fluoride, C₁-C₁₂ alkyl, alkoxy, hydroxyalkyl, cyano, aryloxy, and arylalkyloxy groups.

In copolymers comprising at least one polymerized subunit having structure (III), "copolymer subunit" refers to only the portion of each polymerized subunit derived from the polymerizable group, and does not include the L, or R¹-R⁷ groups, which can be separately defined in any of the ways discussed hereinabove with respect to the polymerizable monomers.

For example, it is well known in the art to copolymerize acrylate, methacrylate, or styrene monomers of formula (Ib) or (Ic), by use of radical initiators. Copolymers derived from copolymerization of monomers of formula (I b) or (Ic) would have at least one polymer subunit having the formulas shown below:

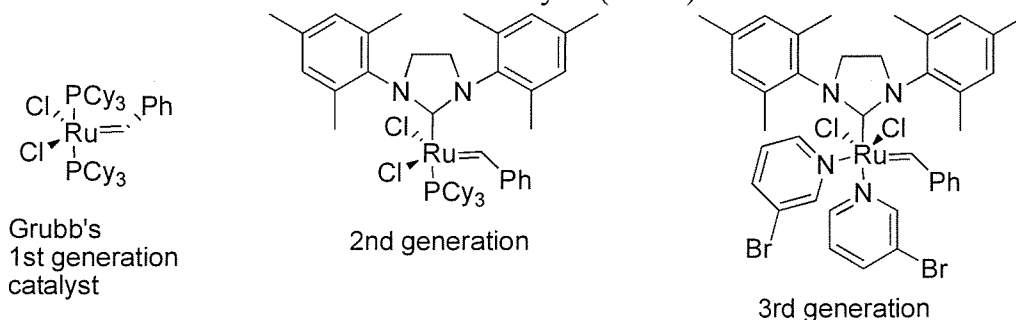
- 20 -



OR

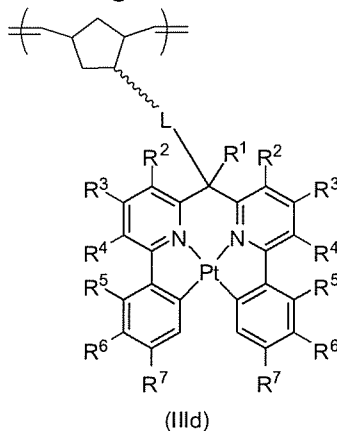
wherein L is a C₁-C₂₀ organic group that links the polymerized norbornene subunit to the ligand of the polycyclic platinum complex, and the R¹, R², R³, R⁴, R⁵, R⁶, and R⁷ peripheral substituents can be any of the R^x groups described above in connection with the Pt complexes of formula (I).

It is also well known in the art that cyclic olefins, including norbornenes, can be polymerized via ring-opening metathesis polymerization (ROMP), a living polymerization method resulting in polymers with controlled molecular weights, low polydispersities, and which also allows for the easy formation of either random or block co-polymers. See, for example, Fürstner, A. *Angew. Chem., Int. Ed.* 2000, 39, 3013; T. M. Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* 2001, 34, 18; *Olefin Metathesis and Metathesis Polymerization, 2nd Ed.*; Ivin, J., Mol, I. C., Eds.; Academic: New York, 1996; and *Handbook of Metathesis, Vol. 3 – Application in Polymer Synthesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003, each of which is respectively incorporated herein by reference for their teachings regarding methods and catalysts for ROMP polymerizations. Catalysts (also termed initiators) commonly used by those skilled in the art include Grubb's ruthenium catalysts (below).



Ruthenium-based ROMP initiators are highly functional-group tolerant, allowing for the polymerization of norbornene monomers linked to fluorescent and phosphorescent metal complexes. ROMP polymerizations can also be carried out with molybdenum or tungsten catalysts such as those described by Schrock (*Olefin Metathesis and Metathesis Polymerization, 2nd Ed.*; Ivin, J., Mol, I. C., Eds.; Academic: New York which is respectively incorporated herein by reference for its teachings regarding molybdenum or tungsten catalysts for ROMP polymerizations).

Attempts to homo-polymerize the norbornene/Pt complexes of formula (Ic) with Grubbs 3d generation ROMP initiator resulted in insoluble materials. Without wishing to be bound by theory, the insolubility may arise from intramolecular interactions between the Pt complexes if the Pt complexes are present in too high a concentration in the polymer. However, copolymerizations of the norbornene/Pt complexes of formula (Id) with other optionally substituted norbornene monomers successfully produced soluble copolymers comprising at least one polymerized subunit having the formula:

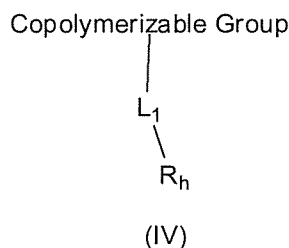


wherein L is a C₁-C₂₀ organic group that links the polymerized norbornene subunit to the ligand of the polycyclic platinum complex, and the R¹, R², R³, R⁴, R⁵, R⁶, and R⁷ peripheral substituents can be any of the R^x groups described above in connection with the Pt complexes of formula (I).

The copolymers containing subunits of formula (III) can be either random or block copolymers, and can have any relative proportion of Pt-linked subunits to "other copolymerized subunits", but in many embodiments are random copolymers that contain a significantly higher proportion of "other copolymerized subunits" than Pt-linked subunits. In many embodiments, the Pt

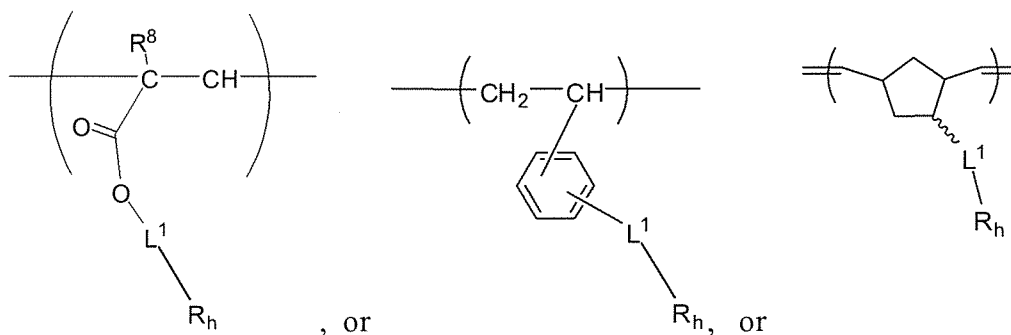
complex would be present in the range from about 0.1 mole % to about 20 mole %.

The copolymers containing subunits of formula (III) can be prepared by mixing at least one monomer of formula (Ib), (Ic), or (Id) with one or more additional comonomers suitable for polymerization, and polymerizing the mixed monomers in the presence of a polymerization initiator. In some embodiments of the norbornene derived copolymers, block copolymers can be readily prepared with "blocks" having differing proportions of the subunits derived from the monomers of formula (Id) with the additional comonomers, in order to either "tune" the wavelength of emissions, or adjust the solubility/processability characteristics of the resulting block copolymers. In some embodiments of the inventions, the additional comonomer having structure (IV) shown below, which have poly-unsaturated and polycyclic aromatic or heteroaromatic "host" group side chains "R_h" that are capable of conducting holes, electrons, and/or excitons.



wherein the copolymerizable group can be any organic group comprising a copolymerizable functional group, including the acrylate, styrene, and norbornene functional groups, L¹ is a linking group similar to the L groups described elsewhere herein, and R_h is a group capable of carrying holes, electrons, and/or excitons, as further described herein.

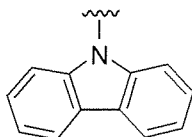
Examples of the corresponding copolymerized acrylate, styrene, and norbornene subunits are shown below:



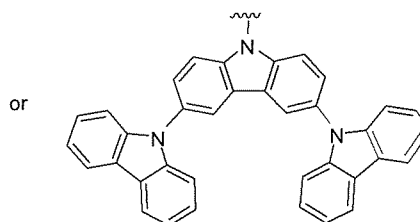
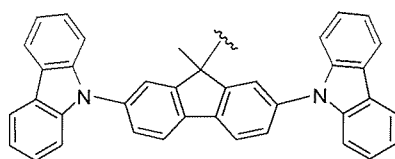
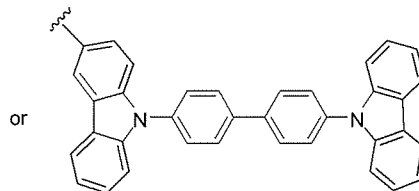
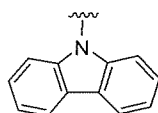
wherein

- i) L^1 is a C_1 - C_{20} organic group linking the polymeric subunit to the R_h group; and
- ii) the R_h group comprises a poly-unsaturated and polycyclic aromatic or heteroaromatic group capable of conducting holes, electrons, and/or excitons, and
- iii) R^8 is H or CH_3 .

A variety of R_h poly-unsaturated and polycyclic aromatic or heteroaromatic "host" compounds that are capable of conducting holes, electrons, and/or excitons are known, and can be linked to norbornene groups to form copolymerizable compounds linked to an R_h group. For example, optionally substituted carbazole groups comprising the core ring structure shown below are well known as hole carrying groups:



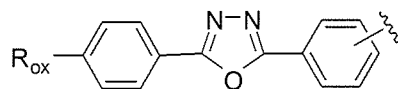
- 15 Examples of R_h groups comprising one or more carbazole rings that have been linked to polymerizable groups include the following:



wherein the carbazole ring structures can optionally be further substituted with 1, 2, or 3 ring substituent groups, such as halides or C_1 - C_{12} alkyl or alkoxy groups;

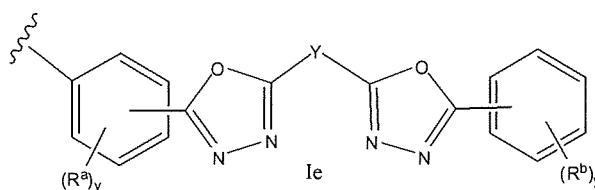
- 20 Furthermore, compounds comprising 2, 5-diaryl oxadiazole groups have been disclosed in the art as suitable for use in OLED devices as hole carrying compounds. Accordingly, in some embodiments, the R_h group can be a mono-oxadiazole group comprising the ring structure:

- 24 -



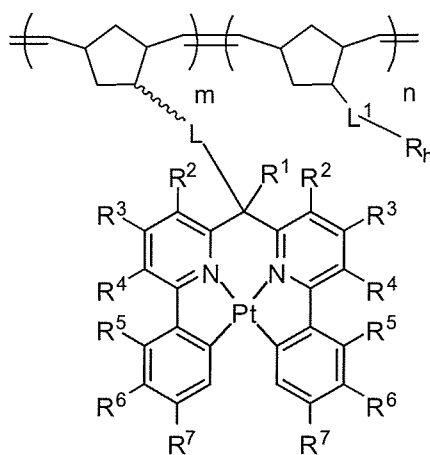
wherein R_{ox} is a C_1 - C_{12} alkyl group, and the mono-oxadiazole ring structure can optionally be further substituted with 1, 2, or 3 C_1 - C_{12} alkyl, perfluoroalkyl, alkoxy, or perfluoroalkoxy groups.

- 5 Alternatively, in additional but related embodiments, the R_h group can be a bis-oxadiazole groups comprising the ring structure:



wherein Y is absent or an arene group, and R^a and R^b are C_1 - C_{12} alkyl, perfluoroalkyl, alkoxy, or perfluoroalkoxy groups, and y is 0, 1, 3, or 3.

- 10 The norbornene copolymers formed by copolymerizing compound (Id) and co-monomers having formula (IV) can have structure shown below.



- wherein L, L^1 , R_h , and the R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , and R^7 peripheral substituents can be any of the R^x groups described above in connection with the Pt complexes of formula (Ic). The (IIIb) copolymers can be either random or block copolymers, and the drawing of those polymers shown above is not intended to imply that the copolymers are necessarily block copolymers.
- 15

The copolymers can have any relative proportion of Pt-linked subunits to “other copolymerized subunits”, but in many embodiments the copolymers are

random copolymers that contain a significantly higher proportion of “other copolymerized subunits” than Pt-linked subunits. In many embodiments, the Pt complexes will be present in the emissive layers of the OLED devices in concentrations from about 0.1 mole % to about 20 mole %. In the drawing shown above, “m” is an integer intended to indicate the total number of copolymer subunits linked to Pt complexes, and can range from about 1 to about 20. Correspondingly, “n” is an integer intended to indicate the total number of copolymer subunits linked to R_h groups, and can range from about 80 to about 100. In some embodiments, the ratio of n/m is between about 5:1 to about 99:1.

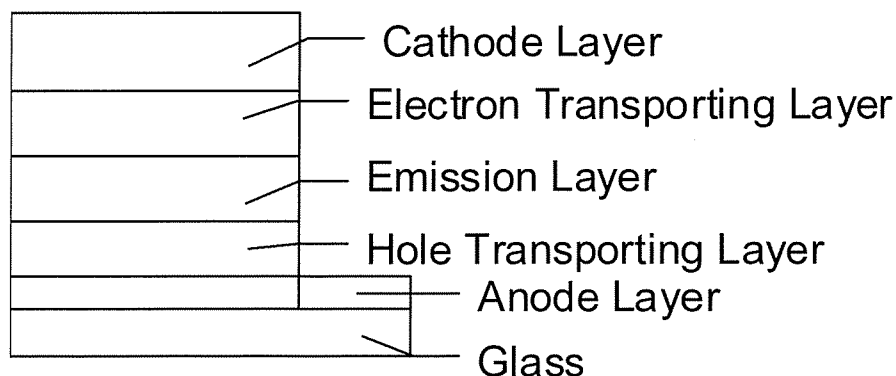
It should be noted that in some embodiments, the copolymers might contain three (or more) types of subunits, for example some subunits linked to the Pt complexes, some subunits linked to hole carrying carbazole groups, and some subunits linked to electron carrying oxadiazole groups.

The copolymers can emit phosphorescent light in various regions of the visible spectrum, depending upon the specific platinum complex employed.

Organic Electronic Devices Comprising the Pt Compounds and/or Copolymers

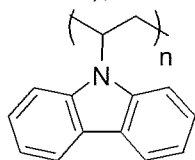
Some aspects of the present inventions relate to novel organic electronic devices, including light emitting diodes and OLED devices that comprise the various platinum complexes and/or Platinum containing copolymers described above. As further described below, such platinum complexes and/or platinum containing copolymers can be solution processed and/or spin coated onto appropriate substrates to form the emission layer of an OLED device.

In some embodiments, light emitting diodes and/or OLED devices comprise an anode layer, a hole transporting layer, an emission layer, an electron transporting layer, and a cathode layer. Such devices are illustrated in the diagram below:

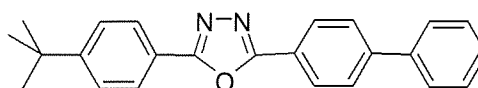


OLED Device

The emission layer comprises the Pt complexes or Pt containing copolymers, and can optionally contain additional hole transporting compounds (such as PVK), or electron transporting compounds (such as PBD)



PVK



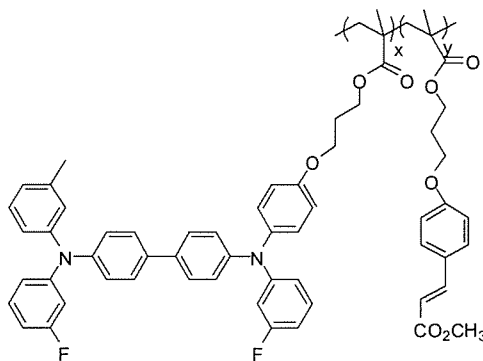
PBD

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Indium tin oxide (ITO) is an example of a suitable material for the anode layers.

Many materials are potentially useful as hole transporting layers. **Poly-TPD-F** (structure shown below, see Zhang, et al., *Synthesis* 2002, 1201 and Domercq, et al., *Chem. Mater.* 2003, 15, 1491, both of which are incorporated herein by reference in their entirety) is especially useful because it is photo cross-linkable and can be used to produce photo-patterned hole transporting layers.

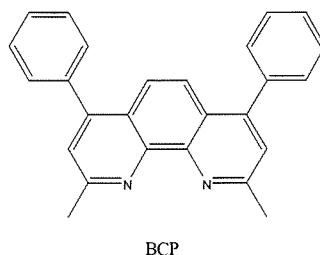
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Poly-TPD-F

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Many materials are suitable as electron transporting and/or hole blocking materials, such as bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, BCP, structure shown below) which can be readily applied to the devices via vacuum/thermal deposition techniques.



Similarly, many materials can be suitable as cathode layers, one example being a combination of lithium fluoride (LiF) as an electron injecting material coated with a vacuum deposited layer of Aluminum.

5 **Photoluminescent Properties of the OLED Devices**

A number of exemplary OLED devices comprising the Pt complexes and/or Pt containing copolymers described above are described in the Examples below, which describe the particular photoluminescence properties measured for those exemplary devices. See Examples 5 and 6, and Figures 8-12.

10 An unexpected and dramatic effect of the degree of loading of the Pt complexes **5a** and **8a** into the emissive layer on the wavelength (and therefore color) of the phosphorescent emissions of the devices was observed. See Figures **10c** and **11b**. See also the chromaticity diagrams in Figures 13 and 14, and Tables 3 and 4, below, which describe the emission maxima observed from the

15 devices comprising compound 5a (Table 3) and 8a (Table 4) in varying concentrations in their emission layers.

Doping Level	CIE Coordinates - xy
5%	(0.32, 0.58)
10%	(0.34, 0.58)
15%	(0.35, 0.56)
20%	(0.39, 0.55)
25%	(0.45, 0.50)
30%	(0.49, 0.48)
35%	(0.51, 0.47)

20 Table 3 – Doping Level of Complex 5a In An OLED Device and Effect on Observed Emission.

Doping Level	CIE Coordinates - xy
5%	(0.29, 0.62)
10%	(0.31, 0.61)
15%	(0.34, 0.58)
20%	(0.40, 0.55)
25%	(0.46, 0.50)
30%	(0.49, 0.48)
35%	(0.53, 0.46)

Table 4 – Doping Level of Complex 8a In An OLED Device and Effect on Observed Emission.

The cause of the observed dramatic shifts in the color and wavelength of the phosphorescence of these OLED devices, from yellowish green at about 5 wt% Pt complex to reddish yellow at 35 wt% Pt complex is not well understood, but certainly provides an unexpected property that can be used to tune the wavelength of the emission from the devices in a rational manner, and hence provides a unexpected advantage useful in manufacturing the resultant OLED devices.

EXAMPLES

The various inventions described above are further illustrated by the following specific examples, which are not intended to be construed in any way as imposing limitations upon the scope of the invention disclosures or claims attached herewith. On the contrary, it is to be clearly understood that resort may be had to various other embodiments, modifications, and equivalents thereof which, after reading the description herein, may suggest themselves to one of ordinary skill in the art without departing from the spirit of the present invention or the scope of the appended claims.

General - All experiments with air- and moisture-sensitive intermediates and compounds were carried out under an inert atmosphere using standard Schlenk techniques. NMR spectra were recorded on either a 400 MHz Varian Mercury spectrometer or a 400 MHz Bruker AMX 400 and referenced to residual proton solvent. UV-vis absorption spectra were recorded on a Varian Cary 5E UV-vis-NIR spectrophotometer, while solution and thin-film PL spectra were recorded on a Fluorolog III ISA spectrofluorometer. Lifetime

measurements were taken using a PTI model C-72 fluorescence laser spectrophotometer with a PTI GL-3300 nitrogen laser. Cyclic voltammograms were obtained on a computer controlled BAS 100B electrochemical analyzer, and measurements were carried out under a nitrogen flow in deoxygenated DMF solutions of tetra-*n*-butylammonium hexafluorophosphate (0.1 M). Glassy carbon was used as the working electrode, a Pt wire as the counter electrode, and an Ag wire anodized with AgCl as the pseudo-reference electrode. Potentials were referenced to the ferrocenium/ferrocene ($\text{FeCp}_2^{+/0}$) couple by using ferrocene as an internal standard. Gel-permeation chromatography (GPC) analyses were carried out using a Waters 1525 binary pump coupled to a Waters 2414 refractive index detector with methylene chloride as an eluent on American Polymer Standards 10 μm particle size, linear mixed bed packing columns. The flow rate used for all measurements was 1 ml/min, and the GPCs were calibrated using poly(styrene) standards. Differential scanning calorimetry (DSC) data were collected using a Seiko model DSC 220C. Thermal gravimetric analysis (TGA) data were collected using a Seiko model TG/DTA 320. Inductively coupled plasma-mass spectrometry (ICP-MS) for platinum and ruthenium was provided by Bodycote Testing Group. ^1H -NMR and ^{13}C -NMR spectra (300 MHz ^1H NMR, 75 MHz ^{13}C NMR) were obtained using a Varian Mercury Vx 300 spectrometer. All spectra are referenced to residual proton solvent. Abbreviations used include singlet (s), doublet (d), doublet of doublets (dd), triplet (t), triplet of doublets (td) and unresolved multiplet (m). Mass spectral analyses were provided by the Georgia Tech Mass Spectrometry Facility. The onset of thermal degradation for the polymers was measured by thermal gravimetric analysis (TGA) using a Shimadzu TGA-50. UV/vis absorption measurements were taken on a Shimadzu UV-2401 PC recording spectrophotometer. Emission measurements were acquired using a Shimadzu RF-5301 PC spectrofluorophotometer. Lifetime measurements were taken using a PTI model C-72 fluorescence laser spectrophotometer with a PTI GL-3300 nitrogen laser. Elemental analyses for C, H, and N were performed using Perkin Elmer Series II CHNS/O Analyzer 2400. Elemental analyses for iridium were provided by Galbraith Laboratories.

Unless otherwise noted, cited reagents and solvents were purchased from well-known commercial sources (such as Sigma-Aldrich of Milwaukee Wisconsin or Acros Organics of Geel Belgium, and were used as received without further purification.

Example 1 – Synthesis of Pt Complexes 5a and 8a

Pt complexes **5a** and **8a** were prepared by the synthetic scheme graphically illustrated in **Figure 3**.

Bis(2-(6-bromopyridyl)ketone (**1a**) was prepared by the procedure described in Parks, J. E.; Wagner, B. E.; Holm, R. H. *J. Organometallic Chem.* **1973**, 56, 53. 1,1-Bis(6-bromo-2-pyridyl)ethan-1-ol (**2a**) was prepared by the procedures described in Stossel, P.; Gerhard, A. *Metal Complexes with Bipodal Ligands* Patent: WO2005042550. PtCl₂(PhCN)₂ was prepared by the procedure described in Uchiyama, Y.; Nakamura, Y.; Miwa, T.; Kawaguchi, S.; Okeya, S. *Chem. Letters* **1980**, 3, 337.

1,1-Bis(6-bromo-2-pyridyl)-1-methoxyethane (3a). 1,1-Bis(6-bromo-2-pyridyl)ethan-1-ol (1.00 g, 2.79 mmol) was added to a suspension of sodium hydride (0.50 g, 20.8 mmol) in 40 ml of THF. When the evolution of hydrogen gas had ceased, iodomethane (1.30 ml, 20.8 mmol) was added. After the mixture was stirred for 2 h, the reaction was quenched with 10% aqueous HCl until acidic and then basified with 10% aqueous potassium carbonate. The crude product was extracted with dichloromethane (50 ml × 3 times) and dried over anhydrous magnesium sulfate. Finally, a silica gel column purification (hexane:EtOAc = 5:1) gave a white solid (0.75 g, 2.02 mmol, yield 72%). TLC, R_f = 0.55 (hexane:EtOAc = 5:1). MS (EI): *m/z* = 372 (M⁺). ¹H NMR (400 MHz, CDCl₃) δ: 7.48 (d, 2H, *J* = 1.6 Hz), 7.47 (s, 2H), 7.29 (dd, 2H, *J* = 5.2 and 2.9 Hz), 3.21 (s, 3H), 1.97 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ: 164.36, 140.83, 138.62, 126.52, 120.17, 82.69, 51.12, 21.72.

1,1-Bis(6-(2,4-difluorophenyl)-2-pyridyl)-1-methoxyethane (4a). Compound **3a** (0.71 g, 1.91 mmol), 2,4-difluorophenylboronic acid (1.20 g, 7.60 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.25 g, 0.216 mmol) were added to a round-bottomed flask equipped with a reflux condenser and dissolved in 20 ml of THF. After 15 ml of aqueous 2N Na₂CO₃ was delivered, the reaction mixture was refluxed for 24 h. The cooled crude mixture was poured onto water and extracted with CH₂Cl₂ (50 ml × 3 times) and then dried over anhydrous magnesium sulfate. Finally, a silica gel column purification (hexane:EtOAc = 10:1) gave a transparent oil (0.73 g, 1.67 mmol, yield 88%). TLC, R_f = 0.65 (hexane:EtOAc = 8:1). ¹H NMR (400 MHz, CDCl₃) δ: 8.03 (dt, 2H, *J* = 10 and 6.8 Hz), 7.70 (d, 2H, *J* = 7.6 Hz), 7.65 (ddd, 2H, *J* = 8.0 and 2.0 and 1.2 Hz), 7.54 (dd, 2H, *J* = 8.0 and 1.0 Hz), 6.84-6.96 (m, 4H), 3.34 (s, 3H), 2.17 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ: 163.53, 161.94 (dd, *J* = 224

and 12 Hz), 159.43 (dd, $J = 225$ and 12 Hz), 150.51 (d, $J = 3$ Hz), 136.76, 132.29 (dd, $J = 10$ and 5 Hz), 123.62 (dd, $J = 11$ and 4 Hz), 122.02 (d, $J = 11$ Hz), 119.84, 111.54 (dd, $J = 21$ and 4 Hz), 103.87 (dd, $J = 27$ and 25 Hz), 84.08, 51.28, 22.01; ^{19}F NMR (376 MHz, CDCl_3) δ : -110.55 (F pos. 2 with respect to phenylpyridine), -113.07 (F pos. 4 with respect to phenylpyridine).

[1,1-Bis(6-(4,6-difluorophenyl)-2-pyridyl- N,C^2)-1-methoxyethane]platinum(II) (5a). A mixture of compound **4a** (200 mg, 0.46 mmol), $\text{PtCl}_2(\text{PhCN})_2$ (220 mg, 0.46 mmol) and xylene (15 ml) was refluxed for 60 min. under an argon flow. The xylene was removed by distillation and the crude product was purified by silica gel column chromatography (dichloromethane) to give compound **5** as a yellow solid (145 mg, 0.23 mmol, yield 50%). TLC, $R_f = 0.6$ (hexane:dichloromethane = 1:1). FAB-MS: $m/z = 631.1$ (M^+). ^1H NMR (400 MHz, CDCl_3) δ : 8.10 (d, 2H, $J = 8.4$ Hz), 7.95 (pseudo t, 2H, $J = 8.0$ Hz), 7.73 (dd, 2H, $J = 8.0$ and 1.0 and 1.2 Hz), 7.54 (dd, 2H, $J = 10$ and 2.4 Hz), 6.56-6.64 (m, 4H), 3.47 (s, 3H), 1.95 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 162.89 (d, $J = 7$ Hz), 161.99 (dd, $J = 252$ and 12 Hz), 160.01, 159.42 (dd, $J = 255$ and 12 Hz), 152.76 (d, $J = 5$ Hz), 139.28, 130.23 (pseudo t, $J = 3$ Hz), 121.38 (d, $J = 21$ Hz), 119.50, 117.39 (dd, $J = 18$ and 3 Hz), 99.87 (pseudo t, $J = 27$ Hz), 89.05, 53.57, 33.76; ^{19}F NMR (376 MHz, CDCl_3) δ : -108.35 (F pos. 2 with respect to phenylpyridine), -110.95 (F pos. 4 with respect to phenylpyridine); ^{195}Pt NMR (86 MHz, CDCl_3) δ : -3583 (referenced to aqueous K_2PtCl_4). Anal. Calcd for $\text{C}_{25}\text{H}_{16}\text{F}_4\text{N}_2\text{OPt}$: C, 47.55; H, 2.55; N, 4.44. Found: C, 47.50; H, 2.55; N, 4.41. A single crystal X-ray diffraction study confirmed the structure indicated by **Formula 5a**.

1,1-Bis(6-bromo-2-pyridyl)-1-fluoroethane (6a) was prepared by the procedures described in Stossel, P.; Gerhard, A. *Metal Complexes with Bipodal Ligands* Patent: WO2005042550.

1,1-Bis(6-(2,4-difluorophenyl)-2-pyridyl)-1-fluoroethane (7a). Compound **6a** (0.68 g, 1.89 mmol), 2,4-difluorophenylboronic acid (1.20 g, 7.60 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.25 g, 0.216 mmol) were added to a round-bottomed flask equipped with a reflux condenser and dissolved in 20 ml of THF. After the addition of 15 ml of aqueous 2N Na_2CO_3 , the reaction mixture was refluxed for 24 h. The cooled crude mixture was poured onto water and extracted with CH_2Cl_2 (50 ml $\times$ 3 times) and then dried over anhydrous magnesium sulfate. Finally, a silica gel column purification (hexane:EtOAc = 10:1) gave a transparent oil (0.71 g, 1.66 mmol, yield 88%).

TLC, R_f = 0.75 (hexane:EtOAc = 5:1). ^1H NMR (400 MHz, CDCl_3) δ : 8.11 (dt, 2H, J = 10 and 6.8 Hz), 7.76 (m, 4H), 7.56 (d, 2H, J = 7.2 Hz), 6.86-7.00 (m, 4H), 2.33 (d, 3H, J = 12 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 162.05 (dd, J = 235 and 12 Hz), 161.14 (d, J = 27 Hz), 159.54 (dd, J = 236 and 12 Hz),
 5 151.05, 137.10, 132.31 (dd, J = 10 and 5 Hz), 123.34 (dd, J = 11 and 4 Hz), 122.76 (d, J = 11 Hz), 118.65 (d, J = 7 Hz), 111.59 (dd, J = 21 and 4 Hz), 103.95 (dd, J = 27 and 25 Hz), 97.95 (d, J = 172 Hz), 25.28 (d, J = 3 Hz); ^{19}F NMR (376 MHz, CDCl_3) δ : -109.95 (F pos. 2 with respect to phenylpyridine), -112.91 (F pos. 4 with respect to phenylpyridine), -146.66.

10 **[1,1-Bis(6-(4,6-difluorophenyl)-2-pyridyl- N,C^2)-1-fluoroethane]platinum(II) (8a).** A mixture of compound **7** (200 mg, 0.47 mol), $\text{PtCl}_2(\text{PhCN})_2$ (225 mg, 0.48 mmol) and xylene (15 ml) was refluxed for 60 min. under an argon flow. The xylene was removed by distillation and the crude product was purified by silica gel column chromatography (dichloromethane) to
 15 give compound **8** as a yellow solid (170 mg, 0.27 mmol, yield 59%). TLC, R_f = 0.65 (hexane:dichloromethane = 1:1). MALDI-TOF MS: m/z = 619.1 (M^+). ^1H NMR (400 MHz, CDCl_3) δ : 8.11 (d, 2H, J = 8.4 Hz), 7.96 (pseudo t, 2H, J = 8.2 z), 7.66 (d, 2H, J = 8.0 Hz), 7.54 (d, 2H, J = 10 Hz), 6.62 (pseudo t, 4H, J = 9.8 Hz), 2.12 (d, 3H, J = 24 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 162.84
 20 (d, = 5 Hz), 162.38 (dd, J = 228 and 12 Hz), 159.81 (dd, J = 229 and 12 Hz), 158.03 (d, J = 30 Hz), 152.06 (d, J = 6 Hz), 139.49, 130.07 (pseudo t, J = 3 Hz), 121.89 (d, J = 21 Hz), 117.28 (dd, J = 18 and 2 Hz), 116.83 (d, J = 15 Hz), 100.06 (pseudo t, J = 26 Hz), 99.86 (d, J = 181 Hz), 33.56 (d, J = 13 Hz); ^{19}F NMR (376 MHz, CDCl_3) δ : -107.64 (F pos. 2 with respect to phenylpyridine), -
 25 110.47 (F pos. 4 with respect to phenylpyridine), 167.22; ^{195}Pt NMR (86 MHz, CDCl_3) δ : -3613 (referenced to aqueous K_2PtCl_4). Anal. Calcd for $\text{C}_{24}\text{H}_{13}\text{F}_5\text{N}_2\text{Pt}$: C, 46.53; H, 2.12; N, 4.52. Found: C, 46.34; H, 2.05; N, 4.53. A single crystal X-ray diffraction study confirmed the structure indicated by **Formula 8a**.

Example 2 - Synthesis of Pt Complexes 13a and 16a

30 Pt Complexes **13a** and **16a** were prepared by the overall synthetic scheme disclosed in **Figure 4**.

5-(5-bromopentyl)bicyclo[2.2.1]hept-2-ene (mixture of *endo* and *exo* isomers, **9a**) was prepared by the procedure described in Stubbs, L. P.; Weck, M. *Chem. Eur. J.* 2003, 9, 992.

35 **Bis(6-bromo-2-pyridyl)(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)methanol (mixture of *endo* and *exo* isomers) (10a).** Compound **9a**

(1.30 g, 5.35 mmol) and magnesium (0.26 g, 10.7 mmol) was stirred for 4 h in 40 ml of THF under an argon flow. The obtained Grignard reagent (norbornenylmagnesium bromide) was added to a THF (20 ml) solution of compound **1** (0.90 g, 2.63 mmol) via a cannula. After the mixture was stirred for 2 h, the reaction was quenched with 1 ml methanol followed by 5 ml of 10% aqueous ammonium chloride. The crude product was extracted with dichloromethane (30 ml $\times$ 3 times) and dried over anhydrous magnesium sulfate. Finally, a silica gel column purification (hexane:EtOAc = 7:1) gave a yellow oil (0.85 g, 1.68 mmol, yield 64%). TLC, R_f = 0.75 (hexane:EtOAc = 5:1). *Endo* isomer: ^1H NMR (400 MHz, CDCl_3) δ : 7.82 (d, 2H, J = 7.6 Hz), 7.53 (pseudo t, 2H, J = 8.0 Hz), 7.32 (d, 2H, J = 7.6 Hz), 6.06 (dd, 1H, J = 5.6 and 3.2 Hz), 5.86 (dd, 1H, J = 5.6 and 3.2 Hz), 5.78 (s, 1H), 2.70 (m, 2H), 2.25 (m, 2H), 1.90 (m, 1H), 1.78 (m, 1H), 0.90-1.42 (m, 10H), 0.38-0.47 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 164.53, 139.98, 139.14, 136.74, 132.38, 126.35, 119.92, 77.92, 49.46, 45.29, 42.42, 42.02, 38.60, 34.60, 32.32, 29.89, 28.41, 23.41.

Bis(6-bromo-2-pyridyl)(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)methoxymethane (mixture of *endo* and *exo* isomers) (11a).
Compound **10a** (0.85 g, 1.68 mmol) was added to a suspension of sodium hydride (0.30 g, 12.5 mmol) in 40 ml of THF. Iodomethane (0.80 ml, 12.8 mmol) was added as the evolution of hydrogen gas had ceased. The mixture was stirred for 2 h, the reaction was quenched with 10% aqueous HCl until it became acidic, and then basified with 10% aqueous potassium carbonate. The crude product was extracted with dichloromethane (30 ml $\times$ 3 times) and dried over anhydrous magnesium sulfate. Finally, a silica gel column purification (hexane:EtOAc = 7:1) gave a yellow oil (0.63 g, 1.21 mmol, yield 72%). TLC, R_f = 0.6 (hexane:EtOAc = 5:1). MS (EI): m/z = 520 (M^+). *Endo* isomer: ^1H NMR (400 MHz, CDCl_3) δ : 7.42-7.50 (m, 4H), 7.25 (dd, 2H, J = 6.8 and 2.0 Hz), 6.04 (dd, 1H, J = 6.0 and 3.0 Hz), 5.85 (dd, 1H, J = 6.0 and 3.0 Hz), 3.11 (s, 3H), 2.70 (m, 2H), 2.55 (m, 2H), 1.90 (m, 1H), 1.77 (m, 1H), 0.90-1.42 (m, 10H), 0.39-0.46 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 163.94, 140.80, 138.35, 136.63, 132.28, 126.28, 120.72, 84.60, 50.52, 49.39, 45.21, 42.33, 38.53, 34.52, 32.26, 31.83, 29.80, 28.45, 22.41.

Bis(6-(2,4-difluorophenyl)-2-pyridyl)(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)methoxymethane (mixture of *endo* and *exo* isomers) (12a).
Compound **11a** (0.63 g, 1.21 mmol), 2,4-difluorophenylboronic acid (0.75 g, 4.75 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.16 g, 0.138 mmol)

were added to a round-bottomed flask equipped with a reflux condenser and dissolved in 20 ml of THF. After the addition of 15 ml of aqueous 2N Na₂CO₃, the reaction mixture was refluxed for 24 h. The cooled crude mixture was poured onto water, extracted with CH₂Cl₂ (50 ml × 3 times) and dried over anhydrous magnesium sulfate. Finally, a silica gel column purification (hexane:EtOAc = 10:1) gave a transparent oil (0.63 g, 1.07 mmol, yield 88%). TLC, R_f = 0.7 (hexane:EtOAc = 8:1). *Endo* isomer: ¹H NMR (400 MHz, CDCl₃) δ: 8.02 (dt, 2H, *J* = 10 and 6.8 Hz), 7.68 (d, 2H, *J* = 8.0 Hz), 7.63 (d, 2H, *J* = 8.0 Hz), 7.53 (d, 2H, *J* = 8.0 Hz), 6.82-6.97 (m, 4H), 6.06 (dd, 1H, *J* = 5.6 and 3.2 Hz), 5.86 (dd, 1H, *J* = 5.6 and 2.8 Hz), 3.26 (s, 3H), 2.78 (m, 2H), 2.70 (m, 2H), 1.89 (m, 1H), 1.77 (m, 1H), 0.90-1.44 (m, 10H), 0.40-0.46 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ: 163.06, 161.92 (dd, *J* = 222 and 12 Hz), 159.41 (dd, *J* = 223 and 12 Hz), 150.45 (d, *J* = 3 Hz), 136.72, 136.52, 132.34, 132.27 (dd, *J* = 9 and 5 Hz), 123.66 (dd, *J* = 11 and 3 Hz), 121.77 (d, *J* = 11 Hz), 120.37, 111.50 (dd, *J* = 21 and 4 Hz), 104.10 (dd, *J* = 24 and 24 Hz), 85.99, 50.68, 49.46, 45.30, 42.44, 38.65, 34.69, 32.32 (2C), 30.23, 28.64, 22.80; ¹⁹F NMR (376 MHz, CDCl₃) δ: -109.97 (F pos. 2 with respect to phenylpyridine), -112.38 (F pos. 4 with respect to phenylpyridine).

[Bis(6-(4,6-difluorophenyl)-2-pyridyl-*N,C*²)(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)methoxymethane]platinum(II) (mixture of *endo* and *exo* isomers) (13a). A mixture of compound **12a** (200 mg, 0.34 mmol), PtCl₂(PhCN)₂ (165 mg, 0.34 mmol) and xylene (15 ml) was refluxed for 60 min. under an argon flow. The xylene was removed by distillation and the crude product was purified by silica gel column chromatography (dichloromethane) to give compound **13a** as a yellow solid (100 mg, 0.13 mmol, yield 38%). TLC, R_f = 0.7 (hexane:dichloromethane = 1:1). MALDI-TOF MS: *m/z* = 779.2 (*M*⁺). *Endo* isomer: ¹H NMR (400 MHz, CDCl₃) δ: 8.15 (d, 2H, *J* = 8.0 Hz), 7.98 (pseudo t, 2H, *J* = 8.0 Hz), 7.73 (dd, 2H, *J* = 8.0 and 0.8 Hz), 7.57 (dd, 2H, *J* = 10 and 2.0 Hz), 6.62 (ddd, 2H, *J* = 12, 8.8 and 2.0 Hz), 6.01 (dd, 1H, *J* = 5.6 and 3.2 Hz), 5.76 (dd, 1H, *J* = 5.8 and 3.0 Hz), 3.41 (s, 3H), 2.58 (d, 2H, *J* = 28 Hz), 2.23 (m, 4H), 0.70-1.94 (m, 10H), 0.29-0.34 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ: 162.92 (d, *J* = 7 Hz), 162.07 (dd, *J* = 254 and 12 Hz), 159.42 (dd, *J* = 255 and 12 Hz), 158.65, 153.20 (d, *J* = 5 Hz), 138.85, 136.80, 132.23, 130.23 (pseudo t, *J* = 3 Hz), 121.36 (d, *J* = 21 Hz), 120.87, 117.54 (dd, *J* = 18 and 2 Hz), 99.83 (pseudo t, *J* = 27 Hz), 92.79, 53.81, 49.46, 47.26, 45.27, 42.44, 38.50, 34.45, 32.31, 29.28, 28.07, 23.29; ¹⁹F NMR (376 MHz, CDCl₃) δ: -108.13 (F

pos. 2 with respect to phenylpyridine), -110.80 (F pos. 4 with respect to phenylpyridine); ^{195}Pt NMR (86 MHz, CDCl_3) δ : -3602 (referenced to aqueous K_2PtCl_4). Anal. Calcd for $\text{C}_{36}\text{H}_{32}\text{F}_4\text{N}_2\text{OPt}$: C, 55.45; H, 4.41; N, 3.59. Found: C, 55.74; H, 4.19; N, 3.45.

5 **Bis(6-bromo-2-pyridyl)(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)fluoromethane (mixture of *endo* and *exo* isomers) (14a).**

Diethylaminosulfur trifluoride (DAST, 0.46 ml, 3.72 mmol) was added to a dichloromethane (20 ml) solution of compound **10a** (0.65 g, 1.28 mmol) at 0°C. After the mixture was stirred at room temperature for 60 min., it was quenched
 10 with 10 ml ice-cooled water (caution: strongly exothermic reaction) and then basified with 10 ml 3M sodium hydroxide. The crude product was extracted with dichloromethane (30 ml $\times$ 3 times) and dried over anhydrous magnesium sulfate. Finally, a silica gel column purification (hexane:EtOAc = 10:1) gave a yellow oil (0.58 g, 1.14 mmol, yield 88%). TLC, R_f = 0.65 (hexane:EtOAc = 5:1). *Endo*
 15 isomer: ^1H NMR (400 MHz, CDCl_3) δ : 7.52 (m, 4H), 7.36 (dd, 2H, J = 7.0 and 1.8 Hz), 6.06 (dd, 1H, J = 5.6 and 3.2 Hz), 5.86 (dd, 1H, J = 5.8 and 3.0 Hz), 2.70 (m, 2H), 2.51 (m, 2H), 1.91 (m, 1H), 1.78 (m, 1H), 0.90-1.40 (m, 10H), 0.40-0.47 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 161.05 (d, J = 26 Hz), 141.22 (d, J = 2 Hz), 138.81, 136.74, 132.33, 127.20, 119.37 (d, J = 8 Hz), 97.87
 20 (d, J = 179 Hz), 49.44, 45.27, 42.40, 38.56, 37.78 (d, J = 21 Hz), 34.50, 32.31, 29.65, 28.30, 22.85 (d, J = 3 Hz); ^{19}F NMR (376 MHz, CDCl_3) δ : -161.34.

Bis(6-(2,4-difluorophenyl)-2-pyridyl)(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)fluoromethane (mixture of *endo* and *exo* isomers) (15a). Compound
 14a (0.60 g, 1.18 mmol), 2,4-difluorophenylboronic acid (0.80 g, 4.75 mmol)
 25 and tetrakis(triphenylphosphine)palladium(0) (0.14 g, 0.121 mmol) were added to a round-bottomed flask equipped with a reflux condenser and dissolved in 20 ml of THF. After the addition of 15 ml of aqueous 2N Na_2CO_3 , the reaction mixture was refluxed for 24 h. The cooled crude mixture was poured onto water, extracted with CH_2Cl_2 (50 ml $\times$ 3 times) and dried over anhydrous magnesium
 30 sulfate. Finally, a silica gel column purification (hexane:EtOAc = 10:1) gave a transparent oil (0.60 g, 1.04 mmol, yield 88%). TLC, R_f = 0.8 (hexane:EtOAc = 5:1). *Endo* isomer: ^1H NMR (400 MHz, CDCl_3) δ : 8.13 (dt, 2H, J = 10 and 6.8 Hz), 7.74 (m, 4H), 7.56 (d, 2H, J = 7.2 Hz), 6.85-7.00 (m, 4H), 6.08 (dd, 1H, J = 5.6 and 3.0 Hz), 5.87 (dd, 1H, J = 6.0 and 2.8 Hz), 2.78 (m, 2H), 2.71 (m, 2H),
 35 1.92 (m, 1H), 1.79 (m, 1H), 0.95-1.47 (m, 10H), 0.42-0.48 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 162.07 (dd, J = 230 and 12 Hz), 160.61 (d, J =

27 Hz), 159.56 (dd, $J = 232$ and 12 Hz), 151.03, 136.99, 136.79, 132.40 (dd, $J = 10$ and 5 Hz), 132.35, 123.43 (dd, $J = 11$ and 4 Hz), 122.50 (d, $J = 11$ Hz), 118.85 (d, $J = 8$ Hz), 111.57 (dd, $J = 21$ and 4 Hz), 103.97 (dd, $J = 27$ and 25 Hz), 99.85 (d, $J = 176$ Hz), 49.51, 45.37, 42.50, 38.69, 38.02 (d, $J = 21$ Hz),
 5 34.64, 32.93, 30.01, 28.47, 23.24 (d, $J = 3$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ : -110.04 (F pos. 2 with respect to phenylpyridine), -112.85 (F pos. 4 with respect to phenylpyridine), -162.31 (bridge pos.).

[Bis(6-(4,6-difluorophenyl)-2-pyridyl- N, C^2)(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)fluoromethane]platinum(II) (mixture of *endo* and *exo* isomers) (16a). A
 10 mixture of compound 12 (200 mg, 0.35 mmol), $\text{PtCl}_2(\text{PhCN})_2$ (165 mg, 0.35 mmol) and xylene (15 ml) was refluxed for 60 min. under an argon flow. The xylene was removed by distillation and the crude product was purified by silica gel column chromatography (dichloromethane) to give 16 as a yellow solid (80 mg, 0.10 mmol, yield 30%). TLC, $R_f = 0.7$ (hexane:dichloromethane = 1:1).
 15 FAB-MS: $m/z = 768.2$ ($M+1$) $^+$. *Endo* isomer: ^1H NMR (400 MHz, CDCl_3) δ : 8.10 (d, 2H, $J = 8.4$ Hz), 7.94 (pseudo t, 2H, $J = 8.0$ Hz), 7.63 (dd, 2H, $J = 7.8$ and 1.8 Hz), 7.55 (dd, 2H, $J = 10$ and 2.0 Hz), 6.61 (ddd, 2H, $J = 12$, 8.8 and 2.0 Hz), 6.02 (dd, 1H, $J = 5.6$ and 3.0 Hz), 5.78 (dd, 1H, $J = 5.8$ and 3.0 Hz), 2.60 (d, 2H, $J = 26$ Hz), 2.50 (m, 4H), 0.73-1.93 (m, 10H), 0.31-0.37 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$
 20 NMR (100 MHz, CDCl_3) δ : 162.83 (d, $J = 6$ Hz), 162.38 (dd, $J = 226$ and 12 Hz), 159.81 (dd, $J = 229$ and 12 Hz), 157.24 (d, $J = 30$ Hz), 152.07 (d, $J = 7$ Hz), 139.07, 136.85, 132.24, 130.10 (pseudo t, $J = 3$ Hz), 121.76 (d, $J = 21$ Hz), 117.81 (d, $J = 16$ Hz), 117.25 (dd, $J = 18$ and 2 Hz), 101.97 (d, $J = 181$ Hz), 100.03 (pseudo t, $J = 27$ Hz), 49.48, 45.29, 45.16 (d, $J = 23$ Hz), 42.45, 38.53,
 25 34.42, 32.33, 29.03, 28.17, 22.87 (d, $J = 2$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ : -107.54 (F pos. 2 with respect to phenylpyridine), -110.45 (F pos. 4 with respect to phenylpyridine), 157.15 (bridge pos.); ^{195}Pt NMR (86 MHz, CDCl_3) δ : -3610 (referenced to aqueous K_2PtCl_4). Anal. Calcd for $\text{C}_{35}\text{H}_{29}\text{F}_5\text{N}_2\text{Pt}$: C, 54.76; H, 3.81; N, 3.65. Found: C, 54.46; H, 3.79; N, 3.53.

30 **Example 3 - Synthesis and Polymerization of Carbazole Monomer 22**

Bicyclo[2,2,1]hept-5-en-2-ylmethyl-3,5-di(carbazol-9-yl)benzoate (mixture of *endo* and *exo* isomers) (22) is a novel polymerizable norbornene derivative of mCP (1,3-di(carbazol-9-yl)benzene). mCP has been used in the prior art as a monomeric hole carrying compound for fabricating blue-emitting
 35 OLEDs due to its high triplet energy (3.0 eV). The polymerizable norbornene

derivative was synthesized by the procedure shown in Figure 5, and further detailed below.

3,5-diiodobenzoic acid (**18a**) was prepared by the procedure described in Endres, A.; Maas, G *Tetrahedron* **2002**, 58, 3999. Methyl 3,5-diiodobenzoate (**19a**) was synthesized by the procedure reported in Kvam, P. I.; Puzyk, M. V.; Balashev, K. P.; Songstad, J. *Acta Chem. Scand.* **1995**, 49, 335.

Methyl 3,5-di(carbazol-9-yl)benzoate (20). To a stirred solution of methyl 3,5-diiodobenzoate (3.00 g, 7.73 mmol), carbazole (3.00 g, 17.94 mmol), Cu (6.40 g, 100.7 mmol) and 18-crown-6 (65 mg, 0.25 mmol) in 30 ml 1,2-dichlorobenzene was added potassium carbonate (12.60 g, 91.17 mmol) under a nitrogen flow. The reaction was stirred at 180°C for 10 h then cooled to room temperature, filtered and the solid residues were washed with THF. After the solvents were removed by evaporation from the combined filtration solution, the crude product was purified by silica gel column chromatography using toluene as the eluent. The target compound was obtained as a white product in 72% yield (2.60 g, 5.58 mmol) by recrystallization from acetone/methanol. MS (EI): m/z = 466 (M^+). 1H NMR (400 MHz, $CDCl_3$) δ : 8.37 (d, 2H, J = 1.6 Hz), 8.15 (dd, 4H, J = 7.2 and 0.8 Hz), 8.02 (t, 1H, J = 1.6 Hz), 7.52 (dd, 4H, J = 7.2 and 0.8 Hz), 7.45 (td, 4H, J = 7.2 and 1.6 Hz), 7.32 (td, 4H, J = 7.2 and 1.2 Hz), 3.99 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ : 165.39, 140.18, 139.54, 133.63, 129.09, 126.45, 126.20, 123.62, 120.55, 120.43, 109.42, 52.82. Anal. Calcd for $C_{32}H_{22}N_2O_2$: C, 82.38; H, 4.75; N, 6.00. Found: C, 82.34; H, 4.66; N, 6.03.

3,5-Di(carbazol-9-yl)benzoic acid (21). A mixture of methyl 3,5-di(carbazol-9-yl)benzoate (1.00 g, 2.14 mmol), 2 ml aq. KOH (30 wt%), 15 ml of THF and 10 ml methanol was stirred at room temperature for 5 h. After the organic solvent was removed under reduced pressure, 20 ml of methanol and 80 ml of 2M aq. HCl were added subsequently to the residues. The reaction mixture was stirred for an additional hour. A pale yellow solid was obtained by filtration. The crude product was purified by recrystallization from acetone/water in 98% yield (0.95 g, 2.10 mmol). MS (EI): m/z = 452.1 (M^+). 1H NMR (400 MHz, $CDCl_3$) δ : 8.37 (d, 2H, J = 2.4 Hz), 8.21 (dt, 4H, J = 7.2 and 0.8 Hz), 8.19 (t, 1H, J = 2.4 Hz), 7.63 (dd, 4H, J = 7.2 and 0.8 Hz), 7.47 (td, 4H, J = 7.2 and 1.2 Hz), 7.30 (td, 4H, J = 7.2 and 1.2 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ : 166.04, 141.19, 140.34, 135.14, 130.08, 127.31, 127.11, 124.38, 121.32, 121.17, 110.42.

Bicyclo[2,2,1]hept-5-en-2-ylmethyl-3,5-di(carbazol-9-yl)benzoate (mixture of *endo* and *exo* isomers) (22). A mixture of 3,5-di(carbazol-9-yl)benzoic acid (0.50 g, 1.10 mmol), 5-(bromomethyl)bicyclo[2,2,1]hept-2-ene (0.30 g, 1.60 mmol), potassium carbonate (4.00 g, 28.94 mmol) and 6 ml of DMF was stirred at 60°C for 26 h. After the reaction mixture was cooled to room temperature, 40 ml water was added. A white solid was obtained by filtration which was purified by silica gel column chromatography using toluene and hexanes (3:2) as eluents. The isolated glassy solid was dissolved in a small mount of acetone (2 ml) and added dropwise to a mixture of methanol and water (20 ml, 4:1) to give a white precipitate. After filtration and drying, host monomer **22** (0.48 g, 0.86 mmol, yield 78%) was obtained. MS (EI): $m/z = 558.2$ (M^+). ^1H NMR (400 MHz, CDCl_3) δ : 8.38 (m, 2H), 8.16 (d, 4H, $J = 7.2$ Hz), 8.19 (m, 1H), 7.53 (d, 4H, $J = 7.2$ Hz), 7.46 (t, 4H, $J = 7.2$ Hz), 7.33 (t, 4H, $J = 7.2$ Hz), 6.19 (dd, 0.7H, $J = 5.6$ and 2.4 Hz, *endo*), 6.09 (m, 0.6H, *exo*), 6.00 (dd, 0.7H, $J = 5.6$ and 1.4 Hz, *endo*), 4.49 (dd, 0.3H, $J = 10.4$ and 6.8 Hz, *exo*), 4.33 (dd, 0.3H, $J = 9.2$ and 9.2 Hz, *exo*), 4.18 (dd, 0.7H, $J = 10.4$ and 6.8 Hz, *endo*), 4.00 (dd, 0.7H, $J = 10.8$ and 9.2 Hz, *endo*), 2.87 (m, 2H), 2.53 (m, 1H), 1.88 (m, 1H), 1.45 (m, 2H), 0.67 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 165.01, 140.31, 139.62, 137.82 (*endo*), 136.98 (*exo*), 136.12 (*exo*), 134.16, 132.06 (*endo*), 129.09, 126.51, 126.31, 123.69, 120.63, 120.53, 109.48, 69.80 (*exo*), 69.16 (*endo*), 49.40 (*endo*), 44.97 (*exo*), 43.93 (*endo*), 43.65 (*exo*), 42.17 (*endo*), 41.57 (*exo*), 37.98 (*exo*), 37.77 (*endo*), 29.55 (*exo*), 28.92 (*endo*). Anal. Calcd for $\text{C}_{39}\text{H}_{30}\text{N}_2\text{O}_2$: C, 83.85; H, 5.41; N, 5.01. Found: C, 83.89; H, 5.35; N, 4.98.

Example 4 - Homopolymerization of Compound 22 to Produce The Carbazole Homopolymer (22)

The ring-opening metathesis polymerization (ROMP) the carbazole containin host monomer (**22**) was carried out using Grubbs' 3rd-generation initiator to form homopolymers having structure **23** as shown in **Figure 8**. Four different polymerizations were carried out with monomer to initiator ratios of 25:1, 50:1, 75:1, and 100:1. **Figure 9a** shows the molecular weights of these homopolymers versus the monomer to initiator ratios. A linear relationship was obtained indicating that the polymerization is controlled. Furthermore, ^1H NMR spectroscopy experiments showed the complete disappearance of the carbene signal of the initiator around 19.10 ppm, and the formation of two new, broad carbene signals at 18.61 (*endo* isomer) and 18.84 (*exo* isomer) ppm, indicating

complete initiation (**Figure 7b**). Both experiments strongly suggest that the ROMP of **22** to form the hole-carrying polymer **23** proceeds in a living fashion.

Example 5 – Copolymerization of Norbornene/Pt Complexes 13a and 16a with Norbornene/Carbazole Monomer 22

Attempts to ROMP homo-polymerize Norbornene/Pt complexes **13a** or **16a** resulted in insoluble materials. However, co-polymerizations of the Norbornene/Pt complexes **13a** or **16a** with the norbornene/carbazole monomer **22** to form copolymers **24** and **25** (see **Figure 8**) were carried out in distilled methylene chloride at room temperature for 20 min. using Grubbs' 3rd-generation ROMP initiator. The ratio of Norbornene/Carbazole monomer **22** to the platinum complex-containing monomers was 9:1 (wt %). Monomer to initiator ratios of 50:1 were employed. The polymerizations were quenched by addition of ethyl vinyl ether and stirring for 20 minutes, then the solutions were concentrated and precipitated into methanol. The work up procedure was repeated five times until hexane solutions were clear, then the polymers **24** and **25** were collected.

Copolymers **24** and **25** are highly soluble in common organic solvents, suggesting a random distribution of the two types of co-monomers. The copolymers were characterized by gel permeation chromatography (see **Table 1** below). Molecular weights around 27 kDa and polydispersity indices around 2.7 were obtained. The platinum content feed ratios of copolymers **24** and **25** are 2.50% and 2.54% respectively, slightly larger than the experimental data of 2.05% and 1.77% measured using ICP-MS, indicating that the doubly cyclometalated Pt moieties are generally stable during ROMP polymerizations. Ruthenium contents in all the copolymers are below 10 ppm, suggesting good removal of the Ru initiators from the copolymers. All polymers showed glass-transition temperatures around 190°C and good thermal stabilities with decomposition temperatures above 380°C at 5% weight loss.

Table 1. Polymer characterization data of Copolymers **23-25**.

Polymer	M _n	M _w	PDI	T _g (°C)	T _d (°C) ^a	Pt(%) ^{b,c}	Ru(ppm) ^b
23	30 000	75 000	2.50	189	387	-	-
24	27 000	72 000	2.64	189	382	2.05(2.50)	9.7
25	27 000	74 000	2.74	187	380	1.77(2.54)	8.6

^a Temperature at 5% weight loss. ^b ICP-MS measurements. ^c The values in parentheses are the feed ratios.

Photophysical Properties of the Pt complexes, Monomers, and Copolymers. Norbornene-substituted platinum complex **13a** exhibits intense

vibronic-structured absorption bands at wavelengths below 350 nm with extinction coefficients (ϵ) on the order of $10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and a medium intensity band in the region around 390 nm (see **Figure 10a**). Without wishing to be bound by theory, these two absorption bands may be ascribed to the intra

5 ligand transition and the transition from the metal-centered d orbitals to π^* orbitals of the ligand, respectively. The absorption properties were found to follow Beer's law below concentrations of about $5 \times 10^{-4} \text{ M}$, suggesting the absence of significant complex aggregation at those concentrations.

A comparison of the both the absorption and photoluminescence spectra of

10 **5a** and **13a** in CH_2Cl_2 are shown in **Figure 10a**. Platinum complex **5a** exhibits an almost identical spectrum to monomer **13a**. This is also true in thin solid films of these compounds. A comparison of the solid-state photoluminescence spectra between complex **5a** dispersed in poly(*N*-vinylcarbazole) (PVK) and copolymer **24** is shown in Figure 8b. Again, the polymeric materials track the emission of

15 their small molecule analogues very well.

Similar results were obtained for the other system based on **8a**, **16a** and **25**, as shown in Figures **11a** and **11b**. The photophysical characterization data are listed in **Table 2** shown below.

Table 2

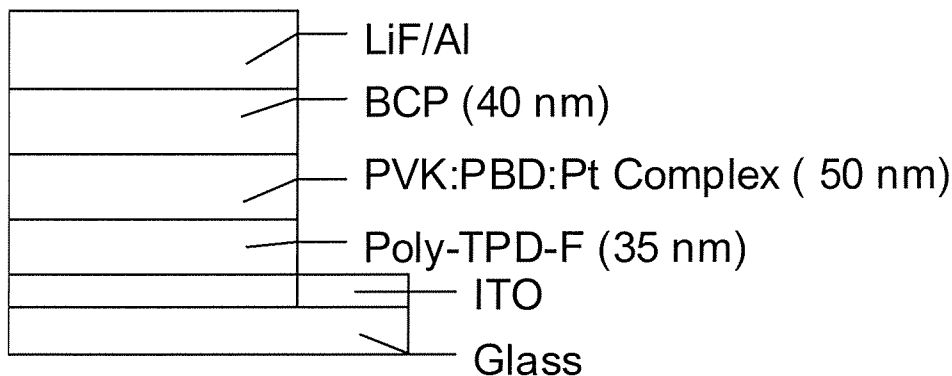
Entry	$\lambda_{\text{abs}}/\text{nm}$ ($\epsilon/10^3 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) ^a	λ_{em} (nm) ^a	λ_{em} (nm)	$\Phi_{\text{f}}^{\text{c}}$	$\Phi_{\text{f}}^{\text{d}}$	$\tau/\mu\text{s}^{\text{c}}$
5a	257 (33.2), 284 (32.3), 319 (19.0), 339 (10.5), 368 (4.92), 390 (9.42), 478 (0.89)	493, 525, 560(sh)	526 ^b	0.54	0.55	0.38
13a	258 (33.3), 285 (31.6), 318 (19.3), 339 (10.8), 369 (5.24), 390 (9.52), 477 (0.81)	492, 520, 560(sh)	-	0.56	0.54	0.39
24	-	-	528	-	-	-
8a	255 (33.8), 284 (32.4), 320 (18.4), 340 (10.3), 369 (4.41), 394 (9.27), 478 (0.78)	492, 520, 564(sh)	526 ^b	0.58	0.57	0.32
16a	255 (33.6), 285 (33.4), 321 (18.2), 341 (10.0), 370 (4.25), 394 (8.84), 478 (0.77)	492, 522, 564(sh)	-	0.55	0.56	0.38
25	-	-	529	-	-	-

^a In CH₂Cl₂. ^b In PVK films. ^c In degassed CH₂Cl₂; reference: *fac*-Ir(ppy)₃ (Φ = 0.40 in toluene). ^d In degassed THF; reference: *fac*-Ir(ppy)₃ (Φ = 0.40 in toluene).

The phosphorescent quantum efficiencies of compounds **5a**, **8a**, **13** and **16** are above 0.5, and significantly higher than that reported for the widely used green emitter Ir(ppy)₃ in toluene (Φ = 0.40), (See (a) Adachi, C.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **2000**, 77, 904. (b) Kawamura, Y.; Brooks, J.; Brown, J. J.; Sasabe, H.; Adachi, C. *Phys. Rev. Lett.* **2006**, 96, 017404. (c) Adachi, C.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *J. Appl. Phys.* **2001**, 90, 5048), suggesting that the Pt complexes and the related copolymers disclosed and claimed herein may be unexpectedly advantageous for use in the manufacture of OLED devices.

Example 6 – OLED Devices Employing the Pt Complexes 5a, 8a, and 24

OLED devices comprising the Pt Complexes **5a**, **8a**, **24** and **25** were constructed and tested as described herein. The devices comprised six layers as shown in the diagram below.



The OLED devices prepared differed only by the nature of the emissive layers. For all preparations of the OLED devices, glass substrates coated with air plasma treated indium tin oxide (ITO) with a sheet resistance of 20 Ω /square were purchased from Colorado Concept Coatings, L.L.C. of Loveland Colorado USA. For the hole-transport/anodic layers, 10 mg of photo-crosslinkable **Poly-TPD-F** was dissolved in 1ml of distilled and degassed toluene under inert atmosphere and stirred overnight. 35 nm thick films of the Poly-TPD-F were spin coated (60s@1500 rpm, acceleration 10,000) onto the (ITO) coated glass substrates, then crosslinked using a standard broad-band UV light with a 0.7 mW/cm² power density for 1 minute.

Subsequently, Pt containing solutions for the emissive layer were spin coated on top of the crosslinked hole-transport layer (60s@1500 rpm, acceleration 10,000) to form a 20 nm thick film of the emissive materials.

For the electron-transport/hole-blocking layers, bathocuproine (BCP) was first purified via gradient zone sublimation, then thermally evaporated onto the top of the emissive layers at a rate of $0.4 \text{ \AA/s}$ and at a pressure below 1×10^{-7} Torr, to form a film 40 nm thick electron carrying/hole blocking layer.

Finally, 2.5 nm of lithium fluoride (LiF) as an electron-injection layer and a 200 nm-thick aluminum cathode were vacuum deposited at a pressure below 1×10^{-6} Torr and at rates of $0.1 \text{ \AA/s}$ and $2 \text{ \AA/s}$, respectively. A shadow mask was used for the evaporation of the Aluminum metal to form five devices with an area of 0.1 cm^2 per substrate. Testing of the resulting OLED devices was done right after the deposition of the metal cathode in inert atmosphere without exposing the devices to air.

OLED Devices comprising Pt Complex 5a. OLED devices having emissive layers comprising various loadings of Pt complex **5a** dispersed in PVK and PBD were prepared by the procedure general device procedures described above. In particular, a first device comprising 5% by weight of Pt Complex 5a in the emissive layer was prepared by dissolving 7 milligrams of polyvinylcarbazole (PVK) as a hole carrying material and 2.5 mg of 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1, 3, 4-oxadiazole (PBD, structure shown below) as an electron carrying material, and 0.5 mg of Pt Complex 5a in 1 ml of distilled and degassed chlorobenzene and stirring under an inert atmosphere overnight.

The solution comprising the PVK, PBD, and Pt complex 5a was spin-coated onto the surface of a previously prepared layer of the poly-TPD-F cross-linked hole transport material, to form a 50 nm thick layer of the emissive material.

An electron transporting layer of BCP and a LiF/Aluminum cathode layer were subsequently deposited over the emissive layers. Similar devices comprising 10, 15, 20, 25, 30, and 35% by weight of the Pt complex 5a were also prepared.

The device performance data for the device comprising 10% of Pt complex 5a in the emissive layer is shown in Figures **12a** and **12b**.

The emission wavelengths and other characteristics of the devices comprising complex 5a in the emissive layer vary strongly depending upon the loading of Platinum complex, see Figure **12c**.

OLED Devices comprising Pt Complex 8a. OLED devices having emissive layers comprising Pt Complex 5a were prepared by the general procedure described above. An OLED device with an emissive layer comprising 5% of Pt complex 8a was prepared by dissolving 7 mg PVK, 2.5 mg PBD, and
5 0.5 mg of Pt Complex 8a was dissolved in the chlorobenzene, and repeating the previously described procedures. Yet another OLED device comprising 10% of Pt Complex 8a was prepared from 6.5 mg of PVK, 2.5 mg of PBD, and 1.0 mg of Pt Complex 8a, and following the previously described procedures.

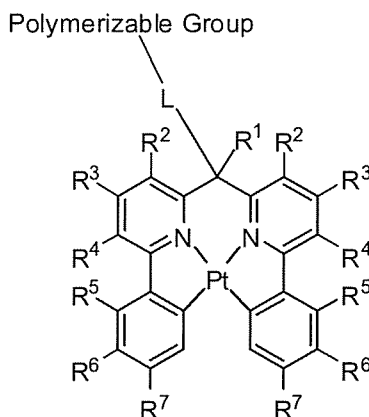
The device performance data for the device comprising 10% of Pt complex
10 5a in the emissive layer is shown in Figures **13a**. The emission wavelengths and other characteristics of the devices comprising complex 5a in the emissive layer vary strongly depending upon the loading of Platinum complex, see Figure **13b**.

OLED Device comprising Pt Copolymers 24 and 25. OLED devices having emissive layers comprising Pt copolymers 24 or 25 were prepared by the
15 general procedure described above. An OLED device with an emissive layer comprising 5% of one of Pt copolymers 24 and 25 was prepared by dissolving 10 mg of Copolymer 24 in 1 or 2 ml of toluene, and repeating the previously described procedures. The device performance data for the devices comprising is shown in Figure 14.

20 The above specification, examples and data provide exemplary description of the manufacture and use of the various compositions and devices of the inventions, and methods for their manufacture and use. In view of those disclosures, one of ordinary skill in the art will be able to envision many additional embodiments of the inventions disclosed and claimed herein to be
25 obvious, and that they can be made without departing from the spirit and scope of the invention. The claims hereinafter appended define some of those embodiments.

What is claimed is:

1. A monomer comprising a polymerizable group linked to a platinum complex, having the formula:



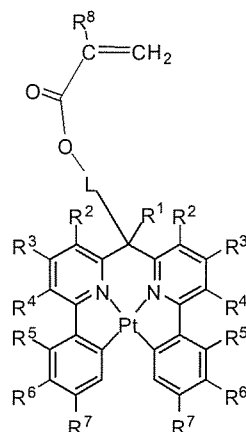
wherein

- 5 a) the polymerizable group comprises from 2 to 20 carbon atoms, and a functional group that can be copolymerized with other comonomers,
- b) L is a C₁-C₂₀ organic group linking the polymerizable group to the platinum complex;
- c) R¹ is fluoride, or a C₁-C₁₂ alkyl, alkoxy, hydroxyalkyl, aryloxy, or
10 arylalkyloxy group;
- d) R², R³, and R⁴ are independently selected from hydrogen and a C₁-C₁₂ organic substituent group;
- e) R⁵, R⁶, and R⁷ are independently selected from hydrogen, fluoride, and a C₁-
15 C₁₂ organic substituent group, or together two of R⁵, R⁶, and R⁷ form a benzene ring that can be optionally substituted by one or two substituent groups independently selected fluoride, C₁-C₁₂ alkyl, alkoxy, hydroxyalkyl, cyano, aryloxy, and arylalkyloxy groups.

2. The monomer of claim 1 wherein the polymerizable group comprises an acrylate, methacrylate, styrene, or norbornene functional group.

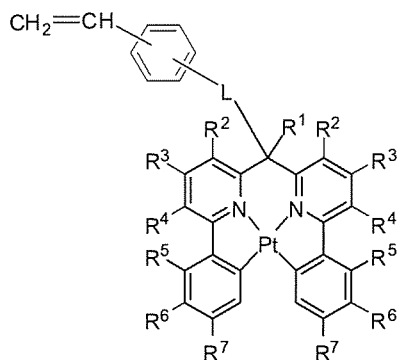
20 3. The monomer of claim 1 having the structure:

- 45 -

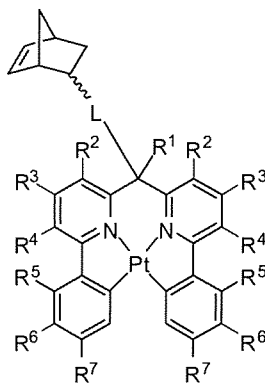


wherein R⁸ is H or CH₃.

4. The monomer of claim 1 having the structure:

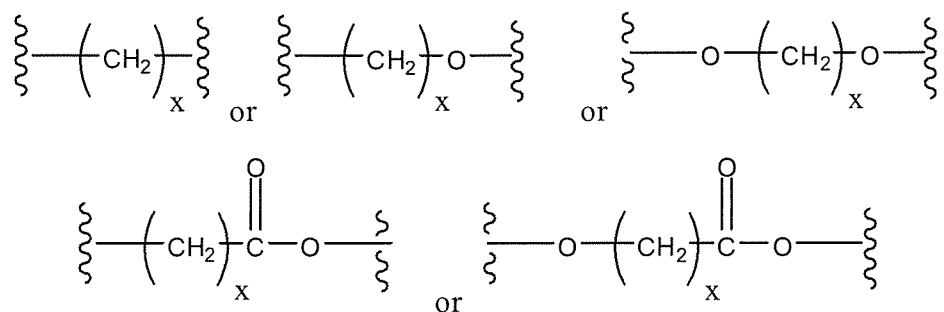


5. The monomer of claim 1 having the structure:



6. A monomer of any one of claims 1-5 wherein L is selected from optionally substituted alkylene, alkoxy, alkylether, alkyl or alkylester, alkylamide, alkylimide, arylene, or arylalkylene, and arylalkoxy groups.

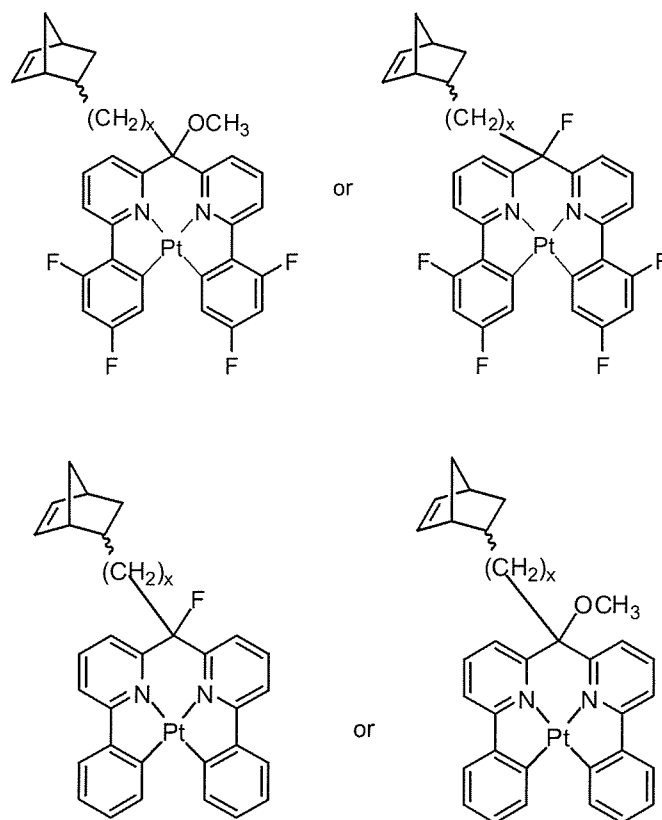
7. A monomer of any one of claims 1-5 wherein L has the formula

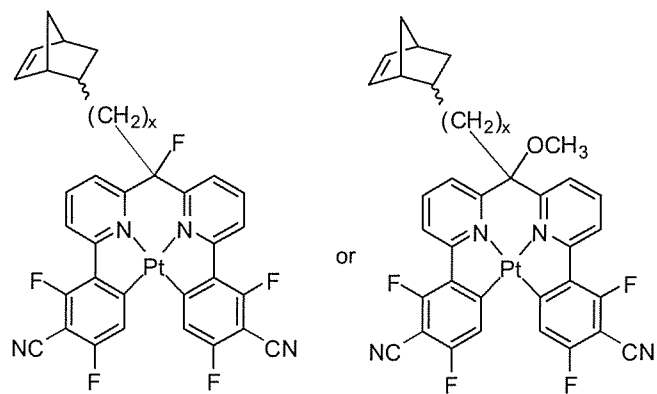
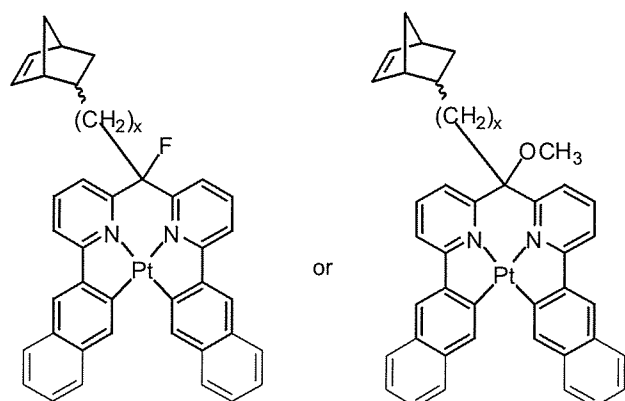
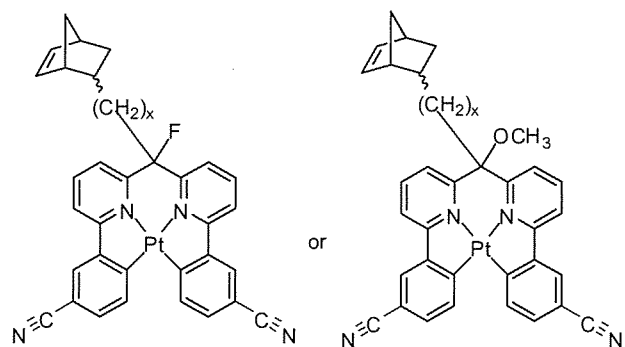


wherein x is an integer from 1 to 20.

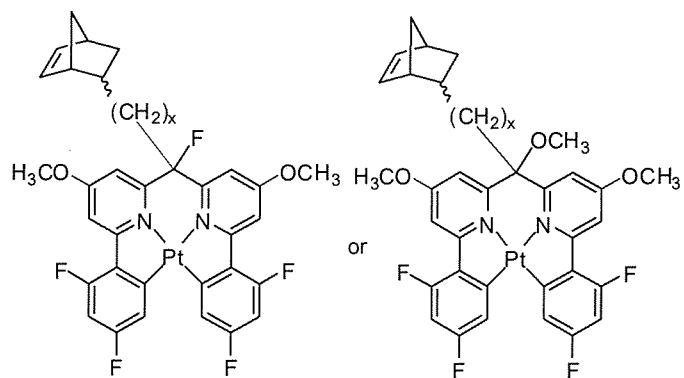
8. A monomer of any one of claims 1-5 wherein R¹ is fluoride or a C₁-C₁₂ alkoxy group.

9. A monomer of claim 1 having the formula:





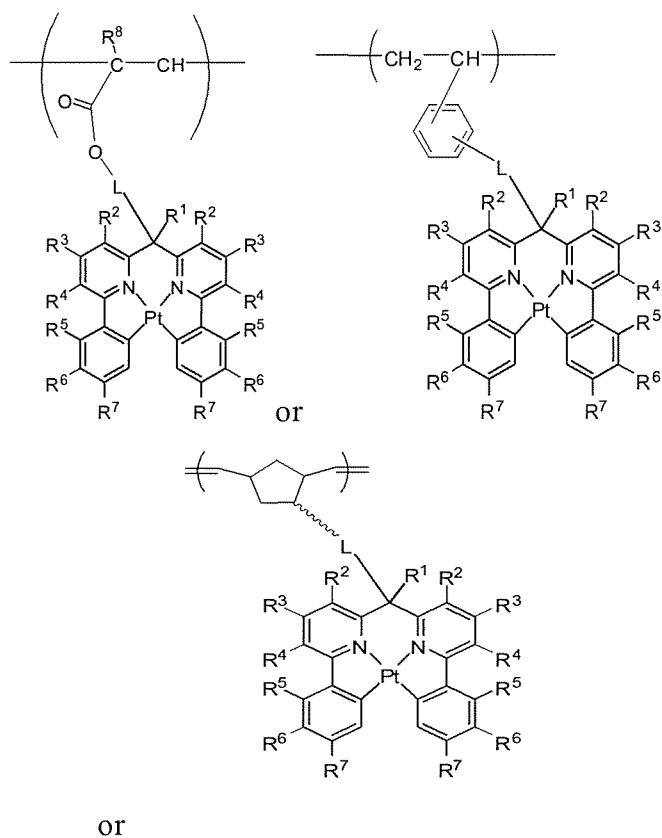
5



wherein x is an integer from 2 to 18.

10. A copolymer prepared by mixing at least one monomer of one of claims 1-9 with one or more additional co-monomers, and polymerizing the mixture of monomers.

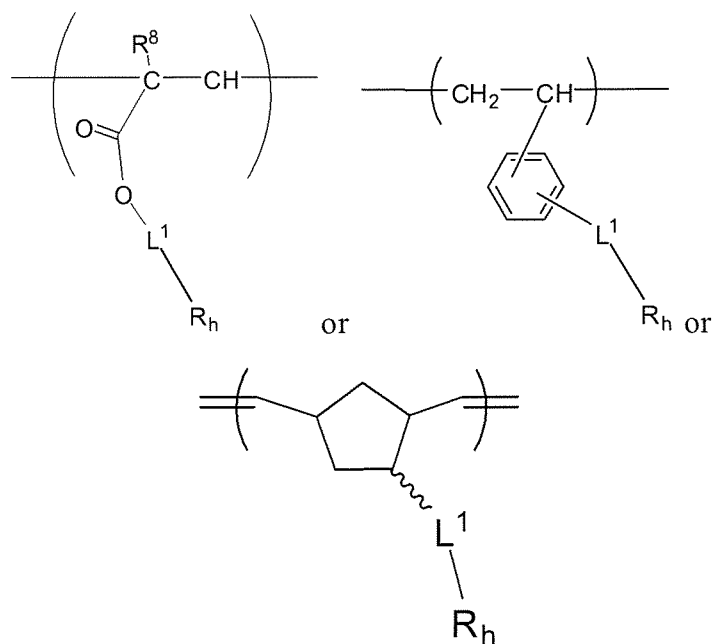
5 11. The copolymer of claim 10 comprising at least one polymerized subunit having the structure:



wherein R^8 is H or CH_3 .

10 12. The copolymer of claim 11 wherein at least one subunit has the structure

- 49 -

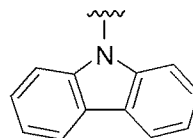


wherein

- i) L^1 is a C_1 - C_{20} organic group linking the polymeric subunit to the R_h group;
- 5 and
- ii) the R_h group comprises a poly-unsaturated and polycyclic aromatic or heteroaromatic group capable of conducting holes, electrons, and/or excitons, and
- iii) wherein R^8 is H or CH_3 .

10 13. The copolymer of claim 12 wherein the R_h groups comprise one or more of the following;

- a) carbazole groups comprising the ring structure,

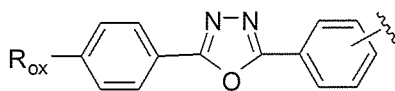


15 wherein the carbazole ring structure can optionally be further substituted with 1, 2, or 3 C_1 - C_{12} ring substituent groups;

or

- b) mono-oxadiazole groups comprising the ring structure:

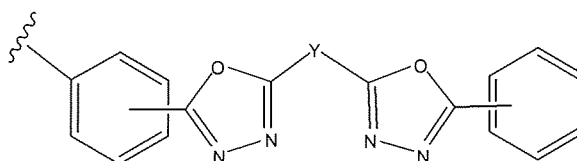
- 50 -



wherein R_{ox} is a C_1 - C_{12} alkyl group, and the mono-oxadiazole ring structure can optionally be further substituted with 1, 2, or 3 C_1 - C_{12} ring substituent groups;

or

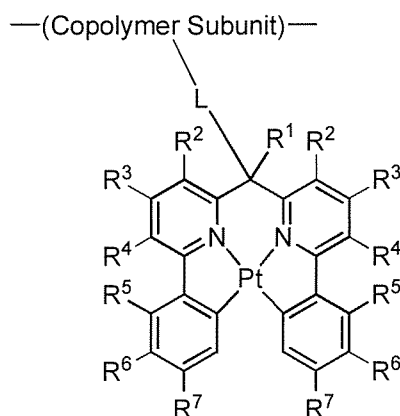
- 5 c) bis-oxadiazole groups comprising the ring structure:



wherein Y is absent or an arene group, and the bis-oxadiazole ring structure may be optionally further substituted with 1, 2, or 3 C_1 - C_{12} ring substituent groups.

- 10 14. An electronic device comprising at least one copolymer of any one of claims 10-13.

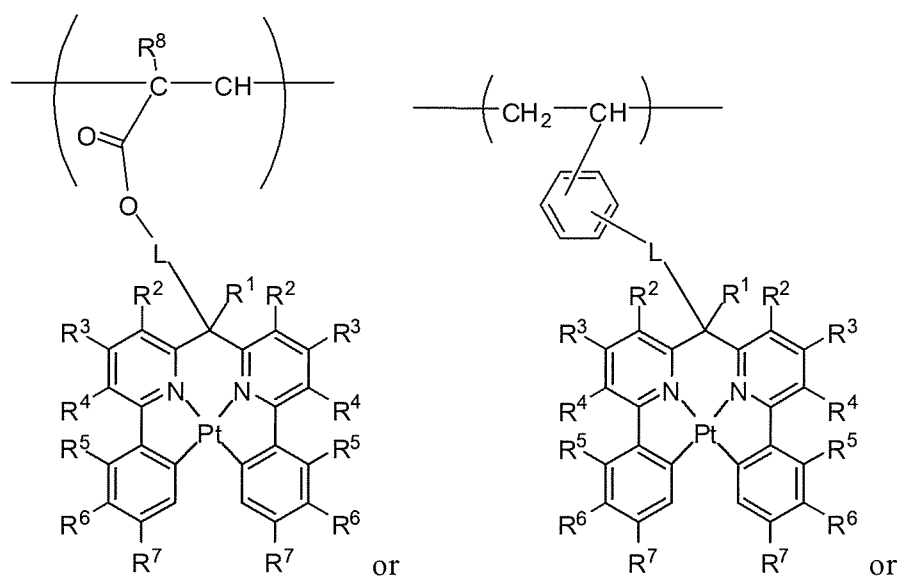
- 15 15. A phosphorescent copolymer having at least one polymerized subunit having the formula:

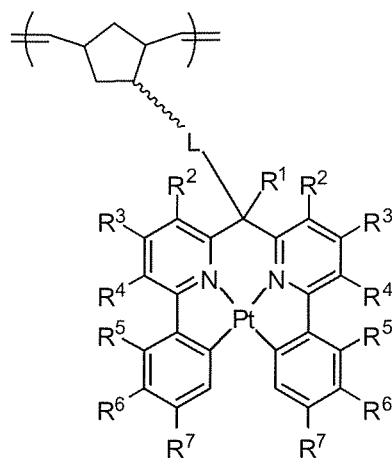


wherein

- 15 a) the copolymer subunit comprises from 2 to 20 carbon atoms,
- b) L is a C_1 - C_{20} organic group linking the copolymer subunit to the platinum complex;

- c) R^1 is fluoride, or a C_1 - C_{12} alkyl, alkoxy, hydroxyalkyl, aryloxy, or arylalkyloxy group;
- d) R^2 , R^3 , and R^4 are independently selected from hydrogen and a C_1 - C_{12} organic substituent group;
- 5 e) R^5 , R^6 , and R^7 are independently selected from hydrogen, fluoride, and a C_1 - C_{12} organic substituent group, or together two of R^5 , R^6 , and R^7 form a benzene ring that can be optionally substituted by one or two substituent groups independently selected fluoride, C_1 - C_{12} alkyl, alkoxy, hydroxyalkyl, cyano, aryloxy, and arylalkyloxy groups.
- 10 16. The copolymer of claim 15 comprising at least one polymerized subunit having the structure:

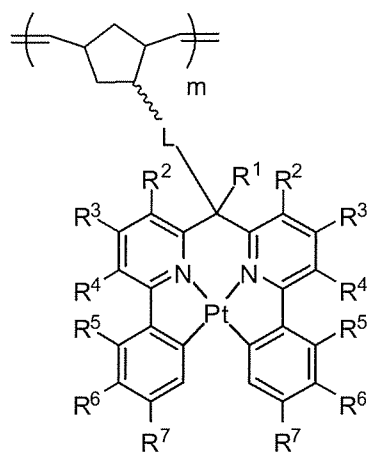




wherein R^8 is H or CH_3 .

17. The copolymer of claim 16 comprising at least

a) one or more polymeric subunits having the structure:



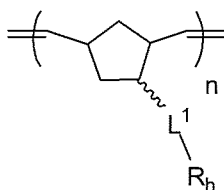
5 wherein

i) L is a C_1 - C_{20} organic group linking the polymerized norbornene group to the polycyclic platinum complex group;

ii) R^1 is fluoride, or a C_1 - C_{18} alkyl, alkoxy, hydroxyalkyl, aryloxy, or arylalkyloxy group;

10 iii) R^2 , R^3 , and R^4 are independently selected from hydrogen or a C_1 - C_{12} organic substituent group;

- iv) R^5 , R^6 , and R^7 are independently selected from hydrogen, cyano, fluoride, or a C_1 - C_{12} organic substituent group; or together two of R^5 , R^6 , and R^7 form a benzene ring that can be optionally substituted by one or two fluorides, or C_1 - C_{12} alkyl, alkoxy, hydroxyalkyl, cyano, aryloxy, or arylalkyloxy groups;
- 5 v) m is a positive integer between 1 and 30; and
- b) one or more subunits having the structure;

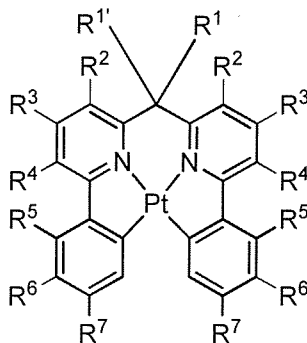


wherein

- i) n is an integer between 1 and 30;
- 10 ii) L^1 is a C_1 - C_{20} organic group linking the polymeric subunit to the R_h group;
- iii) the R_h group comprises a poly-unsaturated and polycyclic aromatic or heteroaromatic group capable of transporting holes, electrons, and/or excitons.

15 17. 18. An electronic device comprising at least one copolymer of claims 15 -

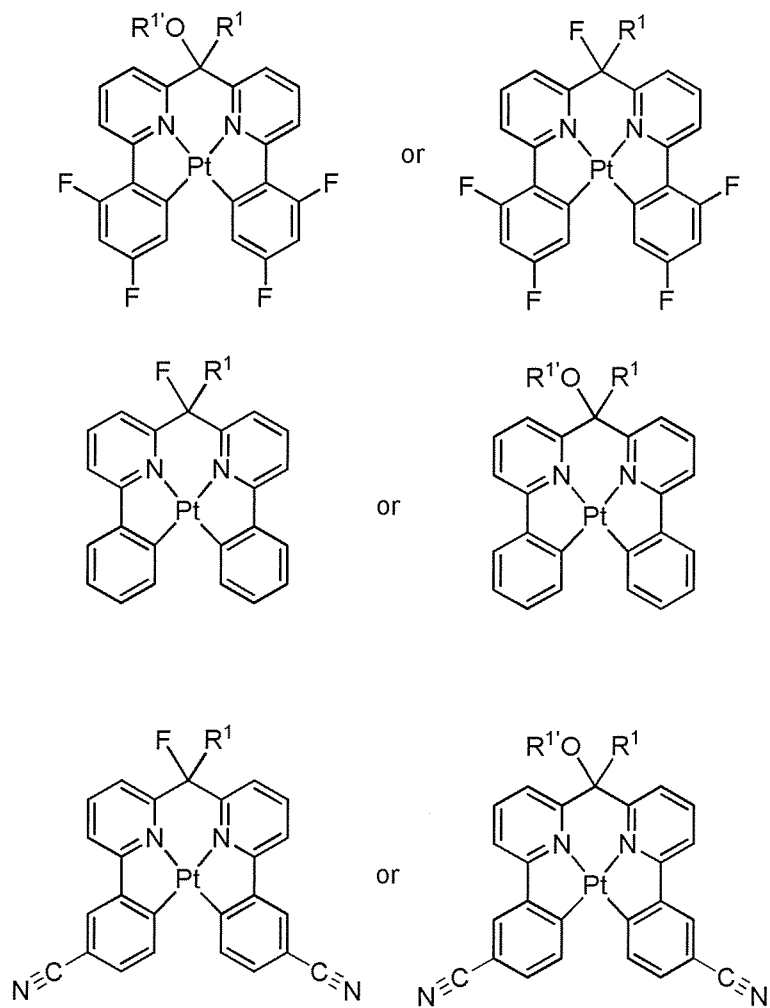
19. A platinum complex having the formula:



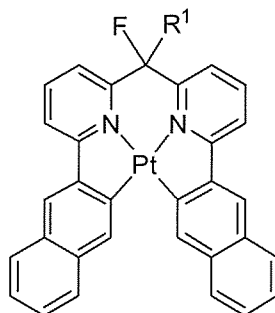
wherein

- a) R^1 and $R^{1'}$ are independently selected from fluoride, or a C_1 - C_{12} alkyl, alkoxy, hydroxyalkyl, aryloxy, or arylalkyloxy group, provided at least one of R^1 and $R^{1'}$ is not alkyl;
- b) R^2 , R^3 , and R^4 are independently selected from hydrogen and a C_1 - C_{12} organic substituent group;
- c) R^5 , R^6 , and R^7 are independently selected from hydrogen, fluoride, and a C_1 - C_{12} organic substituent group, or together two of R^5 , R^6 , and R^7 form a benzene ring that can be optionally substituted by one or two substituent groups independently selected fluoride, C_1 - C_{12} alkyl, alkoxy, hydroxyalkyl, cyano, aryloxy, and arylalkyloxy groups.

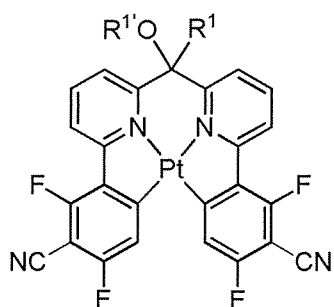
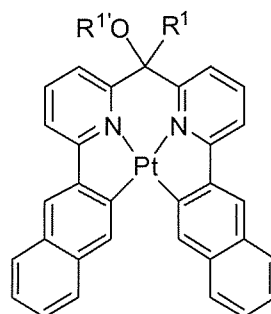
20. A platinum complex of claim 19 having the formula:



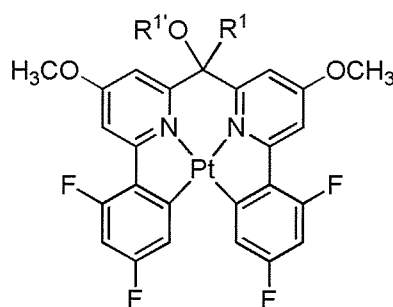
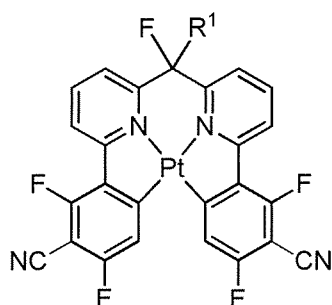
- 55 -



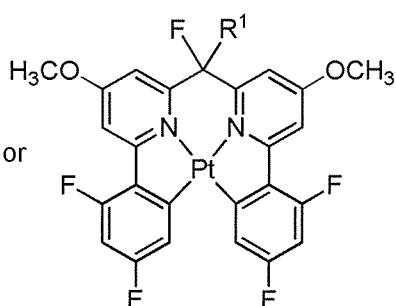
or



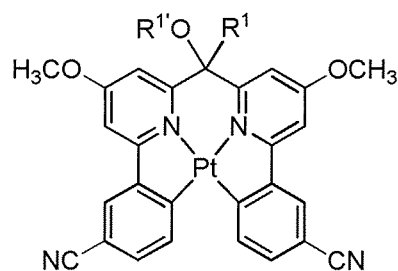
or



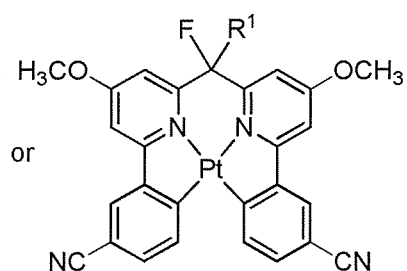
or



5



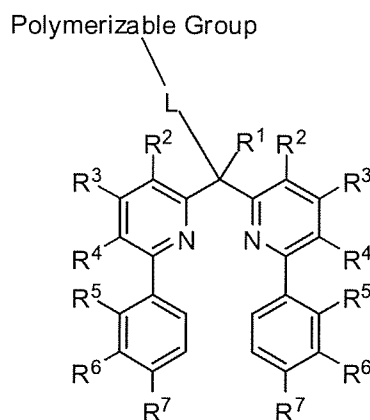
or



wherein R¹ and R^{1'} are independently selected from hydrogen and C₁-C₁₂ alkyl groups.

21. An electronic device comprising at least one copolymer of any of
10 claims 19-20.

22. A compound comprising a polymerizable group linked to a potentially multi-dentate ligand for transition metals, having the formula:



wherein

- 5 a) the polymerizable group comprises from 2 to 20 carbon atoms, and a functional group that can be copolymerized with other comonomers,
- b) L is a C₁-C₂₀ organic group linking the polymerizable group to the platinum complex;
- c) R¹ is fluoride, or a C₁-C₁₂ alkyl, alkoxy, hydroxyalkyl, aryloxy, or
10 arylalkyloxy group;
- d) R², R³, and R⁴ are independently selected from hydrogen and a C₁-C₁₂ organic substituent group;
- e) R⁵, R⁶, and R⁷ are independently selected from hydrogen, fluoride, and a C₁-
15 C₁₂ organic substituent group, or together two of R⁵, R⁶, and R⁷ form a benzene ring that can be optionally substituted by one or two substituent groups independently selected fluoride, C₁-C₁₂ alkyl, alkoxy, hydroxyalkyl, cyano, aryloxy, and arylalkyloxy groups.

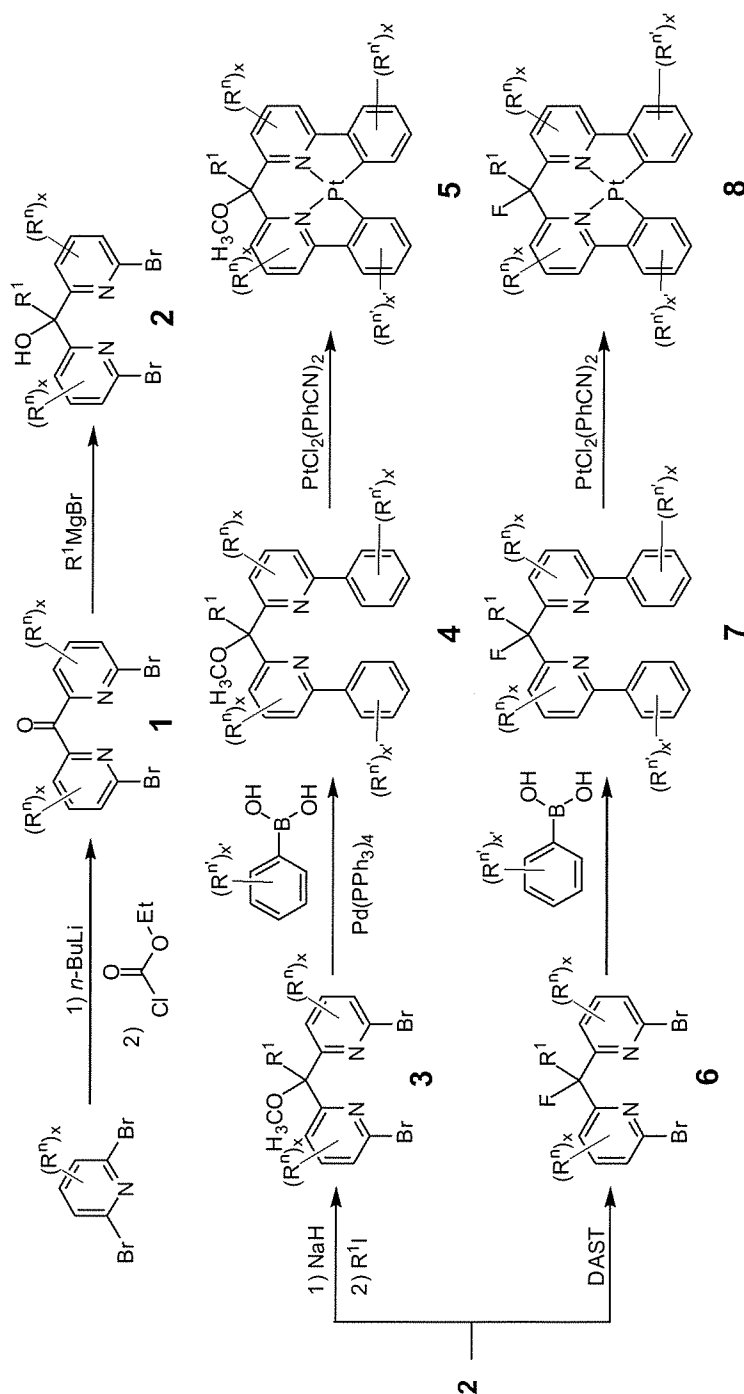


Figure 1

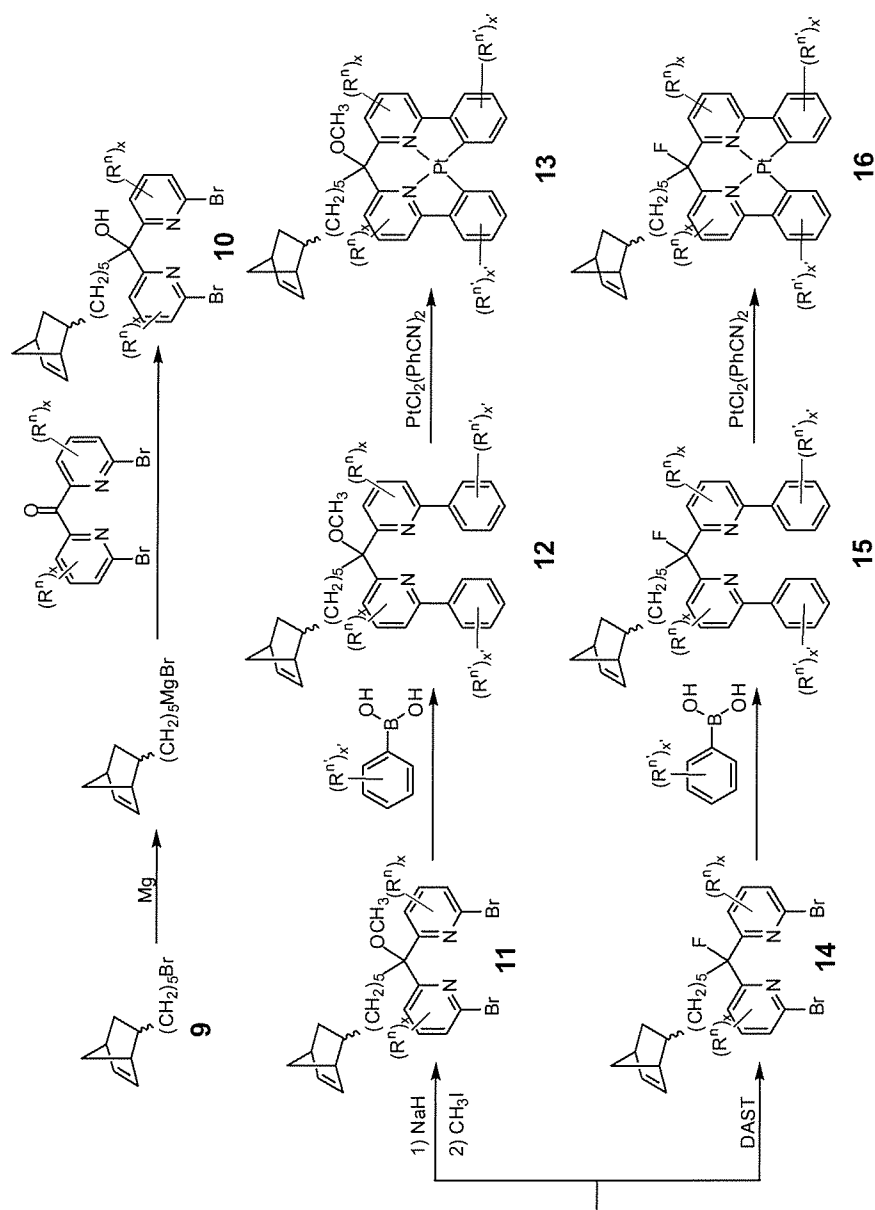


Figure 2

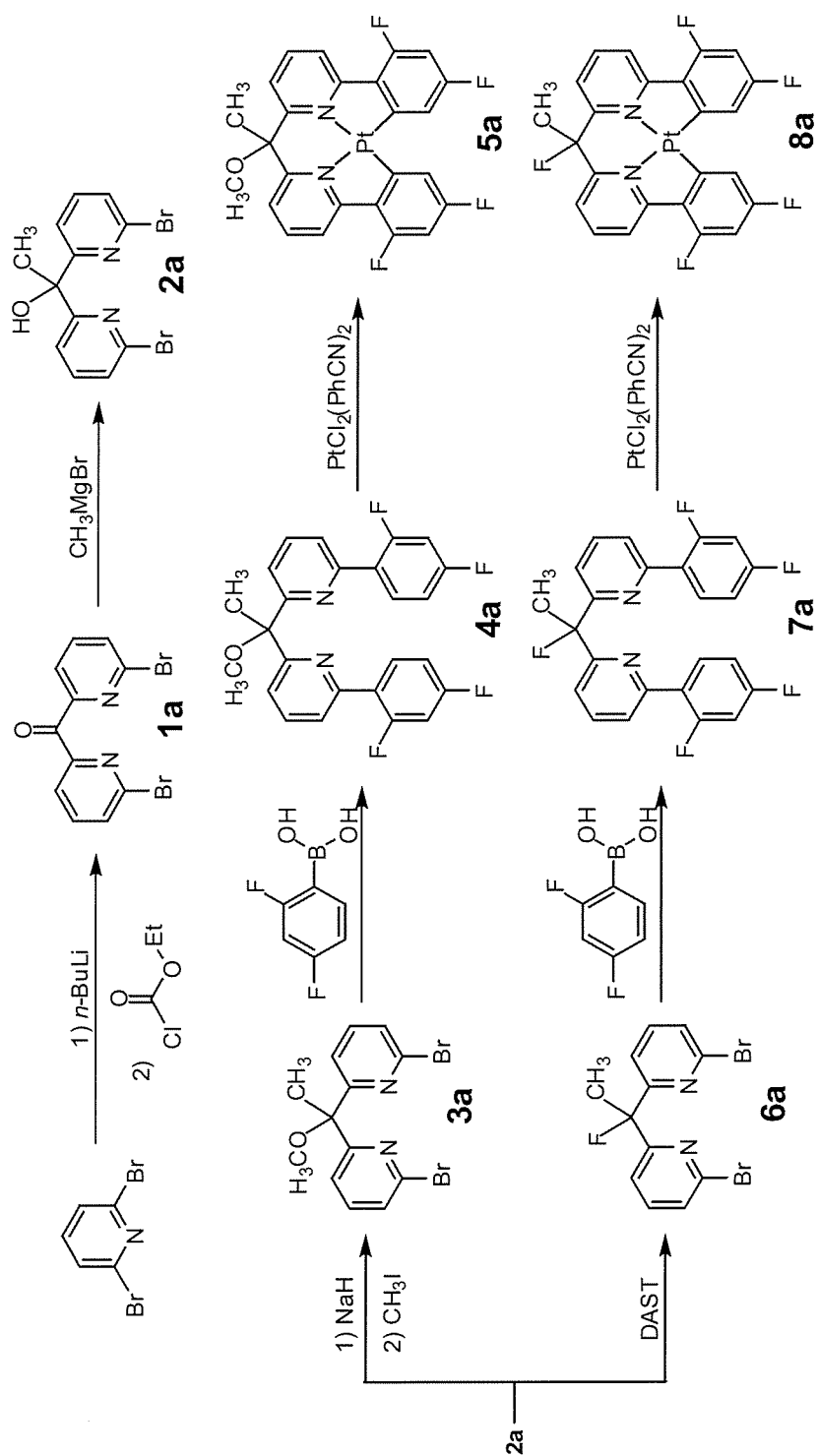


Figure 3

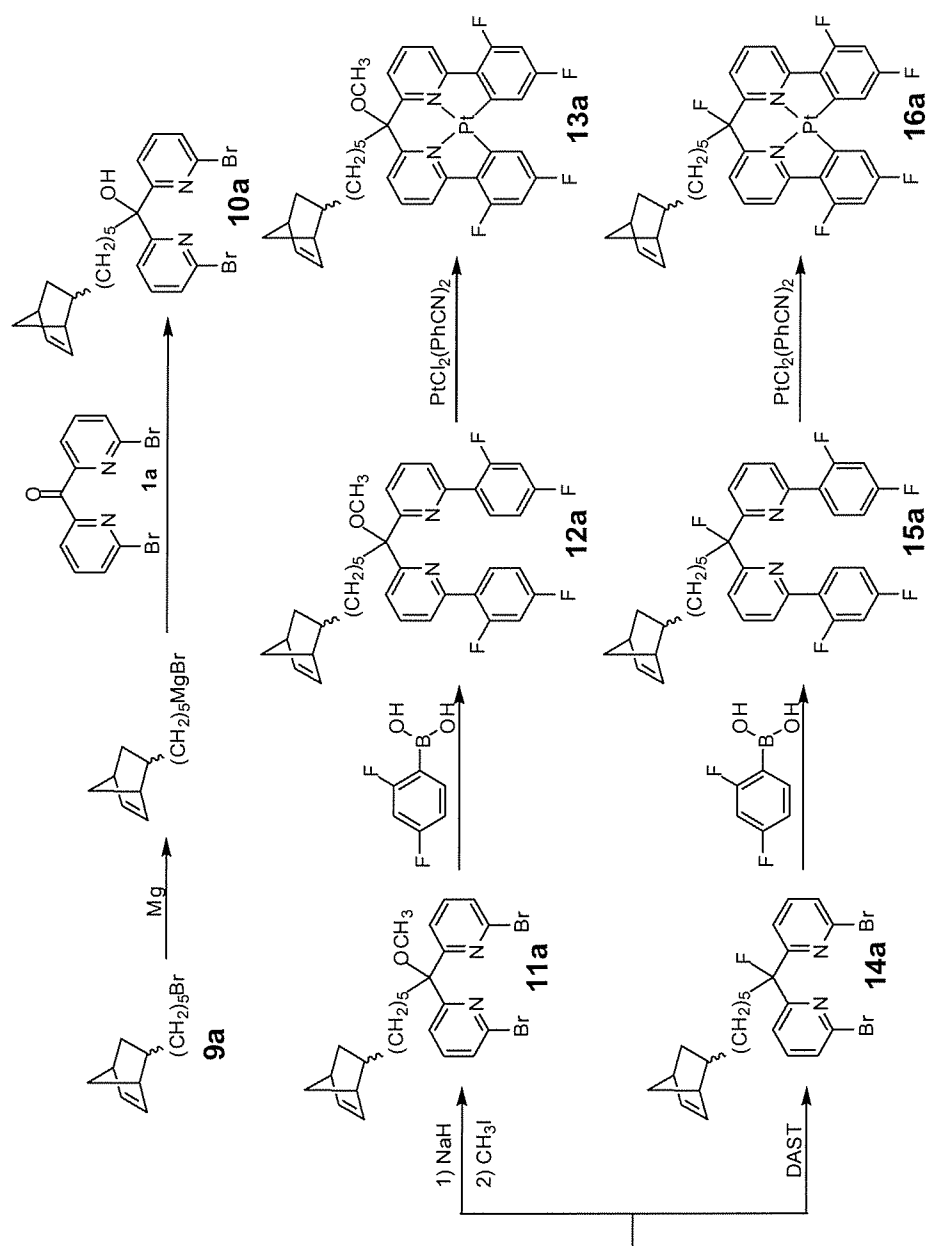


Figure 4

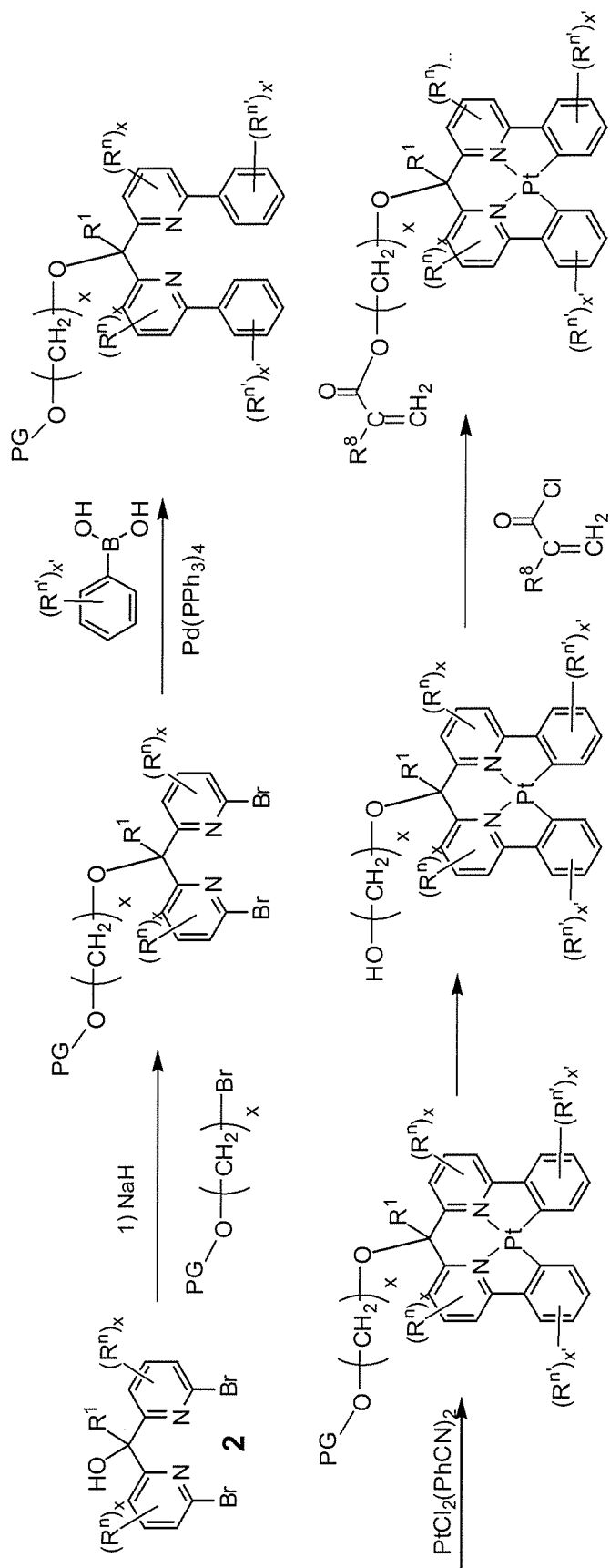


Figure 5

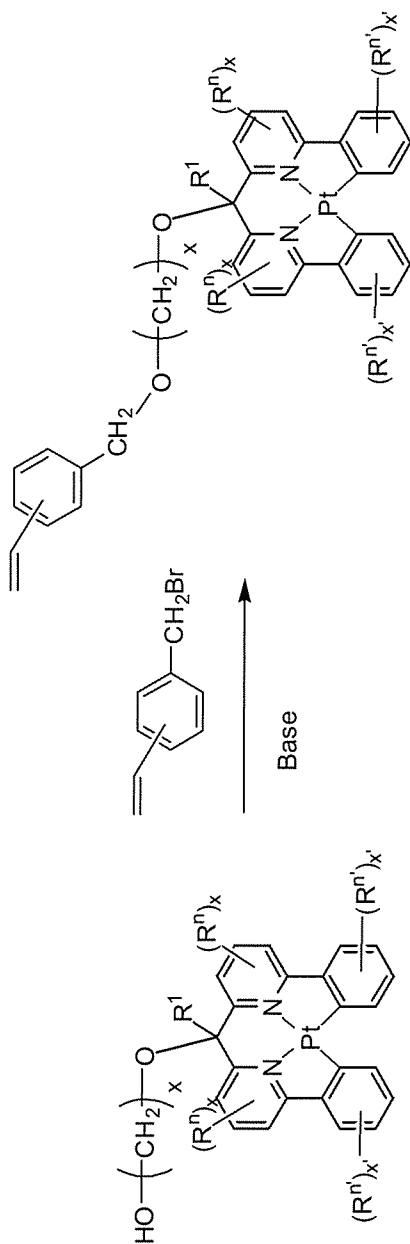


Figure 6

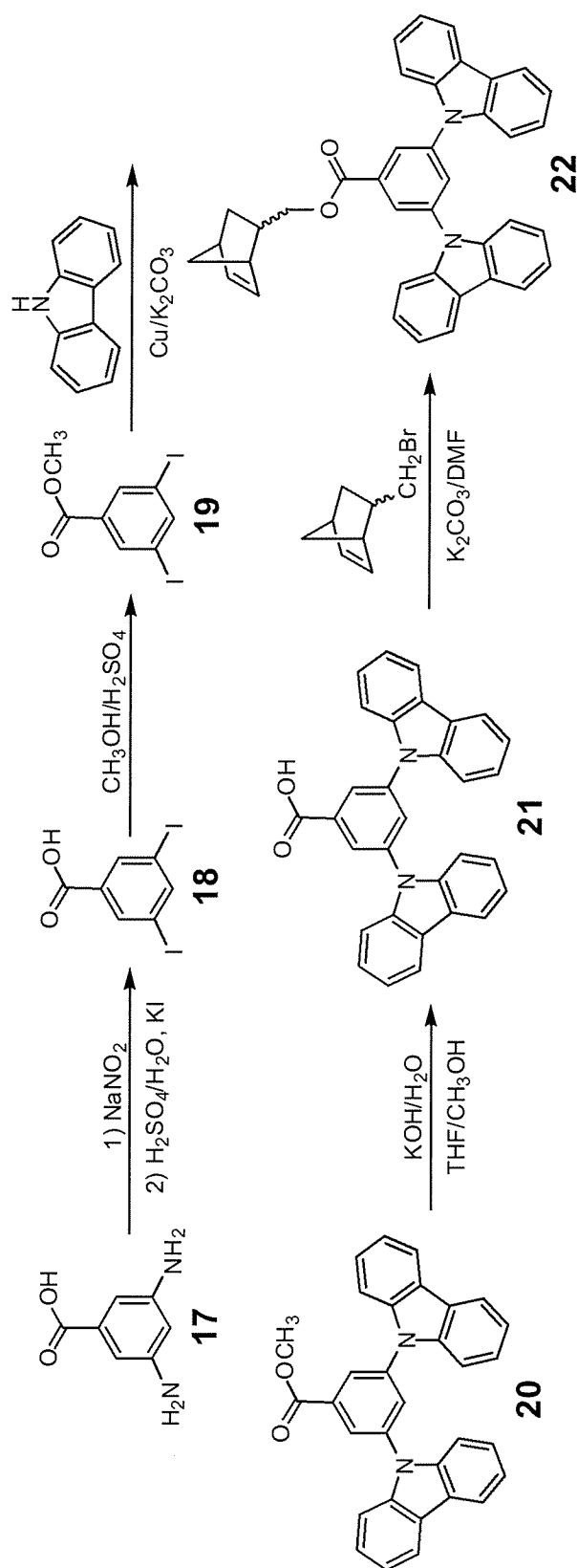


Figure 7

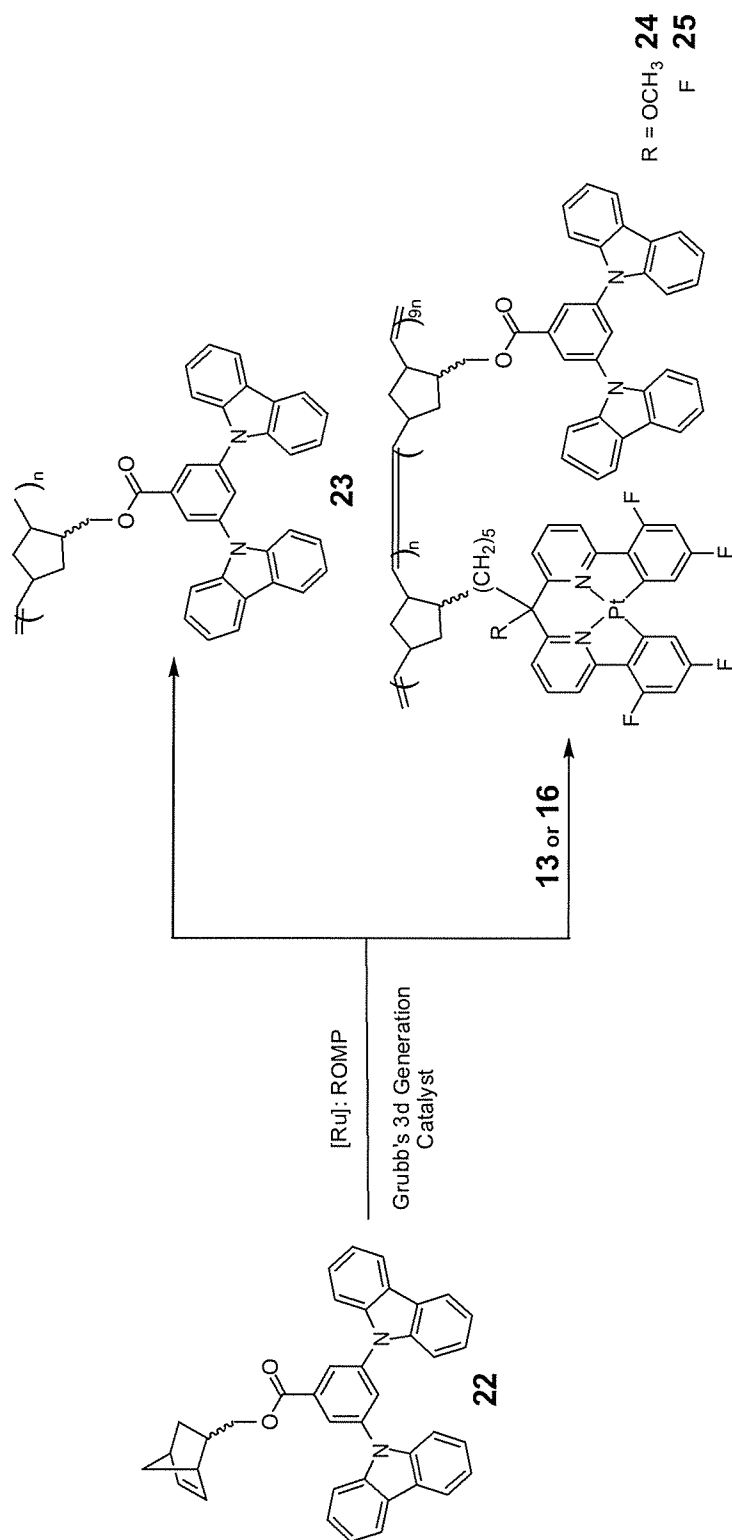


Figure 8

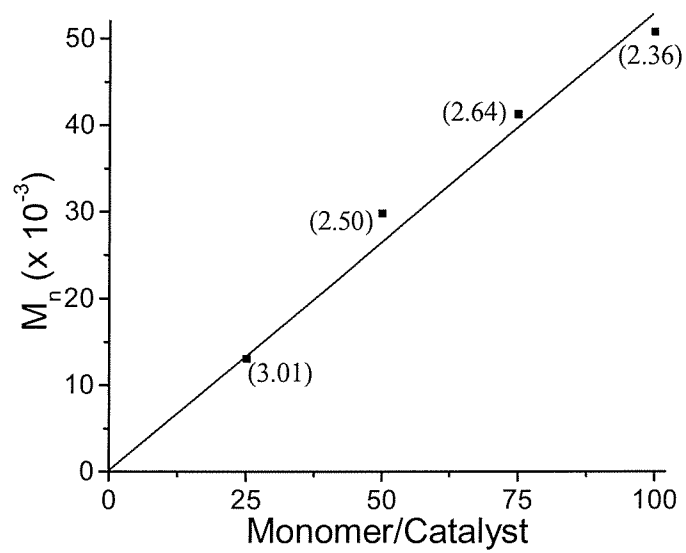


Figure 9a

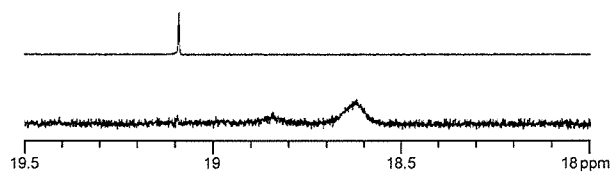


Figure 9b

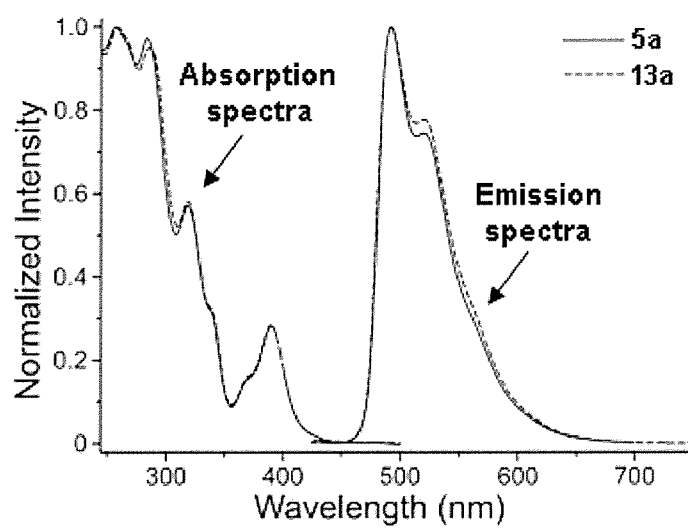


Figure 10a.

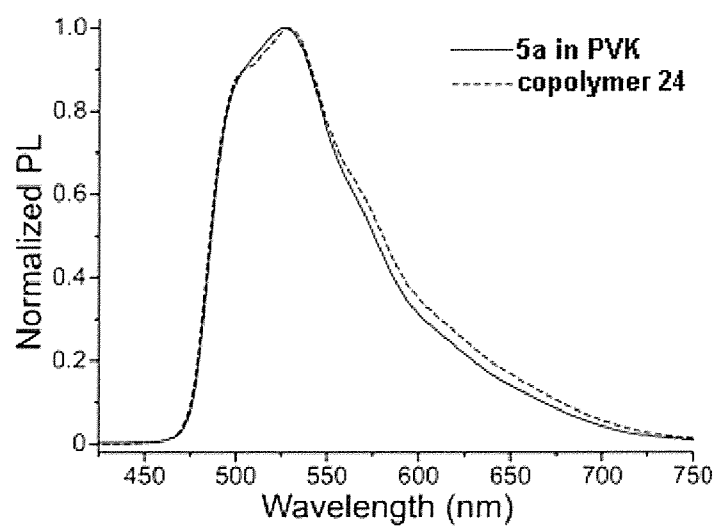


Figure 10b

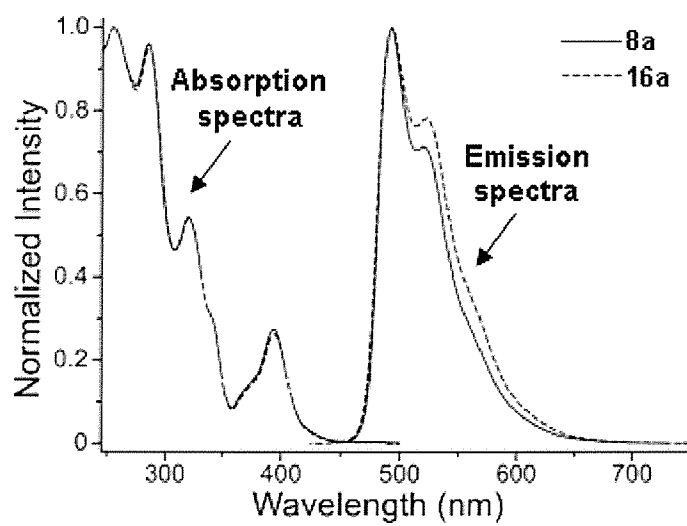


Figure 11a

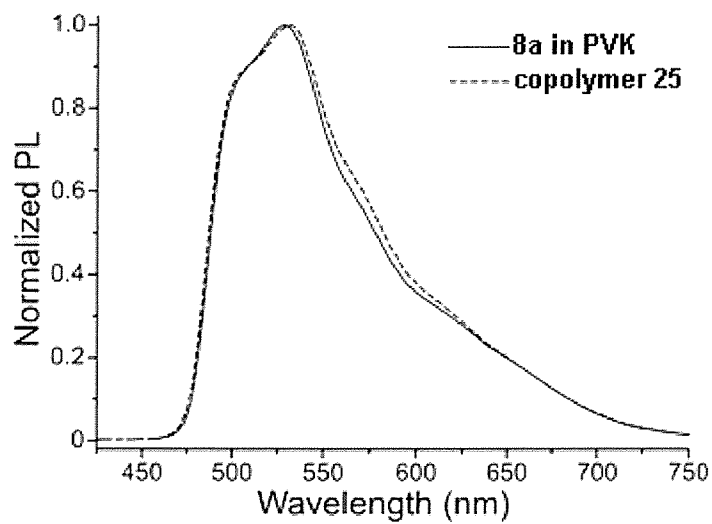


Figure 11b

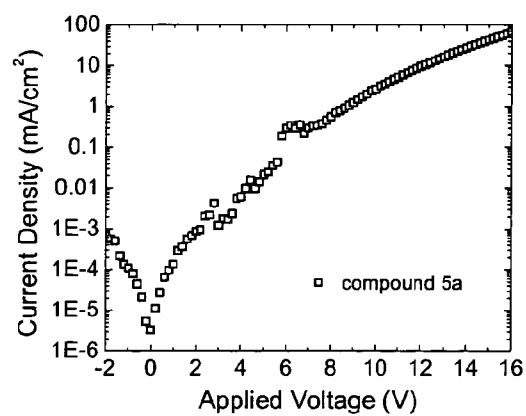


Figure 12a

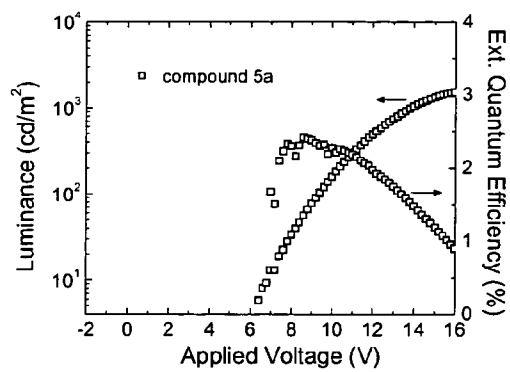


Figure 12b

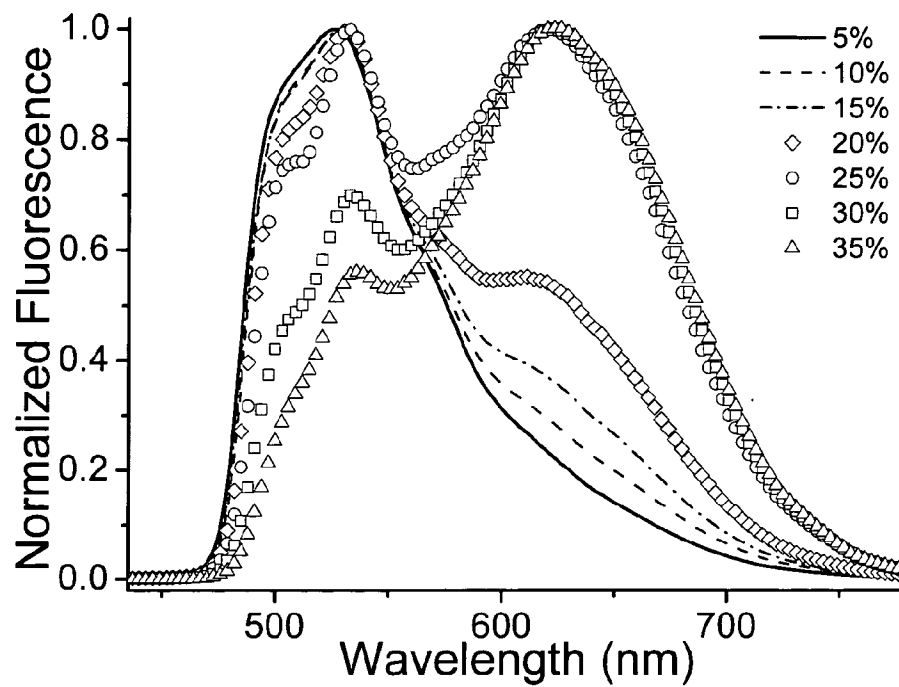


Figure 12c

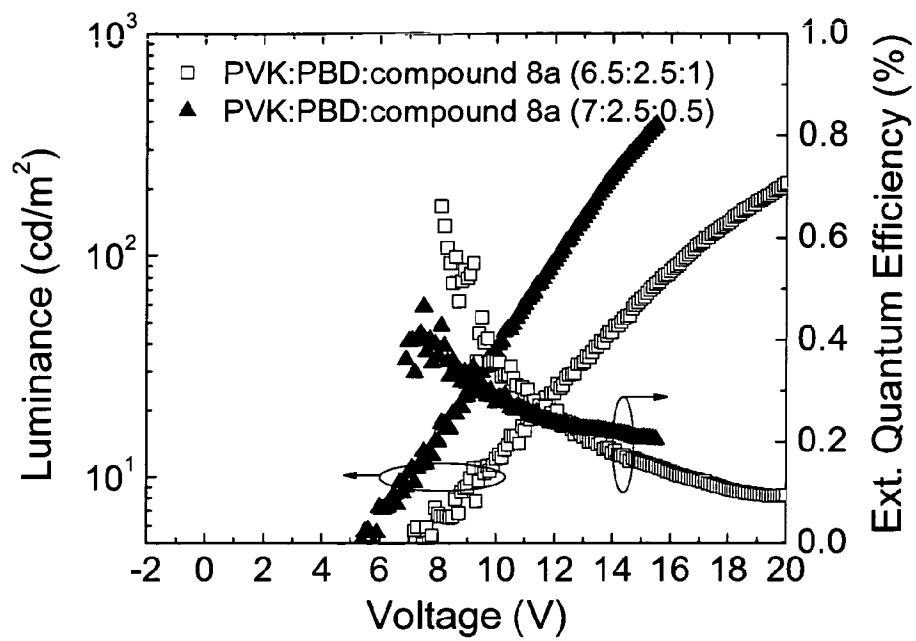


Figure 13a

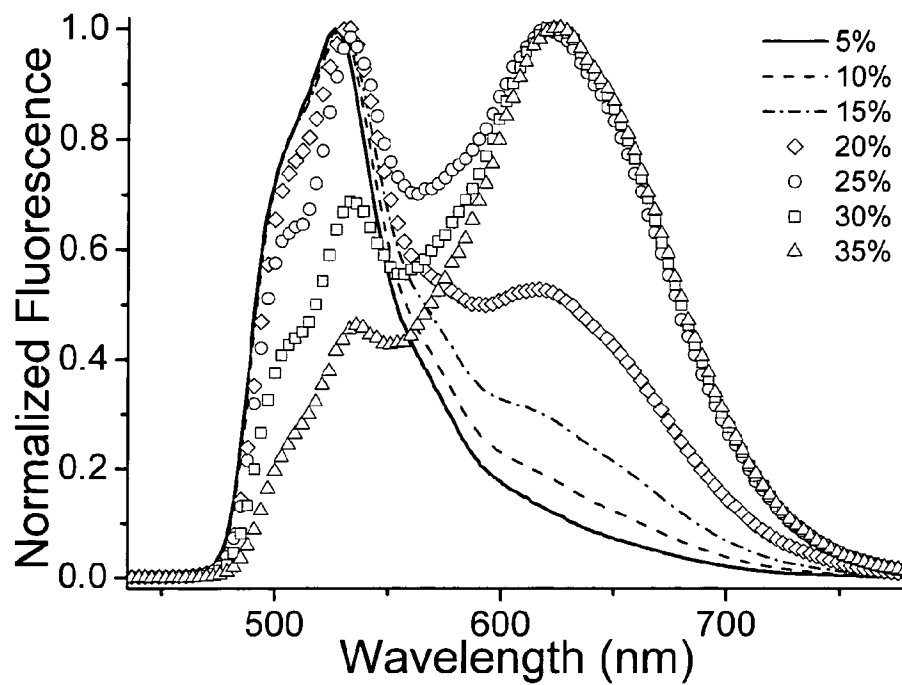


Figure 13b

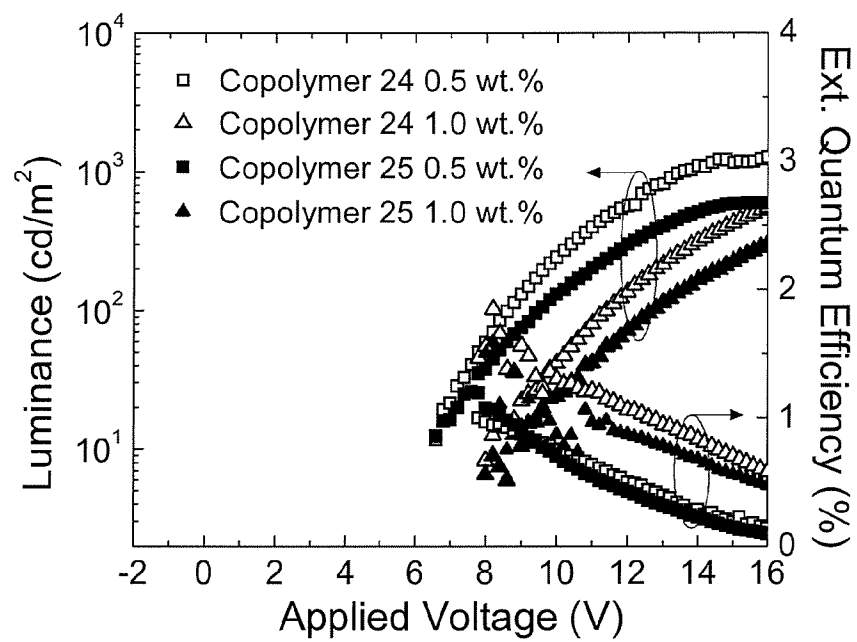


Figure 14

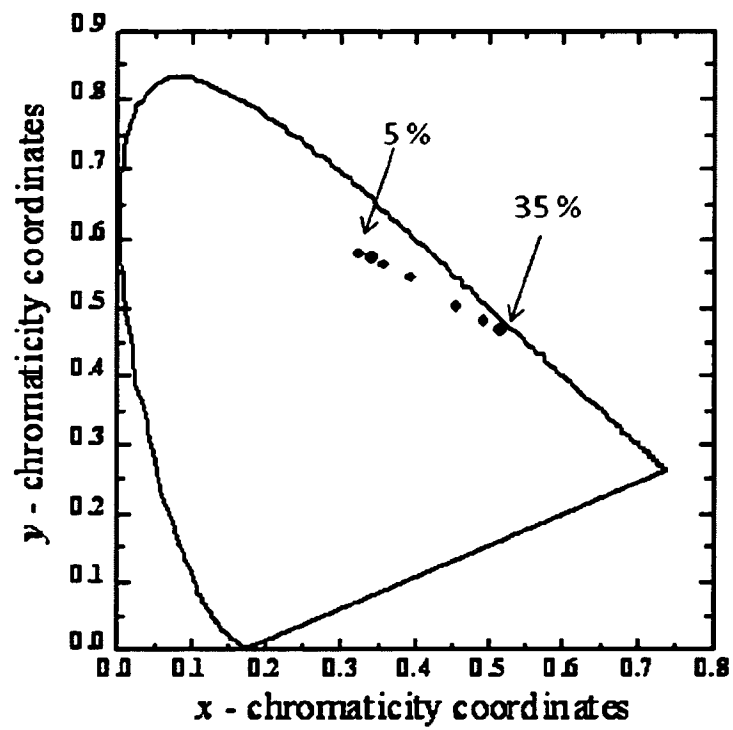


Figure 15

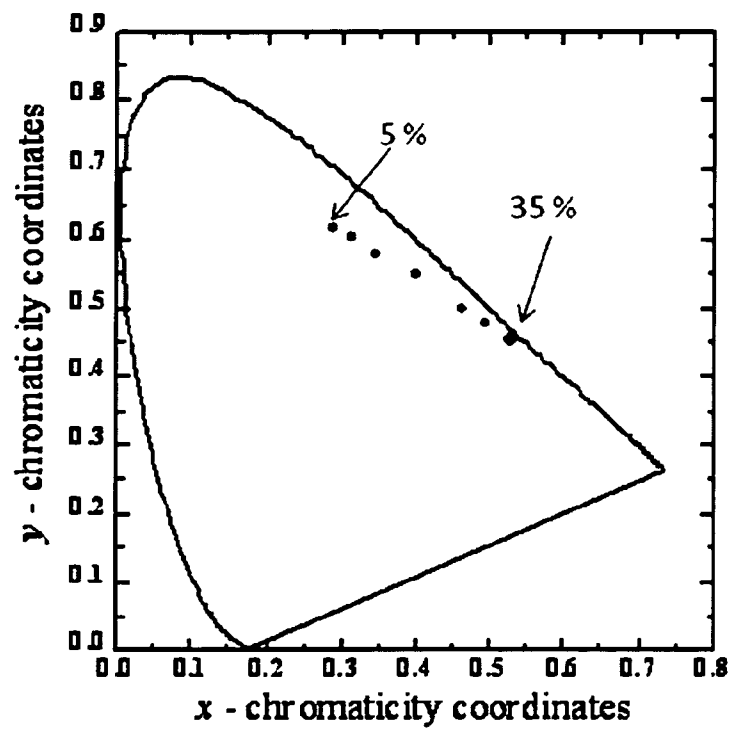


Figure 16

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/059289

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07F15/00 C08F230/04 C09K11/06 H05B33/14 H01L51/00
ADD.

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 C08F C09K H05B 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 practical, search terms used)

EPO-Internal, CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	FENG K ET AL: "Norbornene-Based Copolymers Containing Platinum Complexes and Bis(carbazolyl)benzene in Their Side-Chains" MACROMOLECULES, vol. 42, no. 18, 22 September 2009 (2009-09-22), pages 6855-6864, XP001548720 ISSN: 0024-9297 DOI: 10.1021/MA901280X the whole document	1,2,5-22
X	US 2007/075311 A1 (OKADA) 5 April 2007 (2007-04-05) the whole document in particular, paragraphs [0416]-[0436], especially polymer P4 on page 112 ----- -/--	1-3,10, 11,14-16

☒ 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 document 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

8 October 2010

Date of mailing of the international search report

26/10/2010

Name and mailing address of the ISA/

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Authorized officer

Elliott, Adrian

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2010/059289

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/082284 A1 (STOESSEL ET AL) 12 April 2007 (2007-04-12) paragraph [0101]; example 1 -----	19,20
Y	WO 2008/066192 A1 (FUJIFILM CORPORATION) 5 June 2008 (2008-06-05) page 39; compounds 79,83 page 48; compound 233 -----	1-22
Y	EP 1 516 901 A1 (JSR CORPORATION) 23 March 2005 (2005-03-23) claim 1, especially the definitions of X1 and X2 -----	1-4,6-8, 10-16, 18-22
Y	WO 2009/026235 A2 (GEORGIA TECH RESEARCH CORPORATION) 26 February 2009 (2009-02-26) the whole document -----	1,2,5-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2010/059289

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		EP 1678190 A1	12-07-2006
		WO 2005042550 A1	12-05-2005
		JP 2007519614 T	19-07-2007
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		JP 2008160087 A	10-07-2008
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		JP 2004027088 A	29-01-2004
WO 2009026235 A2	26-02-2009	KR 20100058563 A	03-06-2010