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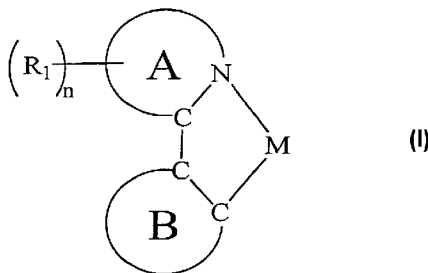
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(54) Title: ORGANIC PHOSPHORESCENT MATERIAL AND ORGANIC OPTOELECTRONIC DEVICE



(57) **Abstract:** The invention provides a cyclometallated complex comprising the structure of formula (I); wherein M is a d-block transition metal; B is a five- or six-membered aryl or heteroaryl ring which is optionally substituted and optionally fused to one or more other aryl or heteroaryl rings; A is a five- or six-membered heteroaryl ring comprising at least three nitrogen atoms; R₁ is a group other than hydrogen; n is zero or an integer equal to or greater than one; and A and B are optionally fused or linked by one or more covalent bonds. The invention also provides the use of such complexes in optoelectronic devices, and in particular in organic light emitting devices.

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ORGANIC PHOSPHORESCENT MATERIAL AND ORGANIC OPTOELECTRONIC DEVICE

Field of the invention

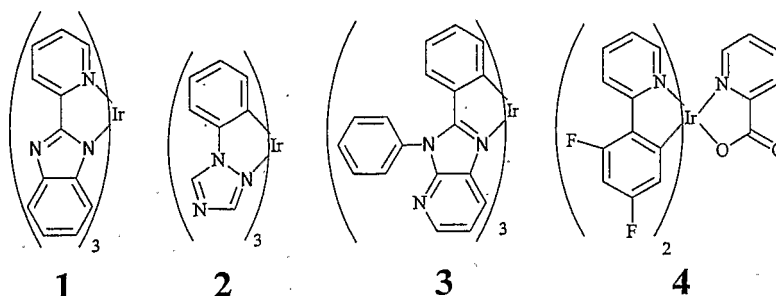
The present invention relates to organic phosphorescent materials, in particular to blue organic phosphorescent materials and to organic electroluminescent devices comprising organic phosphorescent materials.

Background of the invention

Organic electroluminescent devices comprise a layer of organic electroluminescent material positioned between two electrodes. Application of a current between the two electrodes causes the organic material to electroluminescence. The phenomenon of organic electroluminescence has many applications in the fields of displays and lighting. In the late 1980's efficient organic electroluminescence was observed in conjugated polymers, as described in WO90/13148, and in complexes of aluminum 8-hydroxyquinolate, as described in Tang et al Applied Physics Letters 51, 913, (1987). The electroluminescence in such systems is termed fluorescence and is produced by radiative emission from the singlet excited states produced by the electrical excitation of the polymers or molecules. Much research over the last decade has been directed at the investigation of such fluorescent systems.

In the 1990s the efficient emission of light from the triplet excited states of electrically excited molecules was observed, Baldo et al Applied Physics Letters 75, 4, (1999). This electroluminescent system comprised a green light emitting cyclometallated iridium phenylpyridine complex and showed a higher efficiency than had previously been observed in fluorescent systems. This phenomenon, known as phosphorescence, has been widely investigated. US2002/0134984 discloses a series of iridium complexes in which iridium is coordinated to a bidentate ligand via two nitrogen atoms, such as compound 1 below. US2001/0019782 discloses a series of iridium complexes in which iridium is coordinated to a bidentate ligand, the ligand comprising two aryl moieties bonded by a C-N bond, such as compound 2 below. US2002/0055014 discloses a series of iridium complexes in which iridium is coordinated to a ligand comprising a phenylazole derivative, such as compound 3

below. WO02/15645 discloses the blue phosphorescent complex 4, known as Firpic, shown below.



The cyclometallated phosphorescent complexes referred to above have been designed to be volatile to allow their deposition by vacuum evaporation. Vacuum evaporation is a technique commonly used to deposit layers of low molecular weight materials in the manufacture of electroluminescent devices. Other research has focussed on the incorporation of phosphorescent emitters into polymers, as disclosed in WO02/068435 and EP1245659. The incorporation of phosphorescent emitters into polymers allows the phosphorescent systems to be deposited using solution processing techniques such as ink-jet printing and screen printing. The advantage of using solution processing to produce electroluminescent displays has been widely recognised in the field, as disclosed for example in EP 0 880 303.

An alternative approach to provide solution processable phosphorescent materials has been to incorporate the phosphorescent emitters into dendrimers, as disclosed in WO02/066552. Dendrimers are highly branched macromolecules in which branched molecular sub-units, known as dendrons or dendrites, are attached to a core. The dendrimers disclosed in WO02/066552 comprise a cyclometallated phosphorescent core and a series of organic dendrons. The properties of such dendrimers make them ideal for solution processing. Further classes of electroluminescent dendrimers have been developed including dendrimers comprising dendrons based on aryl-aryl moieties, as disclosed in WO02/067343, and asymmetric dendrimers as disclosed in WO02/066575.

Much of the development of organic light emitting devices is aimed at the exploitation of these devices in display applications such as mobile phones and large area displays. Full colour displays require light emitting materials which emit light in the red, green and blue regions of the electromagnetic spectrum. Fluorescent organic materials capable of emitting red, green and blue light have been developed.

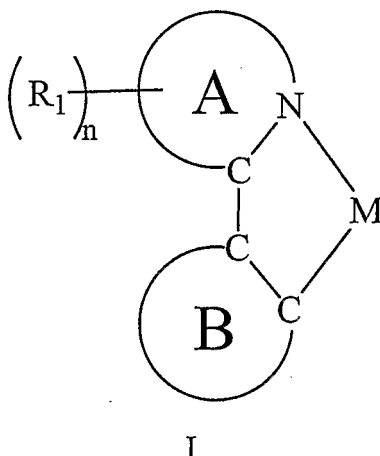
Phosphorescent materials emitting red and green light have been developed but there are relatively few examples of phosphorescent materials capable of emitting blue light. Although the above mentioned iridium complex Firpic emits blue light this is of a light blue colour rather than the deeper blue required for full colour displays.

As is clear from the above brief survey of recent research in the field there is a need for the development of phosphorescent compounds having a high efficiency and available in a range of colours suitable for use in display applications. In particular there is a need for a range of high efficiency phosphorescent complexes emitting light in the blue region of the electromagnetic spectrum. Further there is a need for a range of solution processable phosphorescent light emitting compounds.

Summary of the invention

The present invention provides phosphorescent light emitting compounds suitable for use in electroluminescent devices.

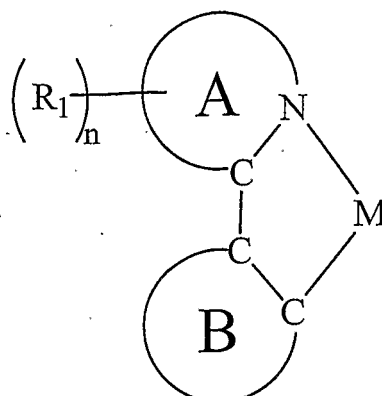
In a first embodiment the present invention provides a complex of formula I:



wherein:

- M is a d-block transition metal;
- B is a five- or six-membered aryl or heteroaryl ring which is optionally substituted and optionally fused to one or more other aryl or heteroaryl rings;
- A is a five- or six-membered heteroaryl ring comprising at least three nitrogen atoms;
- R_1 is a group other than hydrogen;
- n is zero or an integer equal to or greater than one; and
- A and B are optionally fused or linked by one or more covalent bonds.

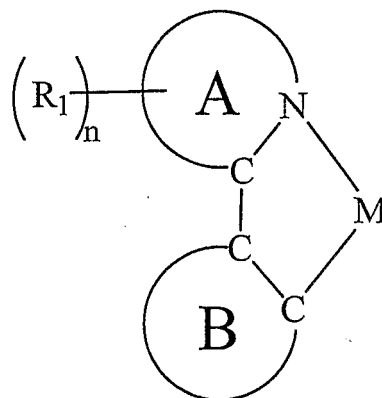
In a second embodiment the present invention comprises a cyclometallated complex comprising the structure of formula II:



II

wherein A is a five- or six-membered heteroaryl ring which comprises at least three heteroatoms and which is optionally substituted or fused, B is a five- or six-membered aryl or heteroaryl ring which is optionally substituted or fused, n is greater than one and R₁ is a dendron or a solubilising group.

In a third embodiment the present invention comprises a polymer comprising a cyclometallated complex comprising the structure of formula III:



III

wherein A is a five- or six- membered heteroaryl ring which comprises at least three heteroatoms and which is optionally substituted or fused, B is a five- or six-membered aryl or heteroaryl ring which is optionally substituted or fused, n is zero or greater than one and R₁ is a substituent other than hydrogen.

The present invention is also directed to an optoelectronic device comprising a cyclometallated complex of the present invention. In a preferred embodiment said optoelectronic device is an organic light emitting diode.

The present invention is further directed to an organic light emitting device comprising a blend comprising a cyclometallated complex according to the present invention and an organic host. Although not wishing to be bound by theory it is thought that the organic host acts as a charge transporter and a source of triplet excitons which are transferred to the light-emitting cyclometallated complex. Alternatively the recombination of the hole and electron charge carriers to form excitons may take place at the cyclometallated complex with the host acting as a charge transporter. Preferably the organic host comprises a carbazole moiety or a triarylamine moiety.

The present invention is also directed to the use of a cyclometallated complex according to the invention in an optoelectronic device.

The invention also provides an organic light-emitting device comprising an phosphorescent layer disposed between two electrodes, said phosphorescent layer, wherein said device has a CIE-y coordinate of less than 0.25.

Brief description of the drawing

Figure 1 shows the photoluminescent spectrum of a cyclometallated complex according to the present invention.

Detailed description of the invention

Unless otherwise stated, the term alkyl represents a linear or branched alkyl group or moiety which preferably contains from 1 to 6 carbon atoms such as a C₁₋₄ alkyl group or moiety. Examples of C₁₋₄ alkyl groups and moieties include methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl and *t*-butyl. For the avoidance of doubt, where two alkyl moieties are present in a group, the alkyl moieties may be the same or different.

As used herein, a halogen is typically chlorine, fluorine, bromine or iodine. It is preferably chlorine, fluorine or bromine.

As used herein the term amino represents a group of formula -NH₂. The term C₁₋₆ alkylamino represents a group of formula -NHR' wherein R' is a C₁₋₆ alkyl group, preferably a C₁₋₄ alkyl group, as defined previously. The term di(C₁₋₆ alkyl)amino represents a group of formula -NR'R'' wherein R' and R'' are the same or different and represent C₁₋₆ alkyl groups, preferably C₁₋₄ alkyl groups, as defined previously. As used herein the term amido represents a group of formula -C(O)NH₂.

As used herein, an aryl group is typically a C₆₋₁₀ aryl group such as phenyl or naphthyl. An aryl group may be unsubstituted or substituted at any position. Typically, it carries 0, 1, 2 or 3 substituents.

As used herein, references to an aryl group include fused ring systems in which an aryl group is fused to a carbocyclyl, heterocyclyl or heteroaryl group. The carbocyclyl, heterocyclyl or heteroaryl group to which the aryl group is fused may itself be fused to a further aryl, heteroaryl, carbocyclyl or heterocyclyl. Accordingly, the term aryl encompasses aryl groups such as phenyl when fused to other monocyclic or polycyclic ring systems. Exemplary fused ring systems include those where a phenyl ring is fused to a monocyclic carbocyclyl ring which is itself fused to a phenyl ring, for instance a carbazolyl group.

As used herein, a heteroaryl group is typically a 5- to 14-membered aromatic ring, such as a 5- to 10-membered ring, more preferably a 5- or 6-membered ring, containing at least one heteroatom, for example 1, 2 or 3 heteroatoms, selected from O, S and N. Examples include pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl, furanyl, thienyl, pyrazolidinyl, pyrrolyl, oxadiazolyl, isoxazolyl, thiadiazolyl, thiazolyl, imidazolyl, pyrazolyl, oxazolyl, isothiazolyl, benzofuranyl, isobenzofuranyl, benzothiophenyl, indolyl, indazolyl, carbazolyl, acridinyl, purinyl, cinnoliny, quinoxaliny, naphthyridinyl, benzimidazolyl, benzoxazolyl, quinoliny, quinazoliny and isoquinoliny.

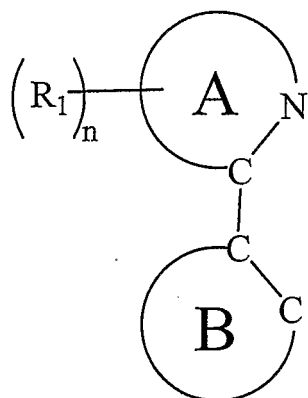
As used herein, references to a heteroaryl group include fused ring systems in which a heteroaryl group is fused to an aryl group. When the heteroaryl group is such a fused heteroaryl group, preferred examples are fused ring systems wherein a 5- to 6-membered heteroaryl group is fused to a phenyl group. Examples of such fused ring systems are benzofuranyl, isobenzofuranyl, benzothiophenyl, indolyl, indazolyl, benzimidazolyl, benzoxazolyl, quinoliny, quinazoliny and isoquinoliny moieties.

A heteroaryl group may be unsubstituted or substituted at any position. Typically, it carries 0, 1, 2 or 3 substituents.

As used herein, an alkoxy group is typically a said alkyl group attached to an oxygen atom. A haloalkyl or haloalkoxy group is typically a said alkyl or alkoxy group substituted by one or more said halogen atoms. Typically, it is substituted by 1, 2 or 3 said halogen atoms. Haloalkyl and haloalkoxy groups include perhaloalkyl and perhaloalkoxy groups such as -CX₃ and -OCX₃ wherein X is a said halogen atom, for example chlorine or fluorine.

Ligands suitable for the cyclometallated complexes of the present invention comprise a five- or six-membered heteroaryl ring comprising at least three heteroatoms, termed A, and a five- or six-membered aryl or heteroaryl ring, termed B.

For the avoidance of doubt, while the cyclometallated complexes are shown in formulae I, II and III as bearing one ligand comprising rings A and B, the complexes may comprise further ligands which are not shown for the sake of clarity. For example, the complexes may comprise a further ligand of the same structure, i.e. a further ligand of structure:



The complexes may alternatively or additionally comprise further ligands of a different structure. These options are discussed later in this description.

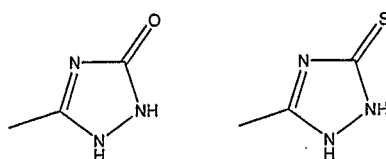
In the embodiment represented by formula I and the subsequent definition, A comprises at least three nitrogen atoms. According to one embodiment, there is provided a cyclometallated complex of formula I wherein M is a d-block transition metal, B is a five- or six-membered aryl or heteroaryl ring which is optionally substituted or fused, and either (i) A is a five membered heteroaryl ring comprising at least three nitrogen atoms, R_1 is a group other than hydrogen and n is equal to or greater than zero, or (ii) A is a six membered heteroaryl ring comprising at least three nitrogen atoms, R_1 is a group other than hydrogen and n is equal to or greater than two.

Rings A and B are linked by a carbon-carbon bond. Ring A comprises a nitrogen atom which coordinates to the metal of the cyclometallated complex. Ring B forms a carbon-metal sigma bond to the metal of the cyclometallated complex. In this way the central metal atom, the nitrogen on ring A, a carbon atom on ring B and the two carbon atoms which form the bond between rings A and B form a five-membered ring. Where ring A is a five-membered ring it may suitably be a triazole, an

oxadiazole, a thiadiazole or a tetrazole. In addition to the carbon-carbon bond between rings A and B discussed above, the rings may also be fused or linked via one or more covalent bonds, as discussed below.

A is a 5- or 6-membered heteroaryl ring having at least three nitrogen atoms in the ring. The heteroaryl ring may be optionally substituted or fused to one or more aryl or heteroaryl groups. Suitable A groups therefore include triazoles, tetrazoles and triazines.

The A groups may also be substituted by one or more ketone or thioketone groups within the ring. Thus, suitable A groups include triazolones and triazolethiones, for example groups of the formula:



In the embodiment where A is a five-membered ring, A is preferably a triazole or tetrazole. In the embodiment where A is a six-membered ring, A is preferably a triazine. It is preferred that A is a five-membered ring.

Ring A may be unsubstituted or substituted by one or more R_1 groups. Suitable R_1 groups include halogen atoms and C_{1-6} alkyl, aryl, C_{1-6} alkoxy, amino, C_{1-6} alkylamine, di(C_{1-6} alkyl)amino and carbazole groups. These substituents may themselves be substituted by, amongst other substituents, halogen atoms, C_{1-6} alkyl groups and C_{1-6} alkoxy groups.

Preferably at least one R_1 group on ring A is electron-donating. More preferably all R_1 substituents on ring A are electron-donating. Particularly preferred R_1 groups include C_{1-6} alkoxy, C_{1-6} alkyl, C_{1-6} alkylamino, di(C_{1-6} alkyl)amino, aryl, carbazole, arylamino and diarylamino. Preferred C_{1-6} alkoxy groups are C_{1-4} alkoxy groups, for example methoxy or ethoxy. Preferred C_{1-6} alkyl groups include ethyl, n-propyl, i-propyl, n-butyl, i-butyl and t-butyl. Preferred diarylamino groups include -NPhPh, wherein the phenyl rings may themselves be substituted by 1, 2 or 3 C_{1-2} alkoxy groups.

In an alternative embodiment the R_1 groups may be electron-withdrawing groups, for example substituted by one or more halogen atom, haloalkyl groups (including perhaloalkyl groups such as perfluoroalkyl groups) or aryl groups.

Ring A may be further substituted. In a preferred embodiment heteroaryl ring A is substituted with at least one dendron. Such an embodiment may have a structure of the form CORE- [DENDRON]_m, in which CORE represents a cyclometallated complex according to the present invention, m represents an integer of 1 or more, each DENDRON, which may be the same or different, represents a dendritic molecular structure. Preferably said dendritic molecular structure comprises aryl and/or heteroaryl groups or nitrogen which are preferably connected by sp² or sp hybridised carbon atoms of said aryl or heteroaryl groups or via single bonds between N and said aryl or heteroaryl groups. CORE is defined as terminating in the single bond from ring A which is connected to an sp² hybridised ring carbon atom of the first aryl or heteroaryl group or nitrogen to which more than one dendritic branch is attached, said ring carbon atom or N forming part of said DENDRON. When present it is preferred that the DENDRON is attached to the CORE via a linking group, more preferably the linking group is a non-conjugated linking group such as an alkylene group, in particular a methylene or ethylene group.

n is preferably zero or an integer from 1 to 5, suitably 1 to 4. More preferably n is zero, one, two or three, most preferably one, two or three.

B is a 5- or 6-membered aryl or heteroaryl group. The aryl or heteroaryl group which may itself be substituted with or fused to one or more further aryl or heteroaryl groups.

When B is a 5- or 6-membered aryl group it is preferably selected from phenyl rings which are optionally fused to other aryl or heteroaryl groups. For example, suitable aryl groups include phenyl, phenanthrenyl, naphthyl, pyrenyl and fluorenyl groups. Most preferably B is a phenyl ring.

When B is a 5- or 6-membered heteroaryl group, the ring preferably comprises 1, 2 or 3 heteroatoms independently selected from oxygen, sulphur and nitrogen. Suitable heteroaryl groups include pyridine, pyrazine, pyrimidine, thiophene, furan and pyrrole, preferably pyridine, pyrazine and pyrimidine. These heteroaryl groups may optionally be fused to other aryl or heteroaryl groups, for example to a phenyl ring. For example, B may be a group selected from benzofuran, benzothiophene, benzoimidazole, indole, quinoline, isoquinoline, quinazoline.

The B group may be unsubstituted or substituted by one or more substituents. Suitable substituents include halogen atoms, C₁₋₆ alkyl, C₁₋₆ alkoxy, sulfoxides, sulfones, =O groups, aryl groups such as phenyl rings, and heteroaryl groups, wherein

these substituents may themselves be substituted by one or more halogen atoms, C₁₋₄ alkyl, C₁₋₄ alkoxy, amino, C₁₋₄ alkylamino or di(C₁₋₄ alkylamino) groups. Preferably the B group is substituted by at least one electron-withdrawing group such as a halogen atom, haloalkyl, haloalkoxy, sulfoxide or sulphone group. Preferred halogen atoms include bromine, chlorine and fluorine, more preferably chlorine and fluorine, and most preferably fluorine. Particularly preferred haloalkyl groups are fluoroalkyl groups. The alkyl group may be substituted in all positions by the halogen atoms, e.g. in order to form trifluoromethyl or -CF₂CF₃. Alternatively, the alkyl portion of the haloalkyl group may be substituted in only some positions, e.g. in order to form difluoromethyl or -CFHCFH₂. Preferred haloalkoxy groups include said haloalkyl groups which are linked via an oxygen atom, for example -OCF₃ or -OCF₂CF₃. Sulphoxide groups are groups of formula -SO₂R' where R' is preferably hydrogen or a C₁₋₆ alkyl group. Sulphone groups are groups of formula -SOR' where R' is preferably hydrogen or a C₁₋₆ alkyl group.

The B group is preferably substituted by one or more substituents, more preferably by one or two substituents. It is particularly preferred if the B group is substituted by two electron-withdrawing groups which are in the meta position relative to the point of attachment to the central metal atom M. Suitable substituents in these positions include fluorine and perfluorinated groups such as trifluoromethyl. The substituents may themselves be unsubstituted or substituted, for example with one or more C₁₋₄ alkyl, C₁₋₄ alkoxy, amino, C₁₋₄ alkylamino or di(C₁₋₄ alkyl)amino groups.

Ring B may also be substituted by one or more dendrons. Such an embodiment may have a structure of the form CORE- [DENDRON]_m, in which CORE represents a cyclometallated complex according to the present invention, m represents an integer of 1 or more, each DENDRON, which may be the same or different, represents a dendritic molecular structure. Preferably said dendritic molecular structure comprises aryl and/or heteroaryl groups or nitrogen which are preferably connected by sp² or sp hybridised carbon atoms of said aryl or heteroaryl groups or via single bonds between N and said aryl or heteroaryl groups. CORE is defined as terminating in the single bond from ring B which is connected to an sp² hybridised ring carbon atom of the first aryl or heteroaryl group or nitrogen to which more than one dendritic branch is attached, said ring carbon atom or N forming part of said DENDRON. When present it is preferred that the DENDRON is attached to the

CORE via a linking group, more preferably the linking group is a non-conjugated linking group such as an alkylene group, in particular a methylene or ethylene group.

Preferably said dendron comprises a carbazole moiety or a diarylamine or triarylamine moiety. Preferably said dendron comprises a 1,3,5-substituted phenyl moiety.

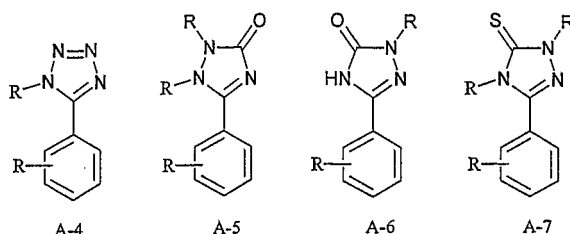
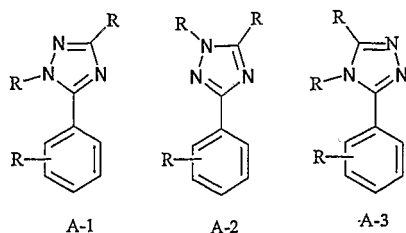
In a preferred embodiment of the cyclometallated complex of the present invention A comprises a triazole group substituted with an electron donating group, preferably an alkyl or alkylamine group, B comprises a phenyl group substituted with at least one fluorine or fluorinated group and said d-block transition metal is iridium. Most preferably said alkyl substituted triazole comprises a 1,2,4-triazole.

In all embodiments of the invention the group M is a d-block transition metal. M is preferably selected from iridium, rhodium, palladium, platinum, gold, osmium and ruthenium. Cyclometallated complexes of these metals have been shown to provide phosphorescent systems for use in organic electroluminescent devices. More preferably M is selected from iridium and platinum, both of which have been shown to provide high efficiency phosphorescent systems.

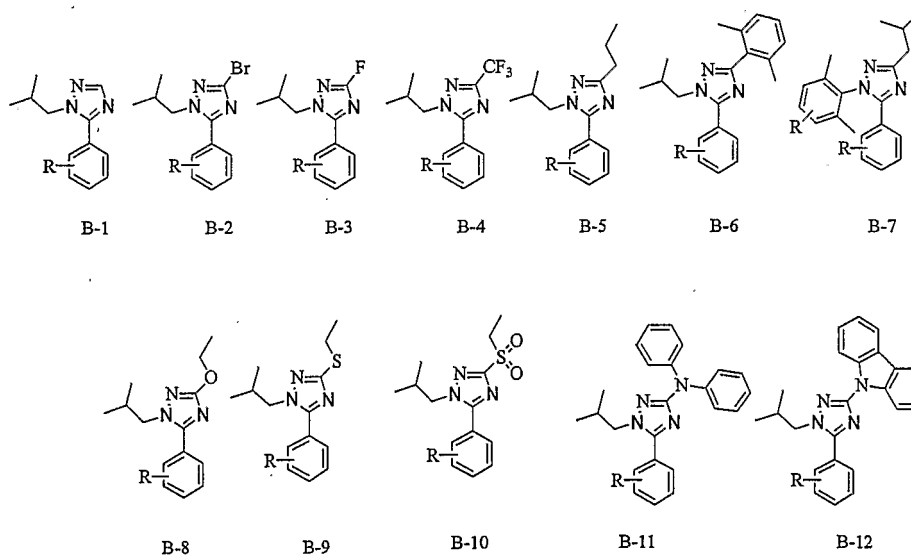
In an alternative embodiment the present invention provides a polymer or oligomer comprising a cyclometallated complex according to the present invention. Said cyclometallated complex may be incorporated into the main chain of the polymer or oligomer or said cyclometallated complex may be pendant to the main chain of the polymer or oligomer. Preferably said polymer or oligomer further comprises carbazole or triarylamine groups.

Further aspects and preferred features of the invention will now be considered with regard to specific compounds.

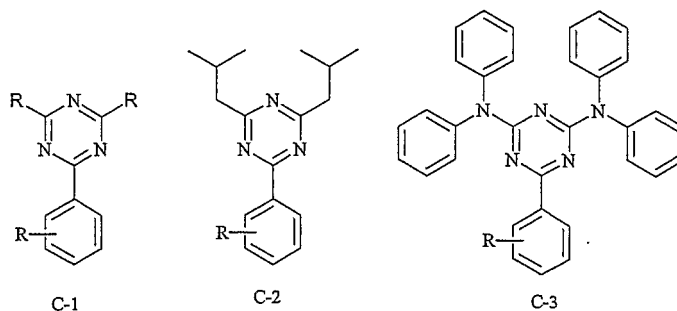
Compounds A-1 to A-7 below are examples of ligands where ring A is a five-membered ring and ring B is a phenyl ring. R represents a substituent, for example, hydrogen, an alkyl or aryl group or a halogen.



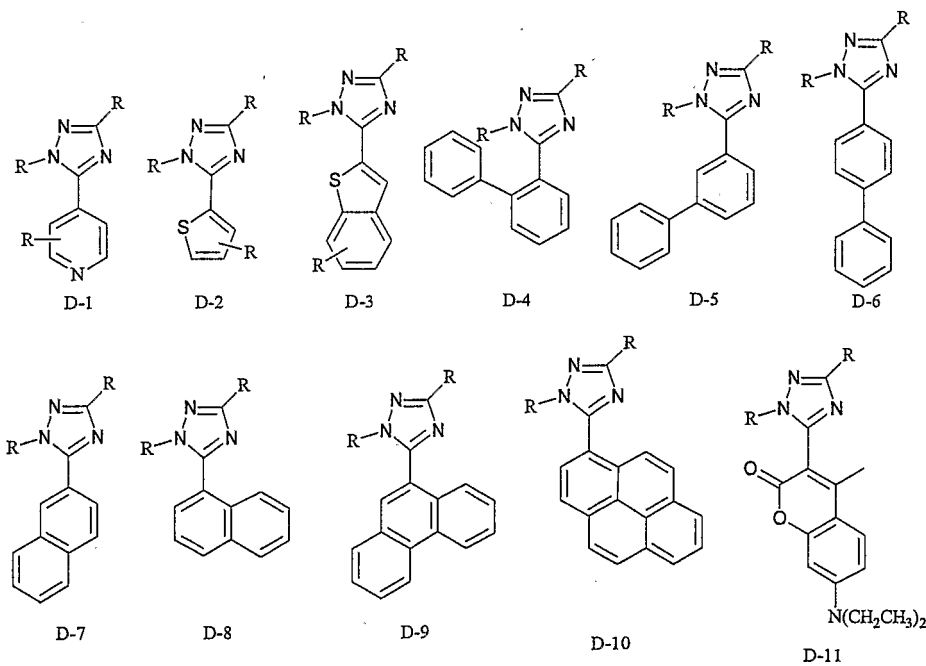
Ring A may be substituted, where ring A comprises a nitrogen this may also be substituted. Suitable substituents include alkyl and aryl groups, alkyloxy groups, alkylamines, arylamines, particularly diarylamines or triarylamines, carbazoles and halogen atoms, in particular fluorine or bromine. Electron donating groups are particularly suitable class of substituents and include alkoxy groups, alkyl groups, alkylamines and arylamines. Compounds B-1 to B-12 are examples of ligands with substituents on ring A.



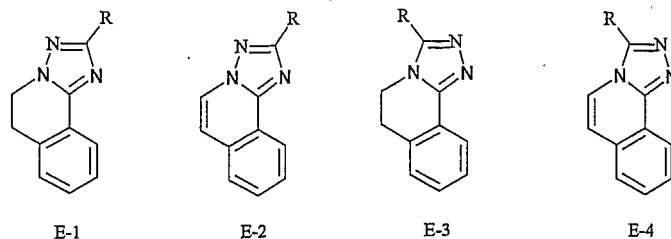
Alternatively ring A may be a six-membered heteroaromatic system, such as a triazine. Where ring A is a six-membered system it may be substituted with alkyl or aryl groups, halides or electron-donating groups. Compounds C-1 to C-3 show examples of suitable ligands wherein ring A is a six-membered ring. R represents a substituent, for example, hydrogen, an alkyl or aryl group or a halogen.



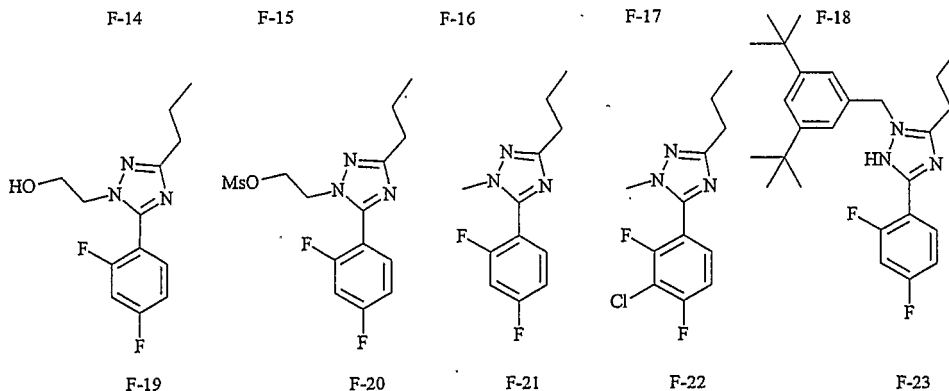
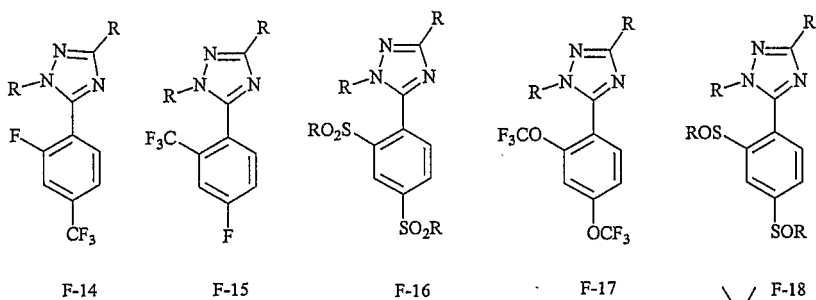
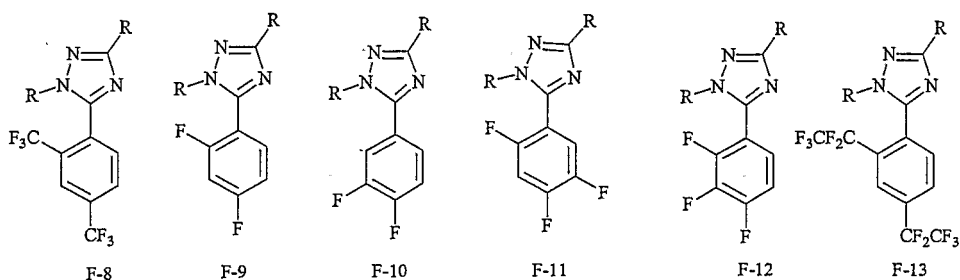
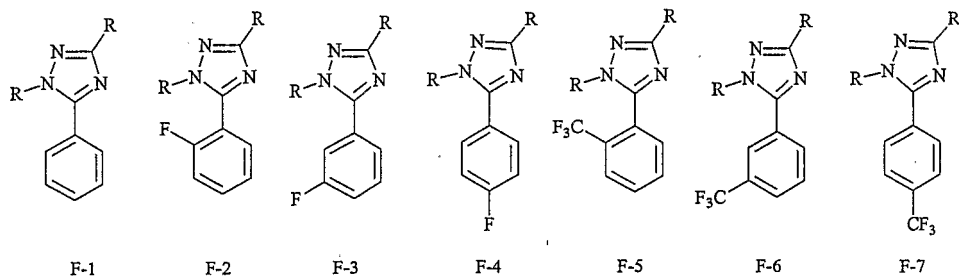
Ring B may be a five or six-membered ring and may be an aromatic or heteroaromatic ring such as benzene, pyridine, pyrazine, pyrimidine, thiophene, furan and pyrrole and derivatives of such groups. Ring B may be substituted or fused. Compounds D-1 to D-11 show suitable ligands wherein ring A is a triazole, clearly many other heteroaryl groups such as those described above may be selected for ring A. R represents a substituent, for example, hydrogen, an alkyl or aryl group or a halogen.



Rings A and B may be fused or linked by covalent bonds as shown in E-1 to E-4 below. R represents a substituent, for example, hydrogen, an alkyl or aryl group or a halogen.

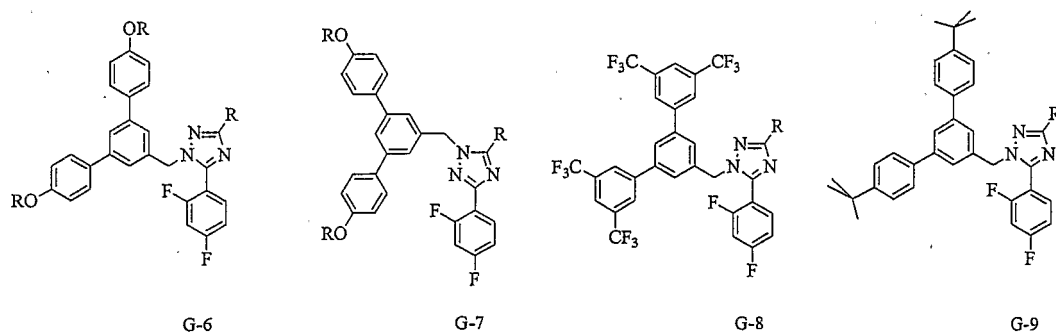
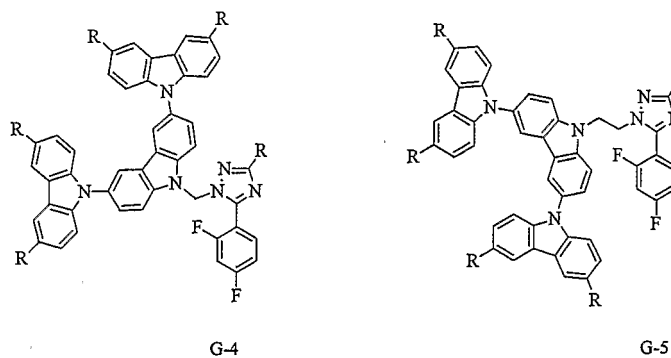
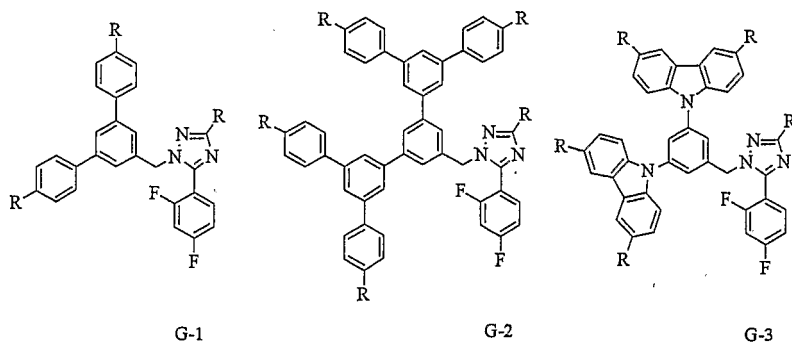


It is preferred that ring B is substituted with electron withdrawing groups such as fluorine, fluoroalkyl, fluoroalkoxy, sulfoxide or sulphone groups. Compounds F-1 to F-23 are examples of ligands substituted with electron withdrawing groups. R represents a substituent, for example, hydrogen, an alkyl or aryl group or a halogen.

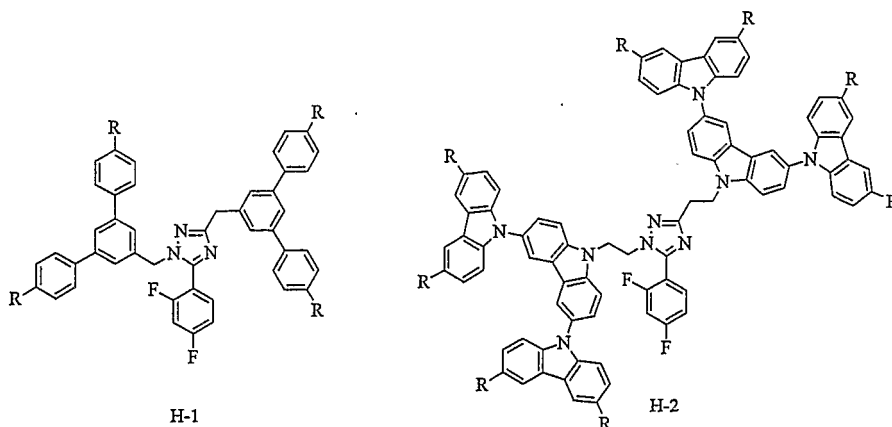


The ligand on metal M may be substituted with dendrons to provide enhanced solution processing properties and to introduce further functionality into the ligand, such as charge transporting functionality. Dendrons are branching structures which allow a high density of functionality to be introduced into the eventual metal complex. In the cyclometallated complexes of the present invention the central metal ion and the ligands forming the first coordination sphere will form the core of the dendrimer with the dendrons substituted onto ring A, B or both. It is preferred that the dendrons are substituted onto ring A of the ligand and that the dendrons are not conjugated to ring A. It has been found particularly advantageous to provide an alkylene linking group between the dendron and ring A, in particular a methylene or ethylene linking group. It is preferred that where ring B has dendron substituents these are in the para position to the carbon of ring B which will form a carbon-metal bond in the cyclometallated complex. Dendrons comprising carbazole, triarylamine and 1,3,5-phenyl groups are particularly suitable for application in light emitting devices. Compounds G-1 to G-9 show ligands according to the present invention substituted with dendrons at ring A. R represents a substituent, for example, hydrogen, an alkyl or aryl group or a halogen or an alkyloxy group.

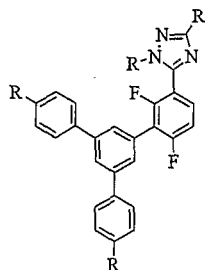
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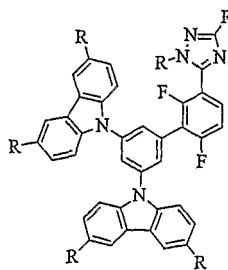
Ring A may also be substituted with a plurality of dendrons, for example, compounds H-1 and H-2 show ligands substituted with a pair of dendrons at ring A. R represents a substituent, for example, hydrogen, an alkyl or aryl group or a halogen.



Ligands of the present invention may also be substituted at ring B with dendrons, as shown by compounds I-1 and I-2 below. R represents a substituent, for example, hydrogen, an alkyl or aryl group or a halogen.

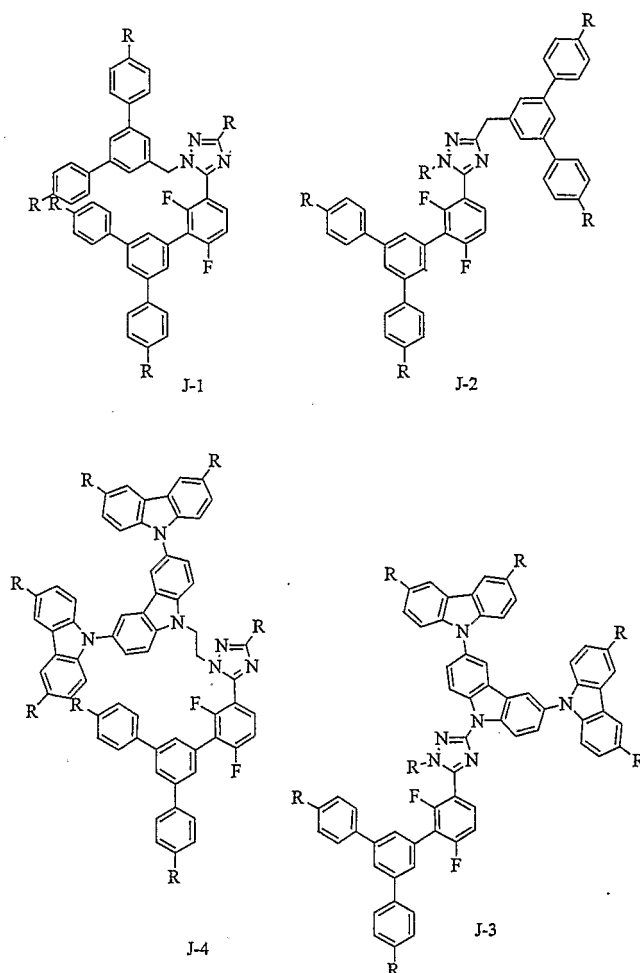


I-1



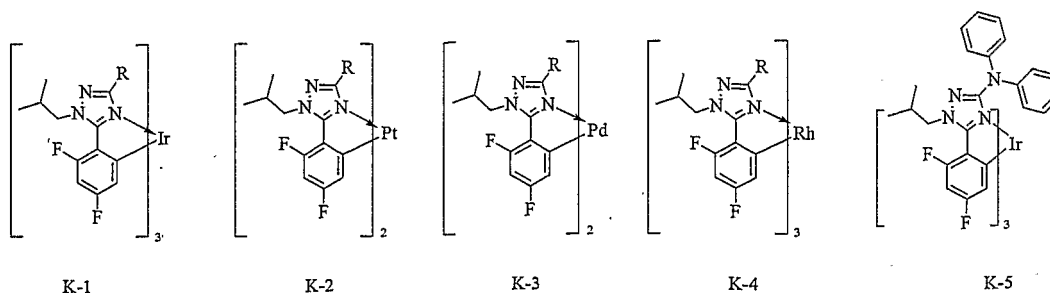
I-2

Alternatively both rings A and B may be substituted with dendrons, as shown by compounds J-1 to J-4 below. R represents a substituent, for example, hydrogen, an alkyl or aryl group or a halogen. United Kingdom patent application GB0219987.5 describes advantages associated with having a plurality of dendrons substituted around a metal core.

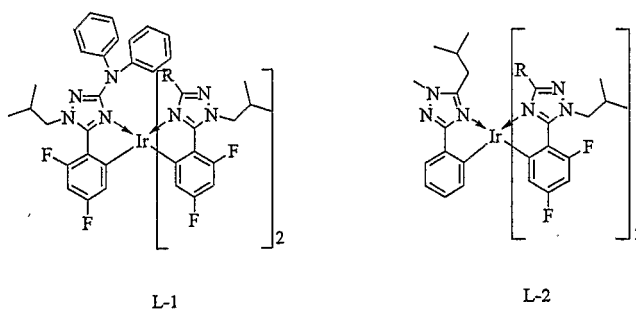


The cyclometallated complex of the present invention may be homoleptic or heteroleptic. In a homoleptic complex all ligands are identical, in a heteroleptic complex different ligands are bound to the metal.

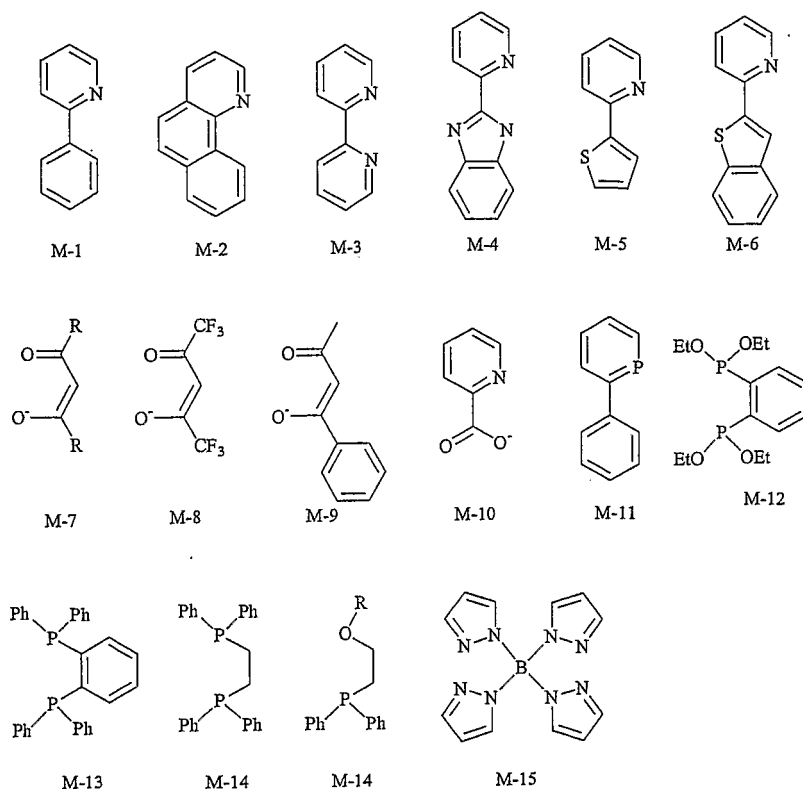
Where said cyclometallated complex is heteroleptic it preferably comprises a ligand selected from the group comprising picolinate, acetylacetonate, phosphines, pyridine and pyridine derivatives, carbonyl, nitrile, isonitrile and halides. Most preferably where said cyclometallated complex is heteroleptic it comprises a picolinate or a tetrakis(1-pyrazolyl)borate co-ligand. Where said cyclometallated complex is heteroleptic it may comprise a further ligand of the same general structure (i.e. having rings A and B linked in the same manner, and having ring A substituted n times by group R_1), but the definitions of A, B, R_1 and n may be different. Suitable homoleptic complexes include those compounds K-1 to K-5 below.



The cyclometallated complexes of the present invention may be heteroleptic complexes comprising different ligands of formula I, examples of such complexes are shown by compounds L-1 and L-2 below.

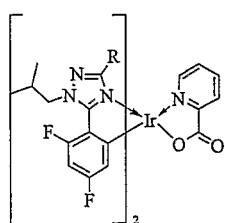


The cyclometallated complexes of the present invention may also be heteroleptic complexes comprising at least one ligand of formula I and other ligands of different structures. Examples of suitable ligands which may be used to form heteroleptic complexes in the present invention include phenylpyridines and other 2-substituted pyridines, 1,3-diones such as picolates, phosphines and diphosphines and carboxylates. Picolates are particularly preferred co-ligands. 1-Pyrazolylborates, such as tetrakis(1-pyrazolyl)borate are a preferred class of co-ligands. Compounds M-1 to M-15 are examples of suitable ligands for use in heteroleptic complexes according to the present invention.

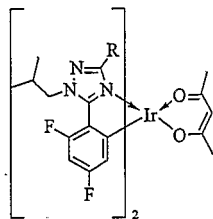


In addition to the bidentate co-ligands, examples of which are illustrated above, monodentate ligands may also be used as co-ligands in the cyclometallated complexes of the present invention. Examples of suitable monodentate ligands include carbonyl, nitrile, isonitrile and alkylisonitriles, thiocyanide, alkylphosphines and arylphosphines, in particular triphenylphosphine, halides, in particular chloride or bromide, heterocyclic compounds such as pyridine and substituted pyridines and alkynes. Preferred monodentate ligands include carbonyl, nitrile, isonitriles, triarylphosphines and halides.

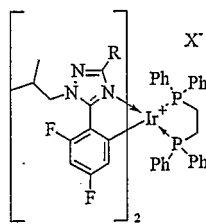
Examples of heteroleptic complexes comprising ligands of formula I and ligands of different structures are shown by compounds N-1 to N-9 below. X represents a charged moiety with a charge sufficient to balance the charge of the metal complex and is preferably chloride, tetrafluoroborate or hexafluorophosphate.



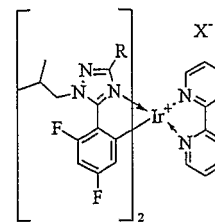
N-1



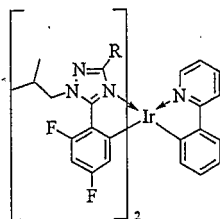
N-2



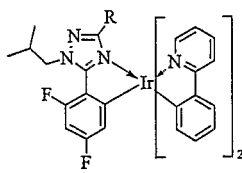
N-3



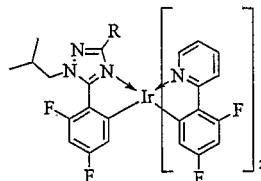
N-4



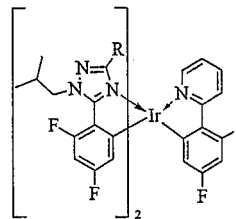
N-5



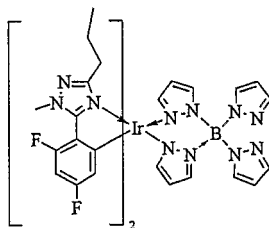
N-6



N-7

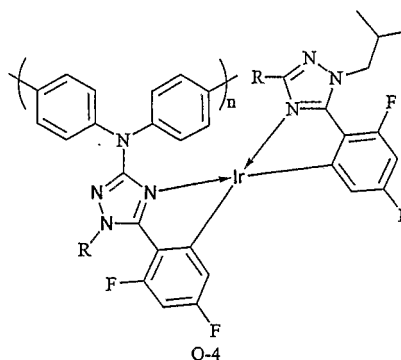
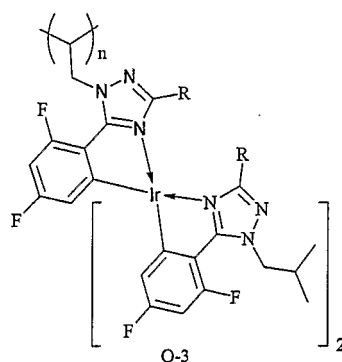
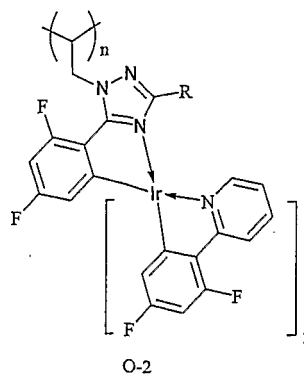
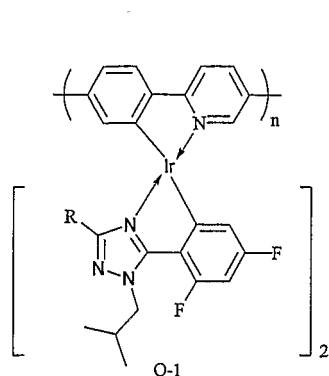


N-8



N-9

The cyclometallated complexes of the present invention may also be incorporated into polymers. The complexes may be incorporated in the main chain of the polymer or as side chains. The polymers incorporating the cyclometallated complexes of the present invention may be homopolymers or copolymers, copolymers may further comprise monomers selected from the group comprising fluorenes, such as 9,9-di-n-octylfluorene, triarylamines, such as N,N-bis(phenyl)-4-sec-butylphenylamine, benzothiadiazoles or phenylene vinylenes. Examples of such systems are shown by polymers O-1 to O-4 below.



A particularly advantageous class of copolymers includes those copolymers which comprise the cyclometallated complexes of the present invention and a comonomer suitable to act as a host material such as carbazole, carbazole derivatives and triarylamines.

In an alternative embodiment of the invention there is provided a cyclometallated complex comprising the structure of formula II wherein A is a five- or six-membered heteroaryl ring which comprises at least three heteroatoms and which is optionally fused to another ring, B is a five- or six-membered aryl or heteroaryl ring which is optionally substituted and is optionally fused to another ring, n is greater than one and R₁ is a dendron or a solubilising group. The heteroatoms in ring A are preferably selected from oxygen, sulphur and nitrogen. More preferably ring A contains at least two nitrogen atoms, more preferably at least three nitrogen atoms. Preferably ring A contains 3, 4 or 5 heteroatoms, more preferably 3 or 4 heteroatoms. The preferred rings for A and B of this embodiment, the preferred R₁ substituents and the preferred values of n are as defined above in relation to the first embodiment of the invention.

Preferred dendrons are as described above in relation to the first embodiment of the invention defined with reference to formula I. Preferred solubilising groups

include alkyl groups having 3 to 12 carbon atoms and heteroalkyl groups such alkoxy groups. Suitable alkoxy groups include C₁₋₆ alkoxy groups.

In a further embodiment of the invention there is provided a polymer comprising a cyclometallated complex comprising the structure of formula III wherein A is a five- or six-membered heteroaryl ring which comprises at least three heteroatoms and which is fused to another ring, B is a five- or six-membered aryl or heteroaryl ring which is optionally substituted and optionally fused to another aryl or heteroaryl ring, n is zero or greater than one and R₁ is a substituent other than hydrogen. The heteroatoms in ring A are preferably selected from oxygen, sulphur and nitrogen. More preferably ring A contains at least two nitrogen atoms, more preferably at least three nitrogen atoms. Preferably ring A contains 3, 4 or 5 heteroatoms, more preferably 3 or 4 heteroatoms.

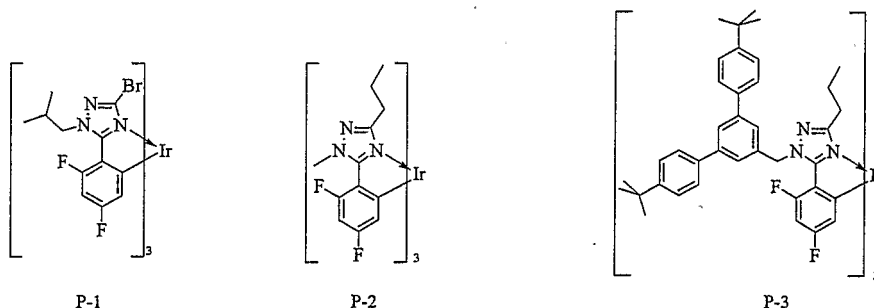
The preferred rings for A and B of this embodiment, the preferred R₁ substituents and the preferred values of n are as defined above in relation to the first embodiment of the invention.

The inventors of the present invention have surprisingly found that a class of cyclometallated iridium complexes of formula I emit light having a blue colour. Cyclometallated iridium complexes of formula I wherein ring A is a five membered ring and is substituted with an electron donating group and wherein ring B is a phenyl ring and is substituted with at least one electron withdrawing group have been shown to emit blue light. In particular cyclometallated iridium complexes of formula I wherein ring A comprises a triazole substituted with an alkyl group and ring B comprises a phenyl ring substituted meta to the carbon-metal bond with two electron withdrawing groups selected from fluorine and trifluoromethane have been shown to emit light of a deep blue colour. Preferably the complexes of the invention have a CIE-y coordinate of less than 0.30, preferably less than 0.25, more preferably between 0.15 and 0.25.

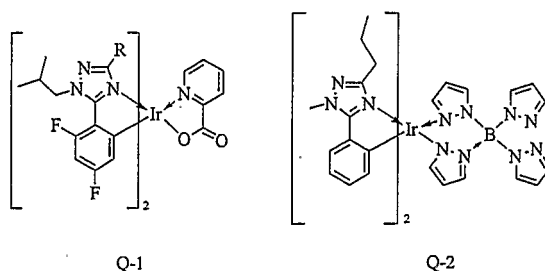
For the purposes of the present invention blue light is considered to comprise light having CIE (Commission Internationale de l'Eclairage) coordinates of $0.3 > x > 0.05$ and $0.3 > y > 0.01$ and a wavelength of between 430 and 490nm and deep blue is considered to comprise light having CIE coordinates of $0.3 > x > 0.1$ and $0.2 > y > 0.01$ and a wavelength of between 430 and 470nm. The CIE defines the primary colour blue to have a wavelength of 435.8nm and the PAL television system uses a blue light source with CIE coordinates of $x=0.15$, $y=0.06$.

The prior art blue phosphorescent light emitting iridium complexes of which Firpic referred to above is an example emit light of a light blue colour having CIE coordinates of $x=0.16$, $y=0.29$ with maximum emission at a wavelength of 470nm.

The cyclometallated complex P-1, shown below, has the photoluminescent spectrum, shown in Figure 1, having a peak emission at a wavelength of 450nm with additional peaks at 428 and 490nm and CIE coordinates of $x=0.15$, $y=0.09$. Clearly the photoluminescence of this cyclometallated complex is significantly blue shifted in comparison with the prior art blue phosphorescent emitter Firpic. The CIE coordinates of the complex are a deeper blue than the prior art blue phosphorescent systems and as such are more suitable for producing full colour displays. The dendron substituted complex P-3 shows CIE coordinates of $x=0.16$, $y=0.14$.



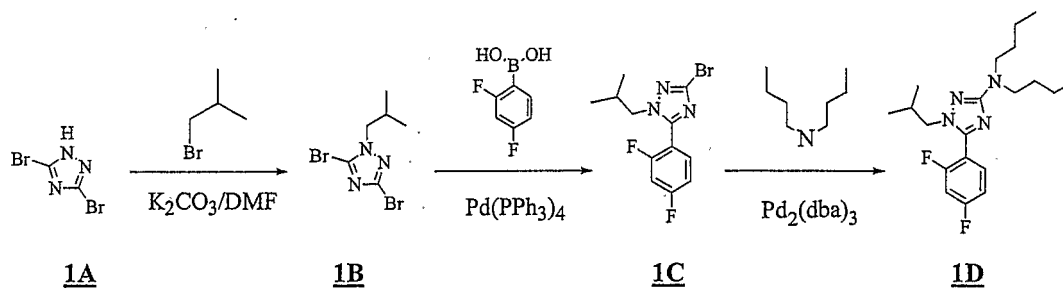
Heteroleptic complexes comprising ligands used in the above-described blue light emitting iridium cyclometallated complexes and further ligands known to shift the colour of light emission of the complexes may also be prepared. Examples of such ligands include anionic ligands such as picolinate, acetylacetonate, tetrakis(1-pyrazolyl)borate and nitrile. Examples of cyclometallated iridium complexes incorporating both the above described ligands and blue shifting coligands are shown below, compounds Q-1 to Q-2.



In order to obtain cyclometallated complexes with deep blue emission it is preferred that substituents on rings A and B are not conjugated to the rings or do not

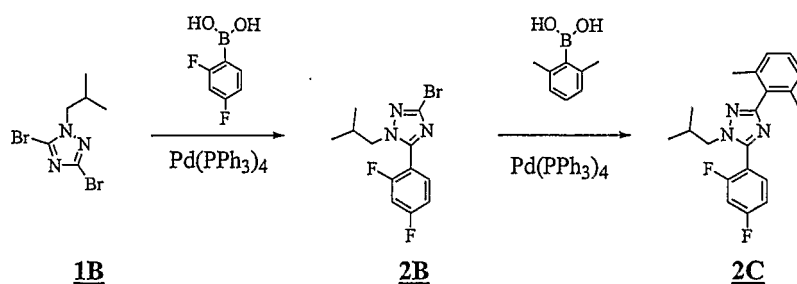
significantly extend the π -conjugated system of rings A or B. The introduction of any such extended conjugation into the cyclometallated complexes serves to red shift the emission. The tetrakis(1-pyrazolyl)borate substituted complex Q-2 has a deep blue photoluminescent emission having CIE coordinates of $x=0.16$, $y=0.19$.

The cyclometallated complexes of the present invention and the ligands of the cyclometallated complexes of the present invention may be prepared according to standard synthetic techniques. A typical synthetic scheme for the preparation of a cyclometallated complex according to the present invention is shown in Scheme 1 below.

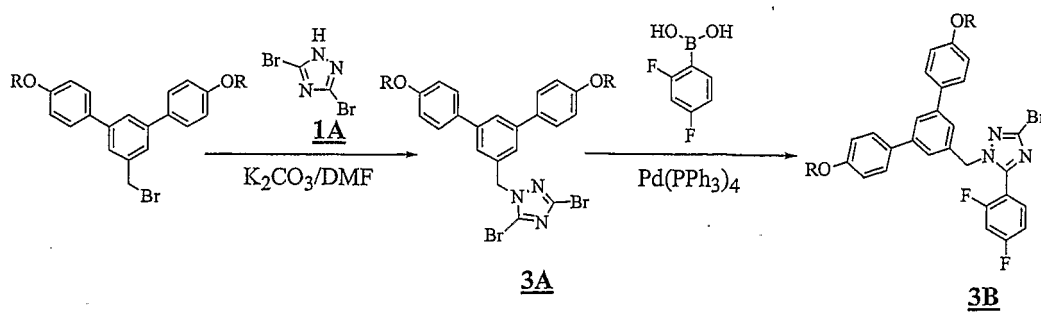


Scheme 1

In the above Scheme 1 a dibrominated triazole 1A is reacted with excess *iso*-butylbromide in the presence of a base to provide the substituted triazole 1B. The substituted triazole 1B is further reacted with a phenyl substituted boronic acid using Suzuki coupling to provide compound 1C. Compound 1C is then further substituted with dipropylamine in the presence of tris(dibenzylideneacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$) to provide the ligand 1D. This synthetic methodology allows a wide range of ligands to be prepared. The flexibility of the synthetic methodology is highlighted by synthetic schemes 2 and 3 shown below for the preparation of a range of ligands including dendron substituted ligands.

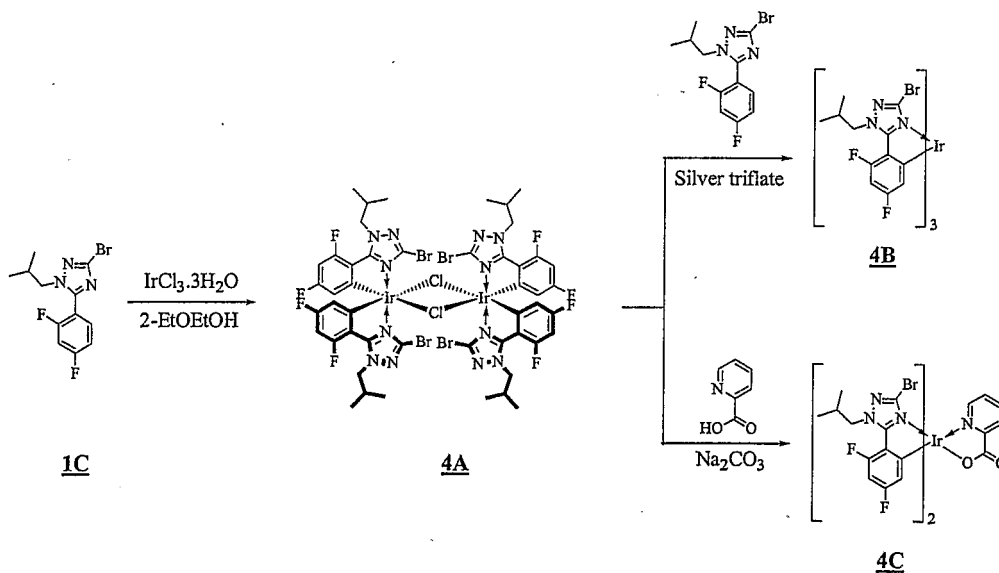


Scheme 2



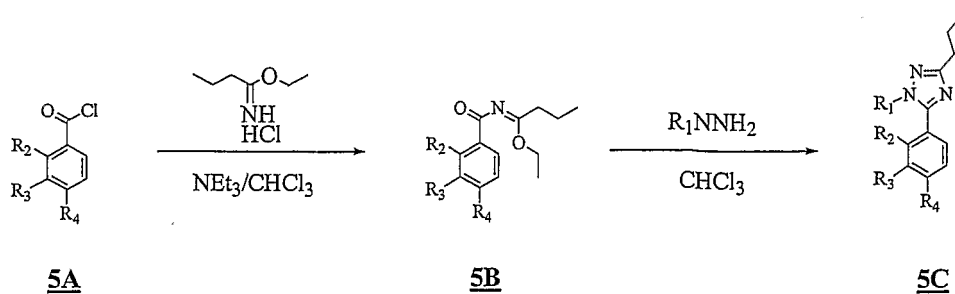
Scheme 3

Metal complexes of the ligands can be prepared by standard synthetic techniques, in particular as described in *Inorganic Chemistry* (1994), 33(3), 545-50. In the procedure shown in Scheme 4 below excess phenyltriazole ligand 1C is reacted with iridium chloride in a protic solvent. The dimer complex 4A is isolated from the reaction mixture and reacted with further phenyltriazole ligand 1C in the presence of silver trifluoromethane sulfonate to give cyclometallated iridium complex 4B. Alternatively the dimer complex 4A may be reacted with a different co-ligand to give a heteroleptic complex such as 4C.



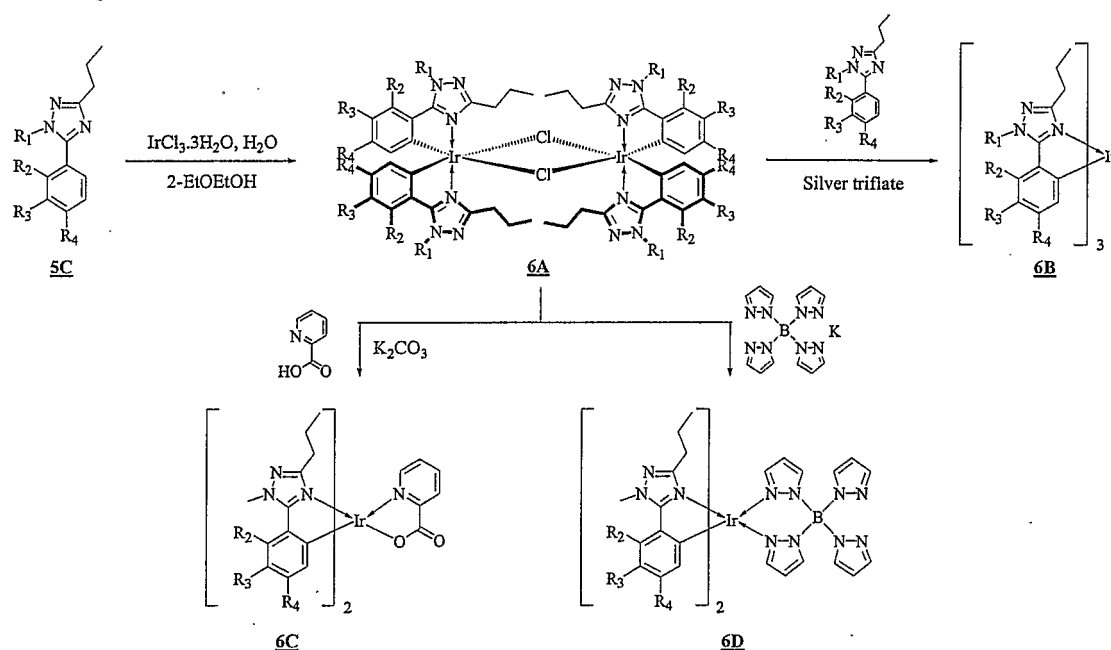
Scheme 4

Scheme 5 shows an alternative and more preferred approach to the preparation of triazole based ligands comprising a triazole ring.



Scheme 5

Scheme 6 illustrates general synthetic approaches to the cyclometallated iridium complex **6B** to **6D**.



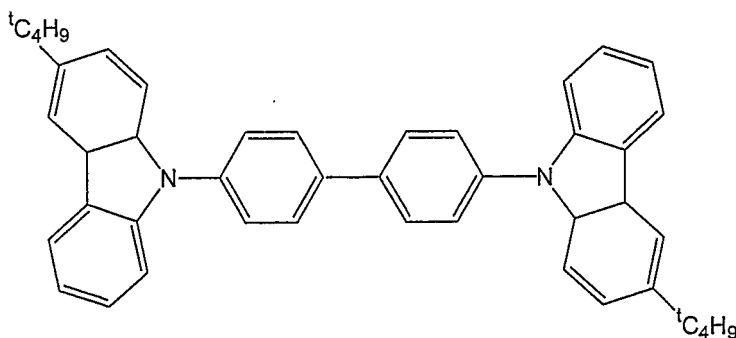
Scheme 6

Where the cyclometallated complexes of the present invention comprise dendrons these may be substituted onto the ligand prior to complexation of the ligand with the metal or alternatively the cyclometallated core may be formed first and the dendrons substituted onto the cyclometallated core.

The cyclometallated complexes of the present invention have application in organic optoelectronic devices. Organic optoelectronic devices include electroluminescent, photoluminescent, fluorescent and photoconductive organic devices and organic transistors. Photoconductive organic devices include photovoltaic devices, photodiodes and photosensors. In particular the cyclometallated complexes of the present invention have application in organic light emitting diodes.

Organic light emitting diodes comprise a layered structure comprising a lower electrode situated on a substrate, a layer, or several layers, of organic light emitting material and an upper electrode. When a voltage is supplied across the electrode of the device opposite charge carriers, namely electrons and holes, are injected into the organic light emitting material. The electrons and holes recombine in the layer of organic light emitting material forming an excited state (or exciton) which can decay radiatively (with the emission of light) or non-radiatively. In the case of fluorescent organic light emitters the radiative excited states are singlet excitons, in the case of phosphorescent organic light emitters the radiative excited states are triplet excitons. The cyclometallated complexes of the present invention are phosphorescent organic light emitters and in particular the cyclometallated complexes of the present invention comprising iridium and platinum form highly efficient phosphorescent light emitters.

The organic light emitting layer of organic phosphorescent light emitting devices generally comprises an organic phosphorescent light emitter, such as the cyclometallated complexes of the present invention, and an organic host. The organic host acts to transport charge to the phosphorescent emitter and also acts as a triplet source whereby triplet excited states are formed in the organic host and then transferred to the phosphorescent emitter where they decay with the emission of light. Prior art organic hosts used in phosphorescent light emitting systems include carbazoles such as polyvinylcarbazole, known as PVK, 4,4'-bis(carbazol-9-yl)biphenyl, known as CBP, N,N -dicarbazolyl-3,5-benzene, known as mCP, diphenyldi(o-tolyl) silane or *p*-bis(triphenylsilyl)benzene, known as UGH1 and UGH2 respectively and described in Holmes et al. (*Appl. Phys. Lett.*, **83**, no. 18, 2003, 3818), and (4,4',4''-tris(carbazol-9-yl)triphenylamine), known as TCTA, such hosts are described in Ikai et al. (*Appl. Phys. Lett.*, **79** no. 2, 2001, 156). One particularly suitable host material is di(tert-butyl)CBP, which has the structure:



Triarylamines may also be used as host materials, in particular tris-4-(N-3-methylphenyl-N-phenyl)phenylamine, known as MTDATA. Where the phosphorescent emitter and the host are both soluble they may be deposited as a blend by solution processing techniques such as spin-coating, doctor blade coating, screen printing or ink-jet printing. Where the phosphorescent emitter and the host are insoluble and volatile they may be deposited by vacuum deposition. The phosphorescent emitter and host are preferably present in a blend comprising 5 to 50 mol % of phosphorescent emitter, preferably 10-30 mol % of phosphorescent emitter. Tetraarylsilane hosts are preferred, the tetraarylsilanes UGH1 and UGH2 are particularly preferred. Wide band gap hosts, such as tetraarylsilanes, are particularly preferred as hosts for cyclometallated complexes of the present invention which emit blue light.

Organic phosphorescent light emitting devices comprising a separate light emitter and host are well known in the prior art. More recently it has been found advantageous to combine the phosphorescent light emitter and the organic host in a single molecule, dendrimer or polymer, examples of such systems are disclosed in GB0206356.8. Advantages of such systems include improved film stability (no phase separation), improved electrochemical stability, improved manufacturability of devices, in particular improved solution processing properties, and improved light emission. As discussed above, in the cyclometallated complexes of the present invention host moieties can be introduced as substituents directly onto the aryl or heteroaryl rings A and/or B, by incorporation of the host moieties into dendrons attached to rings A and/or B or by forming copolymers comprising monomers of the cyclometallated complexes of the present invention and comonomers incorporating host moieties.

The organic light emitting layer of the light-emitting devices of the present invention may further comprise a diluent compound. In particular, polymethylmethacrylate (PMMA) may be admixed with the cyclometallated complex of the invention and the host material. This optional PMMA is used to dilute the concentration of host and dopant materials in the phosphorescent layer in order to prevent quenching effects which can occur at higher concentrations. Since PMMA is not a charge transporting material, the quantity used is a balance between minimising quenching and maintaining good conductivity in the phosphorescent layer. Preferred

levels of PMMA in the phosphorescent layer are from 0 to 90% by weight, more preferably from 30 to 80%, more preferably 50 to 80%, most preferably 50 to 75%.

In addition to increasing quantum efficiency, PMMA may also contribute to improving film formation.

The light emitting organic layer preferably has a thickness of between 5 and 200nm, more preferably of between 10 and 60nm and most preferably of between 20 and 50nm. The light emitting layer incorporating a phosphorescent emitter and a host may also include hole-transport materials examples of which are discussed below.

One of the electrodes of the organic light emitting device, the anode, comprises a high work function material suitable for injecting holes into the layer of organic light emitting material, this material typically has a work function of greater than 4.3 eV and may be selected from the group comprising indium-tin oxide (ITO), tin oxide, aluminum or indium doped zinc oxide, magnesium-indium oxide, cadmium tin-oxide, gold, silver, nickel, palladium and platinum. The anode material is deposited by sputtering or vapour deposition as appropriate. Incorporation of a thin layer of, for example, silicon oxide, over the surface of the anode, in particular over ITO, can improve the performance of organic light emitting devices, as shown in WO02/093662.

The other electrode, the cathode, comprises a low work function material suitable for injecting electrons into the layer of organic light emitting material. The low work function material typically has a work function of less than 3.5 eV and may be selected from the group including Li, Na, K, Rb, Be, Mg, Ca, Sr, Ba, Yb, Sm and Al. The cathode may comprise an alloy of such metals or an alloy of such metals in combination with other metals, for example the alloys MgAg and LiAl. The cathode preferably comprises multiple layers, for example Ca/Al, Ba/Al or LiAl/Al. The device may further comprise a layer of dielectric material between the cathode and the emitting layer, such as is disclosed in WO 97/42666. In particular it is preferred to use an alkali or alkaline earth metal fluoride as a dielectric layer between the cathode and the emitting material. A particularly preferred cathode comprises LiF/Al, with a layer of LiF of thickness from 1 to 10nm and a layer of Al of thickness 10 to 500nm. The cathode materials are deposited by vacuum deposition methods.

For light emission to occur from the device it is preferred that either the cathode, the anode or both be transparent or semi-transparent. Suitable materials for transparent anodes include ITO and thin layers of metals such as platinum. Suitable

materials for transparent cathodes include a thin layer of electron injecting material in proximity to the layer of organic light emitting material and a thicker layer of transparent conductive material overlying the layer of electron injecting material e.g. a cathode structure comprising Ca/Au. Where neither the cathode nor the anode is transparent or semi-transparent light emission occurs through the edge of the device.

The organic light emitting device may include further organic layers between the anode and cathode to improve charge injection and device efficiency. In particular a layer of hole-transporting material may be situated over the anode. The hole-transport material serves to increase charge conduction through the device. The preferred hole-transport material used in the art is a conductive organic polymer such as polystyrene sulfonic acid doped polyethylene dioxythiophene (PEDOT:PSS) as disclosed in WO98/05187. Other hole transporting materials such as doped polyaniline, TPD (N,N'-diphenyl-N,N'-bis(3-methylphenyl)[1,1'-biphenyl]-4,4'-diamine), NPD (4,4'-bis[N-naphthyl]-N-phenyl-amino]biphenyl) and MTDATA may also be used. A hole transport layer which has been shown to be particularly advantageous when used in combination with cyclometallated complexes comprises polymerised divinyl-TPD.

The cyclometallated complexes of the present invention may comprise a hole transporting moiety. The advantages of incorporating the hole transporting function into the cyclometallated complex include improved film stability and improved manufacturability. The hole transporting groups may be incorporated into the cyclometallated complexes as substituents directly on the ligands, for example as dendrons, or by being present as comonomers in copolymers comprising the cyclometallated complexes of the present invention. The cyclometallated complexes of the present invention may also comprise an electron transporting moiety.

A layer of electron transporting/hole blocking material may be positioned between the layer of light emitting material and the cathode, this has been found to improve device efficiency. Suitable materials for electron transporting/hole blocking layers include 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), 1,3,5-tris(2-N-phenylbenzimidazolyl)benzene (TPBI) and 2-biphenyl-5(4'-t-butylphenyl)oxadiazole (PBD). The provision of an electron transporting/hole blocking layer between the light emitting layer and the cathode has been found to significantly improve device performance both in terms of device efficiency and lifetime.

The substrate of the organic optoelectronic device should provide mechanical stability to the device and act as a barrier to seal the device from the environment. Where it is desired that light enter or leave the device through the substrate, the substrate should be transparent or semi-transparent. Glass is widely used as a substrate due to its excellent barrier properties and transparency. Other suitable substrates include ceramics, as disclosed in WO 02/23579 and plastics such as acrylic resins, polycarbonate resins, polyester resins, polyethylene terephthalate resins and cyclic olefin resins. Plastic substrates may require a barrier coating to ensure that they remain impermeable. The substrate may comprise a composite material such as the glass and plastic composite disclosed in EP 0 949 850.

To provide environmental protection the device is encapsulated. Encapsulation may take the form of a glass sheet which is glass bonded to the substrate with a low temperature frit material. To avoid the necessity of using a glass sheet to encapsulate the device a layer of passivating material may be deposited over the device. Suitable barrier layers comprise a layered structure of alternating polymer and ceramic films and may be deposited by PECVD as disclosed in WO 00/36665 and US 5,686,360. Alternatively the device may be encapsulated by enclosure in a metal can.

Preferred device structures for the phosphorescent light emitting cyclometallated complexes of the present invention include:

Glass / ITO / PEDOT:PSS / CBP:emitter / TPBI / LiF / Al

Glass / ITO / poly(vinyl-TPD) / CBP:emitter / TPBI / LiF / Al

Glass / ITO / SiO / PEDOT:PSS / CBP:emitter / TPBI / LiF / Al

Glass / ITO / SiO / poly(vinyl-TPD) / CBP:emitter / TPBI / LiF / Al

Glass / ITO / PEDOT:PSS / PVK:emitter / TPBI / LiF / Al

Glass / ITO / poly(vinyl-TPD) / PVK:emitter / TPBI / LiF / Al

Glass / ITO / SiO / PEDOT:PSS / PVK:emitter / TPBI / LiF / Al

Glass / ITO / SiO / poly(vinyl-TPD) / PVK:emitter / TPBI / LiF / Al

Where the phosphorescent emitter comprises a cyclometallated complex according to the present invention which emits blue light it is preferred that a wide band gap host material is used, such as a tetraarylsilane.

In a most preferred embodiment the phosphorescent emitter and host are combined in a molecule which may be small molecule, a dendrimer or a polymer.

Glass / ITO / PEDOT:PSS / combined host-emitter / TPBI / LiF / Al

Glass / ITO / poly(vinyl-TPD) / combined host-emitter / TPBI / LiF / Al

Glass / ITO / SiO / PEDOT:PSS / combined host-emitter / TPBI / LiF / Al

Glass / ITO / SiO / poly(vinyl-TPD) / combined host-emitter / TPBI / LiF / Al

Organic optoelectronic devices may be prepared by any suitable method known to those skilled in the art. Typically the substrate will comprise a glass sheet upon which a layer of anode material, such as ITO, may be deposited by sputtering. The ITO or other anode material may, if required, be patterned using either additive methods during deposition, such as printing, or using subtractive methods following deposition, such as photolithography. The organic layers of the device may be deposited by vapour deposition, this is a particularly suitable method for the deposition of low molecular weight organic optoelectronic materials.

Where the organic optoelectronic materials are soluble they may be advantageously deposited by solution processing techniques. Solution processing techniques include selective methods of deposition such as screen printing and ink-jet printing and non-selective methods such as spin coating and doctor blade coating. Cyclometallated complexes of the present invention which incorporate host moieties are particularly suited to solution processing as such materials are not present in the form of a blend and therefore will not phase separate on deposition.

The cathode and any additional dielectric or electron transporting/hole blocking layers may be deposited using vapour deposition. Auxiliary layers and

features may be included in the organic optoelectronic device as appropriate to improve charge injection or to facilitate patterning of the device.

Examples

Example 1

3,5-Dibromo-1-iso-butyl-1H-[1,2,4]triazole (Compound 1B)

A mixture of 3,5-dibromo-1H-[1,2,4]triazole (Zumbrunn, *Synthesis*, 1998, 1357) (**1A**) (440 mg, 1.94 mmol), potassium carbonate (483 mg, 3.49 mmol), *iso*-butylbromide (0.4 mL, 3.49 mmol), and *N,N*-dimethylformamide (5 mL) was heated at 103 °C under argon for 4 h. The mixture was allowed to cool to room temperature. Water (20 mL) was added and the mixture was extracted with ether (3 x 20 mL). The ether extracts were combined, washed with brine (1 x 30 mL), dried over anhydrous sodium sulphate, filtered and the solvent was completely removed to leave **1B** as a pale yellow oil (548 mg, 100%); ¹H(200 MHz; CDCl₃) 0.96 (6 H, *J* 6.6 Hz, CH₃), 2.28 (1 H, m, CH), and 3.94 (2 H, d, *J* 7.4 Hz, CH₂); *m/z* [APCI⁺] 280, 282, 284 (M⁺).

Example 2

3-Bromo-1-iso-butyl-5-(2',4'-difluorophenyl)-1H-[1,2,4]triazole (Compound 1C)

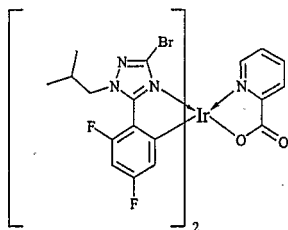
A mixture of **1B** (6.80 g, 24.0 mmol), 2,4-difluorophenylboronic acid (6.07 g, 38.5 mmol), tetrakis(triphenylphosphine) palladium (0) (833 mg, 0.721 mmol), aqueous sodium carbonate (2 M, 21 mL), ethanol (21 mL) and toluene (63 mL) was deoxygenated and heated at 103 °C under argon for 19 h. The mixture was allowed to cool to room temperature. The organic layer was separated. The aqueous layer was extracted with ether (3 x 30 mL). The organic layer and the ether extracts were combined, washed with brine (1 x 50 mL), and dried over anhydrous sodium sulphate and filtered. The solvents were completely removed to give 8.2 g of light yellow oil. The oil was purified by column chromatography over silica gel using a dichloromethane-light petroleum mixture (1:100 to 1:10) as eluent to give **1C** (900 mg, 12%); ¹H(200 MHz; CDCl₃) 0.80 (6 H, d, *J* 6.6 Hz, CH₃), 2.26 (1 H, m, CH), 3.84 (2 H, d, *J* 8.0 Hz, CH₂), 6.92-7.14 (2 H, m, ArH), and 7.45-7.60 (1 H, m, ArH).

Example 3**[BDFIBTriazole]₃Ir (Compound 4B)**

A mixture of **1C** (470 mg, 1.49 mmol), iridium chloride tri-hydrate (131 mg, 0.371 mmol), water (2.0 mL) and 2-ethoxyethanol (6.0 mL) was heated at 130 °C under argon for 13 h before being cooled. The precipitate was separated from the mixture. The solid was washed with ethanol (8 x 3 mL) and light-petroleum (5 x 8 mL) and dried to give dichloro-bridged dimer **4A** (262 mg, 82%) as a pale yellow solid; ¹H(200 MHz; CDCl₃) 0.95-1.10 (24 H, m, CH₃), 2.20-2.43 (4 H, m, CH), 4.40-4.68 (8 H, m, CH₂), 5.74 (4 H, m, ArH), and 6.40 (4 H, m, ArH).

A mixture of the iridium complex (**4A**) (180 mg, 0.210 mmol) and **1C** (370 mg, 1.17 mmol) and silver trifluoromethanesulfonate (108 mg, 0.420 mmol) was heated at 156-160 °C for 38 h under argon. The reaction was then allowed to cool to room temperature. The mixture was dissolved in dichloromethane (~4 mL) and purified by column chromatography over silica gel using a dichloromethane-light petroleum mixture (1:30 to 1:8) as eluent to give a pale yellow solid of **4B** as a mixture of isomers (232 mg, 97%); ¹H(200 MHz; CDCl₃) 0.80-1.02 (18 H, m, CH₃), 2.10-2.31 (3 H, m, CH), 4.40 (6 H, m, CH₂), 6.05 (3 H, m, ArH), and 6.46 (3 H, m, ArH); *m/z* [MALDI] 1133, 1135, 1136, 1137, 1138, 1139, 1140, 1141, 1142 (*M*⁺).

The photoluminescence spectrum of a neat film of complex **4B** spin coated from a 9.5% solution in chloroform is shown in Figure 1. The neat film shows a very good blue emission with clear vibronic structure giving peaks at 428, 450 and 490nm.

**Example 4****(IBBrF₂PhTriazole)₂IrPic (Compound 4C, shown above)**

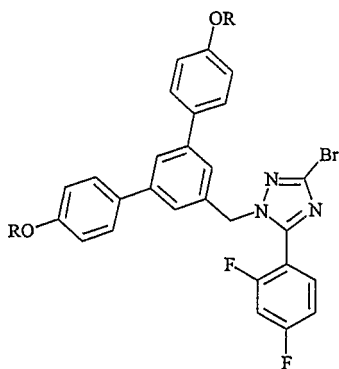
A mixture of the iridium complex (**4A**) (28 mg, 0.033 mmol), picolinic acid (12 mg, 0.098 mmol), sodium carbonate (35 mg, 0.284 mmol) and 1,2-dichloroethane (2 mL) was heated at reflux under Ar(g) for 20 h. The dichloromethane (3 mL) and water (2 mL) were added. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 2 mL). The organic portions were combined and

washed with brine (1 x 5 mL), dried (Na_2SO_4) and the solvent was removed. The residue was purified over silica gel using ethyl acetate-dichloromethane (0:1 to 2:1) as elute to give a yellowish solid **4C** (31 mg, 100%); ^1H (200 MHz; CDCl_3) 0.80-1.02 (12 H, m, Me); 2.13-2.38 (2 H, m, CH), 4.32-4.67 (4 H, m, CH_2), 5.79 (1 H, m, ArH), 6.10 (1 H, m, ArH), 6.49 (2 H, m, ArH), 7.41 (1 H, m, PyH), 7.72 (1 H, m, PyH), 7.93 (1 H, m, PyH), and 8.31 (1 H, m, PyH); m/z [APES^+] 942, 944, 946, 947, 948, 949 (MH^+).

Example 5

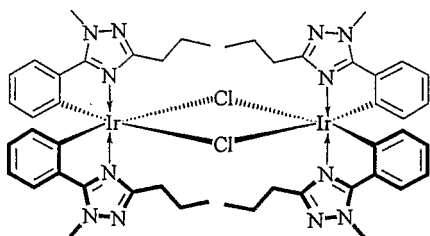
3,5-Dibromo-1-{3',5'-di[4'-(2''-ethylhexyloxy)phenyl]benzyl}-1H-[1,2,4]triazole (Compound 3A of Scheme 3)

A mixture of the dibromo-triazole **1A** (805 mg, 3.55 mmol), the 3,5-di[4'-(2''-ethylhexyloxy)phenyl]benzyl bromide (prepared as disclosed in WO 0159030) (2.67 g, 4.61 mmol), K_2CO_3 (896 mg, 6.48 mmol) and dried DMF (16 cm^3) was deoxygenated and then heated at a bath temperature of 98-108 °C under argon for 46 h. The mixture was allowed to cool to room temperature and poured into 70 cm^3 of water. The mixture was extracted with ether (4 x 30 cm^3). The ether extracts were combined, washed with water (2 x 40 cm^3), and brine (1 x 40 cm^3), and dried over anhydrous sodium sulphate. The solvents were completely removed to leave a yellow oil. The oil was purified by column chromatography over silica gel using DCM-light petroleum (0:1 to 1:10) as eluent to give 1.82 g (71%) of **3A** as a white solid; ^1H (400 MHz; CDCl_3) 0.91-1.02 (12 H, m, 4 x Me), 1.32-1.63 (16 H, m, 8 x CH_2), 1.72-1.83 (2 H, m, 2 x CH), 3.91 (4 H, m, 2 x ArOCH_2), 5.42 (2H, s, ArCH_2), 7.01 (4 H, m, 4 x ArCH), 7.42 (2 H, m, 2 x ArH), 7.54 (4 H, m, 4 x ArCH), and 7.70 (1 H, m, ArH)

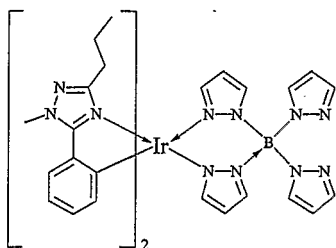


Example 6**3-Bromo-1-{3',5'-di[4''-(2'''-ethylhexyloxy)phenyl]benzyl}-5-(2',4'-difluorophenyl)-1*H*-[1,2,4]triazole (Compound 3B shown above)**

A mixture of the dibromo-triazole **3A** (375 mg, 0.517 mmol), the 2',4'-difluorophenyl boronic acid (146 mg, 0.93 mmol), tetrakis(triphenylphosphine) palladium (0) (42 mg, 0.036 mmol), 2 M Na₂CO_{3(aq)} (0.3 cm³), EtOH (0.3 cm³) and toluene (1.0 cm³) was deoxygenated and heated at reflux (with bath temperature of 110 °C) under argon for 5 days. The mixture was allowed to cool. Water (5 cm³) and ether (10 cm³) were added to the mixture. The organic layer was separated. The aqueous layer was extracted with ether (3 x 6 cm³). The organic layer and the ether extracts were combined, washed with brine (1 x 19 cm³), and dried over anhydrous sodium sulphate. The solvents were completely removed. The residue was purified by column chromatography over silica gel using DCM-light petroleum (0:1 to 1:10) as eluent to give 187 mg (48%) of **3B** as a colourless oil; ¹H(200 MHz; CDCl₃) 0.72-1.04 (12 H, m, CH₃), 1.12-1.84 (18 H, m, CH₂ & CH), 3.89 (4 H, m, OCH₂), 5.37 (2 H, s, ArCH₂), and 6.80-7.62 (14 H, m, ArH).

**Example 7****(MePrPhTriazole)₂IrCl (Compound 6A shown above)**

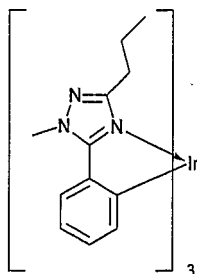
A mixture of the triazole ligand (**MePrPhTriazole**) (**5C**) (1.43 g, 7.09 mmol), iridium chloride trihydrate (1.00 g, 2.84 mmol), water (14 mL) and 2-EtOEtOH (40 mL) was heated at reflux under N_{2(g)} for 13 h. The mixture was allowed to cool to room temperature. Water (48 mL) was added to the mixture to precipitate the yellow solid. The solid was filtered off and washed with water. The mixture was evaporated to dryness to give 1.50 g (84%) of brownish yellow solid of **6A** was obtained; ¹H(200 MHz; CDCl₃) 0.83 (12 H, m, Me), 1.51-1.98 (8 H, m, CH₂), 2.20-2.42 (4 H, m, CH₂), 2.71-2.94 (4 H, m, CH₂), 4.31 (12 H, s, Me), 6.21 (4 H, m, ArH), 6.66 (4 H, m, ArH), 6.80 (4 H, m, ArH), and 7.40 (4 H, m, ArH).



Example 8

(MePrPhTriazole)₂IrTPB (Compound 6D shown above)

A mixture of the iridium complex (**6A**) (250 mg, 0.398 mmol), tetrakis(1-pyrazolyl)borate (**TPB**) potassium salt (250 mg, 0.786 mmol) and dichloromethane (25 mL) was stirred at room temperature under N_{2(g)} for 23 h. The solvent was removed and the mixture was purified over silica gel chromatography using ethyl acetate-light petroleum (1:10 to 1:3) as elute to give a yellow powder of (**6D**) (206 mg, 59%); ¹H(400 MHz; CDCl₃) 0.68 (6 H, m, Me), 1.21-1.28 (2 H, m, CH₂), 1.36-1.58 (6 H, m, CH₂), 4.23 (6 H, s, Me), 6.12 (4 H, m, PyrazolylH), 6.40, (2 H, d, 7.6 Hz, ArH), 6.45 (2 H, m, PyrazolylH), 6.71 (2 H, m, PyrazolylH), 6.88 (2 H, m, ArH), 7.00 (2 H, m, ArH), 7.20 (2 H, m, PyrazolylH), 7.53 (2 H, d, 7.6 Hz, ArH), and 7.68 (2 H, m, PyrazolylH). The photoluminescence quantum yield of a neat film of **6D** spin coated from a solution of chloroform is 1%, having the CIE coordinates x=0.16, y=0.19.



Example 9

(MePrPhTriazole)₃Ir (Compound 6B shown above)

A mixture of the iridium complex (**6A**) (370 mg, 0.589 mmol), the triazole ligand (**MePrPhTriazole**) (**5C**) (710 mg, 3.53 mmol) and silver triflate (303 mg, 1.18 mmol) was heated with oil bath temperature of 170 °C for 19 h under N_{2(g)}. The

mixture was allowed to cool to room temperature and purified over silica gel using ethyl acetate-light petroleum (1:50 to 1:2) as elute to give a yellow powder of **6B** (450 mg, 96%); ^1H (400 MHz; CDCl_3) 0.69 (9 H, t, 7.3 Hz, Me), 1.09-1.22 (3 H, m, CH_2), 1.30-1.44 (3 H, m, CH_2), 1.82-1.94 (3 H, m, CH_2), 2.14-2.26 (3 H, m, CH_2), 4.16 (9 H, s, Me), 6.61 (3 H, d, 7.5 Hz, ArH), 6.81 (3 H, m, ArH), 6.90 (3 H, m, ArH), and 7.52 (3 H, d, 7.7 Hz, ArH). The photoluminescence quantum yield of a neat film of **6B** spin coated from a solution of chloroform is 9%, having the CIE coordinates $x=0.21$, $y=0.30$.

Example 10

Electroluminescent device

An organic electroluminescent device having the structure glass substrate / ITO / Compound 6B (100nm) / TPBI (40nm) / LiF (5nm) / Ca (20nm) / Al (100nm) was prepared. When operated under a forward bias of 5V the device emitted blue light having the CIE coordinates $x=0.21$, $y=0.31$.

Example 11

Electroluminescent device

Onto a glass substrate carrying an ITO anode was deposited a layer of PEDT/PSS (polyethylene dioxythiophene / polystyrene sulfonate available from H. C. Starck of Leverkusen, Germany) by spin-coating. A phosphorescent layer comprising the host material di(t-butyl)CBP, the phosphorescent compound 6B and, optionally, polymethylmethacrylate (PMMA) was deposited over the PEDT/PSS by spin-coating a mixture of the phosphorescent layer components from toluene solution. The quantity of compound 6B in the mixture was 10 % by weight.

A cathode comprising a first layer of lithium fluoride and a second layer of aluminium was then deposited over the phosphorescent layer by vacuum evaporation. The level of PMMA in the phosphorescent layer was varied.

Example 12

Electroluminescent device

Devices according to Example 11 were also formed using a layer of silicon oxide (SiO) in place of PEDT/PSS.

Example 13**Light emission characteristics of the electroluminescent devices**

The devices of Examples 11 and 12 were tested to determine their CIE and quantum efficiency. The results are shown in Table 1 below. The ratio of di(t-butyl)CBP:PMMA:6B is a weight ratio.

Table 1

Device structure	CIE-x	CIE-y	QE Max (%)
PEDT:PSS / di ^t Bu-CBP:6B (9:1)	0.201	0.268	1.15
PEDT:PSS / di ^t Bu-CBP:PMMA:6B (9:9:2)	0.176	0.233	1.93
SiO / di ^t Bu-CBP:PMMA:6B (9:9:2)	0.176	0.284	1.26
PEDT:PSS / di ^t Bu-CBP:PMMA:6B (13:5:2)	0.186	0.245	1.62
SiO / di ^t Bu-CBP:PMMA:6B (13:5:2)	0.177	0.279	0.43
PEDT:PSS / di ^t Bu-CBP:PMMA:6B (5:13:2)	0.175	0.243	2.28
SiO / CBP2:PMMA:PBI (5:13:2)	0.171	0.284	0.19

Example 14**Vacuum evaporation of the electroluminescent layer**

The process of Example 11 was followed except that the devices comprise the following structure:

Glass / ITO / SiO / NPD (optional) / combined host-emitter 6B / TPBI / LiF / Al

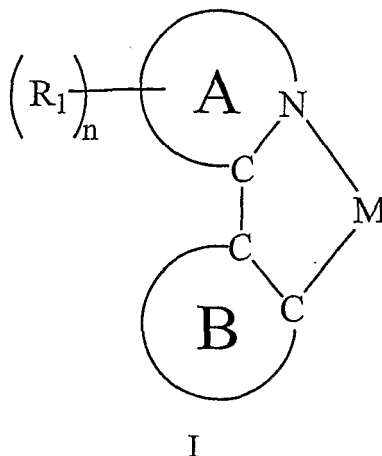
Both the hole transporting NPD layer, when present, and the combined host-emitter layer were formed by vacuum evaporation. The host materials used were CBP and MTDATA.

The best results (i.e. where emission from the host material was minimised) were obtained using mTDATA with the NPD layer present. A device having a hole transport layer of NPD and an electroluminescent layer of mTDATA : Compound 6B (9:1 ratio) gave a maximum quantum efficiency of 0.44%, CIE-x 0.175, CIE-y 0.232.

No doubt the teaching herein makes many other embodiments of, and effective alternatives to, the present invention apparent to a person skilled in the art. The present invention is not limited to the specific embodiments described herein but encompasses modifications which would be apparent to those skilled in the art and lying with the spirit and scope of the attached claims.

Claims:

1. A cyclometallated complex comprising the structure of formula I



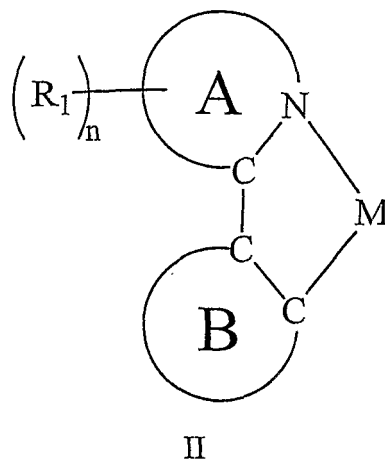
wherein:

- M is a d-block transition metal;
 - B is a five- or six-membered aryl or heteroaryl ring which is optionally substituted and optionally fused to one or more other aryl or heteroaryl rings;
 - A is a five- or six-membered heteroaryl ring comprising at least three nitrogen atoms;
 - R_1 is a group other than hydrogen;
 - n is zero or an integer equal to or greater than one; and
 - A and B are optionally fused or linked by one or more covalent bonds.
2. A cyclometallated complex according to claim 1 wherein A is a five-membered ring.
3. A cyclometallated complex according to claim 2 wherein A is selected from the group comprising triazole and tetrazole.
4. A cyclometallated complex according to claim 1 wherein A is a six-membered ring.
5. A cyclometallated complex according to claim 4 wherein A is a triazine.

6. A cyclometallated complex according to any one of the preceding claims wherein B is a five-membered ring.
7. A cyclometallated complex according to claim 6 wherein B is selected from the group comprising thiophene, furan and pyrrole.
8. A cyclometallated complex according to any one of claims 1 to 5 wherein B is a six-membered ring.
9. A cyclometallated complex according to claim 8 wherein B is selected from the group comprising benzene, pyridine, pyrazine and pyrimidine.
10. A cyclometallated complex according to any preceding claim wherein M is selected from the group comprising iridium, rhodium, palladium, platinum, gold, osmium and ruthenium.
11. A cyclometallated complex according to claim 10 wherein M is selected from the group comprising iridium and platinum.
12. A cyclometallated complex according to any preceding claim wherein said complex is homoleptic.
13. A cyclometallated complex according to any one of claims 1 to 11 wherein said complex is heteroleptic.
14. A cyclometallated complex according to claim 13 wherein said complex further comprises a ligand selected from the group comprising picolines, acetylacetonates, phosphines, pyridine and pyridine derivatives, carbonyl, nitrile, isonitriles, halides and tetrakis(1-pyrazolyl)borates, preferably said complex further comprises a ligand selected from the group comprising picolines and tetrakis(1-pyrazolyl)borates.
15. A cyclometallated complex according to claim 1 wherein R_1 is greater than or equal to one and at least one group R_1 is an electron-donating group.

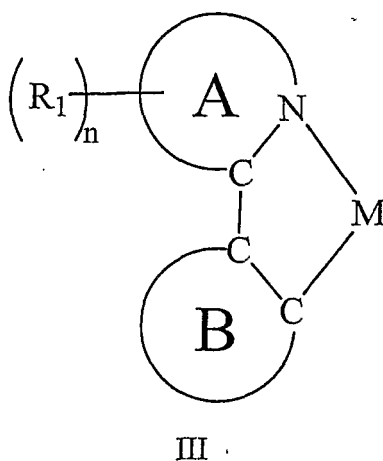
16. A cyclometallated complex according to claim 15 wherein n is greater than one.
17. A cyclometallated complex according to claim 15 or claim 16 wherein said electron-donating group is selected from the group comprising alkylamino, arylamino, alkyl, alkoxy, aryl and carbazole groups.
18. A cyclometallated complex according to any preceding claim wherein said ring B is substituted with at least one electron-withdrawing group.
19. A cyclometallated complex according to claim 18 wherein said electron-withdrawing group is selected from the group comprising halogen atoms, haloalkyl groups, sulfoxides and sulfones.
20. A cyclometallated complex according to claim 19 wherein said electron-withdrawing group is selected from fluorine or perfluorinated C₁₋₆ haloalkyl groups.
21. A cyclometallated complex according to any one of claims 1 to 3 wherein A comprises a triazole group substituted with at least one group R₁ which is an electron donating group, B comprises a phenyl group substituted with at least one fluorine or fluorinated group and said d-block transition metal is iridium.
22. A cyclometallated complex according to any preceding claim wherein ring A is substituted with at least one group R₁ which is a dendron.
23. A cyclometallated complex according to any preceding claim wherein ring B is substituted with at least one dendron.
24. A cyclometallated complex according to claim 22 or claim 23 wherein said dendron comprises a carbazole moiety or a triarylamine moiety.
23. A cyclometallated complex according to claim 20 or claim 21 wherein said dendron comprises a 1,3,5-substituted phenyl moiety.

24. A cyclometallated complex comprising the structure of formula II



wherein M is a d-block transition metal, A is a five- or six- membered heteroaryl ring which comprises at least three heteroatoms and which is optionally substituted or fused, B is a five- or six-membered aryl or heteroaryl ring which is optionally substituted or fused, n is greater than one and R₁ is a dendron or a solubilising group.

25. A cyclometallated complex according to claim 24 wherein rings A and B, substituent R₁ and subscript n are as defined in any one of claims 2 to 23.
26. A polymer comprising a cyclometallated complex according to any one of the preceding claims.
27. A polymer comprising a cyclometallated complex comprising the structure of formula III:



wherein A is a five- or six- membered heteroaryl ring which comprises at least three heteroatoms and which is optionally substituted or fused, B is a five- or six- membered aryl or heteroaryl ring which is optionally substituted or fused, n is zero or greater than one and R₁ is a substituent other than hydrogen.

28. A polymer according to claim 27 wherein rings A and B, substituent R₁ and subscript n are as defined in any one of claims 2 to 23.

29. A polymer according to any one of claims 26 to 28 wherein said cyclometallated complex is incorporated into the main chain of the polymer.

30. A polymer according to any one of claims 26 to 28 wherein said cyclometallated complex is pendant to the main chain of the polymer.

31. A polymer according to any one of claims 26 to 30 wherein said polymer further comprises a carbazole or triarylamine group.

32. An optoelectronic device comprising a cyclometallated complex according to any one of claims 1 to 25.

33. An organic light emitting device comprising a cyclometallated complex according to one of claims 1 to 25.

34. An organic light emitting device according to claim 33 comprising a blend of said cyclometallated complex and an organic host.

35. An organic light emitting device according to claim 33 wherein said cyclometallated complex comprises an organic host, preferably said organic host comprises a carbazole moiety or a triarylamine moiety.

36. An organic light emitting device according to claim 34 or claim 35 wherein said organic host comprises a carbazole moiety or a triarylamine moiety.

37. The use of a cyclometallated complex according to any one of claims 1 to 25 in an optoelectronic device.
38. An organic light-emitting device comprising an phosphorescent layer disposed between two electrodes, wherein said device has a CIE-y coordinate of less than 0.25.
39. An organic light-emitting device according to claim 38 wherein said device has a CIE-y coordinate of between 0.15 and 0.25.
40. An organic light-emitting device according to any one of claims 33 to 36, claim 38 or claim 39 wherein said phosphorescent layer comprises a cyclometallated complex as defined in any one of claims 1 to 25 or a polymer as defined in any one of claims 26 to 31.
41. An organic light-emitting device according to any one of claims 33 to 36 or claims 38 to 40 wherein the phosphorescent layer comprises an organic host material.
42. An organic light-emitting device according to claim 41 wherein the organic host material is di(t-butyl)CBP.
43. An organic light-emitting device according to claim 41 or claim 42 wherein the phosphorescent layer further comprises a diluent compound.
44. An organic light-emitting device according to claim 44 wherein the diluent compound is polymethylmethacrylate (PMMA).
45. An organic light-emitting device according to claim 43 or claim 44 wherein the diluent compound is present in an amount of from 30 to 80% by weight.
46. Use of polymethylmethacrylate in an phosphorescent layer to increase quantum efficiency of an organic light emitting device in which the phosphorescent layer is incorporated.

47. Use of polymethylmethacrylate to improve film formation of an phosphorescent layer.

1 / 1

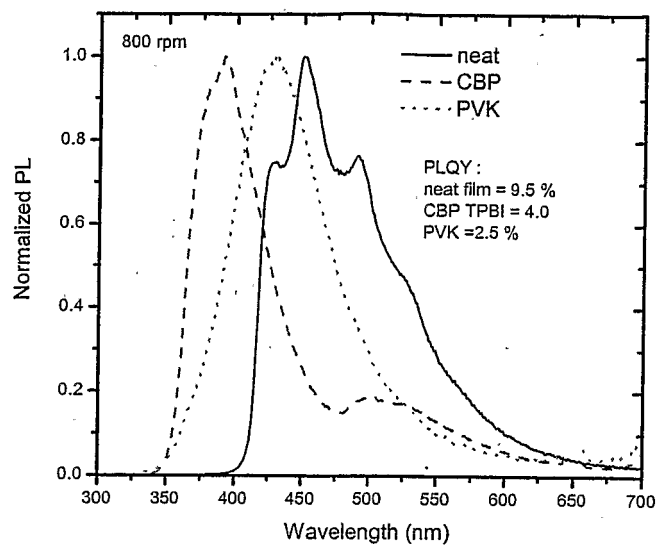


Figure 1

INTERNATIONAL SEARCH REPORT

tional Application No
.../GB2004/002127

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C09K11/06 H05B33/14 H01L51/30 C07F15/00		
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) IPC 7 C09K H05B H01L C07F		
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, WPI Data, PAJ, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/055014 A1 (ISE TOSHIHIRO ET AL) 9 May 2002 (2002-05-09) cited in the application compound K-15, compound K-31, paragraphs '0193!, '0194!, '0196!, '0199!, '0203!, '0204!, '0223!, '0238!; claims -----	1-47
X	US 2001/019782 A1 (KIMURA KEIZO ET AL) 6 September 2001 (2001-09-06) cited in the application	1-20, 26-47
Y	paragraphs '0121!, '0122!, '0124!, '0175! compound (1-34), compound (1-36), claims ----- -/--	22-26
<div style="display: flex; justify-content: space-between;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. </div>		
° Special categories of cited documents :		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*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)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>*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</p> <p>*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</p> <p>*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.</p> <p>*&* document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-size: 1.2em;">8 October 2004</div>		Date of mailing of the international search report <div style="text-align: center; font-size: 1.2em;">18/10/2004</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-size: 1.2em;">Lehnert, A</div>

INTERNATIONAL SEARCH REPORT

International Application No
.../GB2004/002127

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 02/067343 A (SAMUEL IFOR DAVID WILLIAM ; ISIS INNOVATION (GB); LO SHIN-CHUN (GB); B) 29 August 2002 (2002-08-29) cited in the application page 7, line 4 - line 9 page 8, line 15 - line 17 -----	22-26
P,X	EP 1 348 711 A (CANON KK) 1 October 2003 (2003-10-01) page 14; examples	1-20, 32, 33, 38-41
X	& WO 02/44189 A (IGAWA SATOSHI ; CANON KK (JP); FURUGORI MANABU (JP); KAMATANI JUN (JP)) 6 June 2002 (2002-06-06) the whole document -----	1-20, 32, 33, 38-41
X	WO 02/081488 A (COVION ORGANIC SEMICONDUCTORS ; BECKER HEINRICH (DE); SPREITZER HUBERT) 17 October 2002 (2002-10-17) claims 1,17,18 -----	1-20, 26-47
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X	WO 02/15645 A (UNIV PRINCETON ; UNIV SOUTHERN CALIFORNIA (US); UNIVERSAL DISPLAY CORP) 21 February 2002 (2002-02-21) the whole document -----	1-20, 26-47
X	US 2002/134984 A1 (IGARASHI TATSUYA) 26 September 2002 (2002-09-26) the whole document -----	1-20, 26-47
X	WO 02/31896 A (DU PONT) 18 April 2002 (2002-04-18) the whole document -----	1-20, 26-47
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INTERNATIONAL SEARCH REPORT

International Application No

.../GB2004/002127

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>EP 1 175 128 A (FUJI PHOTO FILM CO LTD) 23 January 2002 (2002-01-23) the whole document</p>	<p>1-20, 26-47</p>

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2004/002127

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

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

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Present claims 1-20, 22-47 relate to an extremely large number of possible compounds, products and methods. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds, products and methods claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the compounds and products prepared in the examples, which are cyclometallated complexes comprising a triazole group substituted with at least one group R1 which is an electron donating group (see claim 21) and closely related homologous compounds and methods using these compounds.

The search for claims 1-20, 22-47 has been restricted to the presence of such a triazole group substituted with at least one group R1 which is an electron donating group.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

'GB2004/002127

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专利名称(译)	有机磷光材料和有机光电器件		
公开(公告)号	EP1636322A1	公开(公告)日	2006-03-22
申请号	EP2004733358	申请日	2004-05-17
[标]申请(专利权)人(译)	ISIS创新有限公司 圣安德鲁斯大学		
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发明人	BURN, PAUL LESLIE SAMUEL, IFOR D. W., SCHOOL OF PHYSICS & ASTRONOMY LO, SHIH-CHUN		
IPC分类号	C09K11/06 H05B33/14 H01L51/30 C07F15/00 H01L51/00 H01L51/50		
CPC分类号	H05B33/14 C07F15/0033 C09K11/06 H01L51/0037 H01L51/0062 H01L51/0085 H01L51/5016 Y10S428/917		
优先权	2003011234 2003-05-16 GB		
其他公开文献	EP1636322B1		
外部链接	Espacenet		

摘要(译)

本发明提供一种包含式 (I) 结构的环金属化配合物;其中M是d-区过渡金属; B是五元或六元芳基或杂芳基环, 其任选被取代并任选与一个或多个其他芳基或杂芳基环稠合; A是包含至少三个氮原子的五元或六元杂芳基环; R1是氢以外的基团; n为零或等于或大于1的整数; A和B任选地通过一个或多个共价键稠合或连接。本发明还提供了这种配合物在光电器件中的用途, 特别是在有机发光器件中的用途。