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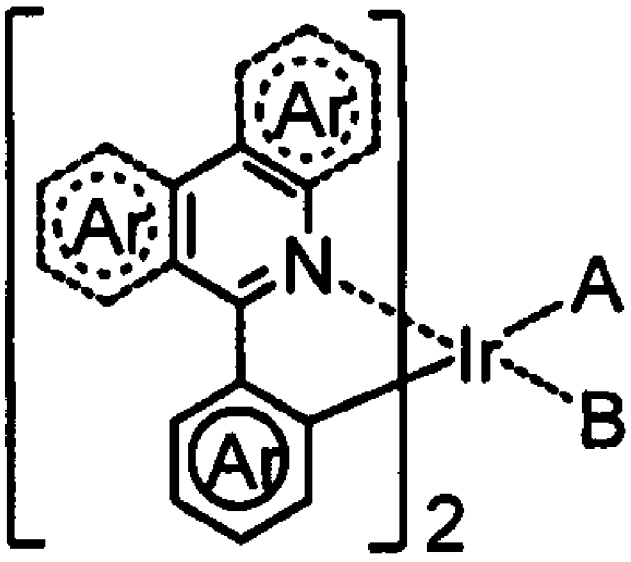
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(54) Title: IRIDIUM BASED COMPLEX FOR WATER SPLITTING



(57) Abstract: In a general form, there is provided a cyclometalated iridium complex, which in one application can be used as a catalyst for water splitting. In one form, the cyclometalated iridium complex includes bandgap lowering ligands, for example aryl quinoline. In another form, the cyclometalated iridium complex includes bandgap widening ligands, for example aryl triazole. In a particular example, one or more additional linking groups are included to improve solubility of the complex. In another particular example, one or more additional linking groups are included to improve attachment of the complex to a semiconductor or an electrode. According to a specific example, there is a cyclometalated iridium complex having the structure wherein, Ar is an aryl group, or a fused or heterocyclic arene or ring.

WO 2012/122605 A1

IRIDIUM BASED COMPLEX FOR WATER SPLITTING

Technical Field

[001] The present invention generally relates to water splitting, and also relates to water oxidation or water photolysis. More specifically, the present invention relates to a complex or a catalyst for water splitting.

Background

[002] Increasing worldwide energy demands, and concerns that such demands and fossil fuel reliance may prove unsustainable or ecologically detrimental have induced research into alternative energy sources. Solar energy is a renewable alternative to fossil fuels and many different systems for harnessing solar energy have been proposed. However, as the intensity of solar energy is variable, for example depending on the time of day or geographic location, many solar energy systems rely on forms of energy storage in order to provide suitable or steady power.

[003] Photoinduced water splitting which produces hydrogen is one such example. Hydrogen produced by light-driven water splitting can be directly used for combustion, used in fuel cells, or stored, for example in the form of liquid fuel. Photoinduced water splitting is a topical area of research as water is the most accessible source of hydrogen on Earth.

[004] In nature, photoinduced water splitting is a finely balanced process, overcoming the energetic barrier of O-H bond cleavage and O-O bond formation by a complex photo synthetic reaction cascade. The energy required to spontaneously dissect water into its elemental constituents at 298 K is 237 kJ/mole. Although the energy needed to directly cleave water using sunlight is available, the absorbance of solar energy by water at such wavelengths is insufficient. One aspect of current research in photoinduced water splitting focuses on designing catalysts to facilitate H-H and O-O bond formation. Additionally, current research strives to design catalysts that operate in the visible light spectrum to induce water splitting.

[005] In currently known work, ruthenium complexes have been proposed as molecular catalysts to oxidise water to dioxygen (see Llobet *et al.*, *Angew. Chem. Int. Ed* 2009, 48, 2842). Relatively recent work has also been performed on iridium(III) [*i.e.* Ir(III)] complexes as catalysts for water oxidation. Since the catalytic process is carried out in an oxidative, and often, either acidic or basic water environment, particularly robust and water soluble catalysts are required. Such requirements can strongly influence suitable types of organic ancillary ligands for a metallic centre, and which can often result in a decrease of catalytic activity over time due to oxidative degradation of organic ligands. A known cyclometalated Ir(III) complex is provided by Thomas *et al.*, (*Inorg. Chem.* 2005, 44, 5677). Ir(III) based materials are continuing to be explored as catalysts in photoinduced water splitting. However, there is significant scope to produce new Ir(III) complexes that provide improved catalytic activity, efficiency, stability, etc.

[006] Research into electron transitions involving Ir(III) complexes demonstrate the complexity of the charge transfer system. Two principle transitions, or a combination thereof, are observed being metal-to-ligand charge transfer (MLCT) in which an electron is promoted from a metal orbital to a vacant orbital on one of the ligands, and ligand-centred (LC) transitions in which an electron is promoted between orbitals on one of the coordinated ligands. Generally, the electron excitation is not pure MLCT but an admixture of MLCT and LC. Strong spin orbit coupling from the Ir(III) centre facilitates intersystem crossing between energetically similar states. In current research, it is sought to tune excited states in an Ir(III) complex to thus provide desirable photo-electro-chemical behaviour which can promote or induce water splitting. There is a need to provide new Ir(III) complexes that can beneficially modify energy bandgaps for use in a photoinduced water splitting system, for example that promotes generation of oxygen gas by the formation of a bond between two oxygen atoms originating from water molecules. Efficient and stable catalysts for oxygen evolution are an important challenge to be addressed for photoinduced water splitting technologies to become more efficient and commercially viable.

[007] There is a need for a new type of catalyst, such as a new iridium complex, and/or a method for producing such a complex, which addresses or at least ameliorates one or more problems inherent in the prior art. In a particular example, there is a need for more

efficient water splitting catalysts. In another particular example, there is a need for improved water soluble catalysts for water splitting. In another particular example, there is a need for catalysts that provide for or otherwise enable to improve attachment to or association with an electrode used for water splitting.

[008] The reference in this specification to any prior publication (or information derived from the prior publication), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that the prior publication (or information derived from the prior publication) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

Brief Summary of the Invention

[009] In various example embodiments there are provided novel catalysts, or families of catalysts, also referenced herein as complexes, for photoinduced water splitting, for example which promote or otherwise improve oxygen evolution, and/or hydrogen evolution.

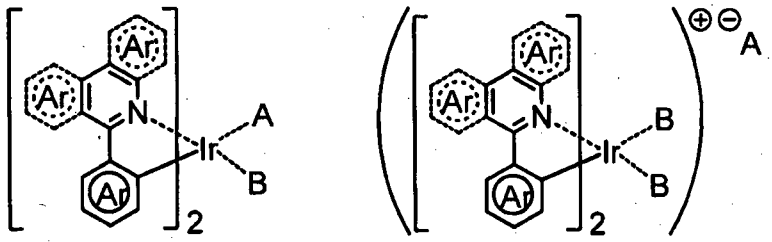
[010] In a general form, there is provided a cyclometalated iridium complex. In one form, the cyclometalated iridium complex includes bandgap widening ligands, for example, aryl triazole, aryl benzimidazole. In another form, the cyclometalated iridium complex includes bandgap lowering ligands, for example, aryl quinoline, aryl pyrazine, aryl quinoxaline.

[011] Example advantageous effects of the catalysts or complexes can include tuneable photo-absorption characteristics to enhance efficiency, and/or functional linker moiety that allows the catalysts and/or complexes to anchor to an electrode or a semiconductor. Significant improvements are observed as a result of the catalysts and/or complexes in more efficient water splitting.

[012] In a particular example, one or more additional linking groups are included to improve solubility of the complex.

[013] In another particular example, one or more additional linking groups are included to improve attachment of the complex to a semiconductor and/or an electrode, for example an electrode used in water splitting and/or photon-driven devices.

[014] In a more specific example, there is provided a cyclometalated iridium complex comprising the structure of formula I:



Ia or Ib

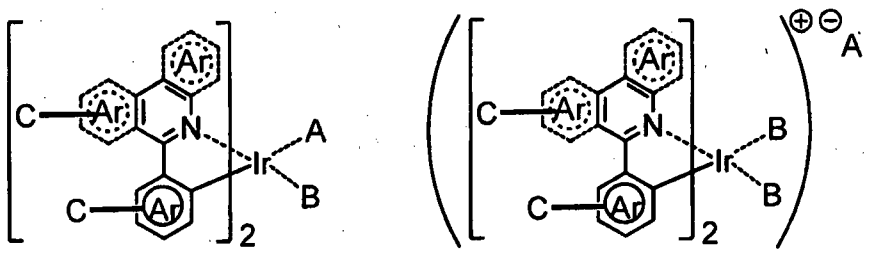
wherein, Ar is an aryl group, or a fused or heterocyclic arene or ring.

[015] In a particular example, the shown pyridine ring in formula I contains more than one nitrogen, derived such as from carbazole, pyrimidine, pyrazine, pyridazine, quinoline, quinoxaline, pyrrole, imidazole, triazine, and/or triazole.

[016] In a particular example, A and/or B are initially part of an electrolyte or a solvent. In another particular example, A and/or B are OH_2, OH, O, bipyridyl, OTf, NO_3, SO_4, PF_6, Cl, or a halo. In another example form, Ar is an aryl ring, or a fused or a heterocyclic arene.

[017] In a particular example, A and/or B are a bidetate ligand, for example diamine, bipyridyl, picolinic acid, picolinamide, quinolone carboxylic acid and/or their derivatives, with an optional counter ion selected from, for example, OH, O, OTf, NO_3, SO_4, PF_6, Cl, or a halo.

[018] In another example, the cyclometalated iridium complex further comprises the structure of formula II:



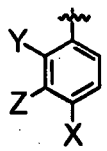
IIa or IIb

wherein, C is one or more linking groups and C is provided on any part of the ligand rings, on either part of the ligand rings, or on the two ligand rings.

[019] In another particular example, C is a water hydrophilic group or an anchor group. C can be derived from, for example, phosphonic acid, carboxylic acid, hydroxamide, amine, ether and/or alcohol.

[020] In another example form, C facilitates or improves the attachment of the complex to a semiconductor and/or an electrode.

[021] In yet another particular example, Ar has the following structure:



wherein X, Y and Z are individually selected from the group consisting of: hydrogen, a halogen, an organofluorine, a trifluoromethyl, an alkyl, a nitro, a cyanide, C_nF_{2n+1}, COOR, C(O)R, OR, an arene, and/or an heteroarene.

[022] Optionally:

X = H, Y = H, Z = H;

X = F, Y = H, Z = H;

X = F, Y = F, Z = H;

X = F, Y = H, Z = CF_3;

X = F, Y = F, Z = CF_3; or

X = H, Y = H, Z = CF_3.

[023] Also optionally, Ar can be selected from the group consisting of: phenyl, a fused arene, for example naphthene, pyrene, fluorene, dibenzofuran, dibenzothiophene,

coumarine, anthracene, indole, benzimidazole, quinazoline, phthalimide, phenanthridine, or a heteroarene, such as pyridine, quinoline, carbazole, pyrimidine, pyrazine, pyridazine, pyrrole, imidazole, triazine, and/or triazole.

[024] In another form, the ligands, attachments and/or linking groups are used to alter or tune the energy bandgap.

[025] In example forms, the cyclometalated complex can be used as a catalyst, photocatalyst, photosensitizer and/or a precursor of active catalytic species in a water splitting device. In a preferred form, there is provided a photoinduced water splitting catalyst including one or more of the cyclometalated complexes and/or one or more of the iridium complexes to act as an active catalytic species or a precursor to promote water splitting.

[026] In another form, an embodiment is directed to the use of one or more of the cyclometalated complexes in a light-driven opto-electronic device.

Brief Description of Figures

[027] Example embodiments should become apparent from the following description, which is given by way of example only, of at least one preferred but non-limiting embodiment, described in connection with the accompanying figures.

[028] Fig. 1 illustrates comparative sacrificial agent, ceric ammonium nitrate (CAN), consumption measurement results from water splitting using novel complexes according to the present invention against a known complex A1 at different concentrations;

[029] Fig. 2 illustrates further comparative CAN consumption measurement results from water splitting using novel complexes according to the present invention;

[030] Fig. 3 illustrates further comparative CAN consumption measurement results from water splitting using novel complexes according to the present invention;

[031] Fig. 4 illustrates comparative oxygen measurement results from water splitting using novel complexes according to the present invention against a known complex A1, where oxygen formation was confirmed by GC;

[032] Fig. 5 illustrates further comparative oxygen measurement results from water splitting using novel complexes according to the present invention;

[033] Fig. 6 illustrates comparative absorption spectra of the novel complexes B1-B3 and E1-E3, and known complex A1, showing the blue-shifted and red-shifted absorption from bandgap increasing and decreasing ligands, respectively (inset shows an expansion of the absorption spectra);

[034] Fig. 7 illustrates comparative absorption spectra of the novel complexes E5-E8, with intense red-shifted absorption spectra (inset shows an expansion of the absorption spectra);

[035] Fig. 8 illustrates results of the measured photocurrents from photoinduced water splitting, showing when complex B1 is present, as a light source was cycled on and off;

[036] Fig. 9 illustrates results of measured photocurrents from photoinduced water splitting, showing when the indicated novel catalysts B1-4 are present, as a light source was cycled on and off;

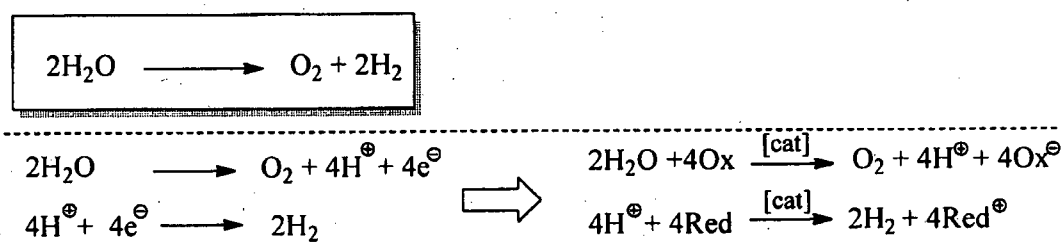
[037] Fig. 10 illustrates results of measured photocurrents from photoinduced water splitting, when complex B1 is continuously irradiated with a light source;

[038] Fig. 11 illustrates results of measured photocurrents from photoinduced water splitting, showing increased photocurrents from the indicated novel metal complex attached to a semiconductor, TiO_2 nanoparticles, as a light source was cycled on and off, compared to those of in the absence of the novel catalyst.

Preferred Embodiments

[039] The following modes, given by way of example only, are described in order to provide a more precise understanding of the subject matter of a preferred embodiment or embodiments.

[040] Water splitting can be achieved by electrolysis which consumes electric power. The free energy of the reaction is 1.23 eV with an activation energy of greater than about 1.85 eV. For photolysis, this energy range is within the visible light spectrum. However, water molecules do not absorb solar radiation effectively in this range. Additionally, the products of the reaction are thermodynamically unfavourable and several bonds are required to be broken and formed. One approach to simplify this complex bond rearrangement is to split the reaction equation into oxidation and reduction half reactions as follows in Scheme 1.



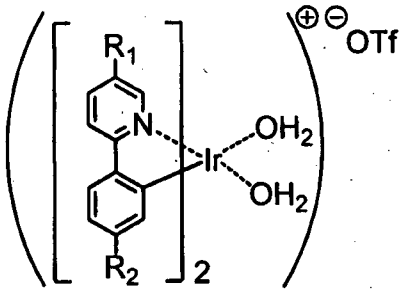
Scheme 1: water splitting process (Ox: sacrificial oxidant, Red: sacrificial reductant, cat: catalyst).

Types of photochemical cells have been proposed to split water, for example containing two catalysts, two electrodes, an electron relay and a photosensitiser. A photosensitiser initiates the redox reaction by transferring excited electrons after photon absorption. There are two major known types of water oxidation catalysts, inorganics and organometallics.

[041] Unlike inorganic water oxidation catalysts, organometallic catalysts consist of one or more organic ligands coordinating to a transition metal. An early coordination complex that was discovered to catalyse water oxidation is a ruthenium blue dimer, $[(bpy)_2(H_2O)Ru(III)ORu(III)(H_2O)(bpy)_2]^{4+}$ (Gersten, *et al., J. Am. Chem. Soc.* 1982, 104, 4029). Over the last two decades, ruthenium catalysts ranging from monomeric to dimeric and more recently tetrameric have been intensively studied (*e.g.* Zong, *et al., J. Am. Chem. Soc.* 2005, 127, 12802; Concepcion, *et al., J. Am. Chem. Soc.* 2008, 130, 16462; Sartorel,

et al., J. Am. Chem. Soc. 2008, 130, 5006; Xu, *et al., Angew. Chem. Int. Ed.* 2010, 49, 8934).

[042] The first aqua Ir(III) complex, $[Ir(ppy)_2(H_2O)_2]^+$, shown below as complex A1, where ppy is phenylpyridine, was synthesised and characterised in 1994, with a structure being determined as the carbon-iridium bond *trans* to the iridium-water coordination. However, the catalytic behaviour on water oxidation using these aqua Ir(III) complexes (A1-5) was not appreciated and investigated until 2008 (McDaniel *et al., J. Am. Chem. Soc.* 2008, 130, 210).



complex A

A1: R_1=H, R_2=H
A2: R_1=CH_3, R_2=H
A3: R_1=CH_3, R_2=Ph
A4: R_1=CH_3, R_2=F
A5: R_1=CH_3, R_2=Cl

wherein, OTf is triflate or trifluoromethanesulfonate, $-OSO_2CF_3$.

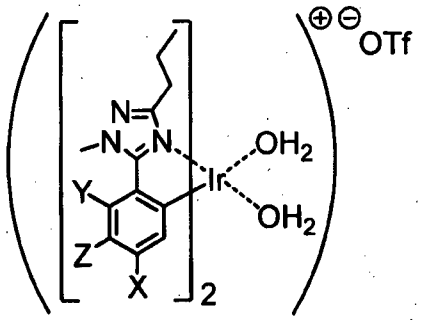
[043] The Applicant has produced one or more novel families of Ir(III) complexes with surprisingly high catalytic activity in water splitting, for example by being ligated with aryl triazole, or aryl quinoline, or aryl pyrazine, aryl quinoxaline, or benzo[*h*]quinoline ligands.

[044] It is believed the aryl triazole and aryl quinoline ligands, as examples, lead to larger (*i.e.* wider) and smaller (*i.e.* narrower) bandgaps, respectively. Furthermore, the Applicant has been able to advantageously influence catalytic activity by tuning of oxidation potentials of the Ir(III) complexes by attaching electron withdrawing groups on one or both of the ligands, such as a ligand phenyl ring, for effective water oxidation. It is believed the addition of one or more electron withdrawing groups, such as for example a fluorine or a trifluoromethyl group to the ligand phenyl ring increases the oxidation potentials of the aqua Ir(III) complexes. Moreover, the Applicant has been able to advantageously influence catalytic activity by tuning of electron density of the Ir(III) complexes by attaching electron donating groups on one or both of the ligands, such as a ligand phenyl ring, for effective water oxidation. It is believed the addition of one or more electron donating

groups, such as for example an alkyl or aryl amino group to the ligand rings, increases the electron density of the aqua Ir(III) complexes for fast oxygen release.

Aryl triazole iridium(III) complexes

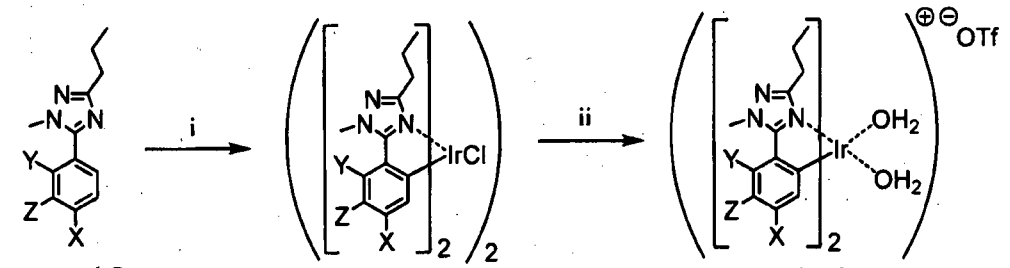
[045] The Applicant has discovered unexpected effects of widened bandgap aqua Ir(III) complexes on improving water oxidation, and synthesised a family of aqua Ir(III) complexes based on aryl triazole ligands, an example of which is shown below as complex B.



complex B

B1: X=H, Y=H, Z=H
B2: X=F, Y=H, Z=H
B3: X=F, Y=F, Z=H
B4: X=F, Y=H, Z=CF_3

[046] Referring to Scheme 2, compound C was formed in two steps (Lo *et al.*, *Chem. Mater.* 2006, 18, 5119) from respective benzoyl chloride by first treating with ethyl butyrimidate hydrochloride in presence of triethylamine to give the corresponding *N*-benzoylbutanimidic acid ethyl ester, which was then reacted with methylhydrazine immediately to give the desired aryl triazole compound C.



compound C

C1: X=H, Y=H, Z=H
C2: X=F, Y=H, Z=H
C3: X=F, Y=F, Z=H
C4: X=F, Y=H, Z=CF_3

complex D

D1: X=H, Y=H, Z=H
D2: X=F, Y=H, Z=H
D3: X=F, Y=F, Z=H
D4: X=F, Y=H, Z=CF_3

complex B

B1: X=H, Y=H, Z=H
B2: X=F, Y=H, Z=H
B3: X=F, Y=F, Z=H
B4: X=F, Y=H, Z=CF_3

Scheme 2: Synthesis of aryl triazole ligands and analogues. Example reagents and conditions: (i): Ir(III) chloride trihydrate, 2-ethoxyethanol, water, heat, $Ar_{(g)}$. (ii): silver trifluoromethanesulfonate, CH_2Cl_2, methanol, water, heat.

[047] The chloro-bridged iridium dimer D1 was prepared in about 78% yields as a yellow solid by cyclometallation of iridium trichloride with compound C in 2-ethoxyethanol and water (Lo *et al.*, *Chem. Mater.* 2006, 18, 5119).

[048] Different methods have been reported for the preparation of the known Ir(III) complex A from a corresponding chloro-bridged iridium dimer in the presence of silver triflate, for example carried out in dichloromethane (DCM) and methanol at room temperature for 1 hour, or heating in ethanol and water at reflux for 16 hours.

[049] Both methods were used to prepare complex B1, however, the conversion was unsatisfactory mainly due to the low solubility of compound D1 in methanol or ethanol (and also the presence of water). The incompletion of the reaction made the isolation of complex B1 problematic due to its poor solubility in most organic solvents and contamination together with compound D1.

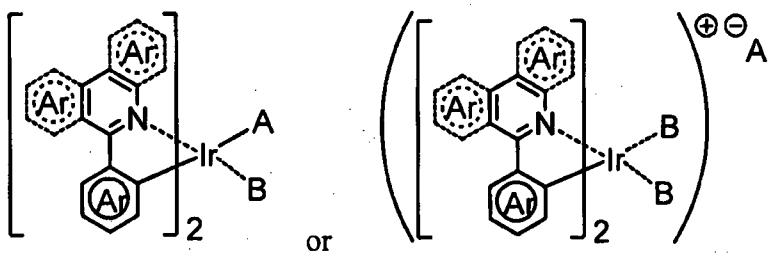
[050] To overcome this, the known method was modified by using excess silver triflate (1.5 equivalents). After removal of the excess of silver triflate by water extraction, complex B1 was obtained in about a 64% yield. Complexes B2–4 were similarly prepared under the same conditions from the corresponding chloro-bridged iridium dimers, D2 – D4.

[051] Mass spectrometry of the synthesised aqua Ir(III) complexes showed major fragmentation peaks at 591.3, 629.1 and 665.1 for B1, B2 and B3, respectively by losing two water ligands and a counter ion, OTf.

Aryl quinoline iridium(III) complexes

The Applicant has also discovered that aqua Ir(III) complexes based on decreased bandgap ligands can provide unexpected improvements in water oxidation, and synthesised another family of aqua Ir(III) complexes based on aryl quinoline ligands.

[052] In an example form there is provided a cyclometalated iridium complex comprising the structure of:



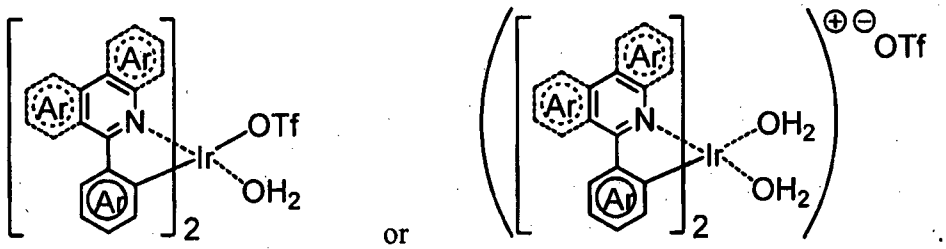
wherein, 'Ar' is an aryl group, such as any functional group or substituent derived from a simple aromatic ring, for example phenyl, a fused ring, for example naphthene, pyrene, fluorene, dibenzofuran, dibenzothiophene, coumarine, anthracene, indole, benzimidazole, quinazoline, phthalimide, phenanthridine, or heteroarene, such as pyridine, quinoline, carbazole, pyrimidine, pyrazine, pyridazine, pyrrole, imidazole, triazine, and/or triazole;

and wherein, A and/or B are OH_2, OTf, OH, O, PF_6, NO_3, and/or a halo such as F, Cl, Br, I, and/or a bidetate ligand, for example diamine, bipyridyl, picolinic acid, picolinamide, quinolone carboxylic acid and/or their derivatives, with an optional counter ion selected from, for example, OH, O, OTf, NO_3, SO_4, PF_6, Cl, and/or a halo.

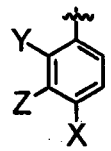
[053] As used herein, an aryl group, typically a C_{6-20} aryl group, refers to any functional group or substituent derived from a simple aromatic ring. An aryl group may be unsubstituted or substituted at any position. Typically, it carries 0, 1, 2 or 3 substituents. References to an aryl group include 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.

[054] For the avoidance of doubt, while cyclometalated complexes are shown as bearing ligands, 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.

[055] In a more specific example form there is provided a cyclometalated iridium complex comprising the structure of:



[056] In another example form Ar is a heterocyclic aromatic ring, for example including nitrogen. In another example form Ar has the following structure:



wherein, X, Y and Z can be individually selected from the non-exclusive group of hydrogen, a halogen (such as fluorine providing a strong electron withdrawing attachment), a halo, a trifluoromethyl, an alkyl, a nitro, a cyanide, C_nF_{2n+1}, COOR, C(O)R, OR, an arene, and/or an heteroarene.

[057] In another specific example, Ar has a structure using:

X = H, Y = H, Z = H;

X = F, Y = H, Z = H;

X = F, Y = F, Z = H;

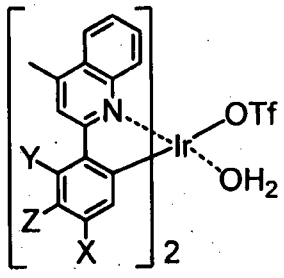
X = F, Y = H, Z = CF_3;

X = F, Y = F, Z = CF_3; or

X = H, Y = H, Z = CF_3.

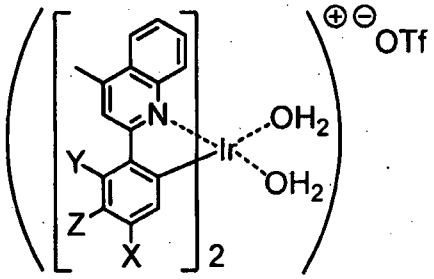
[058] In still another example the cyclometalated iridium complex can include one or more hydrophilic group in any part of the ligand ring. The hydrophilic group can be derived from, for example, phosphonic acid, carboxylic acid, hydroxamide, amine, ether and/or alcohol linking group to improve solubility. Additionally or alternatively, the cyclometalated iridium complex can include one or more linking group C to improve attachment to or association with a semiconductor material or an electrode.

[059] Further example aqua Ir(III) complexes based on aryl quinoline ligands are shown below as complex E. It should be noted that various anions could be used, for example OTf^-, Cl^-, PF_6^-, and/or NO_3^-. In another form, the anion can act as a counter ion.



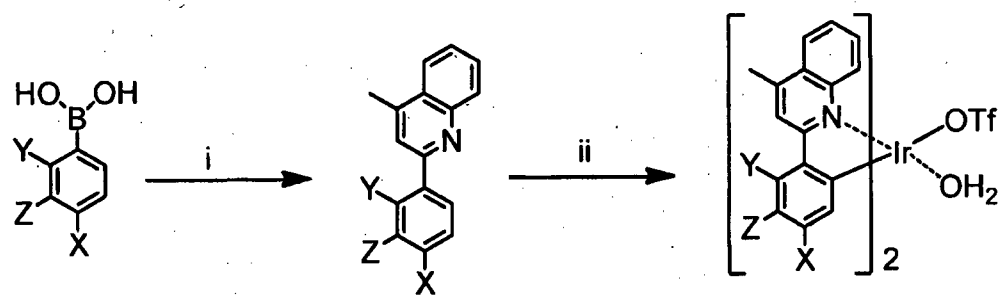
complex E

E(E)1: X= H, Y=H, Z=H
E(E)2: X=F, Y=H, Z=H
E(E)3: X=F, Y=F, Z=H
E(E)4: X=F, Y=H, Z=CF_3



complex EE

[060] Referring to Scheme 3, the synthesis of aryl quinoline ligands, e.g. compound G, was carried out under Suzuki–Miyaura cross-coupling reaction conditions using 2-chloro-4-methylquinoline with corresponding arylboronic acids. The synthesis of complex E involves cyclometallation with iridium trichloride hydrate with corresponding ligand, and followed by ligation with water ligand and anionic exchange.



compound F

F1: X= H, Y=H, Z=H
F2: X=F, Y=H, Z=H
F3: X=F, Y=F, Z=H
F4: X=F, Y=H, Z=CF_3

compound G

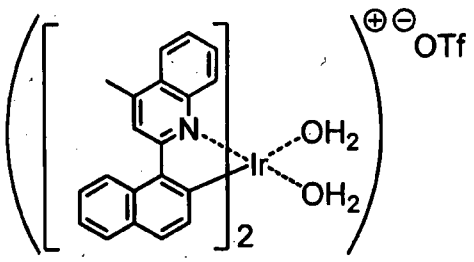
G1: X= H, Y=H, Z=H
G2: X=F, Y=H, Z=H
G3: X=F, Y=F, Z=H
G4: X=F, Y=H, Z=CF_3

complex E

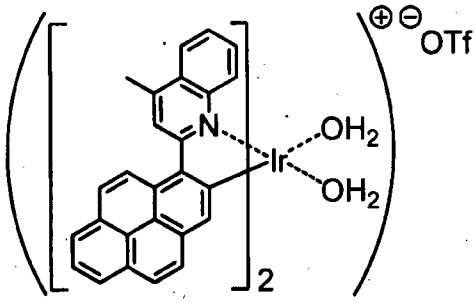
E1: X= H, Y=H, Z=H
E2: X=F, Y=H, Z=H
E3: X=F, Y=F, Z=H
E4: X=F, Y=H, Z=CF_3

Scheme 3: Synthesis of aryl quinoline ligands and analogues. Reagents and conditions: (i): 4-chloro-4-methylquinoline, tetrakis(triphenylphoshine)palladium(0), sodium carbonate, toluene, ethanol, water; heat. $Ar_{(g)}$. (ii): Ir(III) chloride trihydrate, 2-ethoxyethanol, water, heat, $Ar_{(g)}$ followed by silver trifluoromethanesulfonate, CH_2Cl_2, methanol, water, heat.

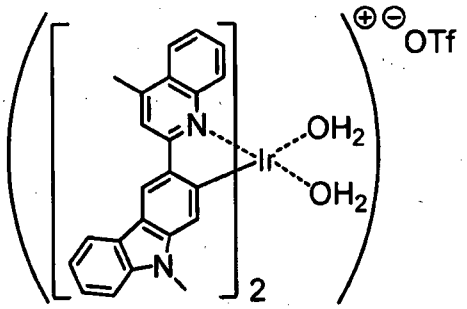
[061] Further example complexes of family E having fused arylquinoline ligands were additionally produced as presented below.



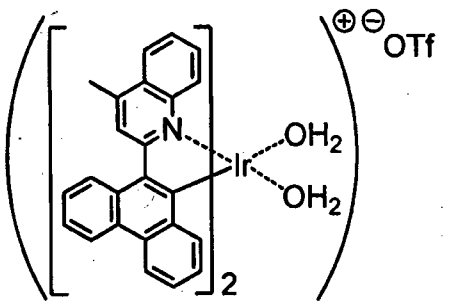
complex E5



complex E6



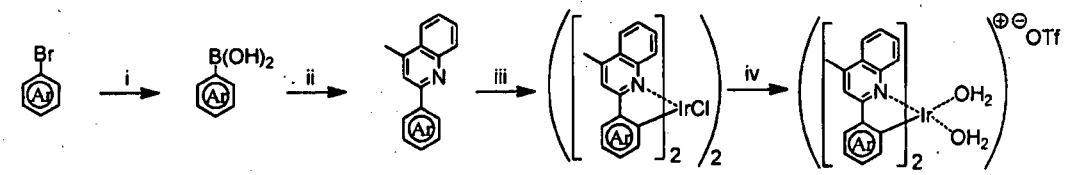
complex E7



complex E8

[062] Referring to Scheme 4, the synthesis of the aryl quinoline ligands, e.g. compound J, was carried out under Suzuki–Miyaura cross-coupling reaction conditions using 2-chloro-4-methylquinoline with corresponding arylboronic acids, which can be available

commercially or prepared from the corresponding bromoarenes. The synthesis of complexes E5-8 involves cyclometallation with iridium trichloride hydrate with the corresponding ligand, and followed by ligation with water ligand in presence of silver triflate.



compound H	compound I	compound J	complex K	complex E
H1: Ar=naphthalene	I1: Ar=naphthalene	J1: Ar=naphthalene	K1: Ar=naphthalene	E5: Ar=naphthalene
H2: Ar=pyrene	I2: Ar=pyrene	J2: Ar=pyrene	K2: Ar=pyrene	E6: Ar=pyrene
H3: Ar=carbazole	I3: Ar=carbazole	J3: Ar=carbazole	K3: Ar=carbazole	E7: Ar=carbazole
H4: Ar=phenanthrene	I4: Ar=phenanthrene	J4: Ar=phenanthrene	K4: Ar=phenanthrene	E8: Ar=phenanthrene

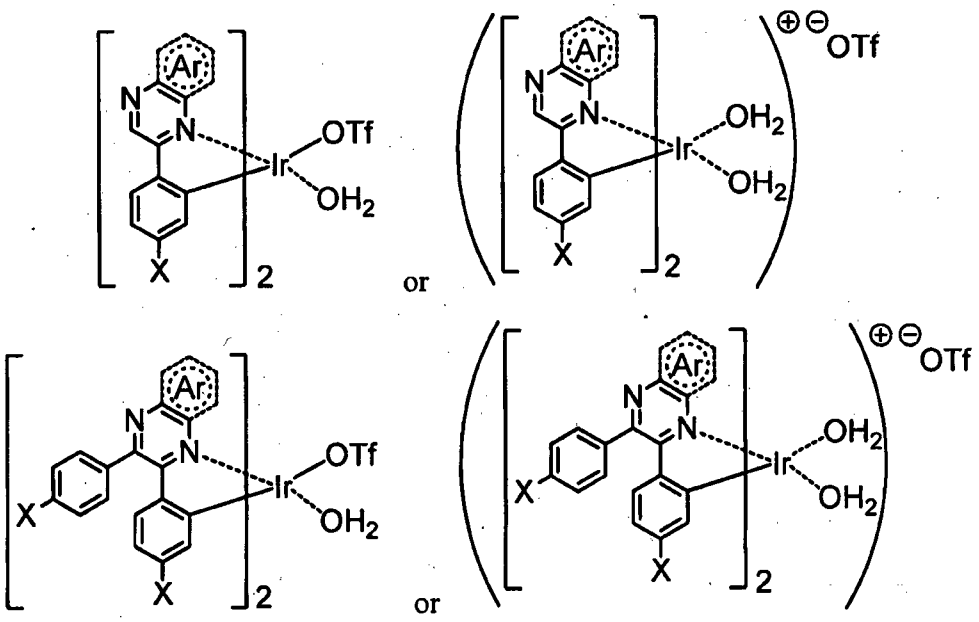
Scheme 4: Synthesis of aryl quinoline ligands and analogues. Reagents and conditions: (i):a. n-BuLi, THF, $Ar_{(g)}$,b. $B(OMe)_3$, c. $HCl_{(aq)}$.(ii): 4-chloro-4-methylquinoline, tetrakis(triphenylphoshine)palladium(0), sodium carbonate, toluene, ethanol, water, heat. $Ar_{(g)}$. (iii): Ir(III) chloride trihydrate, 2-ethoxyethanol, water, heat, $Ar_{(g)}$. (iv): silver trifluoromethanesulfonate, CH_2Cl_2, methanol, water, heat.

[063] The aqua aryl quinoline Ir(III) complexes E were prepared from the ligands via a two step approach, first a cyclometallation to give the chloro-bridged iridium dimer and then the introduction of water ligands under the same conditions as for the aryl triazole family. Notably, all the aryl quinoline Ir(III) dimers were found to have limited solubility in many organic solvents such as dichloromethane, chloroform, acetone, toluene and dimethyl sulphoxide. Hence ^{1}H NMR signals of the chloro-bridged iridium dimers were weak. Nevertheless, the presence of several broadened peaks around 6.0-7.0 ppm could be identified as the phenyl protons *ortho* to an Ir-C bond, supporting the formation of chloro-bridge iridium dimers. The next step to form a target aqua Ir(III) complex E was carried out under the same conditions as described for the formation of aqua Ir(III) complexes B using silver triflate in yields of about 50-60%. Unlike the chloro-bridged dimers and Ir(III) complexes B, the so-formed aqua Ir(III) complexes E showed a dramatic improvement in solubility, being more soluble in DCM but less soluble in acetone.

Aqua aryl quinoxaline and aryl pyrazine iridium(III) complexes

[064] The Applicant has also discovered that decreased bandgap aqua Ir(III) complexes can provide unexpected improvements in water oxidation, and synthesised another families

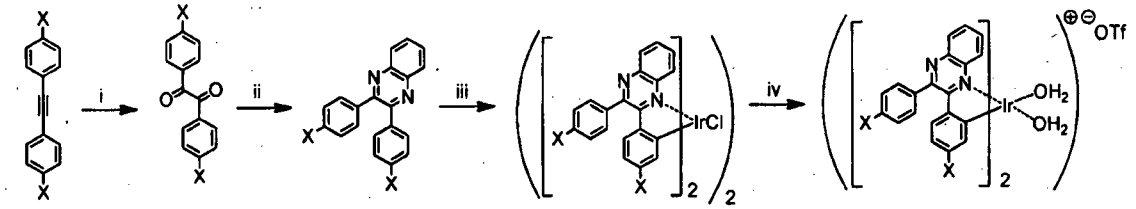
of aqua Ir(III) complexes based on aryl pyrazine, or aryl pyrazine, or aryl quinoxaline, or aryl pyridazine or aryl benzo[h]quinoline.



wherein, X can be selected from the non-exclusive group of hydrogen, a halogen (such as fluorine providing a strong electron withdrawing attachment), a halo, a trifluoromethyl, an alkyl, a nitro, a cyanide,C_nF_{2n+1}, COOR, C(O)R, OR, an arene, and/or an heteroarene.

[065] 'Ar' is an aryl group, such as any functional group or substituent derived from a simple aromatic ring, for example phenyl, a fused ring, for example naphthene, pyrene, fluorene, dibenzofuran, dibenzothiophene, coumarine, anthracene, indole, benzimidazole, quinazoline, phthalimide, phenanthridine, or heteroarene, such as pyridine, quinoline, carbazole, pyrimidine, pyrazine, pyridazine, pyrrole, imidazole, triazine, and/or triazole.

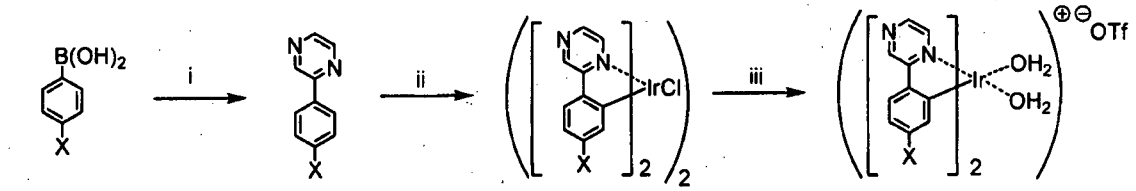
[066] Referring to Schemes 5, the synthesis of aryl quinoxaline ligands, *e.g.* compound O, was carried out under dehydration reaction using diamines with corresponding diketones (*e.g.* compound N), which could be prepared from the respective alkynes (*e.g.* compound M) after oxidation. The synthesis of complex L involves cyclometallation with iridium trichloride hydrate with corresponding ligand, and followed by ligation with water ligand and anionic exchange.



compound M	compound N	compound O	complex P	complex L
M1: X=H	N1: X=H	O1: X=H	P1: X=H	L1: X=H
M2: X=F	N2: X=F	O2: X=F	P2: X=F	L2: X=F
M3: X=CF_3	N3: X=CF_3	O3: X=CF_3	P2: X=CF_3	L3: X=CF_3

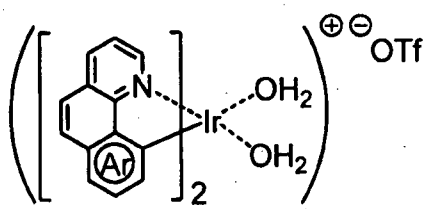
Scheme 5: Synthesis of aryl quinoline ligands and analogues. Reagents and conditions: (i):a. $KMnO_4$.(ii): 1,2-diaminobenzene. (iii): Ir(III) chloride trihydrate, 2-ethoxyethanol, water, heat, $Ar_{(g)}$. (iv): silver trifluoromethanesulfonate, CH_2Cl_2, methanol, water, heat.

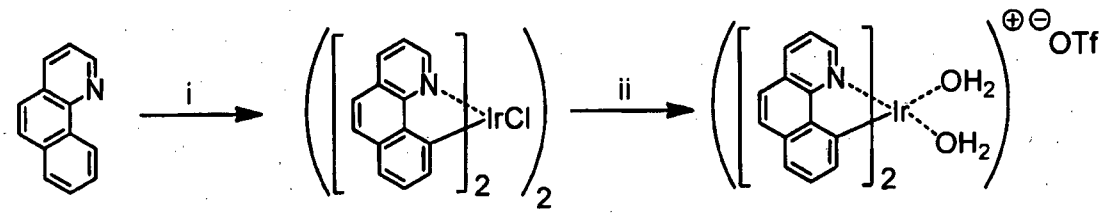
[067] Referring to Scheme 6, the synthesis of aryl pyrazine ligands, *e.g.* compound OO, was carried out under Suzuki cross coupling reaction [*i.e.* using compound NN with 2-chloropyrazine in the presence of *tetrakis(triphenylphoshine)palladium(0)*], The synthesis of complex LL involves cyclometallation with iridium trichloride hydrate with corresponding ligand, and followed by ligation with water ligand and anionic exchange.



compound NN	compound OO	complex PP	complex LL
NN1: X=H	OO1: X=H	PP1: X=H	LL1: X=H
NN2: X=F	OO2: X=F	PP2: X=F	LL2: X=F
NN3: X=CF_3	OO3: X=CF_3	PP2: X=CF_3	LL3: X=CF_3

Scheme 6: Synthesis of aryl pyrazine ligands and analogues. Reagents and conditions: (i)2-chloropyrazine, tetrakis(triphenylphoshine)palladium(0), sodium carbonate, toluene, ethanol, water, heat. $Ar_{(g)}$. (ii): Ir(III) chloride trihydrate, 2-ethoxyethanol, water, heat, $Ar_{(g)}$. (iii): silver trifluoromethanesulfonate, CH_2Cl_2, methanol, water, heat.





compound OOO complex PPP complex LLL

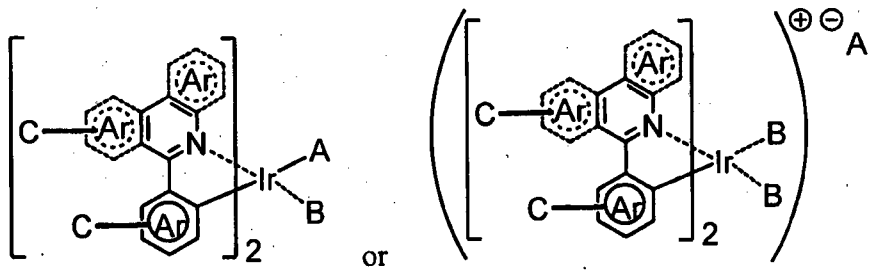
Scheme 7: Synthesis of benzo[h]quinoline ligand and analogues. Reagents and conditions: (i): Ir(III) chloride trihydrate, 2-ethoxyethanol, water, heat, $Ar_{(g)}$. (ii): silver trifluoromethanesulfonate, CH_2Cl_2, methanol, water, heat.

[068] Thus, new families of aqua cyclometalated Ir(III) complexes based on aryl triazole, aryl quinoline and aryl quinoxaline ligands have been successfully synthesised. X-ray crystallography indicates that the triflate anion can alternatively coordinate to the Ir(III) metal in the aqua iridium complexes such as E1. Compared with a known complex A1, UV-visible absorption spectra shows a blue-shift in absorption for iridium complexes B based on aryl triazole, while iridium complexes E based on aryl quinoline or quinoxaline show a red-shift in absorption. For all novel families of aqua Ir(III) complexes, fluorination on the ligand phenyl rings also blue-shifts the absorption spectra.

Aqua iridium(III) complexes with hydrophilic and/or linking groups

[069] Solubility (hydrophilicity) of a catalyst is another important factor for consideration. A phosphonic acid linking group, as used in complex Q, has been identified as having the ability to improve solubility of the catalysts of type E. Improved performance of a sample of complex Q has been presented in Figs. 2 and 5. Improved performance of samples of other complexes Q for different linking groups has been shown in Figs. 2 and 5.

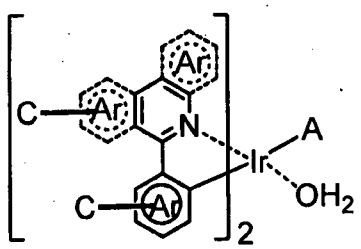
[070] In another example form there is provided a cyclometalated iridium complex comprising the structure of:



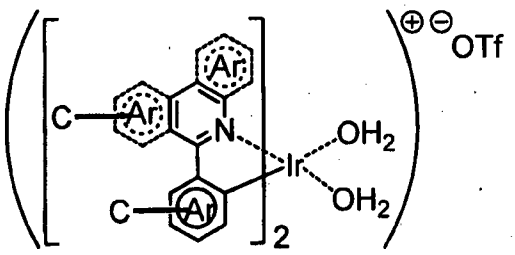
wherein, A and/or B are OH_2, OTf, OH, O, PF_6, NO_3,or a halo such as F, Cl, Br, I; C is one or more linking groups on any part of the ligand rings or on both ligand rings. C is

selected from a functional group derived from, for example, phosphonic acid, carboxylic acid, hydroxamide, amine, ether and/or alcohol. Additionally or alternatively, the ligand of the cyclometalated iridium complex can include one or more halo such as F, Cl. Additionally or alternatively, the cyclometalated iridium complex can include one or more linking group C to improve and/or facilitate attachment to or association with a semiconductor material or an electrode in a photon driven device.

[071] In a more specific example form there is provided a cyclometalated iridium complex comprising the structure of:

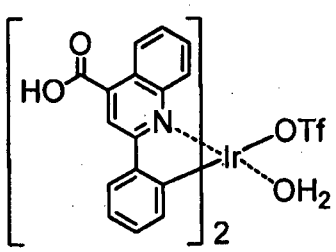


or

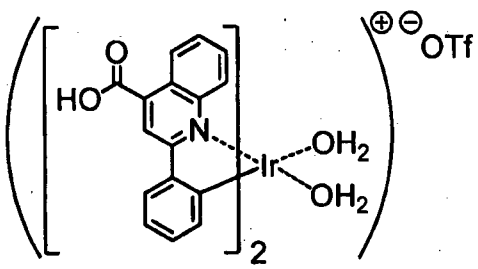


wherein A is a ligand such as OH_2, OTf, OH, O, PF_6, NO_3,or a halo such as F, Cl, Br, I. C is one or more linking groups on any part of the ligand ring. C is selected from a hydrophilic group derived from, for example, phosphonic acid, carboxylic acid, hydroxamide, amine, ether and/or alcohol. Additionally or alternatively, the ligand of the cyclometalated iridium complex can include one or more halo such as F, Cl. Additionally or alternatively, the cyclometalated iridium complex can include one or more linking group C to improve attachment to or association with a semiconductor material or an electrode in a photon driven device.

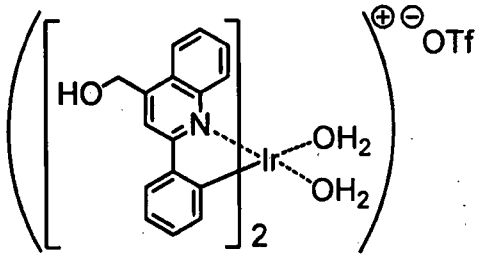
[072] The following further example complexes QI – QIX, including examples of hydrophilic linking groups, can be prepared by reference to Schemes 8–11.



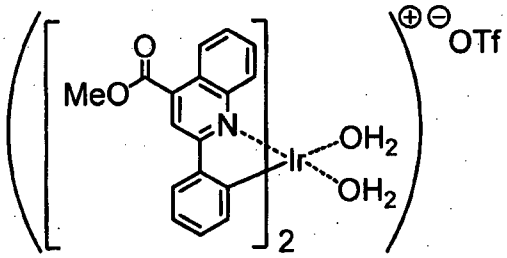
complex QIa



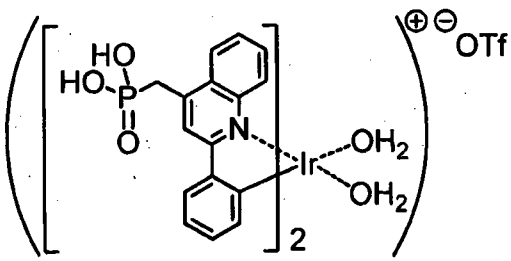
complex QIb



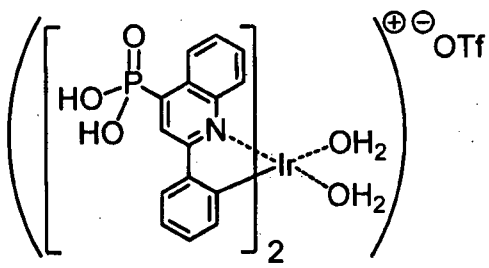
complex QII



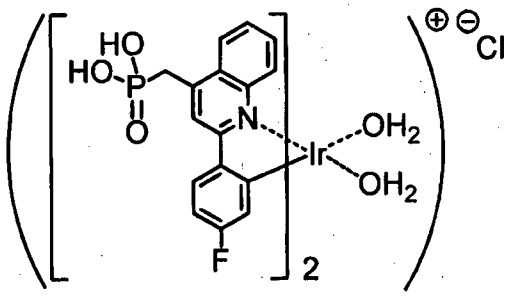
complex QIII



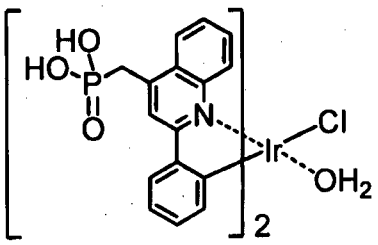
complex QIVa



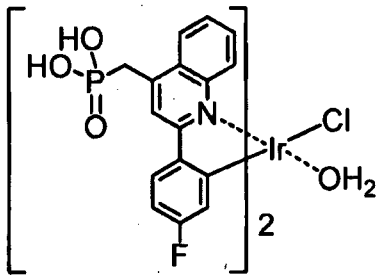
complex QIVaa



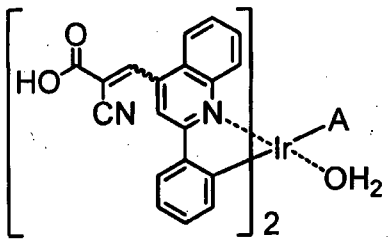
complex QIVb



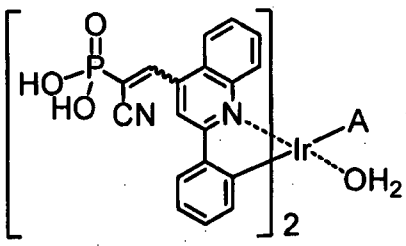
complex QVa



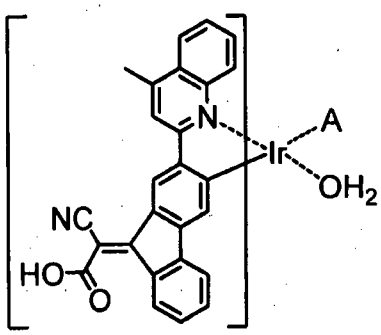
complex QVb



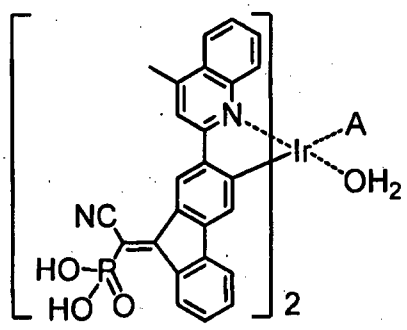
complex QVI



complex QVII

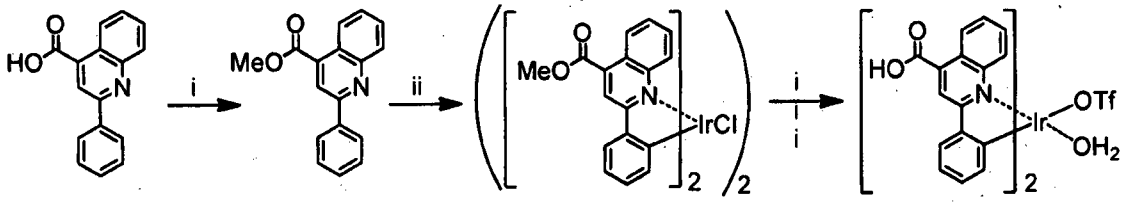


complex QVIII



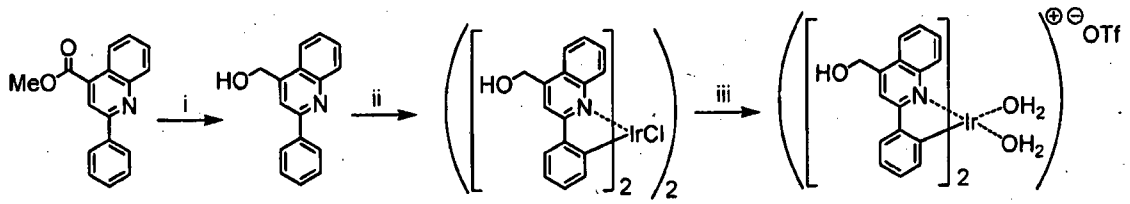
complex QIX

wherein, A can be a selection from OH_2, OTf, OH, O, PF_6, NO_3, SO_4, or a halo such as F, Cl, Br, I as a ligand or as a counter ion while ligated with a solvent such as water, MeOH, MeCN, THF, NEt_3, or an electrolyte.



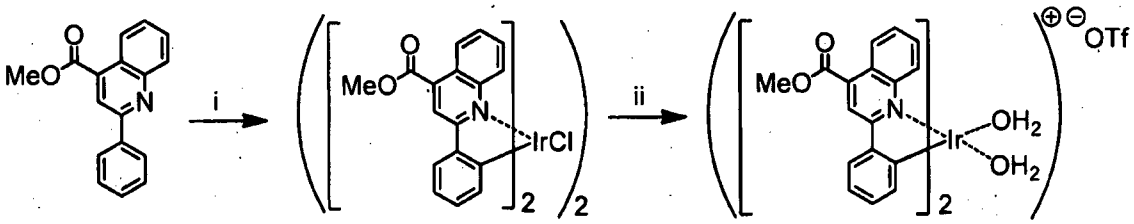
compound R compound S complex T complex QIa

Scheme 8: Synthesis of aryl quinoline ligands and analogues. Reagents and conditions: (i).: $SOCl_2$, MeOH, $Ar_{(g)}$. (ii): Ir(III) chloride trihydrate, 2-ethoxyethanol, heat, $Ar_{(g)}$. (iii):a. LiOH, MeOH, THF; b. $HOTf_{(aq)}$.



compound S compound U complex V complex QII

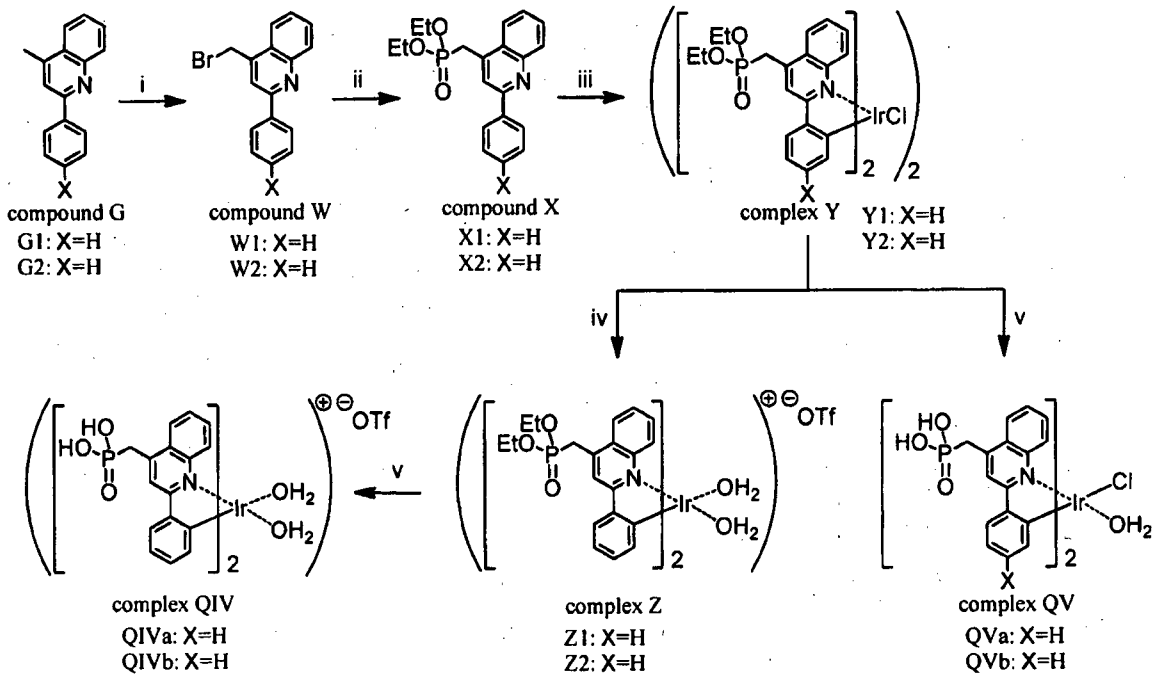
Scheme 9: Synthesis of aryl quinoline ligands and analogues. Reagents and conditions: (i):$NaBH_4$, EtOH, heat. (ii): Ir(III) chloride trihydrate, 2-ethoxyethanol, heat, $Ar_{(g)}$. (iii): silver trifluoromethanesulfonate, methanol, water, heat.



compound S complex T complex QIII

Scheme 10: Synthesis of aryl quinoline ligands and analogues. Reagents and

conditions: (i): Ir(III) chloride trihydrate, 2-ethoxyethanol, heat, $Ar_{(g)}$. (ii): silver trifluoromethanesulfonate, CH_2Cl_2, methanol, water, heat.



Scheme 11: Synthesis of aryl quinoline ligands and analogues. Reagents and conditions: (i): NBS, 1,1-azobis(cyclohexanecarbonitrile), CH_2Cl_2, water, light, heat. (ii): $P(OEt)_3$, heat. (iii): Ir(III) chloride trihydrate, 2-ethoxyethanol, water, heat, $Ar_{(g)}$. (iv): silvertrifluoromethanesulfonate, CH_2Cl_2, methanol, water, heat. (v): $HCl_{(aq)}$, heat.

[073] Electrochemistry of complexes B and E shows reversible oxidation with the oxidation potential higher than water. By fluorination of the ligand phenyl ring, systematic increases in oxidation potential were observed. While the cyclometalated Ir(III) complexes may have either two aqua ligands with triflate counter ion in salt form or single aqua ligand with triflate ion coordinating to iridium directly, the coordination of the triflate ion to Ir(III) seems not to hinder catalytic activity for water oxidation. Water oxidation tests show best results for the aryl quinoline Ir(III) complexes providing a relatively fast oxygen formation rate.

Water Oxidation Performance of Example Complexes

[074] Importantly, water splitting with significant oxygen generation and photocurrents using the new metal complexes developed by the Applicant has been achievable.

[075] Referring to Figs. 1 and 2, there are shown comparative CAN consumption measurement results from water splitting catalysed by the novel complexes B1-3, E1-3, E5, E7 and L against the known complex A1 under the same conditions: In the CAN consumption tests, 4 mL of aqueous CAN solution (2.0 mM) containing 0.1 M HNO_3 was mixed with 20 μL of the catalyst solution in acetonitrile (from 0.25 mM to 4 mM) in a cuvette. CAN consumption was studied by monitoring the absorbance change of Ce(IV) at 340 nm. The concentration of CAN employed was 2 mM whereas the concentrations of the Ir(III) complex catalysts ranged from 1.32 to 21.04 μM. It can be seen that the example complexes exhibited substantial improvements in performance over a known complex A1.

[076] Referring to Fig. 3 there are shown further CAN consumption measurement results from water splitting using other novel complexes bearing with a hydrophilic group as indicated in the figures. Substantial improvements in water oxidation can be observed.

[077] Referring to Fig. 4 there are shown comparative oxygen generation measurement results from water splitting catalysed by the novel complexes E1-3, E5, and E7 against the known complex A1 under the same conditions. In a transparent reactor at 28 °C was water (2 mL), CAN (2 g, 3.6 mmol), and the iridium complex catalyst (0.1 μmol, *ca.* 0.05-0.1 mg, depending on the molecular weight) being tested. Results are presented for a 'dark' scenario (reactor wrapped in Al foil) and a 'light' scenario (reactor exposed to visible light from two LED lamps, each 6 W). It can be seen that the example complexes exhibited substantial improvements in performance over a known complex A1.

[078] Referring to Fig. 5 there are shown further oxygen generation measurement results from water splitting using other novel complexes (Q) bearing with a functional group as indicated in the figures. Substantial improvements in water oxidation can be observed.

[079] Referring to Fig. 6 there are shown comparative absorption spectra of novel complex E1 and a known complex A1. Compared are UV-vis absorption spectra of complexes A1, B1-3 (for blue shifted absorption), and E1-3 (for red-shifted absorption) in methanol, with the inset showing an expansion of the absorption spectra.

[080] Referring to Fig. 7 there are shown comparative absorption spectra of the novel complexes E5-8. Compared are UV-vis absorption spectra of complexes E5-8 in methanol, with the inset showing an expansion of the absorption spectra.

[081] Referring to Fig. 8 there are illustrated controlled potential electrolysis at different potentials vs Ag/AgCl with alternate 25 seconds of illumination (275-750 nm) for complex B1 – with Nafion glassy carbon electrode (diameter 3 mm) in contact with 0.1M Na_2SO_4.

[082] Referring to Fig. 9 there are shown comparative net photocurrents for complexes B1-4 in 0.1 M Na_2SO_4 at different potentials vs Ag/AgCl.

[083] Referring to Fig. 10 there is illustrated controlled potential electrolysis at 1,100 mV vs Ag/AgCl with continuous illumination (275-750 nm) for 32,000 seconds for complex B1 – with Nafion glassy carbon electrode (diameter 3 mm) in contact with 0.1M Na_2SO_4.

[084] Referring to Fig. 11 there are illustrated resulting measured currents from photoinduced water splitting, showing both scenarios for no catalyst and when the indicated novel catalyst is present, as a light source was cycled on and off. As can be seen, there is very little measured current when the catalysts are not present and that the presence of the catalysts substantially improve the measured current resulting from incident light in a water splitting device.

[085] In another example embodiment, a separate photosensitiser and catalyst can be combined as a single 'photocatalyst' material provided by forms of the complexes of type E or Q. Example photocurrent results using a photocatalyst are presented in Table 1. An LED light source is incident on a transparent reactor having a working electrode and a platinum electrode, with the photocurrent measured between the electrodes.

[086] It is believed that a linker group provided with one of the complexes of type E or Q (or alternatively B) mediate direct attachment of an iridium complex to a semiconductor such as titanium dioxide, or a photoanode for photo-driven charge injection to a dye and/or a TiO_2 semiconductor.

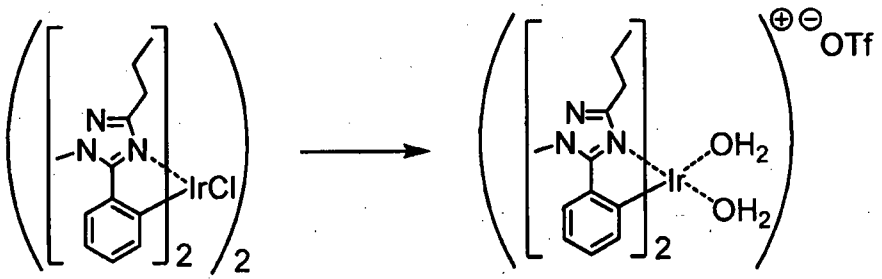
Light Source	*Sample*	*Working Electrode*	*Photocurrent (μA)*
LED	L1	TiO_2	0.6
	L2	TiO_2/complex QIa	11
	L3	TiO_2/complex QIVa	12

Table 1. Sample results for sensitised water splitting using a photocatalyst. Different samples L1 – L3 are trialled, with L1 being a background test. A 6 W LED light source is incident on a transparent reactor having a working electrode and a platinum electrode in 0.1M Na_2SO_4 or 0.1M NaOAc/HOAc.

Examples - Preparation of Ligands and Complexes

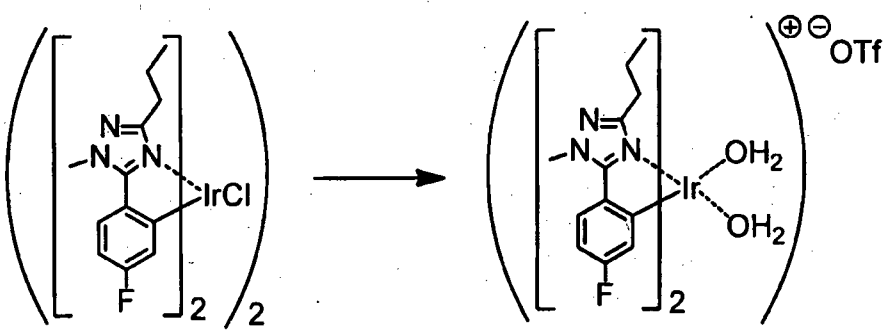
[087] The following further examples discuss various methods of preparing example ligands or complexes. These examples are intended to be merely illustrative and not limiting to the scope of the present invention.

Example 1: Preparation of iridium complex B1



[088] Complex D1 (Lo, *et al.*, *Chem. Mater.* 2006, 18, 5119) (200 mg, 0.319 mmol) was dissolved in a mixture of dichloromethane (5 mL) and methanol (5 mL). Silver triflate (122 mg, 0.478 mmol) in aqueous solution (2 mL) was added and the mixture was refluxed at 50 °C for 5 h under argon. After cooling, the solid suspension was removed through filtration and all solvent was removed to give a solid film. The solid was redissolved in acetone (10 mL) and diluted with hexane (30 mL). The precipitated product was collected and purified by recystallisation through evaporation in dichloromethane (300 mL) to give B1 (158 mg, 64% yield) as a yellow solid. λ_{max}(MeOH)/nm: 262 (logε/dm^3 mol^{-1} cm^{-1} 4.45), 277 (4.60), 332 (4.22), 346 (4.18), 394 (3.64), 441 (3.58), 534 (2.86). ^{1}H NMR (300 MHz, acetone-d_6 + drops of D_2O): δ 0.96 (t, *J*=8.7, 6H), 1.80 (m, 4H, Pr-H), 2.93 (m, 4H, Pr-H), 4.38 (s, 6H, Me), 6.32 (d, *J*=4.2, 2H, Ph-H), 6.68 (t, *J*=5.1, 2H, Ph-H), 6.84 (t, *J*=5.1, 2H, Ph-H), 7.58 (d, *J*=4.8, 2H, Ph-H). *m/z* [ESI$^+$]: 593.1 (M$^+$-OTf-2H_2O).

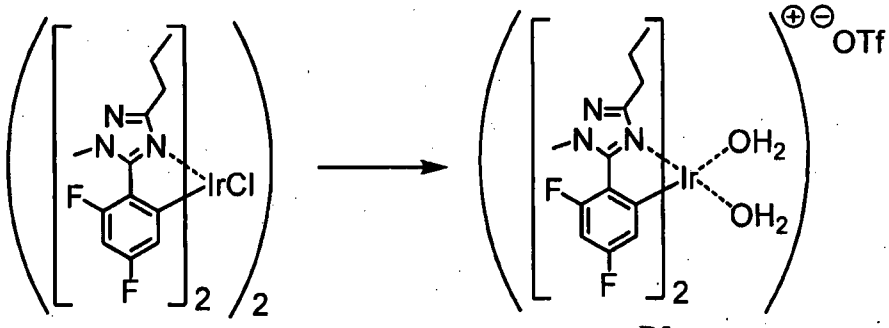
Example 2: Preparation of iridium complex B2



D2 B2

[089] Complex B2 was prepared following the same procedure as for complex B1. Yield: 48%. λ_{max}(MeOH)/nm: 251 (logε/dm^3 mol^{-1} cm^{-1} 4.39), 296 (3.77), 332 (3.45), 385 (3.39), 436 (2.03). ^{1}H NMR (300 MHz, acetone-d_6 + drops of D_2O) δ 0.95 (t, J=8.8, 6H), 1.80 (m, 4H, Pr-H), 2.94 (m, 4H, Pr-H), 4.39 (s, 6H, Me), 5.92 (d, J=6.0, 2H, Ph-H), 6.64 (m, 2H, Ph-H), 7.67 (m, 2H, Ph-H). *m/z* [ESI$^+$]: 629.1 (M$^+$-OTf-2H_2O).

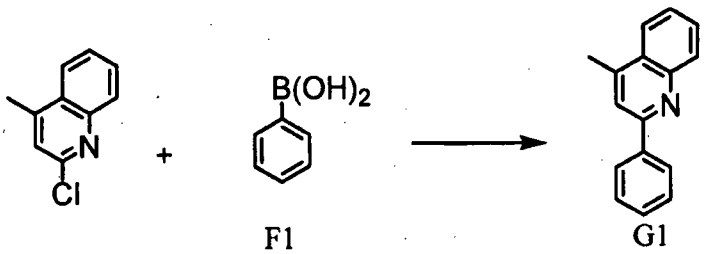
Example 3: Preparation of iridium complex B3



D3 B3

[090] Complex B3 was prepared following the same procedure as for complex B1. Yield: 58%. λ_{max}(MeOH)/nm: 250 (logε/dm^3 mol^{-1} cm^{-1} 4.45), 290 (3.86), 320 (3.59), 360 (3.46), 422 (2.08). ^{1}H NMR (300 MHz, acetone-d_6 + drops of D_2O) δ 0.98 (t, J=7.4, 6H, Pr-H), 1.80 (m, 4H, Pr-H), 2.96 (m, 4H, Pr-H), 4.35 (d, J=7.1, 6H, Me), 5.79 (d, J=9.1, 2H, Ph-H), 6.55 (d, J=5.4, 2H, Ph-H). *m/z* [ESI$^+$]: 665.1 (M$^+$-OTf-2H_2O).

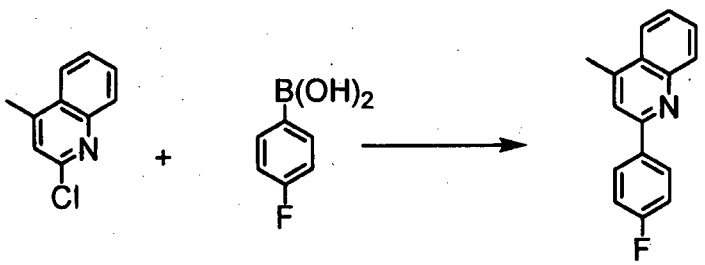
Example 4: Preparation of 4-methyl-2-phenylquinoline (compound G1)



F1 G1

[091] 2-Chloro-4-methylquinoline (600 mg, 3.39 mmol), phenyl boronic acid (620 mg, 5.08 mmol) and sodium carbonate (636 mg) were dissolved in a mixture of toluene (10 mL), ethanol (3 mL) and water (3 mL). The mixture was deoxygenated before and after the addition of tetrakis(triphenylphosphine)palladium(0) (275 mg, 0.23 mmol). The mixture was heated at reflux for 16 h under argon. When cooled, water (15 mL) was added and the two layers were separated. The aqueous layer was extracted with diethyl ether (3 x 15 mL). All the organic portions were combined, washed with brine (10 mL), dried over anhydrous sodium sulphate and filtered. The filtrate was collected and the solvent was removed *in vacuo* to give a yellow oil. The oil was purified by column chromatography over silica using ethyl acetate-hexane (1:50) as eluent to give compound G1 (628 mg, 84%) as a colourless oil, which solidified on standing. ^{1}H NMR (300 MHz, $CDCl_3$)δ 2.78 (d, *J*=0.9, 3H, Me), 7.41-7.57 (m, 4H, Ph-H), 7.73 (t, *J*=6.9, 2H, Qui-H), 7.99 (d, *J*=8.4, 1H, Qui-H), 8.13-8.19 (m, 3H, Qui-H). ^{13}C NMR (125 MHz, $CDCl_3$) δ19.06, 119.83, 123.69, 126.10, 127.63, 127.63, 128.86, 128.86, 129.27, 129.39, 130.41, 139.95, 144.85, 157.15. *m/z* [ESI$^+$]: 220.1 (M^+).

Example 5: Preparation of 2-(4-fluorophenyl)-4-methylquinoline (compound G2)

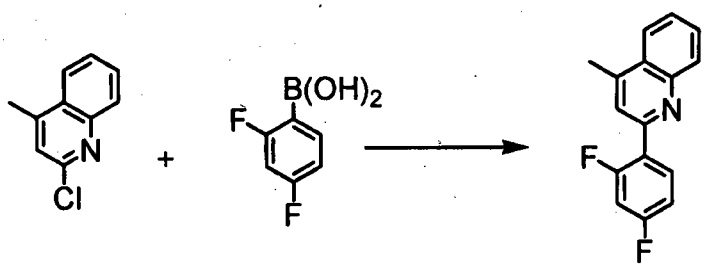


F2 G2

[092] 2-Chloro-4-methylquinoline (3.00 g, 16.9 mmol), 4-fluorophenyl boronic acid (3.55 g, 25.3 mmol) and sodium carbonate (3.18 g) were dissolved in a mixture of toluene (45 mL), ethanol (15 mL) and water (15 mL). The mixture was deoxygenated before and after the addition of tetrakis(triphenylphosphine)palladium(0) (1.37 g, 1.18 mmol). The mixture was refluxed at 110 °C for 16 h under argon. When cooled, water (45 mL) was

added and the two layers were separated. The aqueous layer was extracted with diethyl ether (3 x 40 mL). All the organic portions were combined, washed with brine (40 mL), dried over anhydrous sodium sulphate and filtered. The filtrate was collected and the solvent was removed *in vacuo* to give a yellow oil. The oil was purified by column chromatography over silica using ethyl acetate-hexane (1:50) as eluent to give G2 (2.67 g, 66%) as a colourless oil, which solidified on standing. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.76 (d, *J*=0.9, Me), 7.23-7.15 (m, 2H, Ph-H), 7.54 (t, *J*=8.3, 1H, Qui-H), 7.66 (d, *J*=0.9, 1H, Qui-H), 7.72 (t, *J*=8.4, 1H, Qui-H), 7.73 (d, *J*=8.9, 1H, Qui-H), 8.20-8.00 (m, 3H, Qui-H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.16, 115.87, 115.90, 119.52, 123.76, 126.21, 127.28, 129.45, 129.51, 129.57, 130.33, 136.07, 136.10, 145.10, 148.21, 156.08, 163.86 (d, *J*=197.8). *m/z* [ESI$^+$]: 238.1 (M^+).

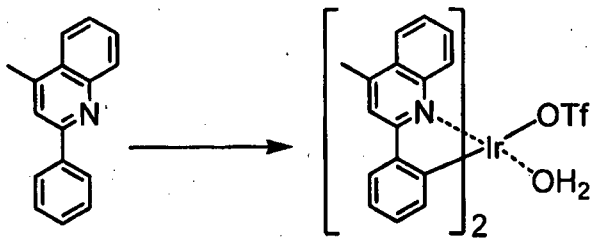
Example 6: Preparation of 2-(2,4-difluorophenyl)-4-methylquinoline (compound G3)



[093] 2-Chloro-4-methylquinoline (2.01 g, 11.3 mmol), 2,4-difluorophenyl boronic acid (2.66 g, 16.9 mmol) and sodium carbonate (2.12 mg) were dissolved in a mixture of toluene (30 mL), ethanol (10 mL) and water (10 mL). The mixture was deoxygenated before and after the addition of tetrakis(triphenylphosphine)palladium(0) (910 mg, 0.79 mmol). The mixture was refluxed at 110 °C for 16 h under argon. When cooled, water (30 mL) was added and the two layers were separated. The aqueous layer was extracted with diethyl ether (3 x 30 mL). All the organic portions were combined, washed with brine (30 mL), dried over anhydrous sodium sulphate and filtered. The filtrate was collected and the solvent was removed *in vacuo* to give a yellow oil. The oil was purified by column chromatography over silica using ethyl acetate-hexane (1:50) as eluent to give G3 (2.83 g, 98%) as a colourless oil, which solidified on standing. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.77 (d, *J*=0.9, Me), 6.94 (m, 1H, Ph-H), 7.04 (m, 1H, Ph-H), 7.58 (t, *J*=8.3, 1H, Qui-H), 7.69 (d, *J*=2.1, 1H, Qui-H), 7.73 (d, *J*=8.4, 1H, Qui-H), 8.20-8.00 (m, 3H, Qui-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.04, 104.48 (t, *J*=26.6), 112.13 (dd, *J*=20.9 & 3.6,), 122.89 (d,

J=8.0), 123.79, 124.57 (dd, J=12.4 & 3.9), 126.56, 127.39, 129.53, 130.35, 132.84 (m), 144.66, 148.24, 152.96 (d, J=1.6), 160.95 (dd, J=250.7 & 11.9), 163.64 (dd, J=249.7 & 11.9). *m/z* [ESI$^+$]: 256.1 (M^+).

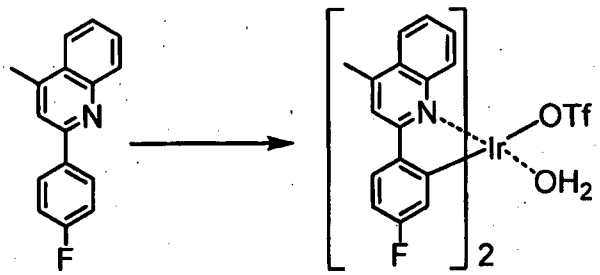
Example 7: Preparation of iridium complex E1



G1 E1

[094] A mixture of compound G1 (406 mg, 1.85 mmol), iridium trichloride hydrate (296 mg, 0.84 mmol), 2-ethoxyethanol (16 mL) and water (8 mL) was heated at 110 °C under argon for 40 h. When cooled, water (40 mL) was added to reaction mixture to give red solid precipitation. The precipitation was filtered and washed with water (3 x 30 mL) and hexane (3 x 150 mL). The dried chloro-bridged dimer was suspended in dichloromethane (30 mL) and methanol (15 mL). An aqueous solution (15 mL) of silver triflate (190 mg, 0.74 mmol) was added and the mixture was heated at 50 °C for 16 h. After cooled, water (30 mL) was added and organic and aqueous layers were separated. Aqueous layer was extracted with dichloromethane (3 x 15 mL). The dichloromethane extracts were combined with organic layer. Insoluble suspension was removed through filtration and a red solid (complex E1) was obtained (340 mg, 51%) after removal of solvents. λ_{max}(MeOH)/nm: 262 (logε/dm^3 mol^{-1} cm^{-1} 4.45), 277 (4.60), 332 (4.22), 346 (4.18), 394 (3.64), 441 (3.58), 534 (2.86). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.00 (s, 6H, Me), 6.33 (d, J=7.2, 2H), 6.59 (t, J=6.3, 2H), 6.92 (t, J=8.4, 2H), 7.62 (m, 4H), 7.73 (d, J=6.6, 2H), 7.94 (s, 2H), 8.05 (m, 2H), 8.69 (m, 2H). *m/z* [ESI$^+$]: 629.1 (M^+-OTf-H_2O).

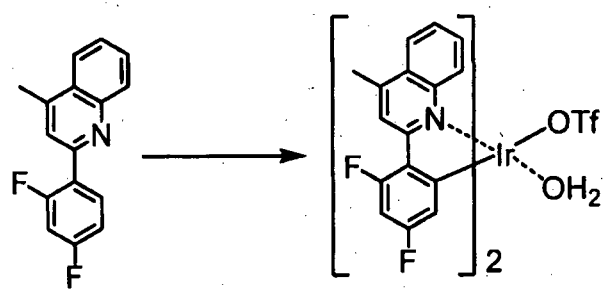
Example 8: Preparation of iridium complex E2



G2 E2

[095] Complex E2 (orange solid) was prepared following the same procedure as for complex E1. Yield: (69%). λ_{max}(MeOH)/nm: 261 (logε/dm^3 mol^{-1} cm^{-1} 4.57), 277 (4.59), 323 (4.22), 339 (4.18), 384 (3.78), 426 (2.66), 518 (2.63). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.01 (s, 6H, Me), 5.96 (d, J=6.8, 2H), 6.69 (td, J=12.6 & 2.49, 2H), 7.65 (m, 4H), 7.72 (m, 2H), 7.87 (s, 2H), 8.05 (m, 2H), 8.61 (m, 2H). *m/z* [ESI$^+$]: 665.1 (M^+-OTf -H_2O).

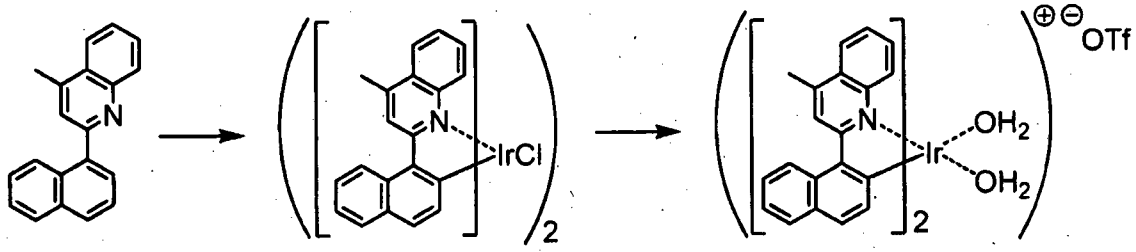
Example 9: Preparation of iridium complex E3



G3 E3

[096] Complex E3 (orange solid) was prepared following the same procedure as for complex E1. Yield: (55%). λ_{max}(MeOH)/nm: 261 (logε/dm^3 mol^{-1} cm^{-1} 4.58), 272 (4.58), 341 (4.20), 383 (3.71), 421 (3.69), 516 (2.54). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.01 (s,6H, Me), 5.76 (d, J=6.7, 2H), 6.46 (td, J=12.7 & 2.4, 2H), 7.69 (m, 4H), 8.08 (m, 2H), 8.36 (d, J=2.25, 2H), 8.61 (d, J=9.45, 2H). *m/z* [ESI$^+$]: 701.1 (M^+-OTf -H_2O).

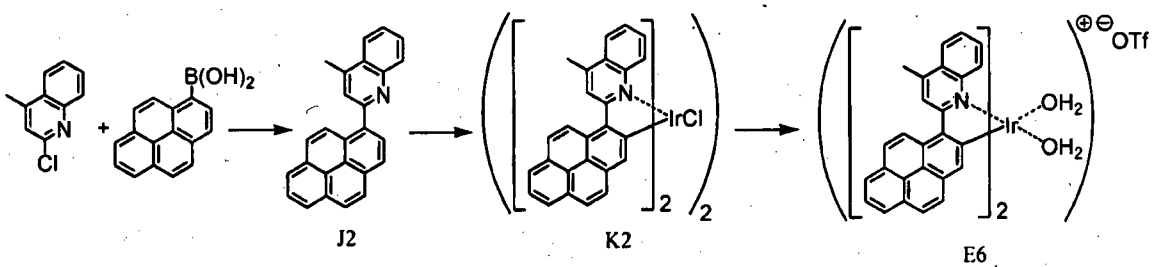
Example 10: Preparation of iridium complex E5



J1 K1 E5

[097] A mixture of compound J1 (303 mg, 1.24 mmol), iridium trichloride hydrate (164 mg, 0.47 mmol), 2-ethoxyethanol (18 mL) and water (6 mL)was heated at 120 °C under argon for 36 h. When cooled, water (40 mL) was added to the reaction mixture to give red solid precipitation. The precipitation was filtered and washed thoroughly with water (100 mL), methanol (50 mL) and diethyl ether (250 mL). After completely dried, 266 mg (74%) of solid (complex K1) was obtained. The chloro-bridged dimer K1 (153 mg, 0.10 mmol) was suspended in dichloromethane (15 mL) and methanol (15 mL). An aqueous solution (3 mL) of silver triflate (62 mg, 0.24 mmol) was added and the mixture was heated at 60 °C for 24 h. After cooled, water (30 mL) was added and dichloromethane and methanol were removed under vacuum. The crude product was then extracted by dichloromethane (2 x 30 mL) and washed by distilled H_2O (2 x 15 mL). A dark red solid (complex E5) was obtained (135 mg, 74%) after filtration of the insoluble solid and removal of the solvents. ^1H NMR (400 MHz, $CDCl_3$) δ 3.06 (s, 6H), 6.44 (d, *J*=8.6,,2H), 7.36 (t, *J*=6.9, 2H), 7.54-7.63 (m, 6H), 7.68 (d, *J*=7.4, 2H), 8.07 (dd, *J*=8.2 &1.6, 2H), 8.48 (d, *J*=8.2, 2H), 8.59 (s, 2H), 8.69 (d, *J*=8.6, 2H). ^{13}C NMR (75 MHz, Acetone-d_6/D_2O) δ 19.41,122.28, 122.65, 124.22, 125.43, 126.81, 127.12, 127.70, 127.85, 129.19, 130.15, 131.82, 132.31, 132.53, 133.78, 141.69, 149.07, 149.24, 149.37, 170.92. *m/z* [ESI$^+$]: 729.2 (M^+-OTf-2H_2O). Anal. Cal. For $C_{41}H_{32}F_3IrN_2O_5S$: C, 53.88; H, 3.53; N, 3.06. Found: C, 53.19; H, 3.24; N, 2.99.

Example 11: Preparation of compound J2 and iridium complex E6

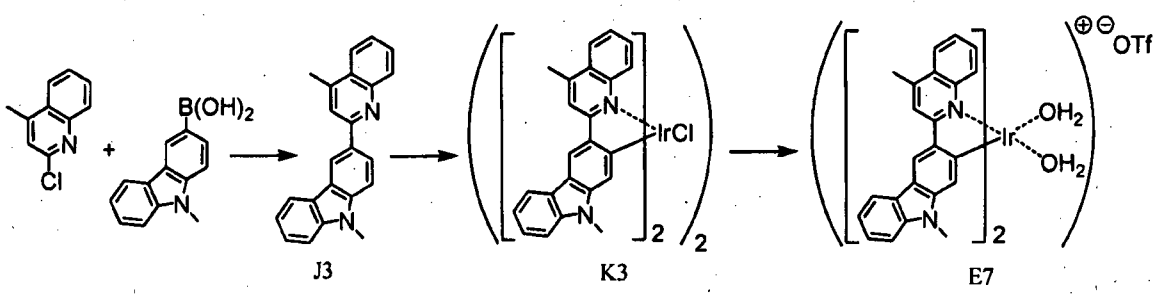


[098] 2-Chloro-4-methylquinoline (500 mg, 2.81 mmol), pyren-1-yl-1-boronic acid (1.03 g, 4.20 mmol) and sodium carbonate (2.06 g) were dissolved in a mixture of toluene (30 mL), ethanol (10 mL) and water (10 mL). The mixture was deoxygenated before and after the addition of tetrakis(triphenylphosphine)palladium(0) (233 mg, 0.20 mmol). The mixture was refluxed at 100 °C for 48 h under argon. When cooled, water (50 mL) was added and the two layers were separated. The aqueous layer was extracted with diethyl ether (3 x 30 mL). All the organic portions were combined, washed with brine (30 mL), dried over anhydrous sodium sulphate and filtered. The filtrate was collected and the

solvent was removed *in vacuo* to give a yellowish solid. The crude solid was purified by column chromatography over silica using ethyl acetate-hexane (1:20) as eluent to give compound J2 as a light yellow solid (950 mg, 99%).. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.85 (s, 3H), 7.66 (dt, *J*=6.87 & 1.26, 1H), 7.71 (s, 1H), 7.81 (dt, *J*=6.9 & 1.4, 1H), 8.00-8.14 (m, 5H), 8.21-8.32 (m, 5H), 8.45 (d, *J*=9.3, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 19.04, 123.92, 124.60, 125.00, 125.04, 125.26, 125.29, 125.31, 125.54, 126.20, 126.55, 127.16, 127.62, 127.88, 128.10, 128.26, 129.04, 129.69, 130.53, 131.11, 131.56, 131.69, 136.28, 144.56, 148.33, 159.62. *m/z* [ESI$^+$]: 344.1 (M+H$^+$). Anal. Cal. For $C_{26}H_{17}N$: C, 90.93; H, 4.99; N, 4.08. Found: C, 90.65; H, 5.05; N, 4.03.

[099] A mixture of compound J2 (384 mg, 1.12 mmol), iridium trichloride hydrate (164 mg, 0.47 mmol), 2-ethoxyethanol (18 mL) and water (6 mL) was heated at 120 °C under argon for 36 h. When cooled, water (40 mL) was added to the reaction mixture to give red solid precipitation. The precipitation was filtered and washed thoroughly with water (100 mL), methanol (100 mL) and diethyl ether (250 mL). After completely dried, a solid (200 mg, 47%) was obtained as complex K2. The chloro-bridged dimer, K2 (111 mg, 0.06 mmol) was suspended in dichloromethane (15 mL) and methanol (15 mL). An aqueous solution (3 mL) of silver triflate (38 mg, 0.15 mmol) was added and the mixture was heated at 60 °C for 24 h. After cooled, water (30 mL) was added and dichloromethane and methanol were removed under vacuum. The crude product was then extracted by dichloromethane (2 x 30 mL) and washed by distilled H_2O (2 x 15 mL). A red solid product was obtained as complex E6 (89 mg, 70%) after filtration of the insoluble solid and removal of the solvents. ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.22 (s, 6H), 6.70 (s, 2H), 7.25 (d, *J*=9.1, 2H), 7.78-7.85 (m, 6H), 7.89 (t, *J*=7.5, 2H), 8.07 (d, *J*=7.3, 2H), 8.22 (d, *J*=7.3, 2H), 8.27 (d, *J*=9.6, 2H), 8.35 (dd, *J*=8.5 & 1.55, 2H), 8.80 (s, 2H), 9.00 (d, *J*=9.5, 2H), 9.13 (d, *J*=8.5, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 19.73, 119.99, 122.03, 122.94, 123.00, 124.94, 125.60, 125.85, 126.47, 126.88, 126.93, 127.61, 127.76, 129.46, 129.51, 129.57, 130.24, 131.28, 131.39, 131.64, 136.14, 141.12, 141.60, 149.34, 149.43, 170.59. [MALDI-TOF]: 1062.6 (M$^+$), 877.4 (M$^+$-OTf-2H_2O). Anal. Cal. For $C_{53}H_{36}F_3IrN_2O_5S$: C, 59.93; H, 3.42; N, 2.64. Found: C, 58.60; H, 3.10; N, 2.59.

Example 12: Preparation of compound J3 and iridium complex E7



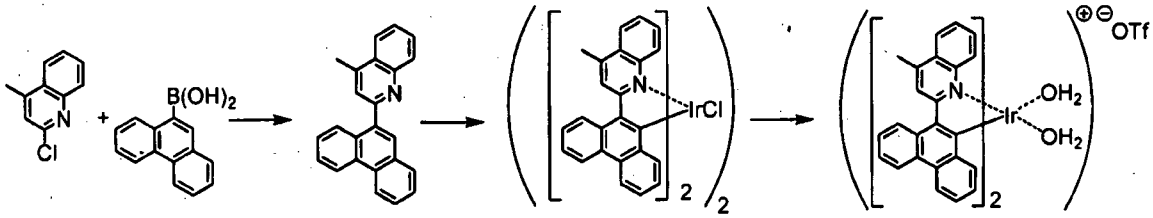
J3 K3 E7

[0100] 2-Chloro-4-methylquinoline (500 mg, 2.81 mmol), 9-methyl-9H-carbazol-3-yl-3-boronic acid (1.10 g, 4.89 mmol) and sodium carbonate (2.06 g) were dissolved in a mixture of toluene (30 mL), ethanol (10 mL) and water (10 mL). The mixture was deoxygenated before and after the addition of tetrakis(triphenylphosphine)palladium(0) (233 mg, 0.20 mmol). The mixture was heated for reflux at 100 °C for 20 h under argon. When cooled, water (50 mL) was added and the two layers were separated. The aqueous layer was extracted with diethyl ether (3 x 30 mL). All the organic portions were combined, washed with brine (30 mL), dried over anhydrous sodium sulphate and filtered. The filtrate was collected and the solvent was removed *in vacuo* to give a yellowish solid. The crude solid was purified by column chromatography over silica using ethyl acetate-hexane (1:20) as eluent to give compound J3 (858 mg, 91%) as a pure white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.81 (s, 3H), 3.91 (s, 3H), 7.28 (t, *J*=1.0, 1H), 7.43 (d, *J*=8.2, 1H), 7.51-7.55 (m, 3H), 7.73 (t, *J*=6.9, 1H), 7.89 (s, 1H), 8.01 (d, *J*=8.3, 1H), 8.23 (t, *J*=7.95, 1H), 8.36 (d, *J*=8.55, 1H), 8.93 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_19.21, 29.38, 108.76, 108.78, 119.41, 119.88, 119.97, 120.78, 123.33, 123.42, 123.77, 125.65, 125.69, 126.07, 127.14, 129.39, 130.12, 130.86, 141.69, 141.96, 144.69, 148.38, 157.90. *m/z* [ESI$^+$]: 323.2 ($M+H^+$). Anal. Cal. For $C_{23}H_{18}N_2$: C, 85.68; H, 5.63; N, 8.69. Found: C, 85.86; H, 5.42; N, 8.47.

[0101] A mixture of compound J3 (480 mg, 1.44 mmol), iridium trichloride hydrate (212 mg, 0.60 mmol), 2-ethoxyethanol (12 mL) and water (4 mL) was heated at 130 °C under argon for 16 h. When cooled, water (40 mL) was added to the reaction mixture to give red solid precipitation. The precipitation was filtered and washed thoroughly with water (100 mL), methanol (100 mL) and diethyl ether (250 mL). After completely dried, a solid (340 mg, 63%) was obtained as complex K3. The chloro-bridged dimer, K3 (270 mg, 0.15 mmol) was suspended in dichloromethane (15 mL) and methanol (15 mL). An aqueous solution (3 mL) of silver triflate (93 mg, 0.36 mmol) was added and the mixture was heated at 60 °C for 6 h. After cooled, water (30 mL) was added and the sovlent evaporated.

The crude product was then extracted with dichloromethane (2 x 30 mL) and washed with distilled H_2O (2 x 15 mL). A red solid (complex E7) was obtained (252 mg, 82%) after filtration of the insoluble solid and removal of the solvents. ^1H NMR (300 MHz, $CDCl_3$) δ 3.05 (s, 6H), 3.19 (s, 6H), 6.33 (s, 2H), 7.11-7.18 (m, 4H), 7.33 (t, *J*=7.1, 2H), 7.56 (m, 4H), 8.04-8.07 (m, 4H), 8.15 (s, 2H), 8.67 (b, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.58, 28.83, 108.59, 114.70, 117.43, 118.47, 119.24, 119.33, 119.53, 123.72, 124.53, 125.17, 126.10, 126.79, 127.46, 131.32, 135.12, 137.68, 140.81, 142.42, 147.83, 148.29, 169.16. *m/z* [ESI^+]: 835.2 (M^+-OTf-2H_2O). Anal. Cal. For $C_{47}H_{38}F_3IrN_4O_5S$: C, 55.34; H, 3.75; N, 5.49. Found: C, 56.07; H, 3.66; N, 5.52.

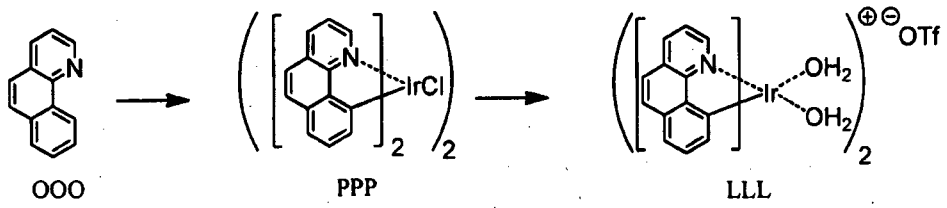
Example 13: Preparation of iridium complex E8



J4 K4 E8

[0102] A mixture of compound J4 (250 mg, 0.78 mmol), iridium trichloride hydrate (108 mg, 0.31 mmol), 2-ethoxyethanol (18 mL) and water (6 mL) was heated at 120 °C under argon for 36 h. When cooled, water (40 mL) was added to the reaction mixture to give red solid precipitation. The precipitation was filtered and washed thoroughly with water (100 mL), methanol (50 mL) and hexane (250 mL) and dried to give complex K4 (70 mg, 26%). The dried chloro-bridged dimer (44 mg, 0.025 mmol) was suspended in dichloromethane (10 mL) and methanol (10 mL). An aqueous solution (1 mL) of silver triflate (15 mg, 0.058 mmol) was added and the mixture was heated at 60 °C for 24 h. After cooled, water (30 mL) was added and dichloromethane and methanol were removed under vacuum. The crude product was then extracted with dichloromethane (2 x 30 mL) and washed by distilled H_2O (2 x 15 mL). A dark red solid was obtained after filtration of the insoluble solid and removal of the solvents as complex E8 (37.5 mg, 72%). ^1H NMR (500 MHz, DMSO-d_6) δ 2.96 (s, 6H), 6.09 (d, *J*=8.35, 2H), 6.36 (t, *J*=6.95, 2H), 7.12-7.17 (m, 4H), 7.34 (t, *J*=6.90, 2H), 7.49 (d, *J*=8.55, 2H), 7.66 (t, *J*=7.10, 2H), 7.82 (t, *J*=8.20, 2H), 8.01 (d, *J*=8.25, 2H), 8.44 (d, *J*=8.45, 2H), 8.74-8.76 (m, 4H), 8.90 (d, *J*=8.25, 2H). *m/z* [MALDI-TOF]: 1015.2 ($M+H^+$), 829.7 (M^+-OTf-2H_2O).

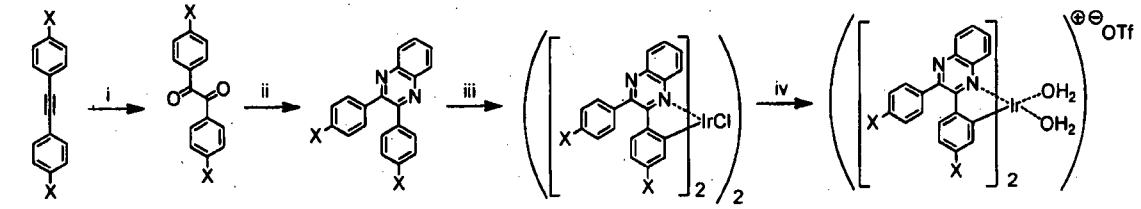
Example 14: Preparation of iridium complexes LLL



OOO PPP LLL

[0103] Benzo[*h*]quinoline (150 mg, 0.84 mmol) and iridium trichloride trihydrate (123 mg, 0.35 mmol) were dissolved in a mixture of 2-methoxyethanol (2.25 mL) and water (0.75 mL). The mixture was heated at 125 °C under argon for 16 hours. When cooled, water (40 mL) was added to the reaction mixture to precipitate a yellow solid. The precipitate was filtered and washed thoroughly with water (100 mL), methanol (50 mL), diethyl ether (100 ml) and dried to give PPP (131 mg, 64%) as a light yellow powder. mp: >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.96 (d, *J*=7.0, 1H), 6.79 (t, *J*=7.6, 1H), 7.21–7.10 (m, 2H), 7.69 (dd, *J*=21.7, 8.7, 4H), 8.26 (dd, *J*=8.0, 1.2, 1H), 9.34 (dd, *J*=5.3, 1.2, 1H). The chloro-bridged dimer PPP (100 mg, 0.085 mmol) was suspended in dichloromethane (15 mL) and methanol (15 ml). An aqueous solution (1.5 mL) of silver triflate (70 mg, 0.27 mmol) was added to the suspension and the mixture was heated at 60 °C for 18 hours. After cooling to room temperature, dichloromethane and methanol were removed under vacuum. The crude product was extracted with dichloromethane (2 x 30 ml) and washed with distilled water (2 x 15 ml) to give LLL as a dark yellow solid (89 mg, 71%). mp: 250 °C (decompose). MS (MALDI-TOF: DCTB): *m/z* 549 (100%, M^+-OTf-2H_2O). ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.91 (d, *J*=7.2, 1H, Ph-H), 7.11 (t, *J*=7.6, 1H, Ph-H), 7.54 (d, *J*=7.8, 1H, Ph-H), 7.96 (q, *J*=8.8, 2H, Ph-H), 8.12 (dd, *J*=8.0, 5.6, 1H, Qui-H), 8.91 (d, *J*=8.0, 1H, Qui-H), 9.89 (d, *J*=5.4, 1H, Qui-H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 122.59, 123.95, 124.80, 127.91, 128.04, 129.50, 129.57, 133.65, 138.37, 139.65, 144.00, 152.00, 155.69. λmax(MeOH)/nm: 255 (log ε/dm^3 mol^{-1} cm^{-1} 4.49), 255 (4.49), 330 (4.12), 358 (4.01), 435 (3.56).

Example 15: Preparation of iridium complexes L1 & L2



compound M	compound N	compound O	complex P	complex L
M1: X=H M2: X=F	N1: X=H N2: X=F	O1: X=H O2: X=F	P1: X=H P2: X=F	L1: X=H L2: X=F

[0104] A mixture of M1 (100 mg, 0.56 mmol), potassium permanganate (532 mg, 3.30 mmol), tetrabutylammonium bromide (75 mg, 0.23 mmol), and acetic acid (0.25 mL) was heated at 50 °C under argon for 5 hours. The reaction was cooled and transferred to a separating funnel before sodium metabisulfate (5 g in 100 ml water) was added until no more potassium permanganate colouration was visible. The aqueous layer was separated and extracted with dichloromethane (3 x 50 mL). All the dichloromethane extracts were combined and washed with brine (50 mL) before passing through a silica plug to give N1 (81 mg, 69%) as a yellow solid. mp: 93-95 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (dd, *J*=8.2, 1.0, 4H), 7.65 (t, *J*=7.4, 2H), 7.50 (t, *J*=7.6, 4H).

[0105] A mixture of N1 (900 mg, 3.60 mmol), *o*-phenylenediamine (470 mg 4.00 mmol), acetonitrile (4.5 mL) and iodine (110 mg) was stirred at room temperature for 2 hours. The yellow brown mixture was passed through a silica plug using dichloromethane as eluent and the solvent was removed under vacuum to give O1 (733 mg, 73%) as a yellow solid. mp: 123-125 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.42–7.31 (m, 6H), 7.47 (dd, *J*=8.1, 1.6, 4H), 7.89 (dd, *J*=6.4, 3.4, 2H), 8.16 (dd, *J*=6.3, 3.4, 2H). λmax(MeOH)/nm: 244 (log ε/dm^3 mol^{-1} cm^{-1} 4.68), 344 (4.16).

[0106] A mixture of O1 (700 mg, 2.50 mmol), iridium trichloride trihydrate (360 mg, 1.00 mmol) 2-ethoxyethanol (44 mL) and water (15 mL) was heated at 130 °C under argon for 16 hours. When cooled, water (40 mL) was added to the reaction mixture to give precipitate a red solid. The precipitate was filtered and washed thoroughly with water (100 mL), methanol (100 mL) and diethyl ether (250 mL) and dried to give P1 (540 mg, 68%) as a dark brown powder. mp: >300 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.20 (d, *J*=7.5, 1H), 6.54–6.38 (m, 2H), 6.88–6.81 (m, 1H), 7.66 (d, *J*=3.1, 3H), 7.97–7.69 (b, 4H), 8.16 (dd, *J*=8.1, 1.3, 1H), 9.00 (d, *J*=8.1, 1H).

[0107] The chloro-bridged dimer P1 (540 mg, 0.50 mmol) was suspended in dichloromethane (123 mL) and methanol (123 ml). An aqueous solution (10 mL) of silver triflate (430 mg, 1.70 mmol) was added and the mixture was heated at 60 °C under argon for 18 hours. After being cooled, dichloromethane and methanol were removed under vacuum. The crude product was passed through filter paper and the product was washed with acetone and dried under vacuum to give L1 as a dark brown powder (894 mg, 95%). mp: >300 °C. MS (MALDI-TOF: DITH): *m/z* 755 (100%, M^+-OTf-2H_2O). ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.21 (dd, *J*=6.0, 3.1, 1H), 6.61–6.50 (m, 2H), 6.82 (dd, *J*=6.4, 3.4, 1H), 7.65 (dd, *J*=5.1, 1.7, 3H), 7.85–7.73 (m, 2H), 8.08–7.90 (m, 2H, Qx-H), 8.31–8.22 (m, 1H, Qx-H), 8.85 (d, *J*=9.9, 1H, Qx-H). ^{13}C (100 MHz, DMSO-d_6) δ 115.9, 119.1, 121.7, 122.3, 122.3, 125.9, 129.1, 129.2, 129.4, 129.8, 130.1, 130.2, 130.9, 131.77, 135.2, 139.3, 140.5, 140.8, 145.1, 153.2, 163.4. λmax(MeOH)/nm: 265 (log ε/dm^3 mol^{-1} cm^{-1} 4.49), 286 (4.25), 293 (4.32), 379 (4.19), 491 (3.45).

[0108] A mixture of M2 (386 mg, 02.50 mmol), ground potassium hydroxide pellets (2.80 g, 50 mmol) and toluene (15 mL) was degassed under vacuum and purged with argon, which was repeated three times. The reaction was heated at 70 °C under argon overnight until the yellow solution became a red colour. 1-Fluoro-4-iodobenzene (0.35 mL, 3.00 mmol), tetrakis(triphenylphosphine)palladium(0) (200 mg, 0.18 mmol), and copper(I) iodide (48 mg, 0.30 mmol) were added to the reaction mixture. The reaction was further degassed and purged with argon for three times. The reaction was heated at 70 °C for five days, monitoring from TLC for when the reaction was complete. The solvent was removed under vacuum and the mixture was separated by column chromatograph over silica using hexane as eluent to give N_2 as a white solid. (331 mg, 62%). mp: 94-95 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09–6.96 (m, 4H), 7.53–7.42 (m, 4H).

[0109] A mixture of potassium permanganate (4.70 g, 30.0 mmol), dichloromethane (50 mL), tetrabutylammonium bromide (750 mg, 0.20 mmol), acetic acid (2.5 mL) and M2 (1.07 g, 0.50 mmol) was heated at 50 °C under argon for 5 h. The reaction was cooled and passed through a silica plug to give N2 as a yellow crystalline solid (1.16 g, 94%) after removing the solvent. mp: 119-120 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (dd, *J*=9.0, 8.3, 4H), 8.08–7.96 (m, 4H).

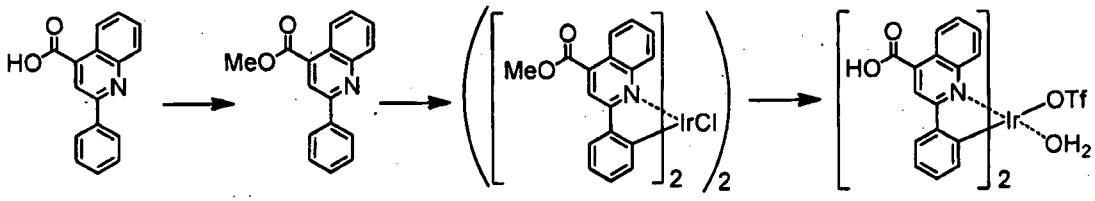
[0110] A mixture of N2 (1.01 g, 4.10 mmol), *o*-phenylenediamine (460 mg 0.50 mmol), acetonitrile (5 ml) and iodine (100 mg, 0.40 mmol) was stirred at room temperature for 2 hours under argon. After five minutes an orange colour could be seen. The resultant brown/green mixture was passed through a silica plug using dichloromethane as the eluent to give O2 (1.22 g, 94%) as a cream coloured solid after the removal of solvents by vacuum. mp: 133-134.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (t, *J*=8.7, 4H, Ph-H), 7.49 (dd, *J*=8.8, 5.4, 4H, Ph-H), 7.77 (dd, *J*=6.4, 3.4, 2H, Qx-H), 8.14 (dd, *J*=6.4, 3.5, 2H, Qx-H). λmax(MeOH)/nm: 243 (log ε/dm^3 mol^{-1} cm^{-1} 4.51), 346 (4.00).

[0111] O2 (750 mg, 2.35 mmol) and iridium trichloride trihydrate (346.5 mg, 0.98 mmol) were dissolved in 2-methoxyethanol (11.25 mL) and water (3.75 mL). The mixture was heated at 125 °C under argon for 16 h. When cooled, water (40 mL) was added to the reaction mixture to give red solid precipitation. The precipitation was filtered and washed thoroughly with water (300 mL), and a mixture of methanol (100 mL) and water (50 mL) and fully dried to give P2 as a red powder (712 mg, 85%). mp: >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.26 (dd, *J*=9.4, 2.5, 1H), 6.24 (td, *J*=8.8, 2.6, 1H), 6.67 (ddd, *J*=8.6, 7.0, 1.4, 1H), 6.89 (dd, *J*=9.0, 5.8, 1H), 7.33 (b, *J*=28.2, 20.2, 3H), 7.68 (dd, *J*=8.3, 1.4, 1H), 7.94 (b, 1H), 8.16 (b, 1H), 8.24 (d, *J*=8.4, 1H).

[0112] The chloro-bridged dimer P2 (300 mg, 0.17 mmol) was suspended in dichloromethane (35 mL) and methanol (35 mL). An aqueous solution (3.5 mL) of silver triflate (180 mg, 0.70 mmol) was added and the mixture was heated at 60 °C under argon for 18 hours. After being cooled, dichloromethane and methanol were removed under vacuum. The crude product was extracted with dichloromethane (2 x 30 mL) and washed with distilled water (2 x 15 mL). The organic layer was combined and passed through filter paper. The solvent was removed under vacuum and the crude was recrystallised from dichloromethane and hexane. The precipitate was collected and fully dried to give L2 as a dark brown powder (347 mg, 98%). mp: >300 °C. (MALDI: DITH): *m/z* 827 (100%, M$^+$-OTf-2H_2O). ^{1}H NMR (300 MHz, methanol-d_4) δ 5.93 (dd, *J*=9.5, 2.5, 1H, Ph-H), 6.45 (td, *J*=8.8, 2.6, 1H, Ph-H), 7.04 (dd, *J*=9.0, 5.8, 1H, Ph-H), 7.38 (t, *J*=8.8, 2H, Ph-H), 7.93–7.85 (m, 2H, Ph-H), 8.04–7.93 (m, 2H, Qx-H), 8.31 (d, *J*=8.0, 1H, Qx-H), 8.70 (d, *J*=8.3, 1H, Qx-H). ^{13}C NMR (101 MHz, methanol-d_4) δ 109.48 (d, *J*=23.0), 116.27 (d, *J*=22.0), 119.06, 121.59 (d, *J*=18.2), 122.26, 125.42, 129.37, 130.65, 131.48 (d, *J*=8.6), 131.8,

132.27 (d, *J*=9.7), 135.53 (d, *J*=3.2), 140.38 (d, *J*=14.0), 141.36, 147.52 (d, *J*=7.5), 152.21, 159.91, 161.78, 162.49 (d, *J*=7.9), 164.24. λmax(MeOH)/nm: 262 (log ε/dm^3 mol^{-1} cm^{-1} 4.32), 286 (4.25), 379 (4.04), 464 (3.48).

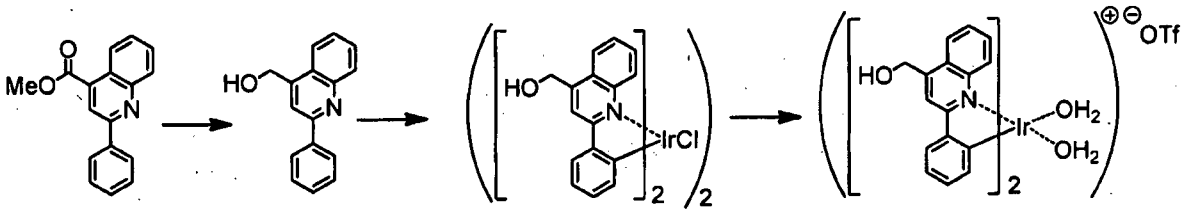
Example 16: Preparation of compound S and iridium complexes T & QIa



R S T QI

[0113] A mixture of compound S (400 mg, 1.50 mmol), iridium trichloride hydrate (220 mg, 0.63 mmol), 2-ethoxyethanol (6 mL) (*note: H_2O should be avoided*) was heated at 120 °C under argon for 20 h. When cooled, water (20 mL) was added to the reaction mixture to give red solid precipitation. The precipitation was filtered and washed thoroughly with water (100 mL), methanol (50 mL) and diethyl ether (250 mL). The dried chloro-bridged dimer (complex T) (150 mg, 0.10 mmol) and LiOH (29 mg, 1.20 mmol) were dissolved in a mixed solvent of THF (30 mL) and EtOH (10 mL). The mixture was stirred at room temperature for 2 h. H_2O (15 mL) was added to the mixture. The solution was heated at 80 °C for 24 h. The reaction was cooled to room temperature and solvent was completely removedto leave a solid. The solid was dissolved in H_2O (50 mL) and 0.1 M HOTf aqueous solution was dropped to the solution until pH=3. The precipitation was collected, washed with H_2O thoroughly and dried in the air to give complex QIa (113 mg, 75%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.10 (d, *J*=8.05, 1H), 6.22 (d, *J*=7.45, 1H), 6.51 (t, *J*=7.35, 1H), 6.61 (t, *J*=7.35, 1H), 6.91 (m, 2H), 7.56 (t, *J*=7.9, 1H), 7.71 (t, *J*=7.9, 1H), 7.85 (t, *J*=7.9, 1H), 8.00-8.08 (m, 3H), 8.29-8.66 (m, 4H), 8.78 (d, *J*=8.8, 1H), 8.83 (d, *J*=8.05, 1H). ^{13}C NMR is not measured due to the very low solubility. *m/z* [MALDI-TOF]: 811.5 (M^+-COOH), 712.1 ([M+Na]$^+$-OTf-H_2O), 689.3 (M^+-OTf-H_2O), 645.2 (M^+-OTf-H_2O-COOH).

Example 17: Preparation of compound U and iridium complexes V & QII

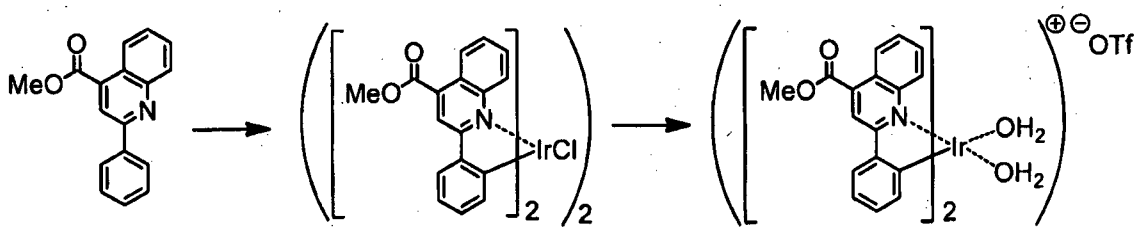


S U V QII

[0114] A solution of compound S (263 mg, 1 mmol), sodium borohydride (113.5 mg, 3 mmol) in 30 mL of absolute ethanol was heated at reflux for 3 h, before being cooled to room temperature. H_2O (30 mL) was added to the mixture. The ethanol was evaporated and the resulting suspension was extracted with diethyl ether (3 x 20 mL). The combined organic layer was dried over anhydrous $MgSO_4$, and filtered. The filtrate was collected and the solvent was removed. The crude was purified by column chromatography over silica using dichloromethane/methanol (20:1) as eluent to give compound U (200 mg, 85%). ^1H NMR (300 MHz, acetone-d_6) δ 4.98 (b, 1H), 5.24 (s, 2H), 7.44-7.56 (m, 4H), 7.74 (dt, J=6.9 & 1.4, 1H), 8.01 (d, J=8.04, 1H), 8.15-8.20 (m, 2H), 8.27-8.30 (m, 2H). ^{13}C NMR (75 MHz, acetone-d_6) δ 60.73, 115.35, 123.12, 125.00, 126.12, 127.30, 128.69, 129.27, 129.33, 130.05, 139.58, 148.02, 148.37, 156.51. *m/z* [ESI$^+$]: 236 ([M+H]$^+$).

[0115] A mixture of compound U (428 mg, 1.82 mmol), iridium trichloride hydrate (268 mg, 0.76 mmol), 2-ethoxyethanol (10 mL) and water (3 mL) was heated at 120 °C under argon for 20 h. When cooled, water (40 mL) was added to the reaction mixture to give red solid precipitation. The precipitation was filtered and washed thoroughly with water (100 mL), dichloromethane (50 mL) and diethyl ether (100 mL). After completely dried, 420 mg (79%) of complex V was obtained. The chloro-bridged dimer (complex V) (111 mg, 0.08 mmol) was suspended in methanol (20 mL). An aqueous solution (2 mL) of silver triflate (50 mg, 0.19 mmol) was added and the mixture was heated at 70 °C for 36 h. After completion, all solvents were removed under vacuum. The crude product was then dissolved in 30 mL of methanol and kept overnight. The insoluble solid was filtered off and complex QII was obtained (90 mg, 67%) after removal of methanol. ^1H NMR (300 MHz, methanol-d_4) δ 5.47 (s, 4H), 6.11 (d, J=7.8, 2H), 6.54 (t, J=7.3, 2H), 6.89 (t, J=7.6, 2H), 7.71-7.88 (m, 6H), 8.18 (d, J=8.1, 2H), 8.43 (s, 2H), 9.03 (d, J=8.85, 2H). ^{13}C NMR (75 MHz, methanol-d_4) δ 61.49, 114.93, 123.70, 125.04, 127.00, 127.21, 127.33, 128.03, 130.64, 132.38, 135.49, 138.64, 148.36, 149.70, 153.05, 170.95. *m/z* [MALDI-TOF]: 661.1 (M^+-OTf-2H_2O).

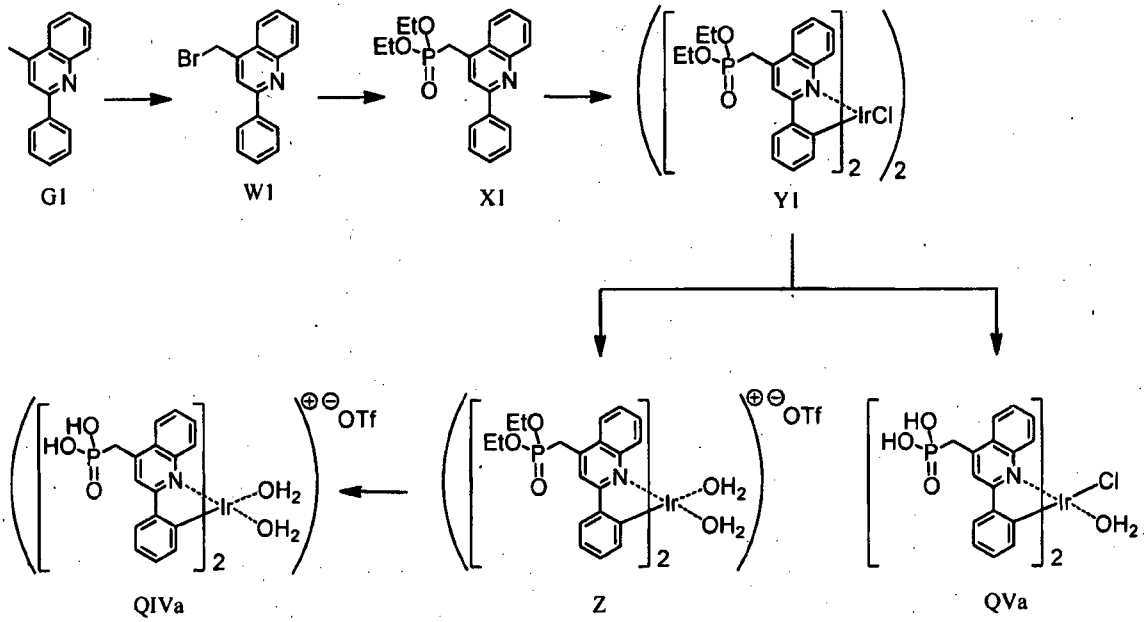
Example 18: Preparation of iridium complex QIII



S T QIII

[0116] A mixture of compound S (400 mg, 1.50 mmol), iridium trichloride hydrate (220 mg, 0.63 mmol) and 2-ethoxyethanol (6 mL) (*note: H_2O should be avoided*)was heated at 120 °C under argon for 20 h. When cooled, water (20 mL) was added to the reaction mixture to give red solid precipitation. The precipitation was filtered and washed thoroughly with water (100 mL), methanol (50 mL) and diethyl ether (250 mL). The dried chloro-bridged dimer (150 mg, 0.10 mmol) was suspended in dichloromethane (10 mL) and methanol (10 mL). An aqueous solution (3 mL) of silver triflate (62 mg, 0.24 mmol) was added and the mixture was heated at 60 °C for 16 h. After cooled, water (30 mL) was added and dichloromethane and methanol were removed under vacuum. The crude product was then extracted with dichloromethane (2 x 20 mL) and washed with distilled H_2O (2 x 15 mL). A dark red solid product was yielded after filtration of the insoluble solid and removal of the solvents to give complex QIII (128 mg, 71%). ^{1}H NMR (400 MHz, methanol-d_4) δ 4.19 (s, 6H), 6.11 (d, *J*=7.8, 2H), 6.64 (t, *J*=7.3, 2H), 6.97 (t, *J*=7.4, 2H), 7.82 (t, *J*=7.8, 2H), 7.89 (t, *J*=8.0, 2H), 7.94 (d, *J*=7.7, 2H), 8.71 (s, 2H), 8.83 (d, *J*=8.2, 2H), 9.06 (d, *J*=8.7, 2H). ^{13}C NMR (100 MHz, methanol-d_4) δ 53.84, 119.23, 124.27, 126.18, 127.08, 127.77, 128.06, 129.34, 131.46, 133.14, 135.50, 138.60, 140.75, 147.44, 150.87, 167.06, 171.22. *m/z* [MALDI-TOF]: 717.4 (M^+-OTf-2H_2O). Anal. Cal. For $C_{35}H_{28}F_3IrN_2O_9S$: C, 46.61; H, 3.13; N, 3.11. Found: C, 45.32; H, 2.73; N, 2.71.

Example 19: Preparation of compounds W1 & X1 and complexes Y1, Z, QIVa & QVa



[0117] 1,1-Azobis(cyclohexanecarbonitrile) (ABCN, 194 mg, 0.80 mmol) was added to a mixture of compound G1 (1.74 g, 7.95 mmol) *N*-bromosuccinimide (NBS, 1.71 g, 9.54 mmol), dichloromethane (75 mL) and H_2O (75 mL). The mixture was vigorous stirred,exposed to a 150 W halogen lamp and heated at reflux for 5 h. The mixture was then cooled to room temperature. The organic layer was collected and the water layer was extracted with dichloromethane (2 × 50 mL). The combined organic layer was then washed with brine, dried over anhydrous $MgSO_4$ and filtered. The filtrate was collected and the solvent was removed under vacuum. The crude was purified by column chromatography over silica using dichloromethane-hexane (1:1) as eluent to afford compound W1 as a colourless solid (1.94 g, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.92 (s, 2H), 7.45-7.57 (m, 3H), 7.63 (dt, *J*=6.9 & 1.3, 1H), 7.76 (dt, *J*=8.4 & 1.5, 1H), 7.91 (s, 1H), 8.11-8.18 (m, 3H), 8.23(dd, *J*=8.5 & 0.7, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.83, 119.36, 123.17, 124.86, 126.75, 127.49, 128.90, 129.61, 129.92, 130.62, 139.03, 142.90, 148.78, 157.08. *m/z* [ESI$^+$]: 298.0 ($M+H^+$). Anal. Cal. For $C_{16}H_{12}BrN$: C, 64.45; H, 4.06; N, 4.70. Found: C, 64.31; H, 4.03; N, 4.97.

[0118] A mixture of compound W1 (596 mg, 2 mmol) and triethylphosphite (2.5 mL) was heated at 100 °C overnight. The excess triethyl phosphite was then removed by distillation at 80 °C under high vacuum. The crude product was purified by column chromatography over silica using dichloromethane-hexane (2:1) and then dichloromethane-methanol (20:1) as eluent to give compound X1 as a colorless oil (631 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, *J*=7.05, 6H), 3.65 (d, J =22.7, 2H), 3.95-4.02 (m, 4H), 7.44-7.57 (m,

4H), 7.70 (dt, *J*=6.9 & 1.35, 1H), 7.87 (d, *J*=3.6, 1H), 8.07 (dd, *J*=8.4 & 1.0, 1H), 8.14-8.19 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.11 (d, *J*=6.1), 30.37 (d, *J*=137.0), 62.20 (d, *J*=7.0), 120.54 (d, *J*=7.0), 123.78 (d, *J*=1.6), 126.07, 126.11, 126.14, 127.25, 128.58, 129.17, 129.34, 130.16, 138.67, 138.74, 139.06, 148.36 (d, *J*=1.65), 156.29 (d, *J*=3.55). *m/z* [ESI$^+$]: 356.1 ($M+H^+$). Anal. Cal. For $C_{20}H_{22}NO_3P$: C, 67.60; H, 6.24; N, 3.94. Found: C, 67.26; H, 6.21; N, 3.92.

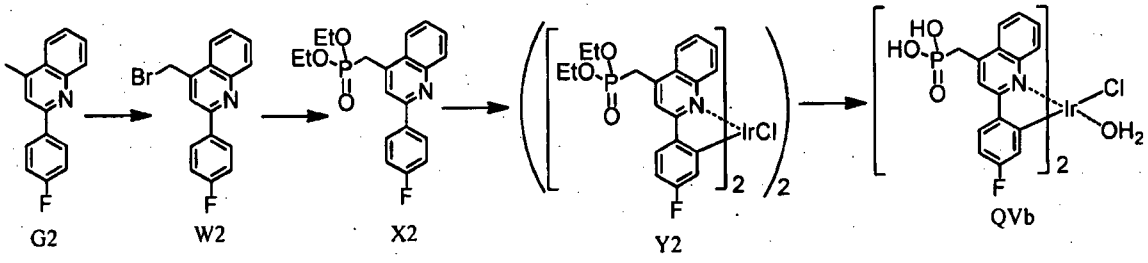
[0119] Compound X1 (470 mg, 1.33 mmol) and iridium trichloride hydrate (195 mg, 0.55 mmol) were dissolved in a mixture of 2-ethoxyethanol (12 mL) and water (4 mL). The mixture was heated at 130 °C under argon for 24 h. When cooled, water (40 mL) was added to the reaction mixture to precipitate a red solid. The precipitation was filtered and washed with water (3 x 30 mL) and hexane (3 x 150 mL). After completely dried, complex Y1 (334 mg, 65%) was obtained. The chloro-bridged dimer (complex Y, 247 mg, 0.13 mmol) was suspended in dichloromethane (15 mL) and methanol (15 mL). An aqueous solution (3 mL) of silver triflate (339 mg, 1.32 mmol) was added and the mixture was heated at 50 °C for 16 h. After cooled, water (30 mL) was added. The solvent was removed under vacuum. The crude product was extracted by dichloromethane (2 x 30 mL) and washed by distilled H_2O (2 x 15 mL). A red solid (130 mg, 46%) was yielded as complex Z after complete removal of the solvent. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19-1.22 (m, 12H), 3.74 (d, *J*=22.4, 4H), 4.02 (m, 8H), 6.32 (d, *J*=7.8, 2H), 6.59 (t, *J*=7.5, 2H), 6.93 (t, *J*=6.3, 2H), 7.56-7.69 (m, 6H), 8.03 (s, 4H), 8.85 (b, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.66 (d, *J*=5.8), 30.45 (d, *J*=127.4), 62.41 (t, *J*=5.7), 119.53, 122.40, 122.82, 126.59, 127.01, 127.24, 127.28, 129.81, 131.61, 134.58, 141.34, 144.72 (d, *J*=9.4), 147.08, 148.91, 169.08. *m/z* [ESI$^+$]: 901.1 (M^+-OTf-$2H_2O$).

[0120] Complex Z (109 mg, 0.1 mmol) was added to 15 mL of aqueous HCl solution (5.7 M) and refluxed at 100 °C for 24 h. After cooled to room temperature, crude complex Z was obtained by removing the solvent as a yellow solid. Complex Z was dissolved in 2 mL methanol and purified by column chromatography over Sephadex LH-20 using methanol as eluent to give complex QIVa (29.2 mg, 30%). λ_{max}(MeOH)/nm: 233 (log ε/dm^3 mol^{-1} cm^{-1} 4.54), 260 (4.54), 280 (4.53), 294 (4.43), 324 (4.23), 360 (4.00), 410 (3.76), 438 (3.60). ^{1}H NMR (400 MHz, methanol-d_4): δ 3.90 (d, 6H, *J*=22.9), 7.00 (t, 2H, *J*=6.3), 7.11 (t, 2H, *J*=7.8), 7.58 (d, 2H, *J*=7.8), 7.66 (t, 2H, *J*=7.0), 7.73-7.81 (m, 4H), 8.03 (d, 2H, *J*=3.5),

8.11 (d, 2H, *J*=8.3), 9.59 (d, 2H, *J*=7.9). ^{13}C NMR (100 MHz, MeOD) δ 30.78 (d, *J*=131.31), 117.72 (d, *J*=6.81), 121.59, 124.98, 125.28, 125.65, 125.99 (d, *J*=4.53), 126.920, 128.40, 130.27, 132.85, 134.31, 143.24 (d, *J*=9.40), 147.61, 150.24 (d, *J*=1.94), 171.88(d, *J*=3.35). *m/z* [ESI$^+$]: 893 (M^+-PO_3H_2). *m/z* [MALDI-TOF]: 627.04 (M^+-OTf-$2H_2O$-$2PO_3H_2$).

[0121] Complex Y (187.3 mg, 0.1 mmol) was added to 20 mL of aqueous HCl solution (5.7 M) and heated at reflux for 24 h. After cooled to room temperature, the crude product was obtained by removing the solvent. The resulted yellowish solid was dissolved in 3 mL of methanol and purified by column chromatography over Sephadex LH-20 using methanol as eluent to give complex QVa (48.8 mg, 29%). λ_{max}(MeOH)/nm: 233 (logε/dm^3 mol^{-1} cm^{-1} 4.44), 260 (4.44), 280 (4.42), 294 (4.30), 324 (4.11), 360 (3.89), 410 (3.61), 438 (3.51). ^{1}H NMR (300 MHz, methanol-d_4): δ 3.89 (d, 6H, *J*=23.49), 7.02 (t, 2H, *J*=6.99), 7.11 (t, 2H, *J*=6.75), 7.58 (d, 2H, *J*=7.80), 7.67 (t, 2H, *J*=7.32), 7.75-7.84 (m, 4H), 8.05 (s, 2H), 8.13 (d, 2H, *J*=8.31), 9.58 (d, 2H, *J*=8.76). ^{13}C NMR (75 MHz, methanol-d_4) δ 30.76 (d, *J*=131.87), 117.70 (d, *J*=6.81), 121.56, 124.96, 125.26, 125.62, 125.98 (d, *J*=4.35), 126.90, 128.37, 130.24, 132.83, 134.29, 143.23 (d, *J*=9.05), 147.60, 150.25, 171.85. *m/z* [MALDI-TOF]: 842.13 (M^+), 788.99 (M^+-Cl-H_2O), 710.04 (M^+-Cl-H_2O-PO_3H_2), 663.04 (M^+-H_2O-$2PO_3H_2$), 629.08 (M^+-Cl-H_2O-$2PO_3H_2$+2H).

Example 20: Preparation of compounds W2 & X2 and complexes Y2 & QVb



[0122] 1,1-Azobis(cyclohexanecarbonitrile) (ABCN, 292 mg, 1.20 mmol) was added to a mixture of compound G2 (2.83 g, 11.9 mmol), *N*-bromosuccinimide (2.55 g, 14.3 mmol), dichloromethane (75 mL) and H_2O (75 mL). The mixture was vigorously stirred, exposed to a 150 W halogen lamp and heated at reflux for 5 h. The mixture was then cooled to room temperature. The organic layer was collected and the water layer was extracted with dichloromethane (2 × 100 mL). The combined organic layer was then washed with brine,

dried over anhydrous $MgSO_4$ and filtered. The filtrate was collected and the solvent was removed under vacuum. The crude was purified by column chromatography over silica using dichloromethane-hexane (1:1) as eluent to give compound W2 as a colourless solid (12.19 g, 58%); mp 124 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.88 (s, 2H), 7.18-7.27 (m, 2H), 7.62 (dt, *J*=1.295 & 6.87, 1H), 7.76 (dt, *J*=1.41 & 6.90, 1H), 7.83 (s, 1H), 8.08-8.22 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.67, 115.81 (d, *J*=21.62), 118.97, 123.14, 124.75, 126.80, 129.34 (d, *J*=8.46), 130.02, 130.52, 135.20 (d, *J*=3.16), 143.04, 148.73, 155.98, 163.90 (d, *J*=248.00). *m/z* [MALDI-TOF]: 316.0 ($M+H^+$). Anal. Cal. For $C_{16}H_{11}BrFN$: C, 60.78; H, 3.51; N, 4.43. Found: C, 60.75; H, 3.42; N, 4.46.

[0123] A mixture of compound W2 (2.35 g, 7.4 mmol) and triethylphosphite (10 mL) was heated at 100 °C overnight under argon. The excess triethyl phosphite was removed by distillation. The crude product was purified by column chromatography over silica using dichloromethane-hexane (1:1) and dichloromethane-methanol (20:1) as eluent to give X2 as a colourless oil (2.87 g, 100%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (dt, *J*=0.33 & 6.87, 6H), 3.62 (d, *J*=22.65, 2H), 3.91-4.03 (m, 4H), 7.12-7.18 (m, 2H), 7.49-7.55 (m, 1H), 7.68 (dt, *J*=1.35 & 8.37, 1H), 7.80 (d, *J*=3.60, 1H), 8.04(dd, *J*=1.05 & 8.46, 1H), 8.09-8.16 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.16 (d, *J*=5.99), 30.45 (d, *J*=137.12), 62.34 (d, *J*=6.71), 115.57 (d, *J*=21.41), 120.34 (d, *J*=6.97), 123.81 (d, *J*=1.41), 126.10 (d, *J*=4.90), 126.22, 129.22 (d, *J*=8.34), 129.57, 130.13, 135.28 (d, *J*=3.08), 138.98 (d, *J*=8.97), 148.34 (d, *J*=2.26), 155.35 (d, *J*=3.59), 163.67 (d, *J*=247.59). *m/z* [MALDI-TOF]: 374.1 ($M+H^+$). Anal. Cal: For $C_{20}H_{21}FNO_3P$: C, 64.34; H, 5.67; N, 3.75. Found: C, 63.98; H, 5.67; N, 3.75.

[0124] A mixture of X2 (896 mg, 2.4 mmol), iridium trichloride hydrate (353 mg, 1.0 mmol), 2-ethoxyethanol (12 mL) and water (4 mL) was heated at 130 °C under argon for 20 hours. When cooled, water (40 mL) was added to the mixture to give red solid precipitation. The precipitation was filtered off and washed with water (3 x 30 mL). After being dried, the obtained solid was suspended in a mixture of 10 mL of HCl (2 M) solution and 10 mL acetone and stirred overnight. The precipitate was filtered and dried to give Y2 (757 mg, 78%). A mixture of Y2 (537 mg, 0.28 mmol), 20 mL aqueous HCl solution (6 M) was heated at reflux (100 °C) for 42 h. After being cooled to room temperature, the solvent

was removed by evaporation to give a crude product as a yellow solid. The solid was dissolved in 2 mL methanol and purified by column chromatography over Sephadex LH-20 using methanol as eluent to give QVb as a red solid (210 mg, 42%). ^{1}H NMR (500 MHz, methanol-d_4) δ 3.89 (d, 4H, *J*=23.49), 7.02 (dd, 2H, *J*=10.10 & 2.50), 7.62 (d, 2H, *J*=6.30), 7.63 (d, 2H, *J*=5.95), 7.76 (dt, 2H, *J*=6.90 & 1.15), 7.81 (d, 2H, *J*=3.60), 8.00 (d, 2H, *J*=7.70), 9.53 (d, 2H, *J*=8.75). ^{13}C NMR (100 MHz, MeOD) δ 32.01 (d, *J*=131.43), 109.79 (d, *J*=23.37), 119.30 (d, *J*=6.89), 119.76 (d, *J*=18.96), 126.43, 126.91, 127.17 (d, *J*=4.25), 127.99, 128.49 (d, *J*=9.74), 131.65, 138.72 (d, *J*=7.53), 144.58 (d, *J*=9.22), 145.36, 151.42 (d, *J*=1.96), 162.84 (d, *J*=250.13), 172.13 (d, *J*=3.43). *m/z* [MALDI-TOF, using dithranol as matrix]: 663.22 (M^+-Cl-2H_2O-2PO_3H_2), 825.17 (M^+-Cl-2H_2O), 884.28 ([M-Cl+Na]$^+$), 896.29 [M^+]. *m/z* [MALDI-TOF, using 4-dimethylamino-pyridine as matrix]: Anal. Cal. For $C_{32}H_{19}F_2IrN_2O_4P_2$: 786.1 (59%), 787.1 (21%), 788.1 (100%), 789.1 (35%), 790.1 (7%). Found: 786.3 (46%), 787.3 (25%), 788.3 (100%), 789.3 (48%), 790.3 (38%). (M^+-OTf-2H_2O-2H_2O-H). λ_{max}(MeOH)/nm: 265 (log ε/dm^3 mol^{-1} cm^{-1} 4.40), 278 (4.37), 294 (4.25), 322sh (4.03), 358sh (3.87), 404 (3.61), 428sh (3.52), 487sh (2.67), 527sh (2.43).

[0125] Optional embodiments of the present invention may also be said to broadly consist in the parts, elements and features referred to or indicated herein, individually or collectively, in any or all combinations of two or more of the parts, elements or features, and wherein specific integers are mentioned herein which have known equivalents in the art to which the invention relates, such known equivalents are deemed to be incorporated herein as if individually set forth.

[0126] Although a preferred embodiment has been described in detail, it should be understood that various changes, substitutions, and alterations can be made by one of ordinary skill in the art without departing from the scope of the present invention.

The claims:

1. A water splitting catalyst, comprising a cyclometalated iridium complex including bandgap lowering ligands.

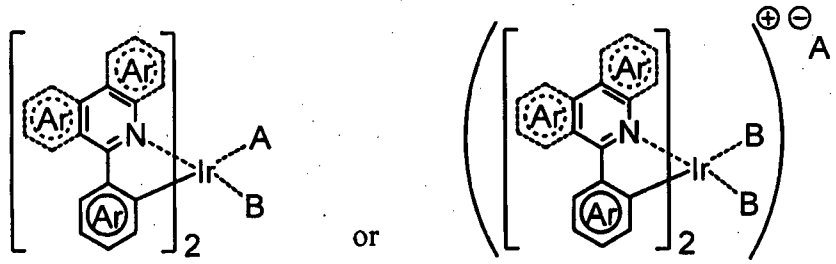
2. The water splitting catalyst of claim 1, wherein the ligands are aryl quinoline ligands.

3. The water splitting catalyst of claim 1, wherein the ligands are derived from aryl pyrazine or aryl quinoxaline.

4. The water splitting catalyst of any one of claims 1 to 3, wherein one or more additional linking groups are included to improve solubility of the complex.

5. The water splitting catalyst of any one of claims 1 to 3, wherein one or more additional linking groups are included to improve attachment of the complex to a semiconductor or an electrode.

6. A cyclometalated iridium complex, comprising the structure of formula I:



Ia Ib

wherein, Ar is an aryl group, or a fused or heterocyclic arene or ring.

7. The cyclometalated iridium complex of claim 6, wherein the represented pyridine ring further comprises two or more nitrogens derived from the group consisting of carbazole, pyrimidine, pyrazine, pyridazine, quinoline, quinoxaline, pyrrole, imidazole, triazine, and triazole.

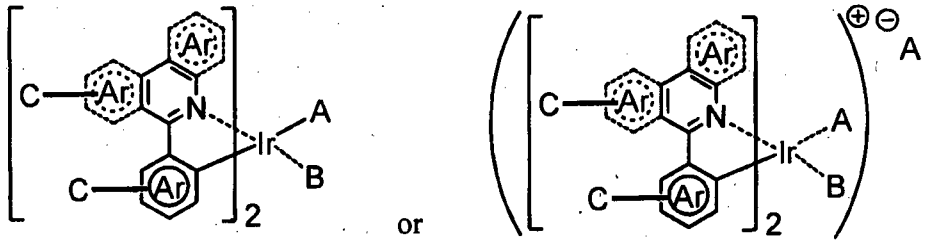
8. The cyclometalated iridium complex of claim 6 or 7, wherein A and/or B are initially part of an electrolyte or a solvent.

9. The cyclometalated iridium complex of claim 6 or 7, wherein A and/or B are initially part of an electrolyte, which can be ligated to a metal or act as a counter ion.

10. The cyclometalated iridium complex of claim 6 or 7, wherein A and/or B are selected from the group consisting of OH_2, OH, O, OTf, SO_4, NO_3, PF_6, Cl, and a halo.

11. The cyclometalated iridium complex of claim 6 or 7, wherein A and/or B are selected from the group consisting of a bidentate ligand, diamine, bipyridyl, picolinic acid, picolinamide, quinolone carboxylic acid, and a derivative thereof.

12. The cyclometalated iridium complex of any one of claims 6 to 11, further comprising the structure of formula II:



IIa IIb

wherein, C is one or more linking groups and C is provided on any part of the ligand rings, on either part of the ligand rings, or on the two ligand rings.

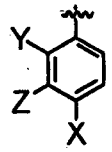
13. The cyclometalated iridium complex of claim 12, wherein C is a hydrophilic group or an anchor group.

14. The cyclometalated iridium complex of claim 12, wherein C is derived from the group consisting of phosphonic acid, carboxylic acid, hydroxamide, amine, ether and alcohol.

15. The cyclometalated iridium complex of claim 14, wherein C facilitates the attachment of the complex to an electrode or semiconductor.

16. The cyclometalated iridium complex of any one of claims 6 to 15, wherein A and/or B are initially part of an electrolyte or a solvent.

17. The cyclometalated iridium complex of any one of claims 6 to 16, wherein Ar has the following structure:



and wherein X, Y and Z are individually selected from the group consisting of hydrogen, a halogen, an organofluorine, a trifluoromethyl, an alkyl, a nitro, a cyanide, C_nF_{2n+1}, COOR, C(O)R, OR, an aryl, and an heteroarene.

18. The cyclometalated iridium complex of claim 17, wherein:

X = H, Y = H, Z = H;

X = F, Y = H, Z = H;

X = F, Y = F, Z = H;

X = F, Y = H, Z = CF_3;

X = F, Y = F, Z = CF_3; or

X = H, Y = H, Z = CF_3.

19. The cyclometalated iridium complex of any one of claims 6 to 18, wherein Ar is selected from the group consisting of phenyl, a fused ring, for example naphthene, pyrene, fluorene, dibenzofuran, dibenzothiophene, coumarine, anthracene, indole, benzimidazole, quinazoline, phthalimide, phenanthridine, or heteroarene, such as pyridine, quinoline, carbazole, pyrimidine, pyrazine, pyridazine, pyrrole, imidazole, triazine, and triazole.

20. The cyclometalated iridium complex of any one of claims 6 to 19, wherein the cyclometalated complex is used as a catalyst, photocatalyst, photosensitizer and/or a precursor of active catalytic species in water splitting.

21. The cyclometalated iridium complex of any one of claims 6 to 20, wherein the cyclometalated complex is used in a light-driven or photon-driven opto-electronic device.

22. A water splitting catalyst, comprising a cyclometalated iridium complex including bandgap widening ligands.

23. The water splitting catalyst of claim 22, wherein the ligands are aryl triazole or aryl benzimidazole ligands.

24. The water splitting catalyst of claim 23, including substitution groups to alter the energy level and energy bandgap.

25. The water splitting catalyst of any one of claims 22 to 24, further including one or more linking groups to improve the solubility of the complex.

26. The water splitting catalyst of any one of claims 22 to 24, further including one or more linking groups to improve the attachment of the complex to a semiconductor or an electrode used in a water splitting or photon-driven device.

FIGURE 1

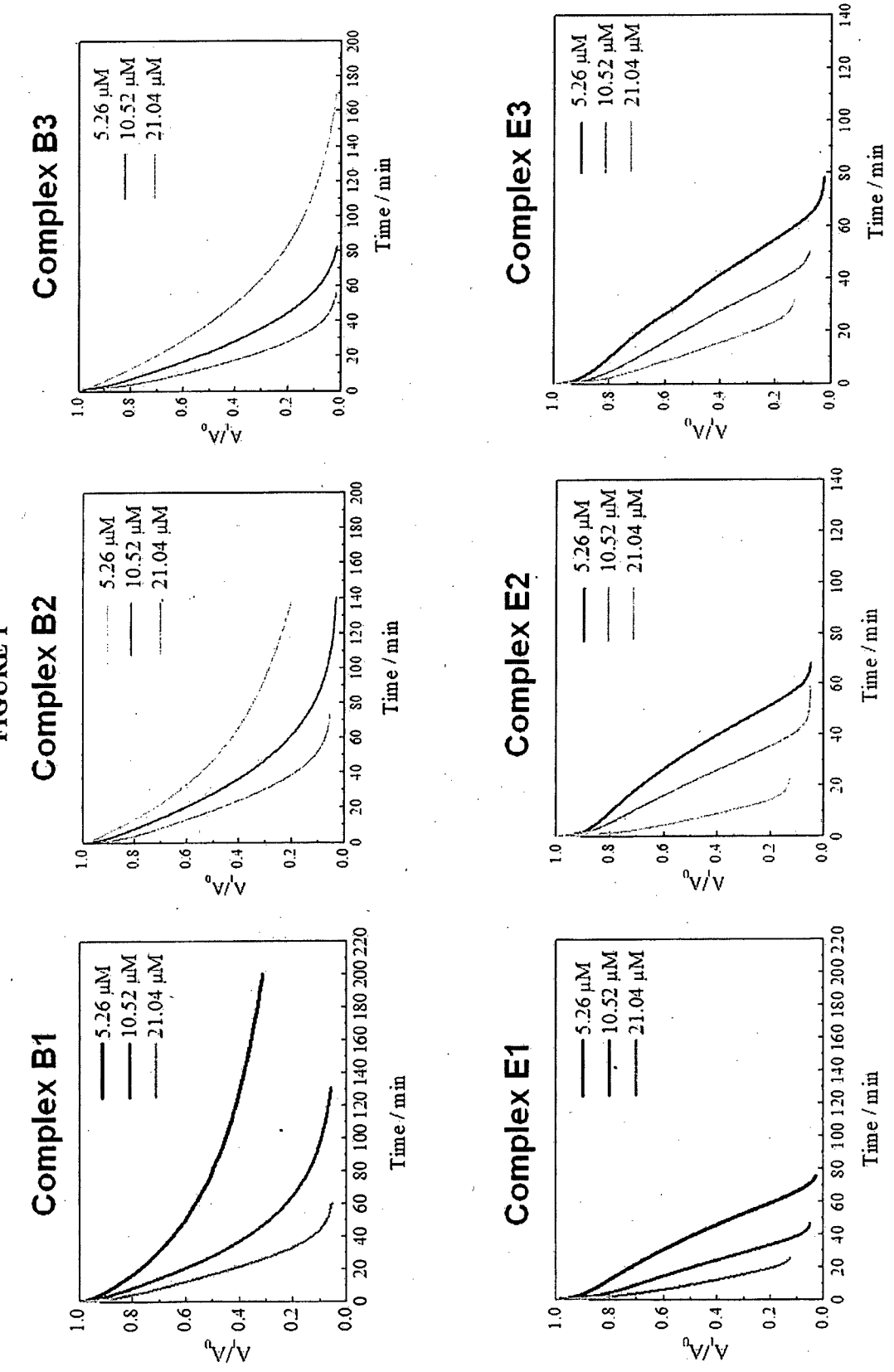

Complex B1
Complex B2
Complex B3
Complex E1
Complex E2
Complex E3
5.26 μM
10.52 μM
21.04 μM
Time / min
A/A0

FIGURE 2

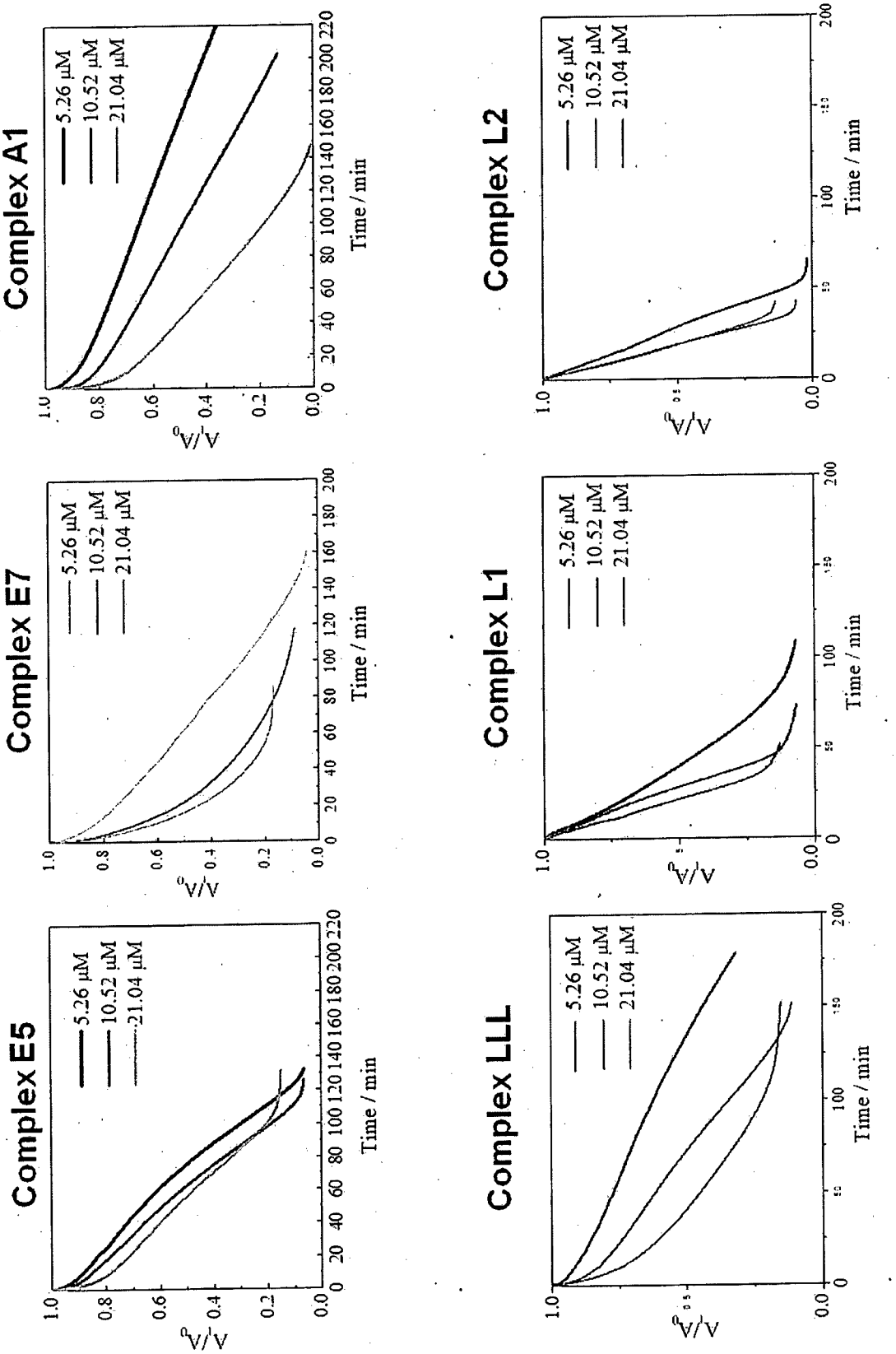

Complex A1
Complex E7
Complex L2
Complex E5
Complex L1
Complex LLL
5.26 µM
10.52 µM
21.04 µM
A/A0
Time / min

FIGURE 3

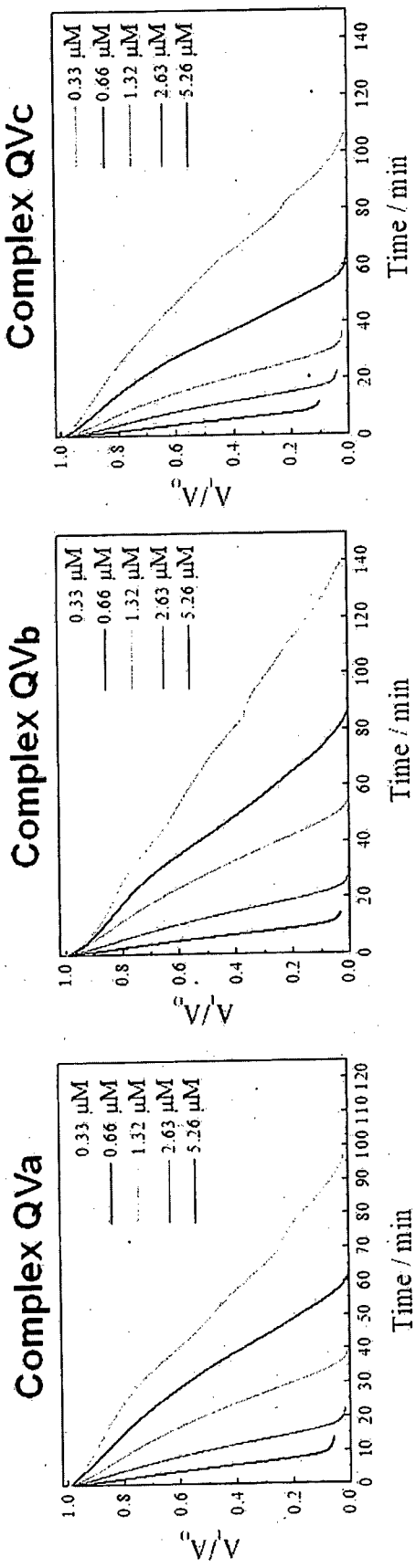

Complex QVa
Complex QVb
Complex QVc
0.33 µM
0.66 µM
1.32 µM
2.63 µM
5.26 µM
Time / min
A/A0

FIGURE 4

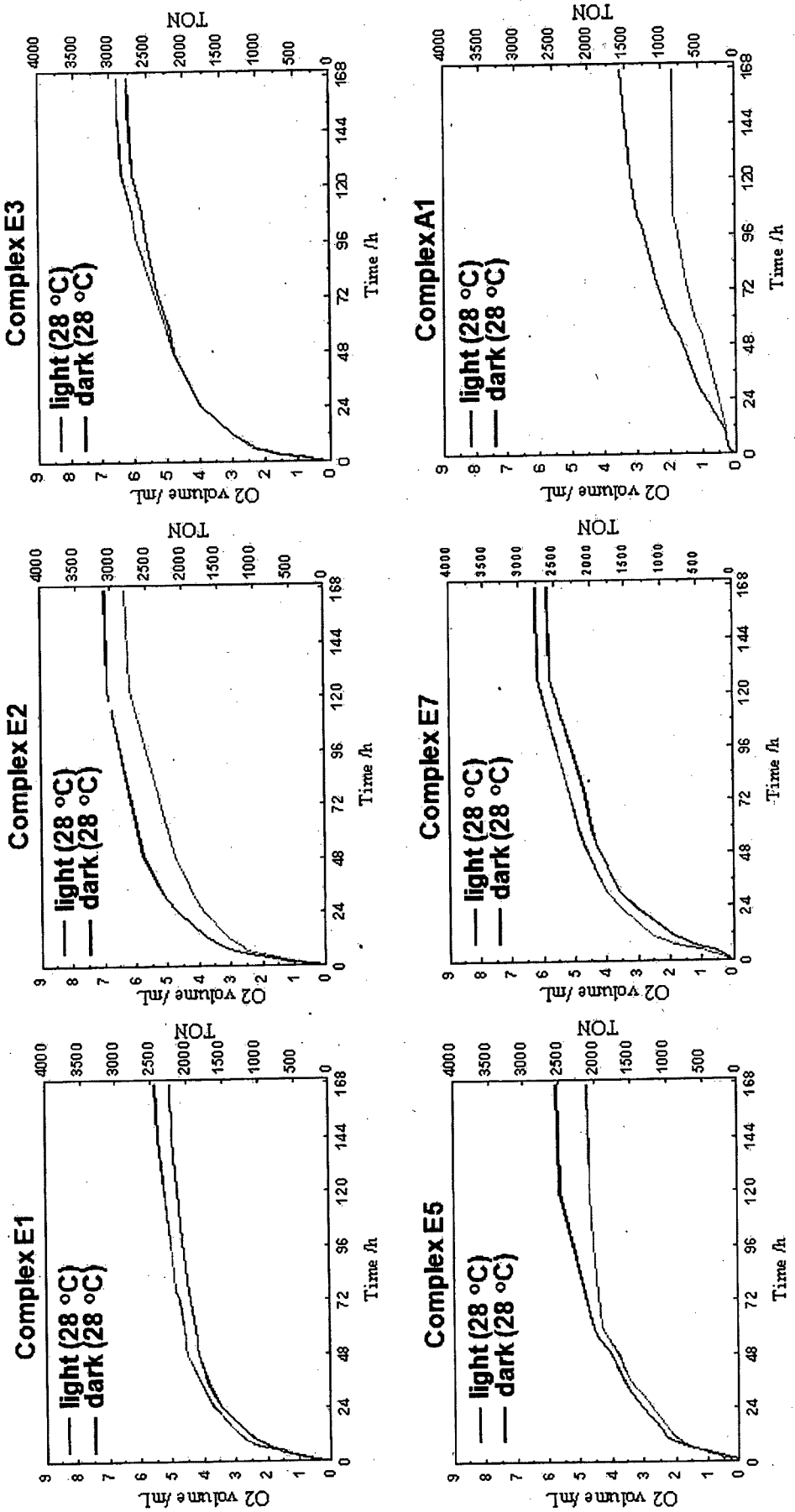

Complex E1
Complex E2
Complex E3
Complex E5
Complex E7
Complex A1
light (28 °C)
dark (28 °C)
O2 volume /mL
Time /h
TON

FIGURE 5

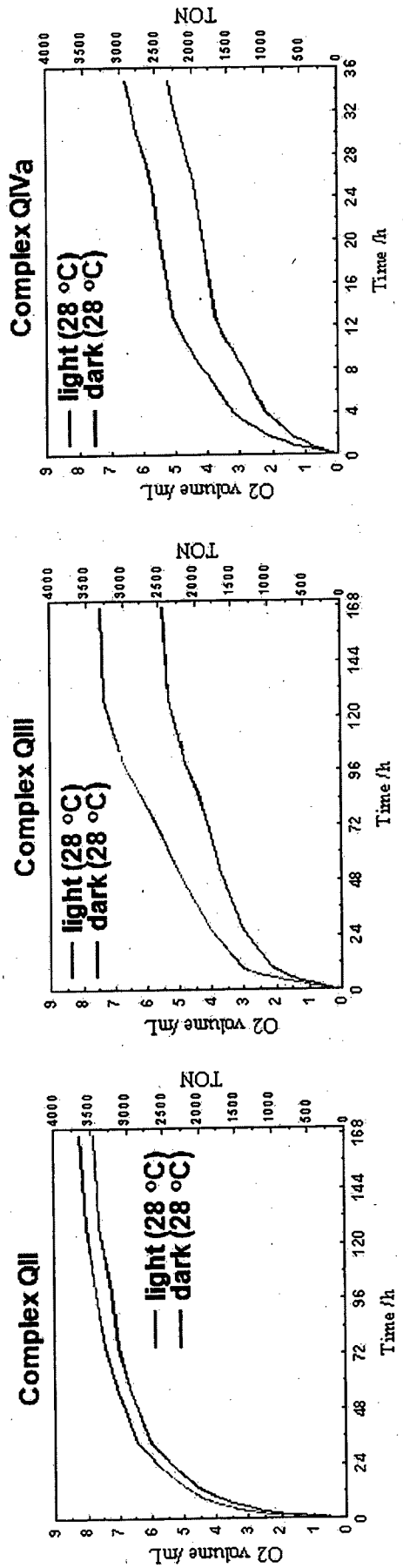

Complex QII
light (28 °C)
dark (28 °C)
O2 volume /mL
Time /h
TON
Complex QIII
light (28 °C)
dark (28 °C)
O2 volume /mL
Time /h
TON
Complex QIVa
light (28 °C)
dark (28 °C)
O2 volume /mL
Time /h
TON

FIGURE 6

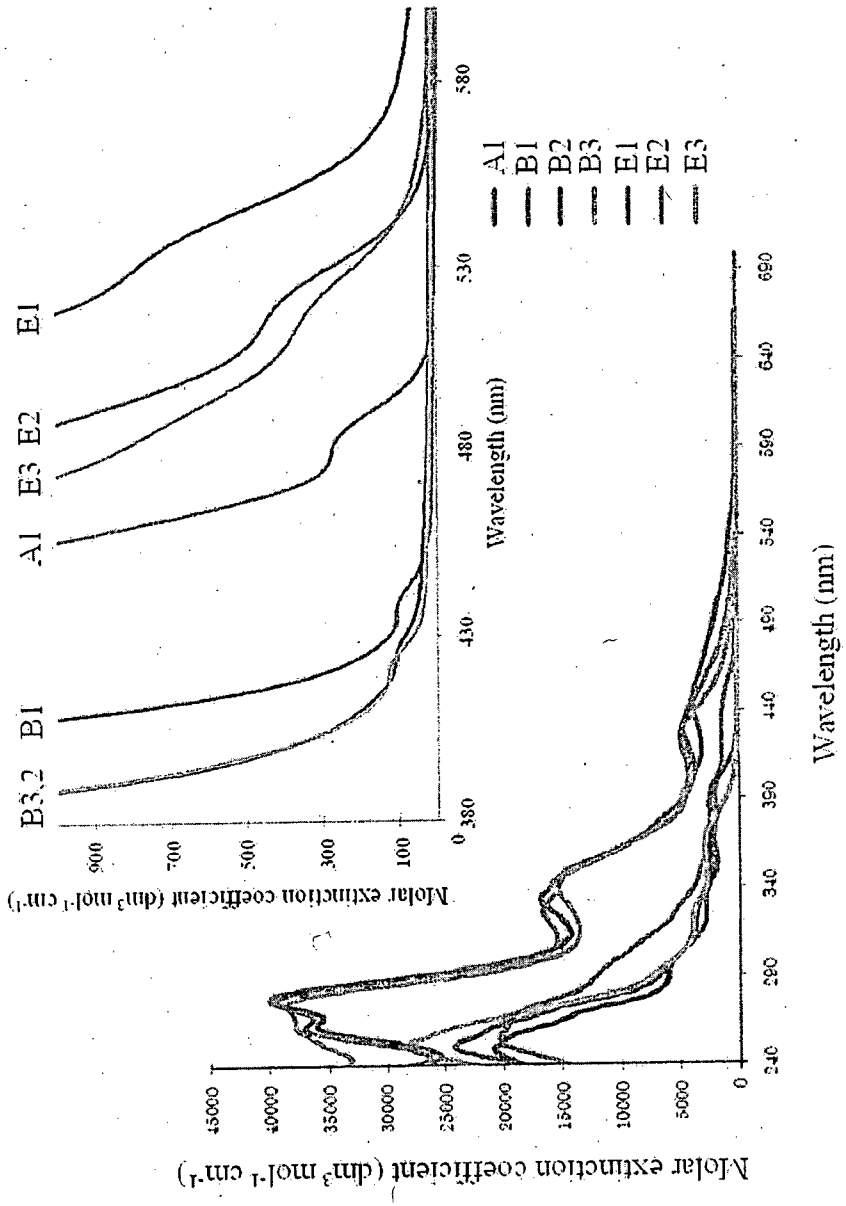

Molar extinction coefficient (dm³ mol⁻¹ cm⁻¹)
Wavelength (nm)
A1
B1
B2
B3
E1
E2
E3
Molar extinction coefficient (dm³ mol⁻¹ cm⁻¹)
Wavelength (nm)
B3,2
B1
A1
E3
E2
E1

FIGURE 7

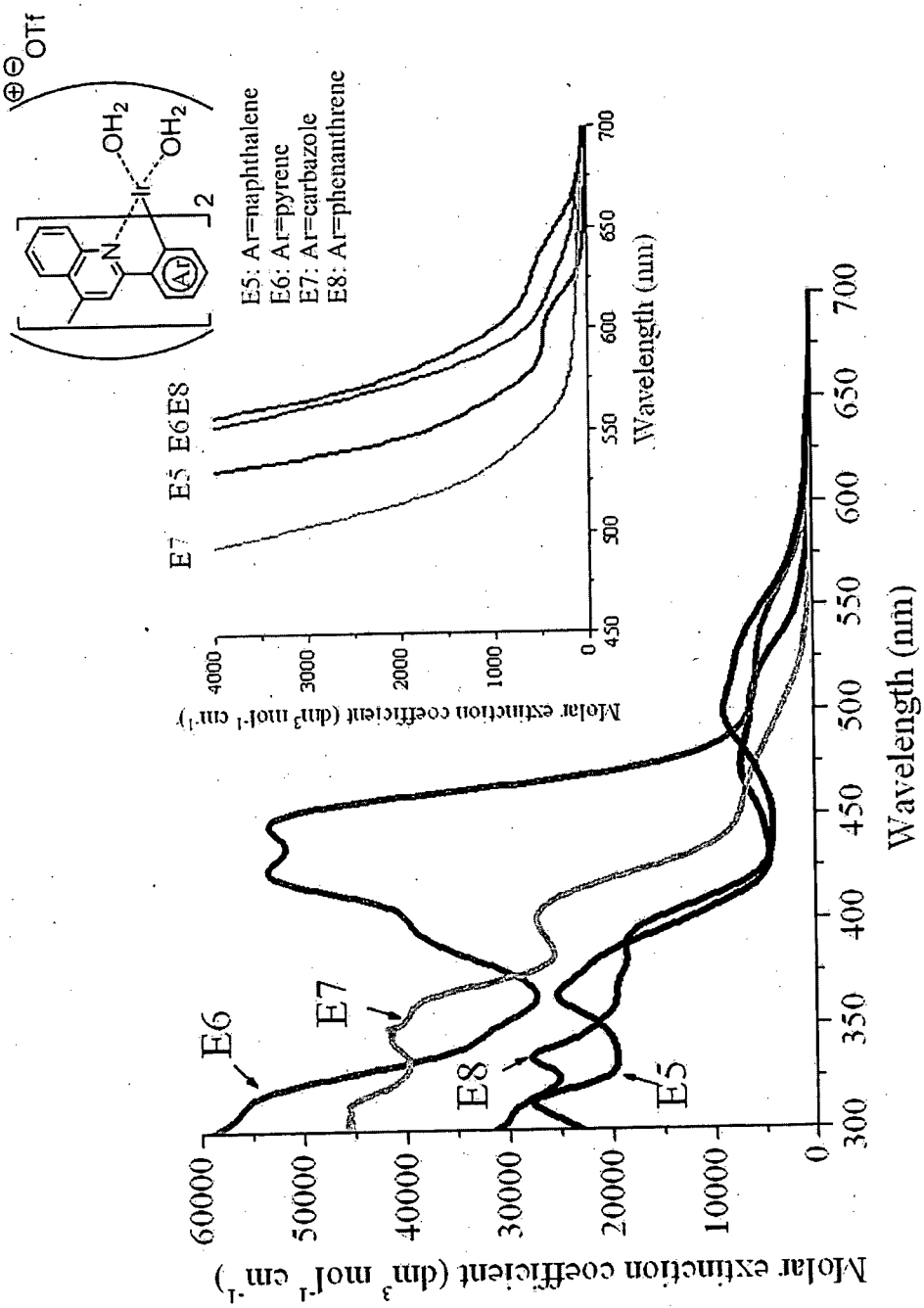

Molar extinction coefficient (dm³ mol⁻¹ cm⁻¹)
Wavelength (nm)
E6
E7
E8
E5
E7 E5 E6 E8
E5: Ar=naphthalene
E6: Ar=pyrene
E7: Ar=carbazole
E8: Ar=phenanthrene
OTf
OH2
Ir
N
Ar

FIGURE 8

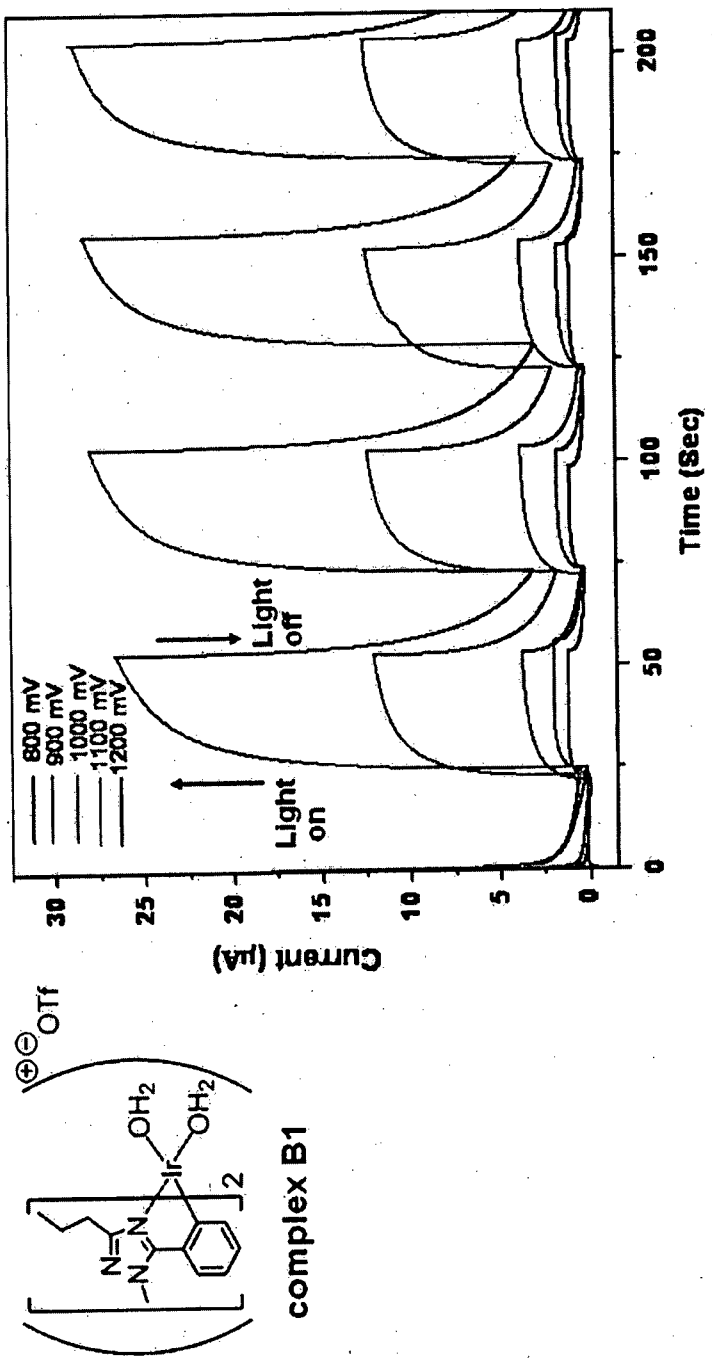

Current (μA)
Time (Sec)
800 mV
900 mV
1000 mV
1100 mV
1200 mV
Light on
Light off
complex B1

FIGURE 9

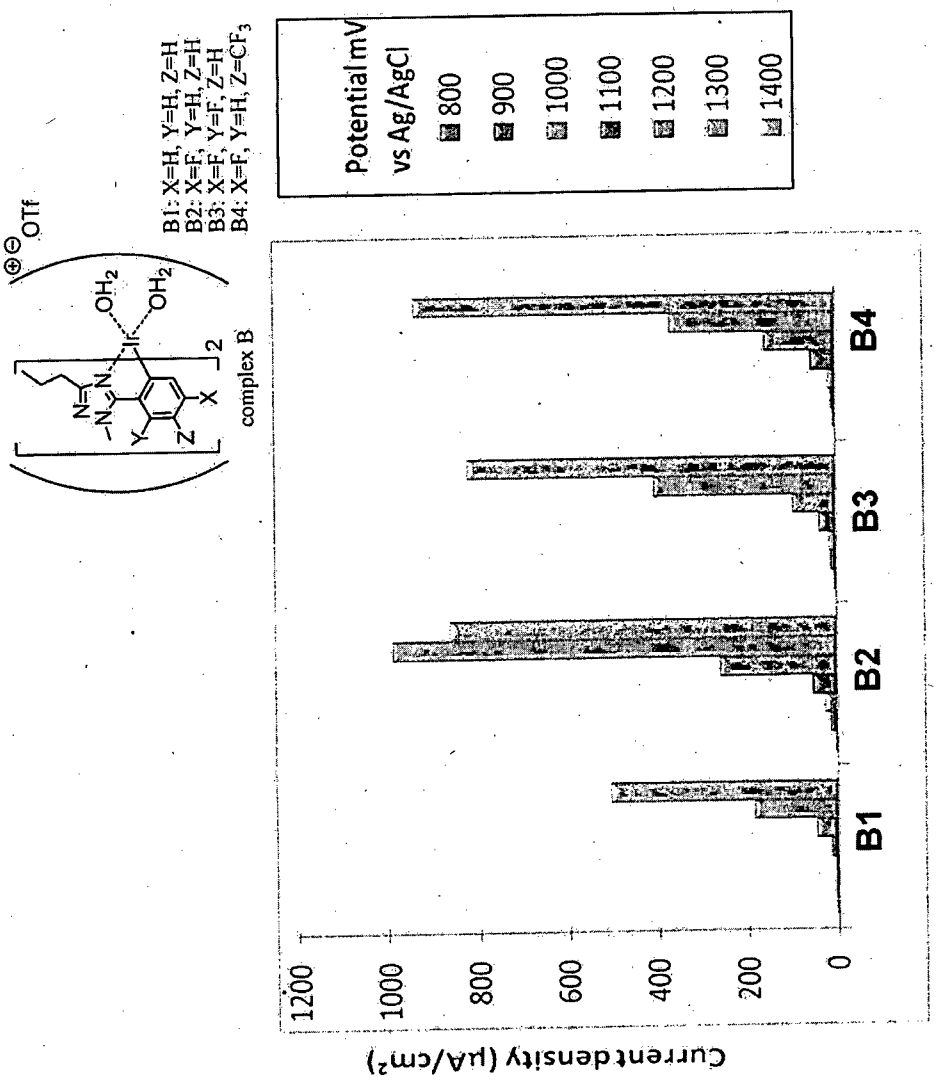

B1: X=H, Y=H, Z=H
B2: X=F, Y=H, Z=H
B3: X=F, Y=F, Z=H
B4: X=F, Y=H, Z=CF3
complex B
Potential mV vs Ag/AgCl
800
900
1000
1100
1200
1300
1400
Current density (μA/cm²)
0
200
400
600
800
1000
1200
B1
B2
B3
B4

FIGURE 10

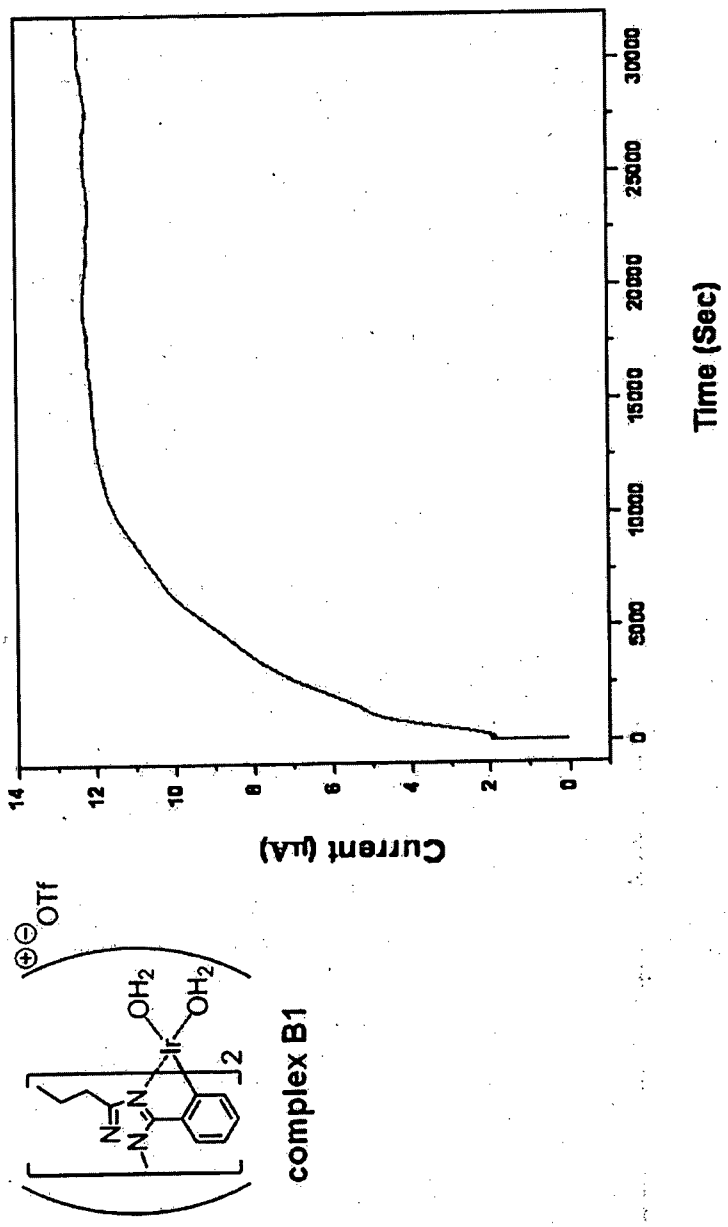
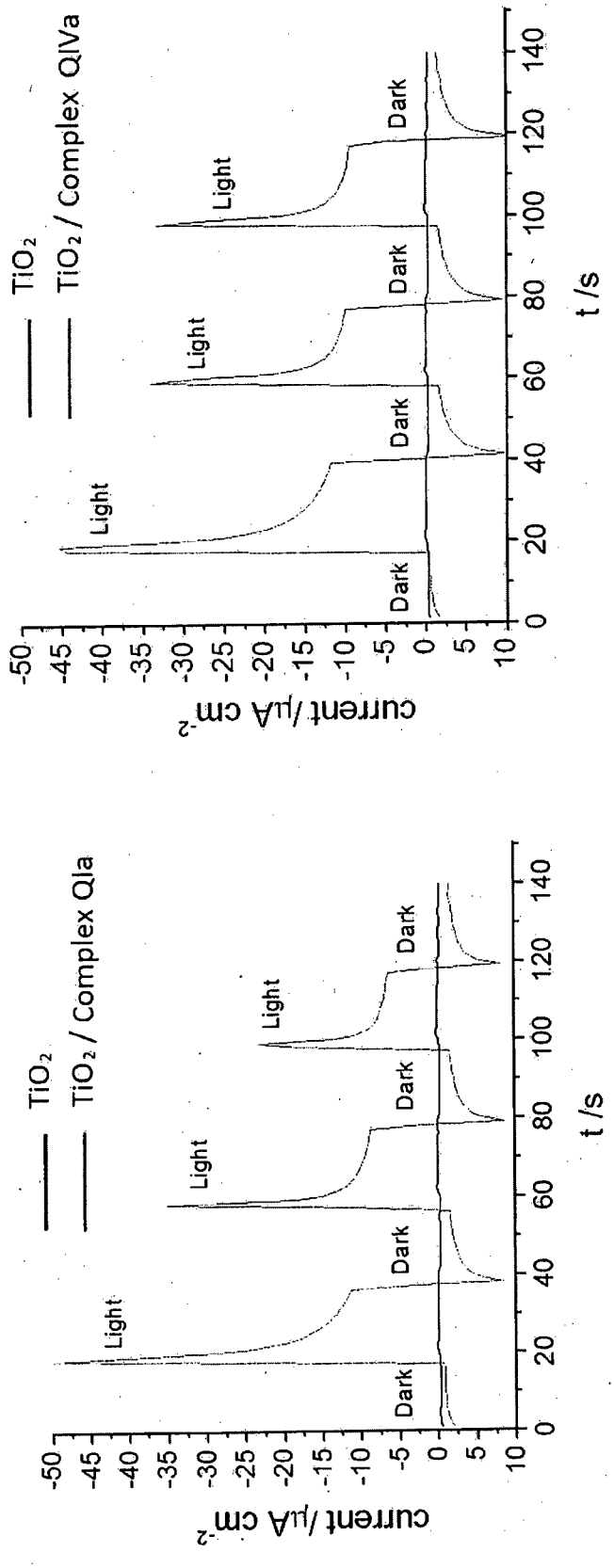

Current (μA)
Time (Sec)
0
2
4
6
8
10
12
14
0
5000
10000
15000
20000
25000
30000
OTf
OH2
OH2
Ir
N
N
2
complex B1

FIGURE 11


TiO2
TiO2 / Complex QIa
TiO2 / Complex QIVa
Light
Dark
current /μA cm-2
t /s

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2012/000277

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

B01J 23/46 (2006.01) ***C07D 241/12*** (2006.01) ***C07D 401/04*** (2006.01)
C07D 215/04 (2006.01) ***C07D 249/08*** (2006.01)

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)

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CAS ONLINE: File REGISTRY, AGRICOLA, ALUMINIUM, ANABSTR, APOLLIT, AQUALINE, BIOTECHNO, CABA, CAPLUS, CBNB, CEABA-VTB, CERAB, CIN, COMPENDEX, CONFSCI, COPPERLIT, CORROSION, DISSABS, ENCOMPLIT, ENCOMPLIT2, GENBANK, INSPEC, INSPHYS, IPA, KOSMET, METADEX, NAPRALERT, NTIS, PASCAL, RAPRA, RDISCLOSURE, SCISEARCH, TULSA, TULSA2, USAN, WATER, WELDASEARCH, WSCA. Structure search based on examples and keyword search (iridium, water, splitting etc.))

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/0223997 A1 (LUSSIER et al) 5 October 2006 Paragraphs [0002]-[0004] and [0050].	1-2, 6-7, 11, 17-19, 22, 24
X	US 2002/0190250 A1 (GRUSHIN et al) 19 December 2002 Abstract; structures IV, V, VI, IX and X; paragraph [0117].	1-2, 6-8, 10-11, 16-19, 22, 24

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

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"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

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Date of the actual completion of the international search	Date of mailing of the international search report
24 April 2012	26 April 2012

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MCDANIEL, N et al, "Cyclometalated Iridium (III) Aquo Complexes: Efficient and Tunable Catalysts for the Homogeneous Oxidation of Water." Journal of the American Chemical Society, 2008, 130(1), 210-217. Abstract; compounds 1-5; page 213, right hand column, second – fourth paragraphs; Figures 3 and 8.	1, 4, 6-20, 22 24-26
X	LO, S-C et al, "Blue Phosphorescence from Iridium (III) Complexes at Room Temperature." Chemistry of Materials, 18(21), 5119-5129. Abstract; compounds 10-14; Figure 1; Tables 1 and 2.	1, 6-7, 11, 17-19, 22-24
X	XU, ML et al, "Crystal Structure of Iridium (III) Bis(2-(*p*-biphenylyl)quinolyl-$N,C^{2'}$) acetylacetonate, $(bpq)_2Ir(acac)$." X-ray Structure Analysis Online, 2005, 21(11), x185-x186. Whole Document.	1-2, 6-7, 11, 17-19
X	PARK, G et al, "Efficient Red-Emitting Phosphorescent Iridium (III) Complexes of Flourinated 2,4-diphenylquinolines." Thin Solid Films, 2007, 515(12), 5090-5094. Abstract; compounds 1-3; figures 1(b), 2 and 3; Table 1; page 5092, right hand column – page 5093, left hand column, second paragraph.	1-2, 6-7, 11, 17-19, 22, 24
X	JIANG, H., "Organic Ambipolar Conjugated Molecules for Electronics: Synthesis and Structure-Property Relationships." Macromolecular Rapid Communications, 2010, 31(23), 2007-2034. Compounds 42-43 and 45-46.	1-2, 6-7, 11, 17-19, 22, 24
X	DRAGONETTI, C et al, "The Role of 5-R-1,10-phenanthroline (R = CH_3, NO_2) on the Emission Properties and Second-Order NLO Response of Cationic Ir (III) Organometallic Chromophores." Inorganica Chimica Acta, 2008, 361(14-15), 4070-4076. Compounds 1-4; Figure 2.	1-2, 6-7, 10-11, 17-19, 22, 24
X	HWANG D-H et al, "Synthesis of a New Plymeric Host Material for Efficient Organic Electro-phosphorescent Devices." Journal of Nanoscience and Nanotechnology, 2008, 8(9), 4649-4652. Abstract; Figure 2.	1-2, 6-7, 11, 17-19, 22, 24
X	LAMANSKY, S. et al, "Synthesis and Characterisation of Phosphorescent Cyclometalated Iridum Complexes." Inorganic Chemistry, 2001, 40(7), 1704-1711. Abstract; page 1705, right hand column, third paragraph – page 1706, left hand column, third paragraph; Figures 2 and 5.	1-2, 6-7, 11, 17-19, 22, 24

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2012/000277

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZHAO, Q. et al, "Highly Selective Phosphorescent Chemosensor for Fluoride Based on an Iridium (III) Complex Containing Arylborane Units." Inorganic Chemistry, 2008, 47(20), 9256-9264. Abstract; Scheme 1, Figure 2.	1-2, 6-7, 10-11, 17-19, 22, 24
X	LI, C et al, "Chlorido(pyridine-κN)bis[2-(quinolin-2-yl)phenyl-κ^2C^1,N]iridium(III) monohydrate." Acta Crystallographica Section E, 2008, E64(9), m1205. Whole document.	1-2, 6-7, 10, 17-19
X	JONES, P et al, "mer-[3-Phenyl-5-(2-pyridyl-κN)-1,2,4-triazol-1-ido-κN^1]bis(2-quinolylphenylκ^2C^1,N)iridium(III) deuterochloroform disolvate." Acta Crystallographica Section E, 2010, E66(11), m1408-m1409. Whole Document.	1-2, 6-7, 11, 17-19
X	LIU, H-W et al, "Cyclometalated Iridium (III) Bipyridine Complexes Functionalised With an N-Methylamino-oxy Group as Novel Phosphorescent Labelling Reagents for Reducing Sugars." Organometallics, 2010, 29(16), 3474-3476. Abstract; Compounds 1-3; Scheme 1, right hand column, page 3474 – right hand column, page 3475; Table 1.	1-2, 6-7, 10-14, 17-19, 22, 24
A	GALOPPINI et al, "Linkers for Anchoring Sensitizers to Semiconductor Particles." Coordination Chemistry Reviews, 2004, 248(13-14), 1283-1297. Figure 3; Tables 1, 2 and 4.	5, 15, 26
P,X	WO 2012/007103 A1 (MERK PATENT GMBH) 19 January 2012 Compounds of formulae 44-46 and 56-85.	1-2, 6-7, 11, 17-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/AU2012/000277

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	2006223997	US	7399857	US	2006224007		
US	2002190250	AU	71550/01	CA	2411624	CA	2455844
		CN	1449640	CN	1520702	EP	1295514
		EP	1424382	EP	1431288	EP	1431289
		EP	1466506	EP	2299785	EP	2306788
		EP	2306789	JP	2005516040	JP	2004503059
		JP	2007524239	US	6670645	US	2004108507
		US	6946688	US	2005165235	US	6979739
		US	2004106007	US	7075102	US	2004191959
		US	7078725	US	2004188673	US	7129518
		US	2004075096	US	7132681	US	2004116696
		US	7161172	US	2004094769	US	7199392
		US	2004089867	US	7276726	US	2005037233
		US	2007292713	US	7476452	US	2009206326
		US	7595501	US	7816016	US	2002121638
		US	2003197183	US	2005095457	WO	0202714
		WO	03063555	WO	2005075597		
WO	2012007103	DE	102010027218				

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX