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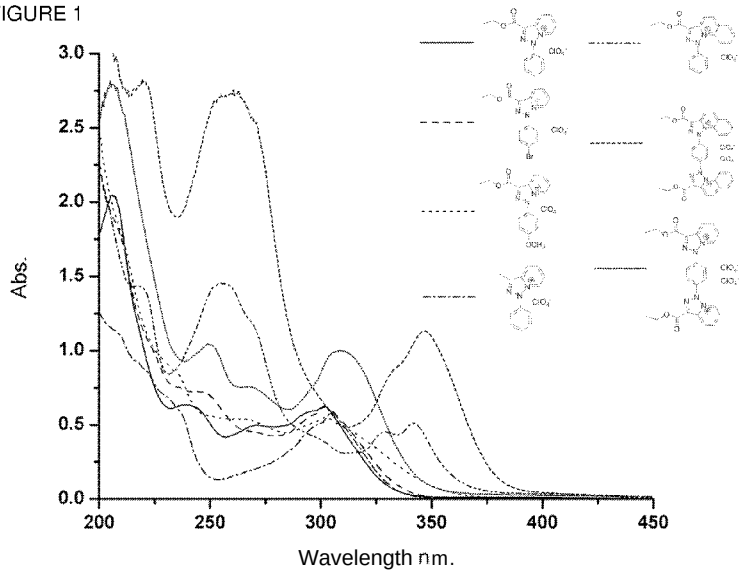
(54) Title: TRIAZOLIUM AND TETRAZOLIUM DERIVATIVES AS ORGANIC LIGHT EMITTERS

FIGURE 1



(57) Abstract: Provided herein are organic compounds useful in a variety of OLED applications.

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TRIAZOLIUM AND TETRAZOLIUM DERIVATIVES AS ORGANIC LIGHT EMITTERS

PRIORITY BENEFIT

This application claims the benefit of U.S. Provisional Application No. 61/570,398 filed on December 14, 2011, the contents of which are hereby incorporated herein in its entirety. The contents of any patents, patent application, and references cited throughout this specification are hereby incorporated by reference in their entireties.

BACKGROUND OF THE INVENTION

Organic light-emitting diodes (OLEDs) exploit the ability of particular materials to emit light when they are excited by means of an electric current. OLEDs have been actively researched because of their capability to emit bright light at a low driving voltage. An OLED generally comprises a light emitting layer (or a plurality of organic layers including a light emitting layer) in between a pair of opposing electrodes. With an electric field applied to the opposing electrodes, electrons and positive holes are injected into the light emitting layer, where they are recombined to form excitons, which emit light. The light emitted from the light emitting layer can be used, for example, to display an image in an electroluminescence device.

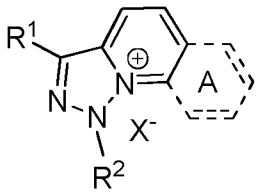
OLEDs that emit red, green, and blue light are employed to prepare a full-colored OLED display. Also, efficient white light producing OLED devices are considered to be useful in several applications, such as paper-thin light sources, backlights in LCD displays, automotive dome lights, and room lighting.

SUMMARY OF THE INVENTION

Provided herein are organic compounds that have been found to display electroluminescence in the visible region of the electromagnetic spectrum. Accordingly, these compounds are useful as emitter molecules for OLED applications. For example, these compounds can be used as host molecules in the emitter layer of an OLED. It is also possible to use these compounds in other layers of OLEDs, for example in the electron transport layer. The compounds can emit white, red, green, or blue light when excited. In one embodiment, these molecules emit white light when excited, thus making them useful for white OLED (WOLED) applications. In another embodiment, these compounds emit blue or green light when excited.

These compounds can be synthesized easily, and can therefore be produced on a large scale.

Accordingly, in one aspect, provided herein is an organic light-emitting diode (OLED) comprising at least one compound of the formula I:



(I)

wherein

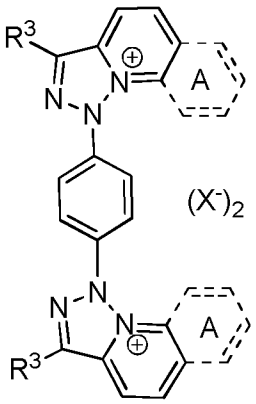
A is an optional fused phenyl ring;

R^1 is selected from the group consisting of H, $Ci-_6$alkyl, $C(0)Ci-_6$alkyl, CN, and $C(0)OCi-_6$alkyl;

R^2 is selected from the group consisting of CN, $N0_2$, Ci_{-6}alkyl and aryl, wherein the aryl is optionally independently substituted one or more times with halogen, Ci_{-6}alkyl or OCi_{-6}alkyl; and

X^- is an anion or a dianion.

In another aspect, provided herein is an organic light-emitting diode comprising at least one compound of the formula IIa:



(Ha)

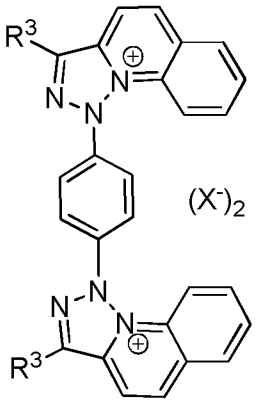
wherein

A is an optional fused phenyl ring;

R^3 is selected from the group consisting of H, $Ci-_6$alkyl, $C(0)Ci_{-6}$alkyl, CN, and $C(0)OCi-_6$alkyl; and

X^- is an anion or a dianion.

In another aspect, provided herein is an organic light-emitting diode comprising at least one compound of the formula II:



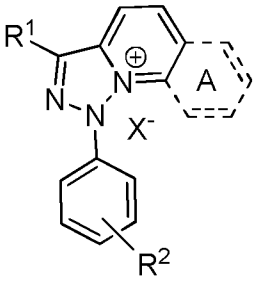
(II)

wherein

R^3 is selected from the group consisting of H, Ci_{-6}alkyl, $C(0)Ci_{-6}$alkyl, CN, and $C(0)OCi_{-6}$alkyl; and

X^- is an anion or a dianion.

In still another aspect, provided herein is a compound of the formula Γ:



(I')

wherein

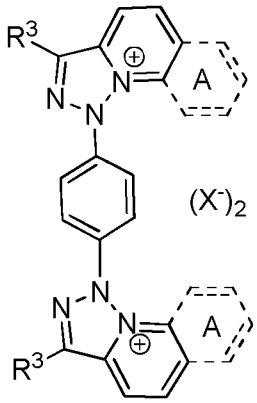
A is an optional fused phenyl ring;

R^1 is selected from the group consisting of H, $C(0)Ci_{-6}$alkyl, CN, and $C(0)OCi_{-6}$alkyl;

R^2 is selected from the group consisting of H, halogen, Ci_{-6}alkyl and OCi_{-6}alkyl; and

X^- is an anion or a dianion.

In another aspect, provided herein is a compound of the formula Ila':



(IIa')

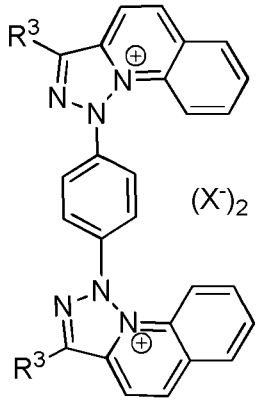
wherein

A is an optional fused phenyl ring;

R^3 is selected from the group consisting of H, C_{i-6}alkyl, C(O)C_{i-6}alkyl, CN, and C(0)OC_{i-6}alkyl; and

X^- is an anion or a dianion.

In another aspect, provided herein is a compound of the formula IT:



(II')

wherein

R^3 is selected from the group consisting of H, C_{i-6}alkyl, C(0)C_{i-6}alkyl, CN, and C(0)OC_{i-6}alkyl; and

X^- is an anion or a dianion.

DETAILED DESCRIPTION OF THE FIGURES

FIGURE 1 shows the UV/Vis spectra of some triazolium derivatives described herein (5×10^{-5} M, CH_3CN).

FIGURE 2 shows fluorescence emission spectra of some triazolium derivatives described herein (5 x 10^{-5}M, CH_3CN).

FIGURE 3 shows the ^{1}H NMR spectrum of **2a,** a salt of formula I, in CD_3CN at 294 K.

FIGURE 4 shows the ^{13}C NMR spectrum of **2a,** a salt of formula I, in CD_3CN at 294 K.

FIGURE 5 shows the ^{1}H NMR spectrum of precursor **1b** in $CDCl_3$ at 294 K in the presence of the minor Z isomer.

FIGURE 6 shows the ^{13}C NMR spectrum of precursor **1b** in $CDCl_3$ at 294 K in the presence of the minor Z isomer.

FIGURE 7 shows the ^{1}H NMR spectrum of **2b,** a salt of formula IIa', in CD_3CN at 294 K.

FIGURE 8 shows the ^{13}C NMR spectrum of **2b,** a salt of formula IIa', in CD_3CN at 294 K.

FIGURE 9 shows the ball and stick drawing of the crystal structure of **2a,** a salt of formula I. The hydrogen atoms and the counterion were omitted for clarity.

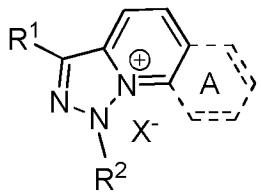
FIGURE 10 shows the UV/Vis absorption (5.0 x 10^{-5} M) and normalized emission spectra of **2a** and **2b** in H_20 .

DETAILED DESCRIPTION OF THE INVENTION

Triazolium and Tetrazolium Compounds

The organic compounds described herein are suitable for use in OLEDs. In particular, they can be used in the electron transport layer or in the light-emitting layer of an OLED. The compounds can be employed as emitter substances in OLEDs, as they display luminescence (electroluminescence) in the visible region of the electromagnetic spectrum. These compounds make it possible to display electroluminescence in the white, red, green and blue regions of the electromagnetic spectrum. It is also possible to display electroluminescence both in the blue region and in the white region of the electromagnetic spectrum.

Accordingly, in one aspect, provided herein is an organic light-emitting diode (OLED) comprising at least one compound of the formula I:



(I)

wherein

A is an optional fused phenyl ring;

R^1 is selected from the group consisting of H, Ci-$_6$alkyl, C(0)Ci$_{-6}$alkyl, CN, and C(0)OCi$_{-6}$alkyl;

R^2 is selected from the group consisting of CN, N0$_2$, Ci$_{-6}$alkyl and aryl, wherein the aryl is optionally independently substituted one or more times with halogen, Ci$_{-6}$alkyl or OCi-$_6$alkyl; and

X^- is an anion or a dianion.

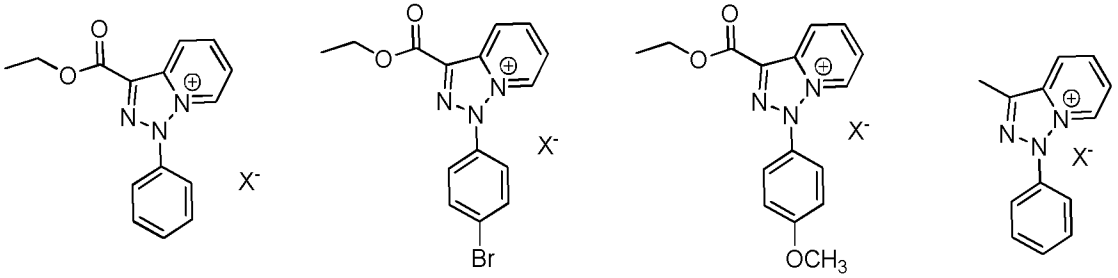
The anion can be a halide ion, a sulfate ion, a perchlorate ion, a hexafluorophosphate ion, or a borate ion *(e.g.* , a tetrafluoroborate ion).

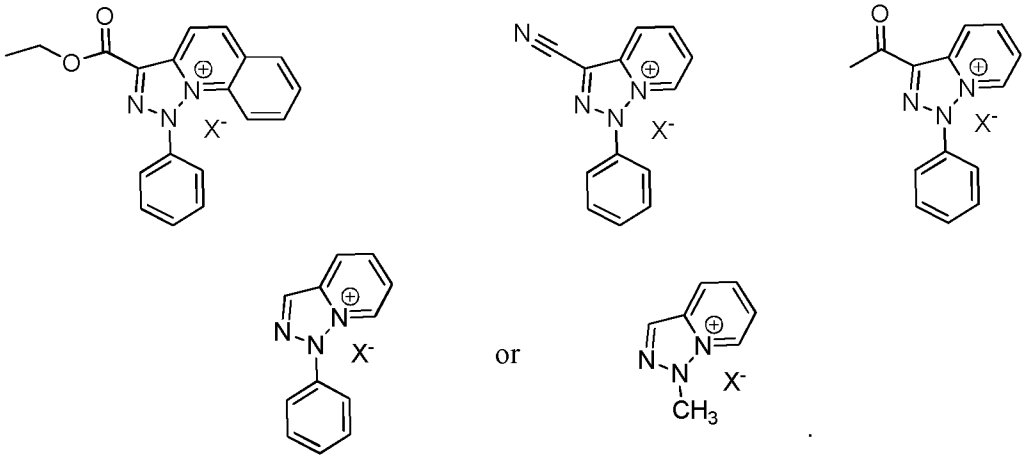
In one embodiment, R^1 is selected from the group consisting of C(0)Ci$_{-6}$alkyl, CN, and C(0)OCi-$_6$alkyl. In another embodiment, R^1 is selected from the group consisting of C(0)Ci$_{-3}$alkyl, CN, and C(0)OCi$_{-3}$alkyl.

In an embodiment, R^2 of formula I can be phenyl that is optionally independently substituted one or more times with halogen, Ci$_{-6}$alkyl or OCi$_{-6}$alkyl.

In one embodiment of formula I, A is not present.

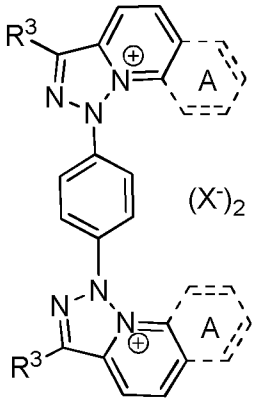
For the OLED described above, the compound of formula I can be in one or more of the following forms:





In one embodiment of these forms, X^- is perchlorate.

In another aspect, provided herein is an organic light-emitting diode comprising at least one compound of the formula Ila:



(Ha)

wherein

A is an optional fused phenyl ring;

R^3 is selected from the group consisting of H, C_{i-6}alkyl, C(0)C_{i-6}alkyl, CN, and C(0)OC_{i-6}alkyl; and

X^- is an anion or a dianion.

The anion can be a halide ion, a sulfate ion, a perchlorate ion, a hexafluorophosphate ion, or a borate ion *(e.g.* , a tetrafluoroborate ion).

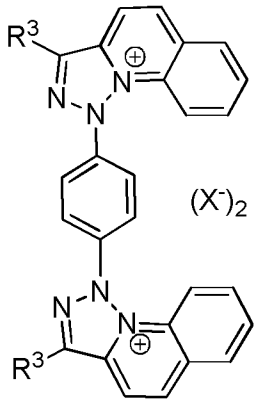
In an embodiment of Formula Ila,

A is not present;

R^3 is selected from the group consisting of H, Ci-$_6$alkyl, C(0)Ci-$_6$alkyl, CN, and C(0)OCialkyl or C(0)OC$_{3-6}$alkyl; and

X^- is an anion or a dianion.

In another aspect, provided herein is an organic light-emitting diode comprising at least one compound of the formula II:



(II)

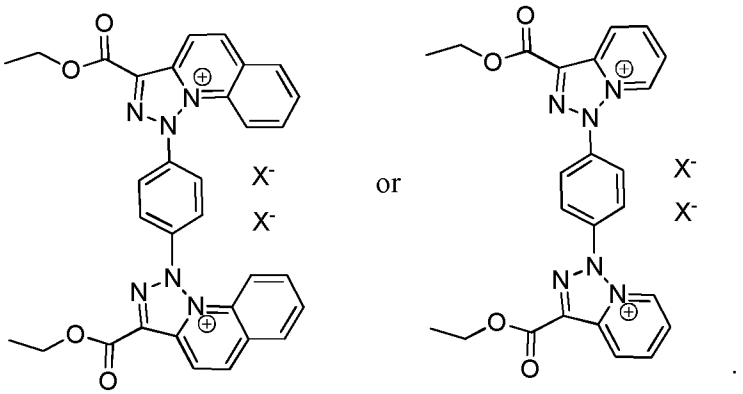
wherein

R^3 is selected from the group consisting of H, Ci-$_6$alkyl, C(0)Ci-$_6$alkyl, CN, and C(0)OCi$_{-6}$alkyl; and

X^- is an anion or a dianion.

The anion can be a halide ion, a sulfate ion, a perchlorate ion, a hexafluorophosphate ion, or a borate ion *(e.g.* , a tetrafluoroborate ion).

Compound Ila can be represented by one of the following compounds:

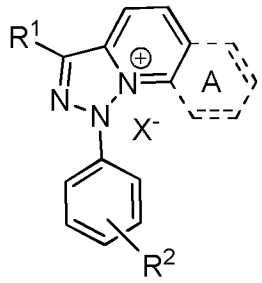


In an embodiment of these compounds, X^- is perchlorate.

In one embodiment of any of the OLEDs comprising a compound of formula I, formula Ila, or formula II, the compounds are used as emitter molecules. In another

embodiment, the compounds are used as host molecules in an emitter layer. In another embodiment, the compound of formula I, Ila, or II emits white, green, or blue light. In a particular embodiment, the compound of formula I, Ila, or II emits white or blue light. Accordingly, the compounds can be used in OLEDs that produce white, green, or blue light.

In another aspect, provided herein is a compound of the formula Γ:



(I')

wherein

A is an optional fused phenyl ring;

R^1 is selected from the group consisting of H, C(0)Ci-$_6$alkyl, CN, and C(0)OCi-$_6$alkyl;

R^2 is selected from the group consisting of H, halogen, Ci-$_6$alkyl and OCi$_{-6}$alkyl; and

X^- is an anion or a dianion.

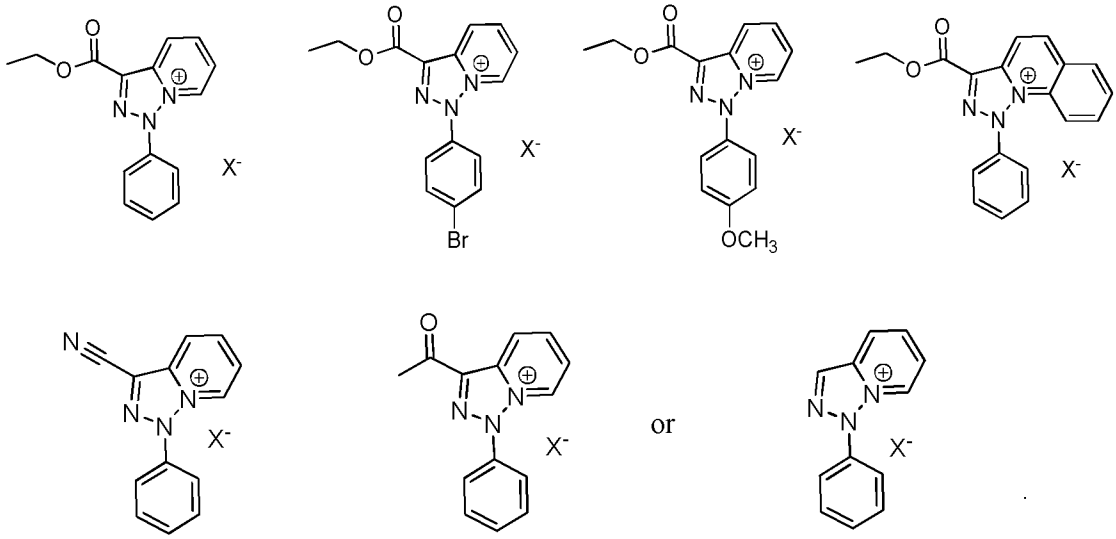
In an embodiment, the halide ion is a sulfate ion, a perchlorate ion, a hexafluorophosphate ion, or a borate ion *(e.g.* , a tetrafluoroborate ion).

In one embodiment of formula Γ, R^1 is selected from the group consisting of C(0)Ci$_-$ $_6$alkyl, CN, and C(0)OCi$_-$ $_6$alkyl. In still another embodiment, R^1 is selected from the group consisting of C(0)d$_-$ $_3$alkyl, CN, and C(0)OCi$_-$ $_3$alkyl.

In another embodiment of formula Γ, R^2 is selected from the group consisting of halogen, Ci-$_6$alkyl, and OCi-$_3$alkyl. In another embodiment, R^2 is in the para position.

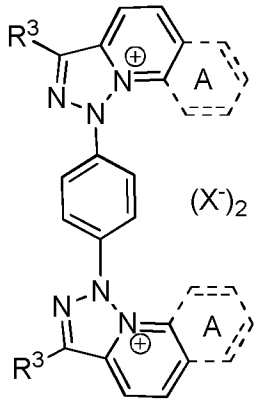
In another embodiment of Γ, A is not present.

Specific, non-limiting examples of compounds of formula Γ are shown below:



In a particular embodiment of these compounds, X^- is perchlorate.

In another aspect, provided here is a compound of claim Ila':



(IIa')

wherein

A is an optional fused phenyl ring;

R^3 is selected from the group consisting of H, C_{i-6}alkyl, $C(0)C_{i-6}$alkyl, CN, and $C(0)OC_{i-6}$alkyl; and

X^- is an anion or a dianion.

The anion can be a halide ion, a sulfate ion, a perchlorate ion, a hexafluorophosphate ion, or a borate ion *(e.g.* , a tetrafluoroborate ion).

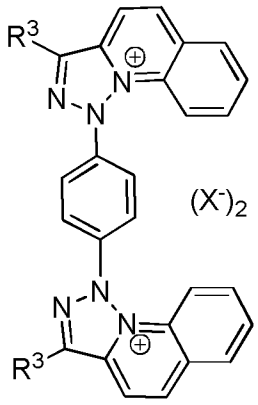
In an embodiment of Formula Ila',

A is not present;

R^3 is selected from the group consisting of H, Ci-$_6$alkyl, C(0)Ci-$_6$alkyl, CN, and C(0)OCialkyl or C(0)OC$_{3-6}$alkyl; and

X^- is an anion or a dianion.

In another aspect, provided here is a compound of claim IΓ:



(II ')

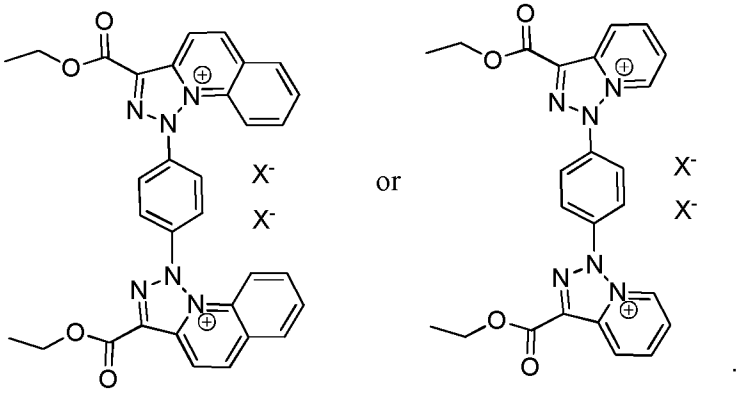
wherein

R^3 is selected from the group consisting of H, Ci-$_6$alkyl, C(0)Ci-$_6$alkyl, CN, and C(0)OCi-$_6$alkyl; and

X^- is an anion or a dianion.

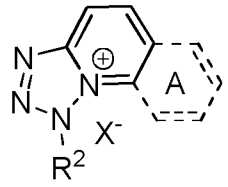
The anion can be a halide ion, a sulfate ion, a perchlorate ion, a hexafluorophosphate ion, or a borate ion *(e.g.* , a tetrafluoroborate ion).

In one embodiment, the compound of formula Ila' is one of the following compounds:



In one embodiment of these compounds, X^- is perchlorate.

In another aspect, provided herein is a compound of formula III:



(III)

wherein R^2, X^- and ring A have the meanings given for Formula I. Also provided herein is an OLED device comprising a compound of formula III.

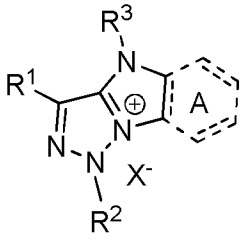
The anion of Formula III can be a halide ion, a sulfate ion, a perchlorate ion, a hexafluorophosphate ion, or a borate ion *(e.g.* , a tetrafluoroborate ion).

In one embodiment of Formula III, R^1 is selected from the group consisting of C(0)Ci- $_6$alkyl, CN, and C(0)OCi- $_6$alkyl. In another embodiment, R^1 is selected from the group consisting of C(0)d_ $_3$alkyl, CN, and C(0)OCi_ $_3$alkyl.

In an embodiment, R^2 of formula III can be phenyl that is optionally independently substituted one or more times with halogen, Ci_$_6$alkyl or OCi_$_6$alkyl.

In one embodiment of formula III, A is not present.

In another aspect, provided herein is a compound of formula IV:



(IV)

wherein R^1, R^2, X^- and ring A have the meanings given for formula I, and R^3 is H or Ci_$_6$alkyl. Also provided herein is an OLED device comprising a compound of formula IV.

The anion of formula IV can be a halide ion, a sulfate ion, a perchlorate ion, a hexafluorophosphate ion, or a borate ion *(e.g.* , a tetrafluoroborate ion).

In one embodiment, R^1 is selected from the group consisting of C(0)Ci_ $_6$alkyl, CN, and C(0)OCi_ $_6$alkyl. In another embodiment, R^1 is selected from the group consisting of C(0)d_ $_3$alkyl, CN, and C(0)OCi_ $_3$alkyl.

In an embodiment, R^2 of formula IV can be phenyl that is optionally independently substituted one or more times with halogen, Ci-$_6$alkyl or OCi-$_6$alkyl.

In another embodiment, R^3 is H or methyl.

In one embodiment of formula IV, A is not present.

As used herein, the term "anion" refers to any anion that is appropriate for use in an OLED. Non-limiting examples of such ions include, but are not limited to, Cl^-, Br^-, I^-, I_3^-, HSO_4^-, SO_4^{2-}, NO_3^-, ClO_4^-, BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, $FeCl_4^-$, $Fe(CN)_6^{3-}$, and anions of various sulfonic acids. In a particular embodiment, the anion is a halide ion, a sulfate ion, a perchlorate ion, a hexafluorophosphate ion, or a borate ion *(e.g.,* a tetrafluoroborate ion).

As used herein, the term "dianion" refers to any dianion that is appropriate for use in an OLED. When a dianion is used with compounds of formulae I, I', III or IV, there will be a 2 to 1 ratio of organic molecule to dianion.

As used herein, the term "alkyl" refers to a fully saturated branched or unbranched hydrocarbon moiety. Preferably the alkyl comprises 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, 1 to 10 carbon atoms, 1 to 7 carbon atoms, 1 to 6 carbons, 1 to 4 carbons, or 1 to 3 carbon atoms. Representative examples of alkyl include, but are not limited to, methyl, ethyl, n-propyl, *iso*-propyl, n-butyl, sec-butyl, *iso*-butyl, *tert*-butyl, n-pentyl, isopentyl, neopentyl, n-hexyl, 3-methylhexyl, 2,2-dimethylpentyl, 2,3-dimethylpentyl, n-heptyl, n-octyl, n-nonyl, n-decyl and the like. Furthermore, the expression "C_x-C_y-alkyl", wherein x is 1-5 and y is 2-10 indicates a particular alkyl group (straight- or branched-chain) of a particular range of carbons. For example, the expression Ci-C4-alkyl includes, but is not limited to, methyl, ethyl, propyl, butyl, isopropyl, tert-butyl and isobutyl.

The term "aryl" includes aromatic monocyclic or multicyclic *e.g.*, tricyclic, bicyclic, hydrocarbon ring systems consisting only of hydrogen and carbon and containing from six to nineteen carbon atoms, or six to ten carbon atoms, where the ring systems may be partially saturated. Aryl groups include, but are not limited to, groups such as phenyl, tolyl, xylyl, anthryl, naphthyl and phenanthryl. Aryl groups can also be fused or bridged with alicyclic or heterocyclic rings which are not aromatic so as to form a polycycle *(e.g.*, tetralin).

OLED Devices Comprising Triazolium and Tetrazolium Derivatives

Also provided herein are OLED devices comprising the compounds provided herein *(i.e.,* compounds of formula I, formula Ila, formula II, formula Ila', formula I', formula

formula III, and formula IV, as well as specific compounds disclosed herein). Essentially, OLEDs are made up of an anode, a hole transport layer, a light-emitting layer, an electron-transport layer, and a cathode. The compounds provided herein can be used as emitter molecules in the light-emitting layer. Also provided herein is a light-emitting layer comprising at least one of the compounds described herein. The further layers in the OLED can be made up of any material which is customarily used in such layers and is known to those skilled in the art. A person skilled in the art will be able to select the structure of the OLEDs in such a way that it is optimally matched to the organic compounds described herein as emitter substances.

The compounds provided herein can be present without further additives in the light-emitting layer. However, it is also possible for further compounds and/or compositions to be present in the light-emitting layer. For example, a fluorescent dye can be present in order to alter the emission color of the organic compound used as emitter molecule. Furthermore, a diluent material can be used. This diluent material can be a polymer, for example poly(N-vinylcarbazole) or polysilane. However, the diluent material can likewise be a small molecule, for example 4,4'-N,N'-dicarbazolebiphenyl (CBP) or tertiary aromatic amines.

The abovementioned individual layers of the OLED can in turn be made up of 2 or more layers. For example, the hole transport layer can be made up of a layer into which holes are injected from the electrode and a layer which transports the holes away from the hole injection layer to the light-emitting layer. The electron transport layer can likewise consist of a plurality of layers, for example a layer into which electrons are injected by the electrode and a layer which receives electrons from the electron injection layer and transports them to the light-emitting layer. These layers can be selected according to factors such as energy level, heat resistance and charge carrier mobility and also energy difference between the layers mentioned and the organic layers or the metal electrodes.

Provided below are brief descriptions of the anode, hole transport layer, light-emitting layer, and cathode components of and OLED. These descriptions are meant to be non-limiting.

The anode is an electrode which provides positive charge carriers. It can, for example, be made up of materials comprising a metal, a mixture of various metals, a metal alloy, a metal oxide or a mixture of various metal oxides. As an alternative, the

anode can be a conductive polymer. Suitable metals include the metals of groups lb, IVa, Va, and Via and the transition metals of group VIII of the periodic table of the elements. The anode can be made to be transparent to light by using mixed metal oxides of groups lib, Illb, and IVb, for example indium-tin oxide (ITO). It is also possible for the anode to comprise an organic material, for example polyaniline. At least one of the anode or cathode should be at least partially transparent to enable the light produced to be emitted.

Suitable materials for the hole transport layer of the OLEDs described herein are disclosed, for example, in Kirk-Othmer Encyclopedia of Chemical Technology, 4th edition, Vol. 18, pages 837 to 860, 1996, which is incorporated herein by reference. Both hole-transporting molecules and polymers can be used as the hole transport material. Non-limiting examples of hole-transporting polymers are selected from the group consisting of polyvinylcarbazoles, (phenylmethyl)polysilanes and polyanilines. It is likewise possible to obtain hole-transporting polymers by doping polymers such as polystyrene and polycarbonate with hole-transporting molecules.

Suitable electron-transporting materials for OLEDs described herein can include, for example, metals chelated with oxinoid compounds, *e.g.,* tris(8-quinolinolato)aluminum (Alq_3), compounds based on phenanthroline, *e.g.,* 2,9-dimethyl-4,7-diphenyl-l,10-phenanthro line (DDPA) or 4,7-diphenyl-l,10-phenanthroline (DPA), and azole compounds such as 2-(4-biphenylyl)-5-(4-t-butylphenyl)-l,3,4-oxadiazole (PBD) and 3-(4-biphenylyl)-4-phenyl-5-(4-t-butylphenyl)-l,2,4-triazole (TAZ). The electron-transporting layer can serve either to aid electron transport or as a buffer layer or barrier layer to avoid quenching of the exciton at the boundaries of the layers of the OLED. The layer preferably improves the mobility of the electrons and reduces quenching of the exciton.

The cathode is an electrode that serves to introduce electrons or negative charge carriers. The cathode can be any metal or nonmetal that has a lower work function than the anode. Suitable materials for the cathode are selected from the group consisting of alkali metals of group la, for example Li, Cs, alkaline earth metals of group Ila, metals of group lib of the periodic table of the Elements including the rare earth metals and the lanthanides and actinides. Metals such as aluminum, indium, calcium, barium, samarium and magnesium and combinations thereof can also be used. Furthermore, lithium-containing organometallic compounds or LiF can also be applied between the organic layer and the cathode to reduce the operating voltage.

The OLEDs comprising the compounds provided herein can further comprise additional layers that are known to those skilled in the art. For example, a further layer can be applied between the hole transport layer and the light-emitting layer in order to aid transport of the positive charge and/or to match the band gap of the layers to one another. As an alternative, this further layer can serve as protective layer. In an analogous way, additional layers can be present between the light-emitting layer and the electron-transport layer to aid transport of the negative charge and/or to match the band gap between the layers to one another. As an alternative, this layer can serve as protective layer.

The OLED comprising the compounds described herein can be produced by well-known methods. The OLED is generally prepared by successive vapor deposition of the individual layers on a suitable substrate. Suitable substrates are, for example, glass or polymer films. The vapor deposition can be carried out using customary techniques such as thermal vaporization, chemical vapor deposition and others. In an alternative process, the organic layers can be applied from solutions or dispersions in suitable solvents, with coating techniques known to those skilled in the art being employed.

The OLEDs comprising the compounds described herein can be used in all devices in which electroluminescence is useful. Examples of such devices include stationary and mobile video display units (VDUs). Stationary VDUs are, for example, VDUs of computers, televisions, VDUs in printers, kitchen appliances and advertising signs, lighting and information signs. Mobile VDUs are, for example, VDUs in mobile telephones, laptops, vehicles and destination displays on buses and trains.

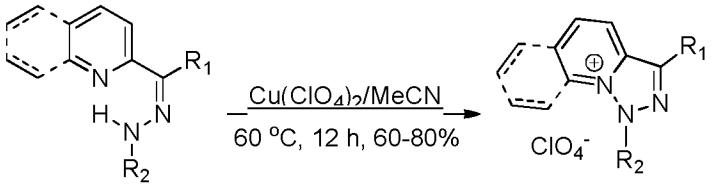
The compounds provided herein also have utility in light emitting electrochemical cells. Accordingly, in one embodiment, provided herein is a light emitting electrochemical cell comprising a compound provided herein.

The compounds provided herein also have utility as an organic semiconductor in optical electronic devices, more typically used as organic field effect transistors (OFET) in integrated electronic devices, such as liquid crystal display (LCD), electronic paper, organic light emitting diode (OLED) display panel, organic radio frequency identification (ORFID) tags, organic photovoltaic (OPV), sensor devices, and analog and digital electronics.

As discussed above, the disclosed compounds also emit white light when excited, which makes them useful for white OLEDs. White OLED emission can be used to prepare a full-color device using red, green, and blue (RGB) color filters. The RGB filters may be deposited on the substrate (when light transmission is through the substrate), incorporated into the substrate, or deposited over the top electrode (when light transmission is through the top electrode). When depositing a RGB filter array over the top electrode, a buffer layer of appropriate thickness, for example from 1 to 1000 nm, may be used to protect the top electrode. The buffer layer may comprise inorganic materials, for example, silicon oxides and nitrides, or organic materials, for example, polymers, or multiple layers of inorganic and organic materials. Methods for providing RGB filter arrays are well known in the art. Lithographic means, inkjet printing, and laser thermal transfer are just a few of the methods RGB filters may be provided.

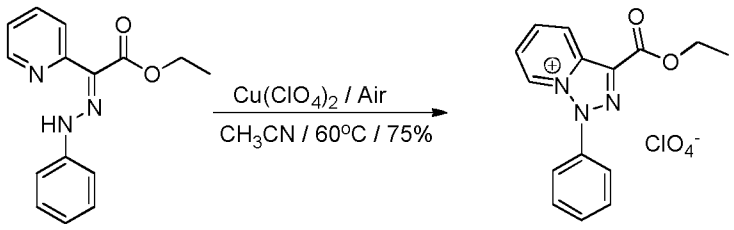
Experimental

General Synthesis of 1,2,3-Triazolium and Tetrazolium Derivatives of Formulae I, I', Ila, II, II a', and II' Formed *via* Cu(II) Oxidative Cyclization of Hydrazones



Scheme 1. Syntheses of derivatives via **Cu(II)** oxidative cyclization of hydrazones.

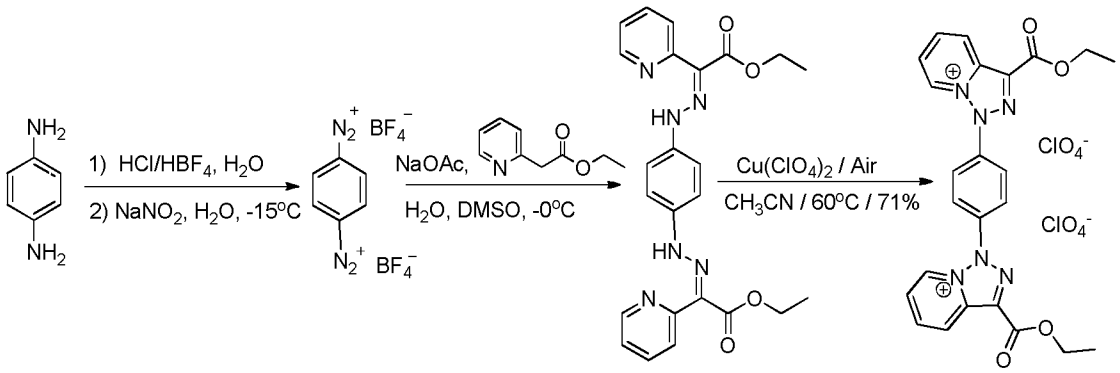
General Procedures: 1 mmol of the appropriate hydrazone starting material was dissolved in 5 mL acetonitrile, and the well stirred solution was heated to 60 °C. Copper**(II)** perchlorate hexahydrate ($Cu(C10_4)_2$-$6H_20$) (4 mmol; 4 equiv) was then added to the solution. The reaction mixture was kept at 60 °C overnight. The reaction mixture was then filtered, and 30 mL 5% (wt.) perchloric acid ($HC10_4$) solution was added to the filtrate. The formed precipitate was collected by filtration and subjected to recrystallization from acetonitrile and 5% (wt.) perchloric acid ($HC10_4$) solution. Yields 60-80%.



l a **2a**

Scheme 2. Synthesis of **2a,** a [l,2,3]triazolo[l,5-a]pyridinium salt of formula Γ.

Procedure for 2a: Compound l a was synthesized according to a literature procedure. [1] Compound **l a** was dissolved in 5 mL of acetonitrile (CH_3CN) and the well-stirred solution was heated to 60°C. Copper(II) perchlorate hexahydrate ($Cu(C10_4)_2$-$6H_20$) (0.741 g, 0.002 mol; 2 equiv.) was then added to the solution. The reaction mixture was kept at 60°C overnight. The reaction mixture was then filtered, and 30 mL 5% (wt.) perchloric acid ($HC10_4$) solution was added to the filtrate. The precipitate was collected by filtration and subjected to recrystallization from acetonitrile and 5% (wt.) $HC10_4$ solution. The final product **2a** was obtained as a light yellow powder (0.276 g, 75%); m.p.: decomposes > 220°C; ^{1}H NMR (500 MHz, CD3CN) δ 8.98 (dd, *J* = 7.1, 0.5 Hz, HI), 8.81 (dd, *J* = 8.8, 1.1 Hz, H4), 8.36 (dd, *J* = 8.3, 7.7 Hz, H2), 8.02 - 7.94 (m, H3), 7.90 (tdd, *J* = 10.4, 5.1, 2.9 Hz, H7), 7.87 - 7.80 (m, H5, H6), 4.61 (q, *J* = 7.1 Hz, -CH_2-), 1.49 (t, *J* = 7.1 Hz, -CH_3) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ 159.06, 137.92, 136.69, 134.61, 134.31, 134.28, 133.48, 132.14, 127.96, 125.59, 125.22, 122.43, 110.60, 64.26, 14.33 ppm. MS (ESI): *m/z* found [M^+] for $C_{15}H_{14}N_30_2^+$ 268.2 (calcd. 268.3).



l b **2b**

Scheme 3. Synthesis of **2b,** a [l,2,3]triazolo[l,5-a]pyridinium salt of formula Ila'.

Procedure for lb: The diazotiation procedure of 1,4-phenylenediamine was modified from a previsouly reported method.[2] 1,4-phenylenediamine (0.54 g, 0.005 mol) was suspended in 2.5 concentrated hydrochloric acid (HCl) and was cooled to 15°C using a dry ice/benzyl alcohol bath. A solution of 4 mL concentrated HCl and 4 mL 40% fluoroboric acid (HBF_4) was precooled to 15 °C and added dropwise to the suspension. After 15 min, a cold solution (2 mL) of sodium nitrite (NaN02 , 1.38 g, 0.02mol; 4 equiv.) was added dropwise to the suspension. After stirring for 1 h, the diazonium salt was collected by filtration. After washing with a small amount of water, the diazonium salt was added in small portions to a suspension of ethyl-2-pyridylacetate (1.5 mL, 0.01 mol; 2 equiv.) and sodium acetate (5.01 g, 0.032 mol; 6.4 equiv.) in an ice bath-cooled solution of 9 mL dimethyl sulfoxide (DMSO) and 15 mL water. The reaction mixture was stirred overnight, during which the product precipitated out. The precipitate was collected by filtration, re-dissolved in methylene chloride (CH_2CI_2), washed twice with 30 mL saturated potassium bicarbonate (K_2CO_3) solution and dried over magnesium sulfate ($MgS0_4$). The crude product was then subjected to silica gel column chromatography (ethyl acetate/hexane 1:5) to give **l b** as a dark yellow powder (2.20 g, 88%) m.p. 155.1 - 155.5 °C; H NMR (300MHz, $CDC1_3$) δ 14.98 (s, N-H), 8.71 - 8.60 (m, HI), 8.28 (d, J = 8.4 Hz, H4), 7.85 - 7.76 (m, H3), 7.39 (s, H5), 7.31 - 7.21 (2m, H2), 4.38 (q, J = 7.1 Hz, $-CH_2-$), 1.45 (t, J = 7.1 Hz, $-CH_3$) ppm; 13C NMR (75 MHz, CDCI3) δ 165.92, 153.11, 146.39, 139.24, 136.85, 124.78, 124.32, 122.15, 116.13, 61.08, 14.58 ppm. MS (EI): *m/z* found $[M^+]$ for $C_{24}H_{24}N_60_4^+$ 460 (calcd. 460).

The ^{1}H NMR spectrum of **2a,** a salt of formula Γ, shows that all aromatic signals are shifted downfield relative to the parent hydrazone, which is consistent with the development of a positive charge in the pyridyl ring.[1] This effect is more pronounced in **2b,** the salt of formula Ila', where the phenyl proton signal is shifted downfield to 8.33 ppm as opposed to 7.38 ppm in **lb.** Moreover, the spectrum does not contain the hydrazone N-H proton, which is an indication that the oxidative cyclization has taken place.

The crystal structure of **2a,** a salt of formula Γ (Figure 9) confirms the formation of the triazolopyridinium ring. The newly formed ring system is perfectly planar, and the distance between N2 and N3 is 1.364(2) Å, which is slightly longer than that in the neutral triazolopyridine (1.351(4)Å).[3] The Cl-Nl bond length is 1.324(2) Å, which is

longer than in hydrazone **l a** (1.305(2) Å), but still within the C=N double bond range. The phenyl substituent at position 2 is not coplanar with the triazolopyridinium ring, and the dihedral angle between them is 63.40(5)°. This is in sharp contrast with the coplanar hydrazone **la,** [1] or 2-substituted [l,2,3]triazoles, [4] in which the aryl substituents are usually coplanar or have very small dihedral angles with the triazole cores. Since no significant intermolecular interactions were observed in the extended structure, the large dihedral angle can be attributed to the electronic structure in N2.

X-ray crystal data were collected using a Bruker CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. Data were measured using w and f scans of 0.5° per frame for 30 s. The total number of images was based on results from the program COSMO[5] where redundancy was expected to be 4.0 and completeness of 100% out to 0.83 Å. Cell parameters were retrieved using APEX II software[6] and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software[7] which corrects for Lp. Scaling and absorption corrections were applied using SADABS[8] multi-scan technique, supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97 program and refined by least squares method on F2 , SHELXL-97, which are incorporated in SHELXTL-PC V 6.10.[9] All non-hydrogen atoms are refined anisotropically. All hydrogens were calculated by geometrical methods and refined as a riding model.

Table 1: Crystal Data and Parameters for **2a,** a salt of formula Γ.

CCDC No.	887676
Empirical formula	$C_{15}H_{14}C1N_3O_6$
Formula weight	367.74
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*Fix I n*
Unit cell dimensions	a = 13.7923(7) Å
	a = 90°

	b = 5.9508(3) Å
	β = 100.5400(10)°
	c = 19.9335(11) Å
	7 = 90°
Volume	1608.44(15) Å3
Z	4
Density (calcd.)	1.519 Mg-m-3
Absorption coefficient	0.277 mm-1
F_{ooo}	760
Crystal size	0.49x0.33x0.04 mm3
Θrange for data collection	1.66 to 25.39°
Index ranges	-16 ≤ h ≤ 16
	-7 ≤ k ≤ 7
	-24 ≤ 1≤ 24
Reflections collected	24909
Independent reflections	2947 [R_{mt} = 0.0287]
Completeness to Θ= 25.36°	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9896 and 0.8758
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2947 / 0 / 254
Goodness-of-fit on F^2	1.047
Final *R* indices [I > 2σ(Γ)]	« 1 = 0.0401, ωR2 = 0.1110
R indices (all data)	Rl = 0.0468, wR2 = 0.1178
Largest diff. peak and hole	0.422 and -0.332 e·Å-3

Both **2a** and **2b** have good solubility in water and polar organic solvents, such as acetone, CH_3CN and EtOH. The UV/Vis spectra of **2a** and **2b** in H_20 (Figure 10) show absorption maxima (λ_{max}) around 300 nm, and no appreciable solvatochromism is observed for both compounds. It is noteworthy that the extinction coefficient of **2b** at λ_{max} is nearly the double of that of **2a.** Considering the fact that the triazolopyridinium ring is

not in conjugation with the phenyl ring, the increase in extinction coefficient in **2b** most probably results from the contribution of the additional triazolopyridinium unit. The H_20 solution of **2a** emits green-blue light upon exicitation at 300 nm with a quantum yield of 0.05+0.02, whereas **2b** emits deep blue light with a much higher quantum yield (0.30+0.02). The more than eight fold enhancement in quantum yield from **2b** to **2a** is much more significant than the increase in extinction coefficient. On one hand, **2b** has one additional fluorophore than **2a.** On the other hand, since the non-conjugated phenyl ring is able to quench fluorescence *via* electron transfer, [10] the introduction of a second electron-withdrawing triazolopyridinium unit in **2b** can help reduce its quenching effect leading to the increase in quantum yield. For comparison, the photopysical properties of **2a** and **2b** were also studied in CH_3CN, and it was found that these properties are almost identical to those in H_20 .

Table *2*. A summary of photophysical properties of 1 and **2** is CH_3CN solution[a]

	Abs. λ_{max} (ε)	PL λ_{em} (Φ^b)	Stokes shift	FWHM
2a	302 (11100)	469 (0,05)	167/11790	131/6008
2b	311 (22100)	412 (030)	101/7882	94/5097

[a] Abs, λ_{max} and PL, λ_{em} are reported in nm, and the extinction coefficient ε is calculated in $L\text{-}mol^{-1}\text{-}cm^{-1}$. Stokes shift and FWHM are reported in both nm and cm^{-1}; [b] ±0.02.

The emission spectra of **2a** and **2b** reveal several interesting photophysical properties (Table 2). Both compounds have very broad emission profiles, spanning over the visible range, especially **2a** that spans from 370 to over 600 nm. Furthermore, the full widths at half maximum (FWHM) for both compounds are as large as 100 nm. Both **2a** and **2b** exhibit mega Stokes shifts (above 100 nm), which is not a common phenomenon for simple organic dyes. [11] As mentioned before, this property is important for preventing self-quenching and light scattering. The CIE (Commission Internationale de l'eclairage) 1931 color space chromaticity diagram was used to determine the color of the emissions, and the results show that from **2a** to **2b,** the color goes from green-blue (0.153, 0.187) to deep blue (0.154, 0.090), demonstrating the color tunability of the triazolopyridinium compounds.

Time-dependent density functional theory (TDDFT) calculations were performed on models of **2a** and **2b** to elucidate the quantum mechanical origins of the

triazolopyridinium UV/Vis and fluorescence spectra. The computations utilized the PBE density functional,[12] a triple-zeta basis set,[13] and the COSMO continuum solvation model as implemented within ORCA 2.9.1.[14] Based upon the TDDFT results, the electronic transition responsible for the prominent UV/Vis transitions near 380 nm can be described as HOMO → LUMO transitions (The experimental and calculated excitation wavelengths are different because of limitations in the TDDFT formalism). Consistent with the experiment, TDDFT predicts that extinction coefficient for **2b** is approximately triple that of **2a.** Inspection of the MOs involved in this transition provides an explanation for the relative intensities of this band in **2a** and **2b.** In both cases, the HOMO is antibonding with respect to the triazolopyridinium-phenyl bond. For **2a,** the LUMO is a triazolopyridinium-based mixture of triazolopyridinium and phenyl π-orbitals, whereas the LUMO is a phenyl-based mixture of the same two orbitals in **2b.** Consequently, there is better orbital overlap of the HOMO and LUMO in **2b** compared to **2a,** resulting in a more intense UV/Vis transition.

The TDDFT calculations also clarify the origin of the broad bandshapes in the UV/Vis and fluorescence spectra of **2a** and **2b.** A TDDFT difference density difference plot shows that the UV/Vis transition has significant charge transfer character with electron density being donated by the phenyl substituent to the triazolopyridinium unit. In contrast, the altered LUMO in **2b** means that the UV/Vis transition may be described as $\pi \rightarrow \pi^*$. Consequently, significant differences are expected between the triazolopyridinium and phenyl π-bond strengths in the ground and excited electronic states, especially for the charge transfer transition of **2a.**

Two [l,2,3]triazolo[l,5-fl]pyridinium salts were synthesized from 2-pyridylphenylhydrazones *via* a novel Cu(II)-mediated oxidative ring closure reaction. The synthesized mono- **(2a)** and bis- **(2b)** triazolopyridiums are water soluble, show blue fluorescence, possess broad emission profiles and exhibit mega-Stokes shifts. Since the positive charge center of the triazolopyridinium ring can be susceptible to nucleophilic attack,[15'16] these compounds can be promising in terms of anion sensing.

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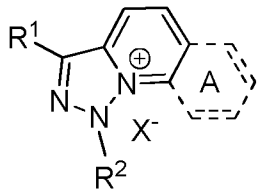
CLAIMS

1. An organic light-emitting diode (OLED) comprising at least one compound of the formula I:



(I)

wherein

A is an optional fused phenyl ring;

R^1 is selected from the group consisting of **H,** $Ci-_6$alkyl, $C(0)Ci-_6$alkyl, CN, and $C(0)OCi-_6$alkyl;

R^2 is selected from the group consisting of CN, $N0_2$, Ci_{-6}alkyl and aryl, wherein the aryl is optionally independently substituted one or more times with halogen, Ci_{-6}alkyl or OCi_{-6}alkyl; and

X^- is an anion or a dianion.

2. The OLED of claim 1, wherein the anion is a halide ion, a sulfate ion, a tetrafluoroborate ion, a perchlorate ion, a hexafluorophosphate ion, or a borate ion.

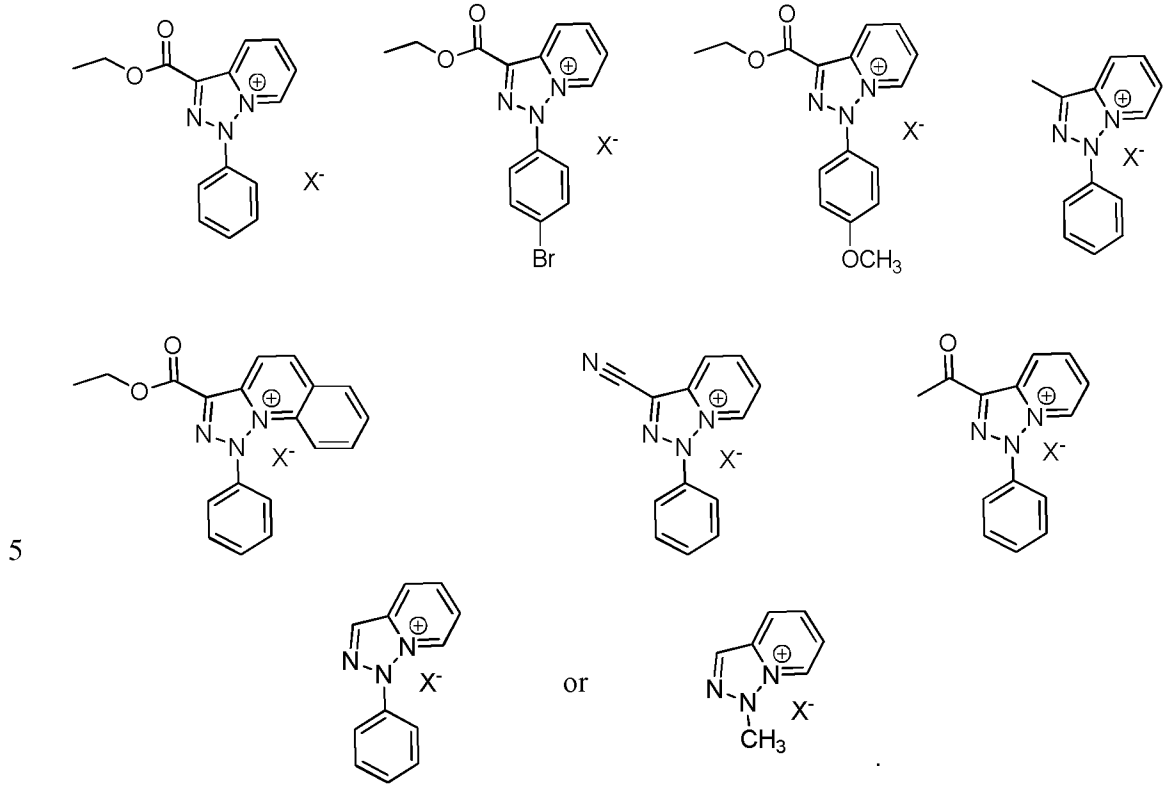
3. The OLED of any one of claims 1-2, wherein **R^1** is selected from the group consisting of $C(0)Ci-_6$alkyl, CN, and $C(0)OCi-_6$alkyl.

4. The OLED of any one of claims 1-3, wherein **R^1** is selected from the group consisting of $C(0)d_{-3}$alkyl, CN, and $C(0)OCi_{-3}$alkyl.

5. The OLED of any one of claims 1-4, wherein **R^2** is phenyl and is optionally independently substituted one or more times with halogen, $Ci-_6$alkyl or $OCi-_6$alkyl.

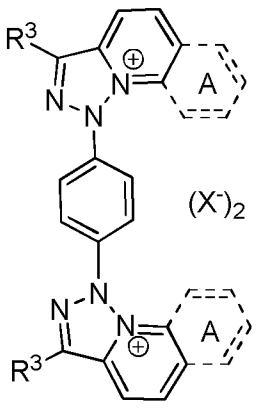
6. The OLED of any one of claims 1-5, wherein A is not present.

7. The OLED of any one of claims 1-6, wherein the compound of formula I is one of the following compounds:



8. The OLED of claim 7, wherein X^- is perchlorate.

9. An organic light-emitting diode comprising at least one compound of the formula IIa:



(Ha)

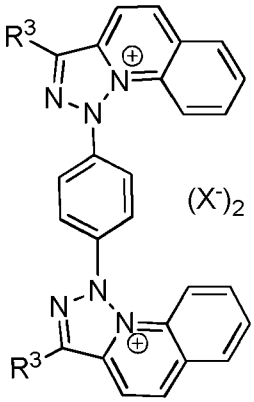
wherein

A is an optional fused phenyl ring;

R^3 is selected from the group consisting of H, Ci_{-6}alkyl, C(0)Ci-$_6$alkyl, CN, and C(0)OCi_{-6}alkyl; and

X^- is an anion or a dianion.

10. An organic light-emitting diode comprising at least one compound of the formula II:



(II)

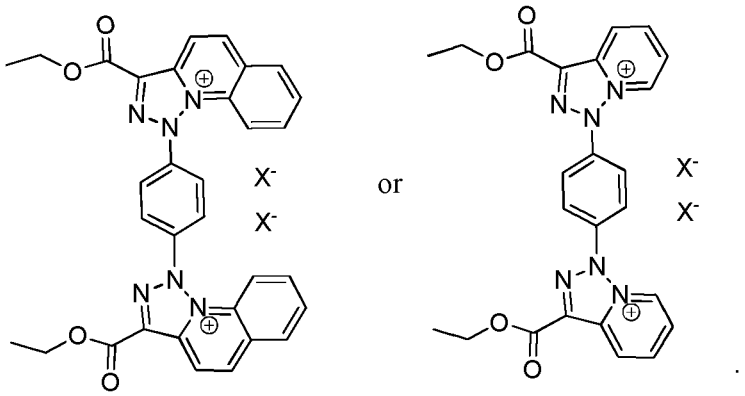
wherein

R^3 is selected from the group consisting of H, Ci^alkyl, C(0)Ci_{-6}alkyl, CN, and C(0)OCi-$_6$alkyl; and

X^- is an anion or a dianion.

11. The OLED of any one of claims 9 or 10, wherein the anion is a halide ion, a sulfate ion, a tetrafluoroborate ion, a perchlorate ion, a hexafluorophosphate ion, or a borate ion.

12. The OLED of any one of claims 9-11, wherein the compound of formula II or Ila is one of the following compounds:



13. The OLED of claim 12, wherein X^- is perchlorate.

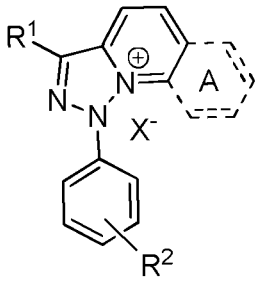
14. The OLED of any of claims 1-13, wherein the compounds are used as emitter molecules.

15. The OLED of any of claims 1-13, wherein the compounds are used as host molecules in an emitter layer.

16. The OLED of any of claims 1-13, wherein the compound emits white, green, or blue light.

17. The OLED of any of claims 1-13, wherein the OLED produces white, green, or blue light.

18. A compound of the formula I':



(I')

wherein

A is an optional fused phenyl ring;

R^1 is selected from the group consisting of H, C(0)Ci-$_6$alkyl, CN, and C(0)OCi-$_6$alkyl;

R^2 is selected from the group consisting of H, halogen, Ci-$_6$alkyl and OCi-$_6$alkyl; and

X^- is an anion or a dianion.

19. The compound of claim 18, wherein the anion is a halide ion, a sulfate ion, a tetrafluoroborate ion, a perchlorate ion, a hexafluorophosphate ion, or a borate ion.

20. The compound of any one of claims 18-19, wherein R^1 is selected from the group consisting of C(0)Ci-$_6$alkyl, CN, and C(0)OCi-$_6$alkyl.

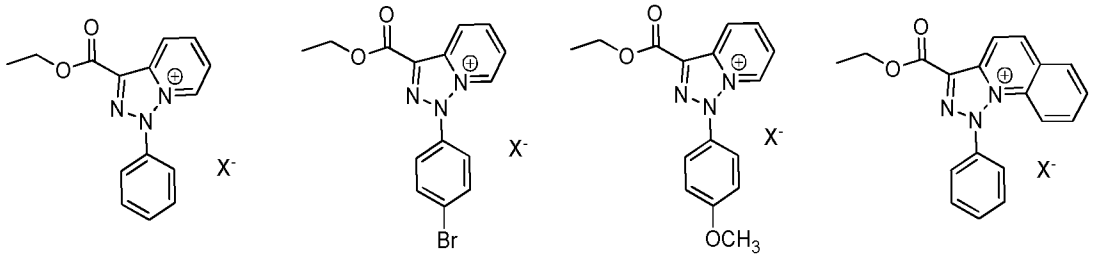
21. The compound of any one of claims 18-19, wherein R^1 is selected from the group consisting of C(0)Ci-$_3$alkyl, CN, and C(0)OCi-$_3$alkyl.

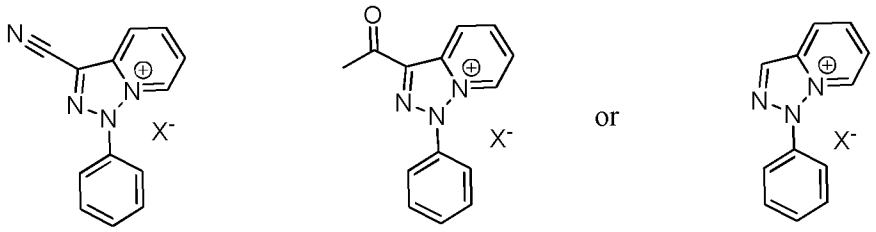
22. The compound of any one of claims 18-21, wherein R^2 is selected from the group consisting of halogen, Ci-$_6$alkyl, and OCi-$_6$alkyl.

23. The compound of any one of claims 18-22, wherein R^2 is in the para position.

24. The compound of any one of claims 18-22, wherein A is not present.

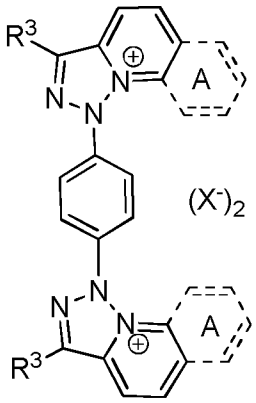
25. The compound of any one of claims 18-24, wherein the compound of formula I is





26. The compound of claim 25, wherein X^- is perchlorate.

27. A compound of formula Ila':



(Ha ')

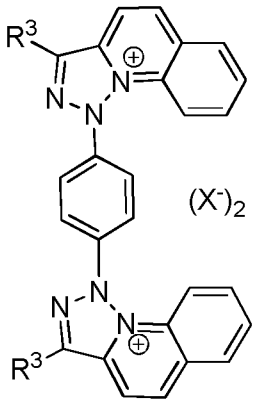
wherein

A is an optional fused phenyl ring;

R^3 is selected from the group consisting of H, Ci-6alkyl, C(0)Ci-6alkyl, CN, and C(0)OCi-$_6$alkyl; and

X^- is an anion or a dianion.

28. A compound of formula IΓ:



(II')

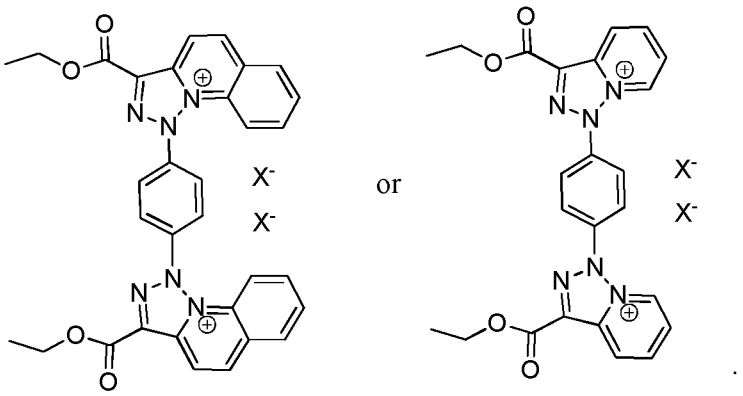
wherein

R^3 is selected from the group consisting of H, C_{i-6}alkyl, $C(0)C_{i-6}$alkyl, CN, and $C(0)OC_{i-6}$alkyl; and

X^- is an anion or a dianion.

29. The compound of any one of claims 27-28, wherein the anion is a halide ion, a sulfate ion, a tetrafluoroborate ion, a perchlorate ion, a hexafluorophosphate ion, or a borate ion.

30. The compound of any one of claims 27-28, wherein the compound of formula IΓ or Ila' is one of the following compounds:



31. The compound of claim 30, wherein X^- is perchlorate.

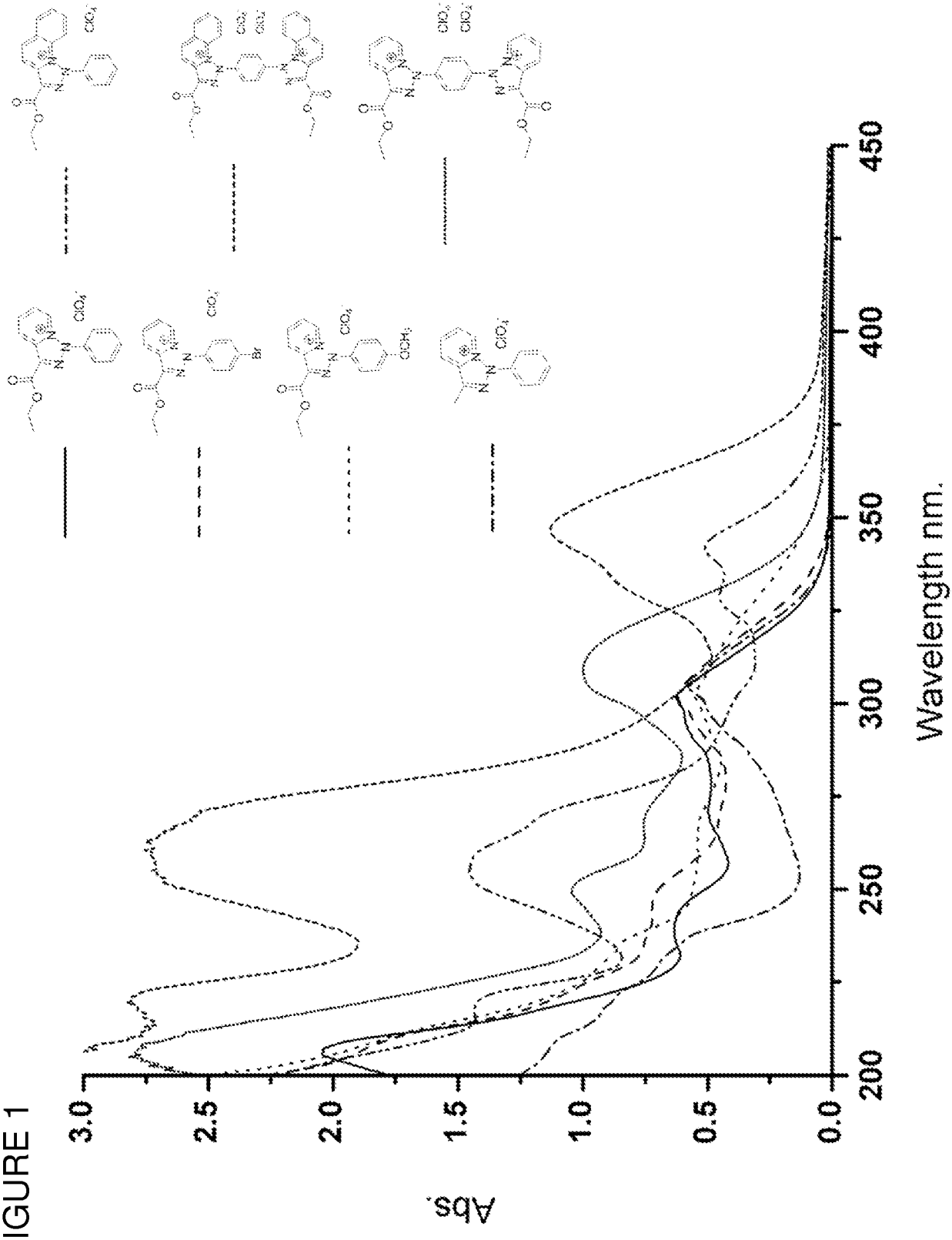


FIGURE 1

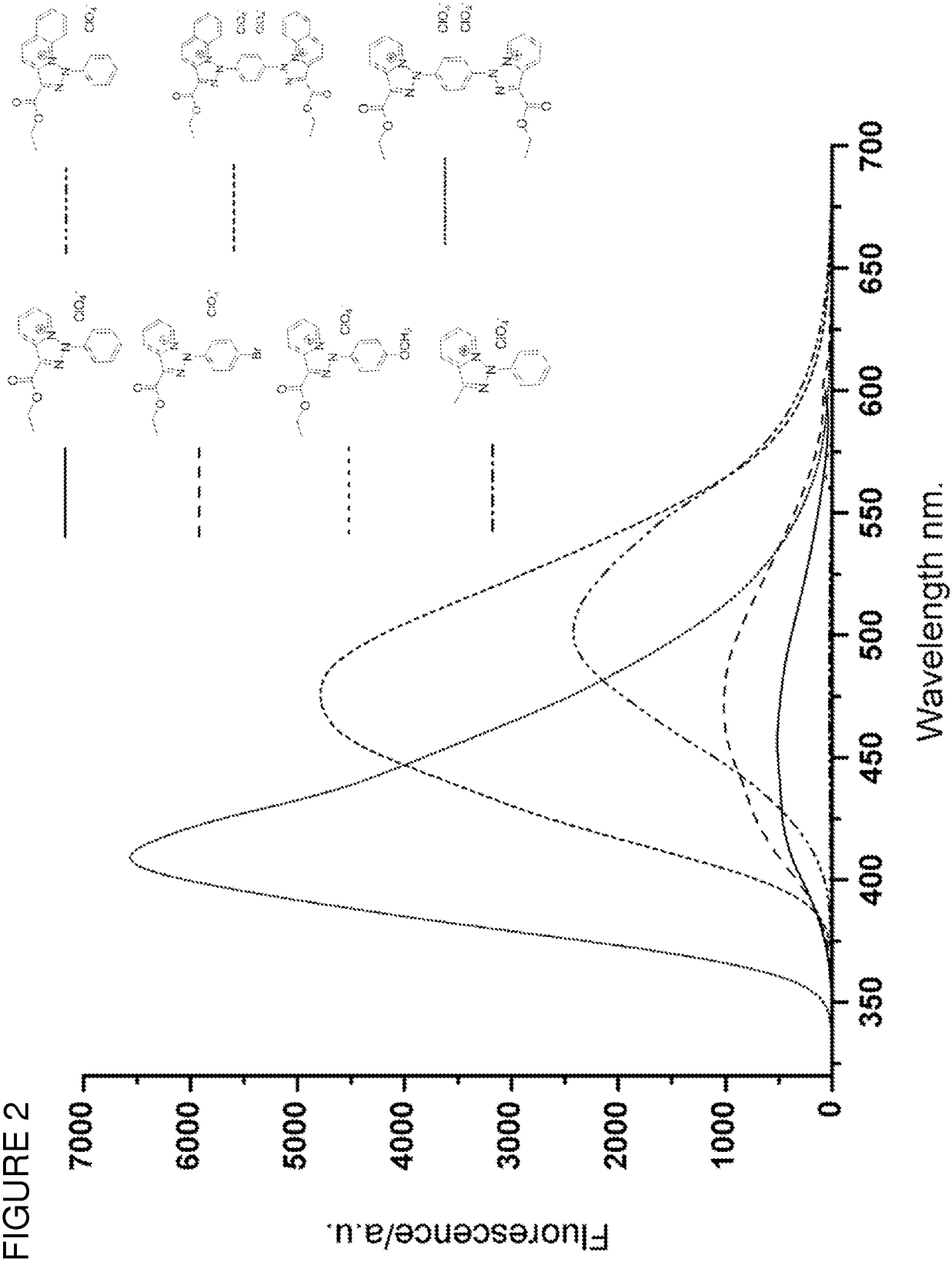

Fluorescence/a.u.
Wavelength nm.
0
1000
2000
3000
4000
5000
6000
7000
350
400
450
500
550
600
650
700

FIGURE 2

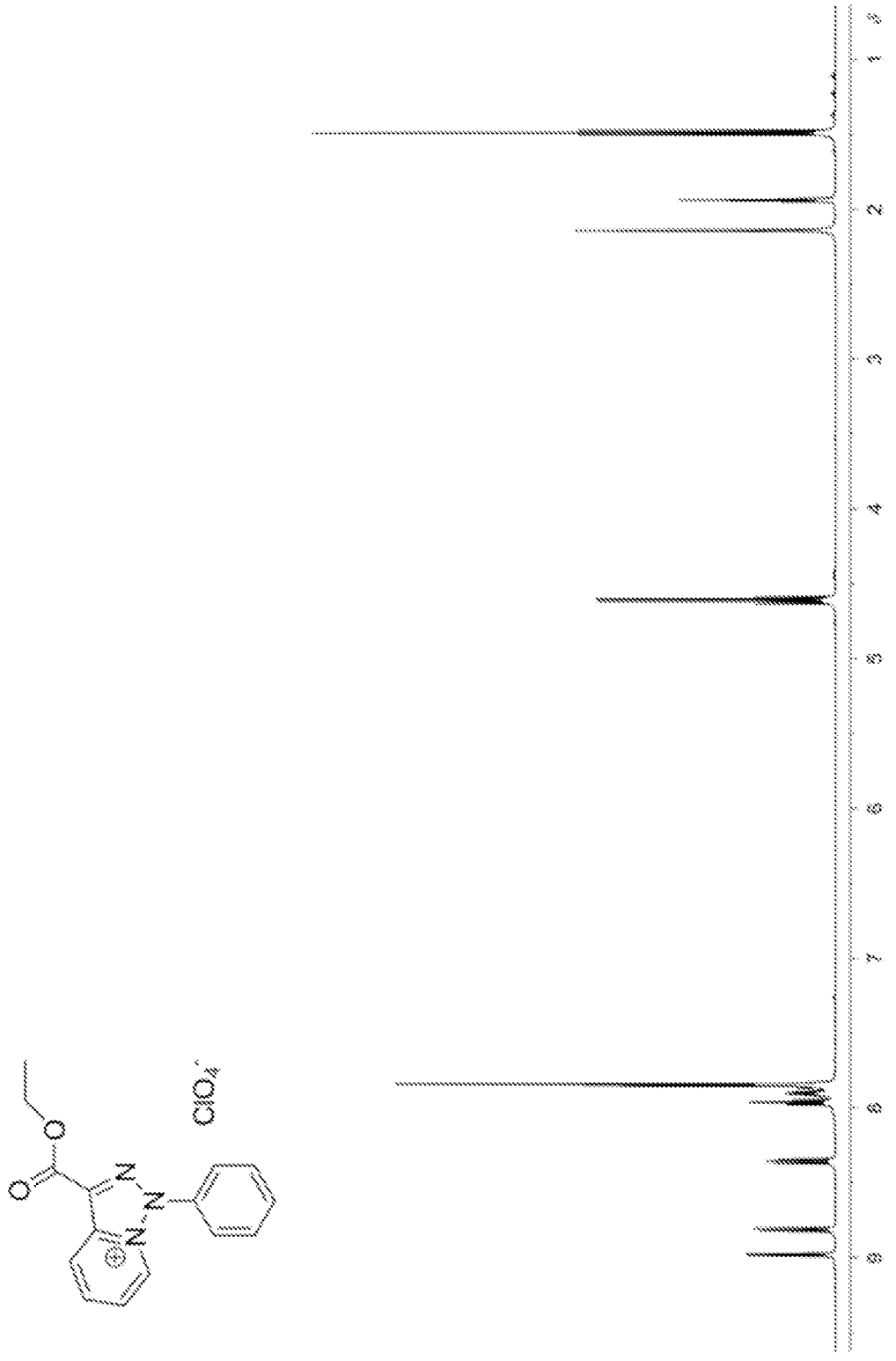


FIGURE 3

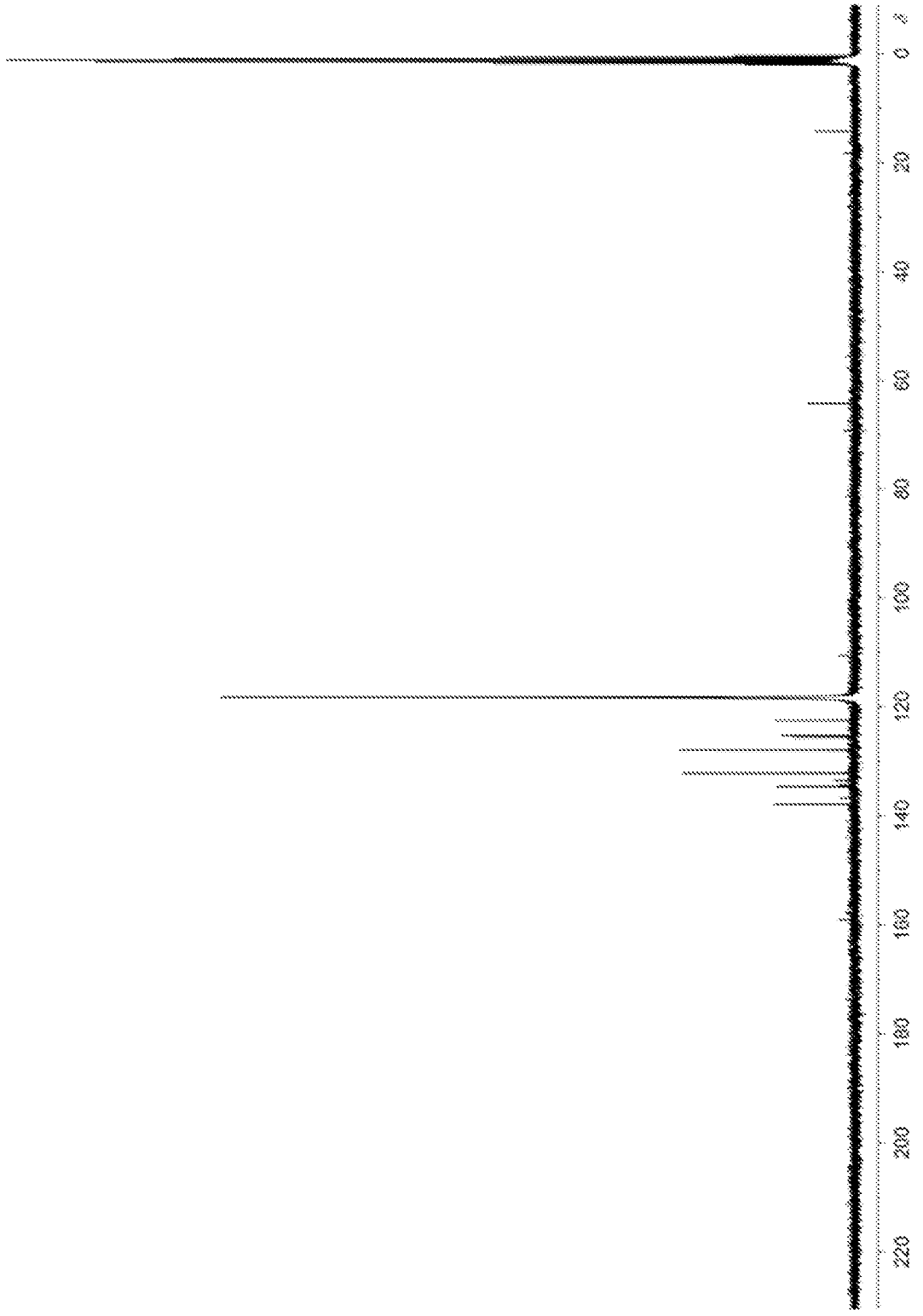
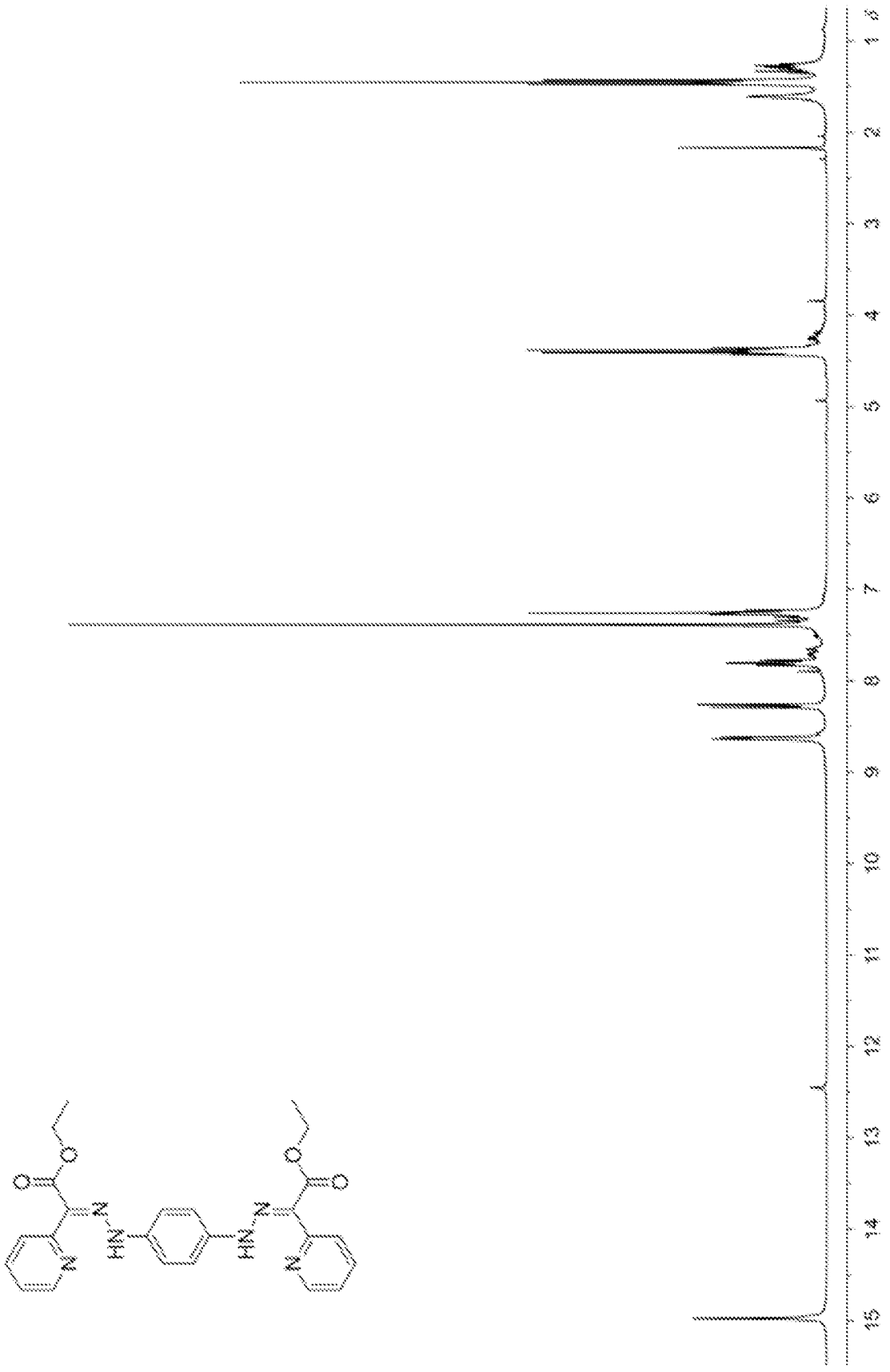


FIGURE 4

FIGURE 5



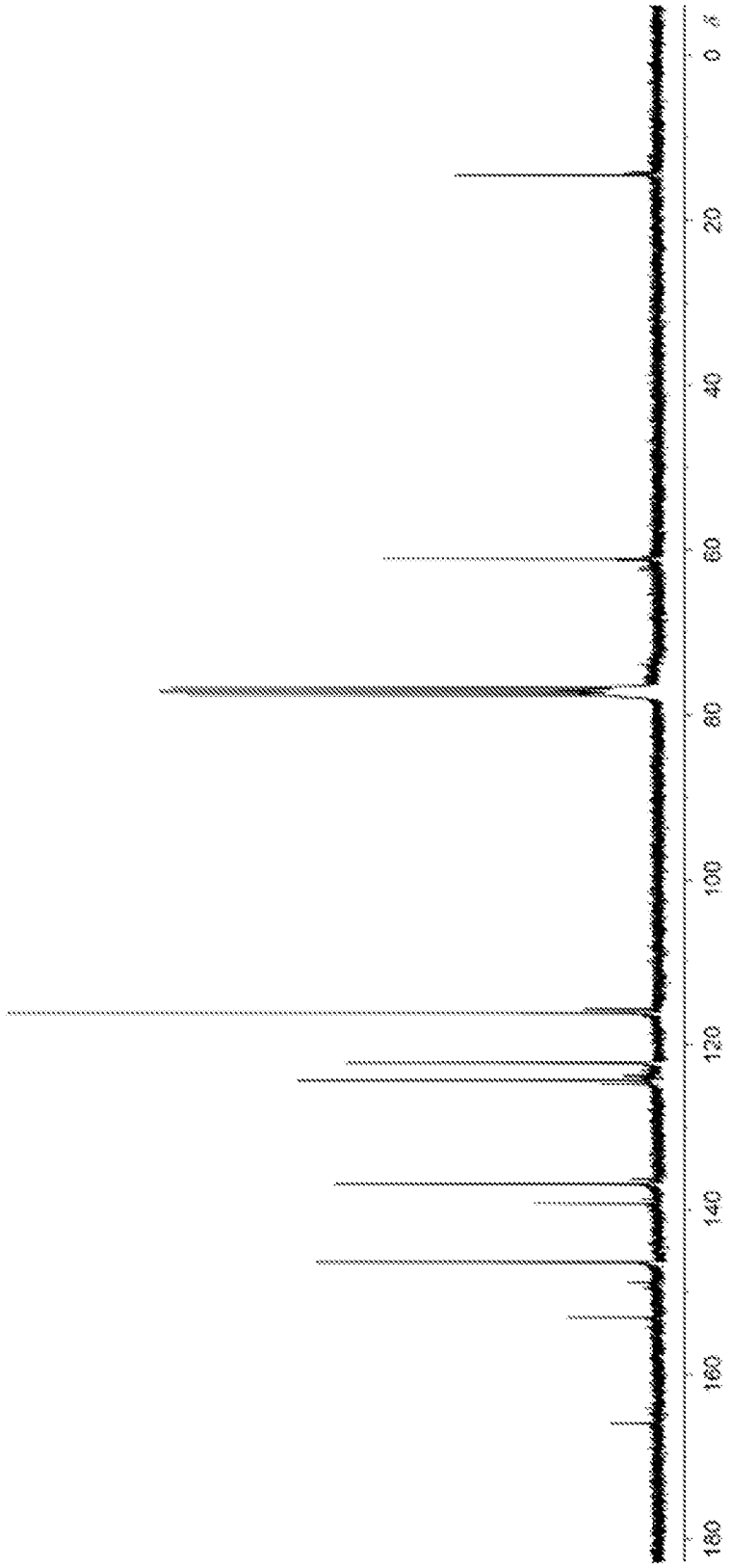


FIGURE 6

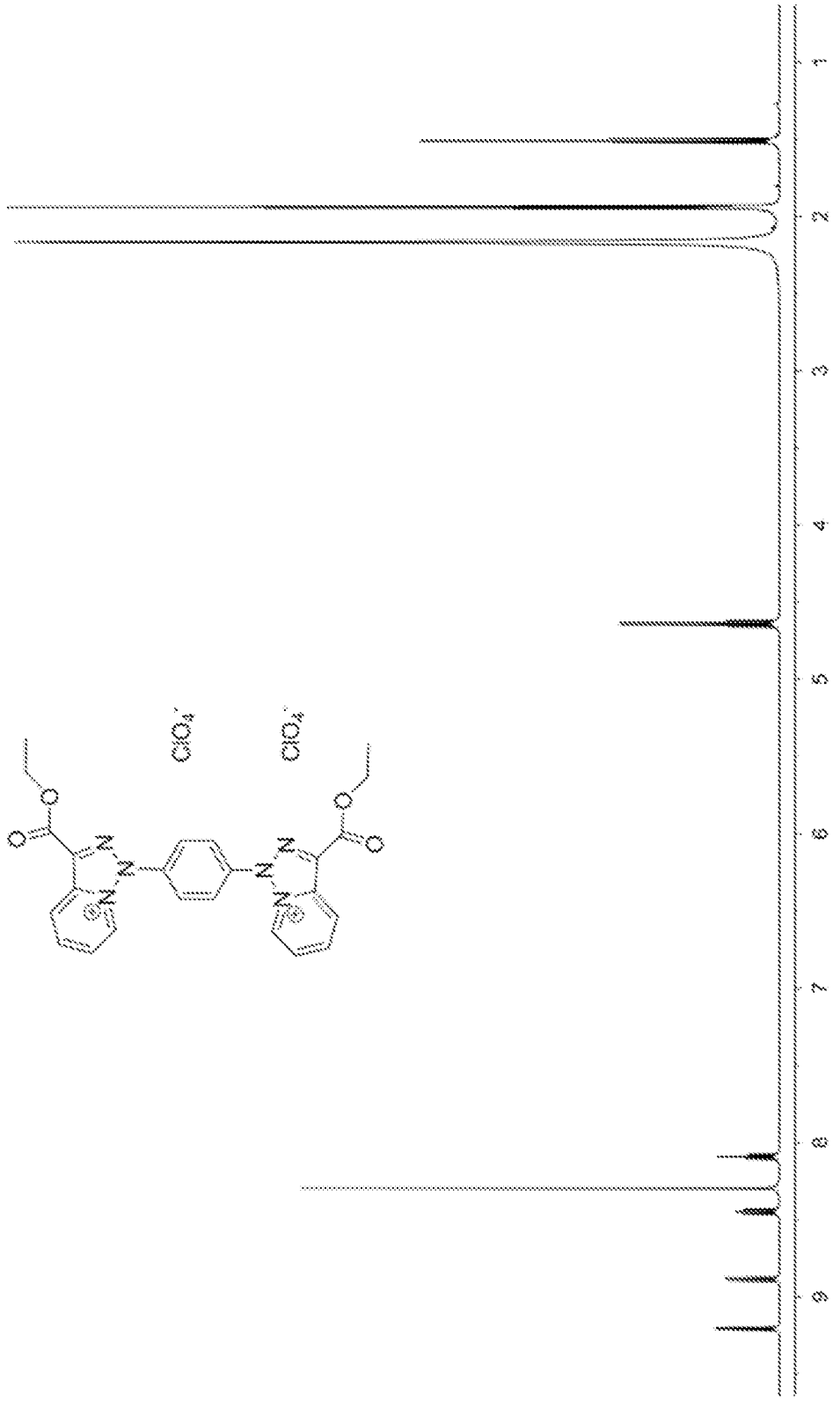


FIGURE 7

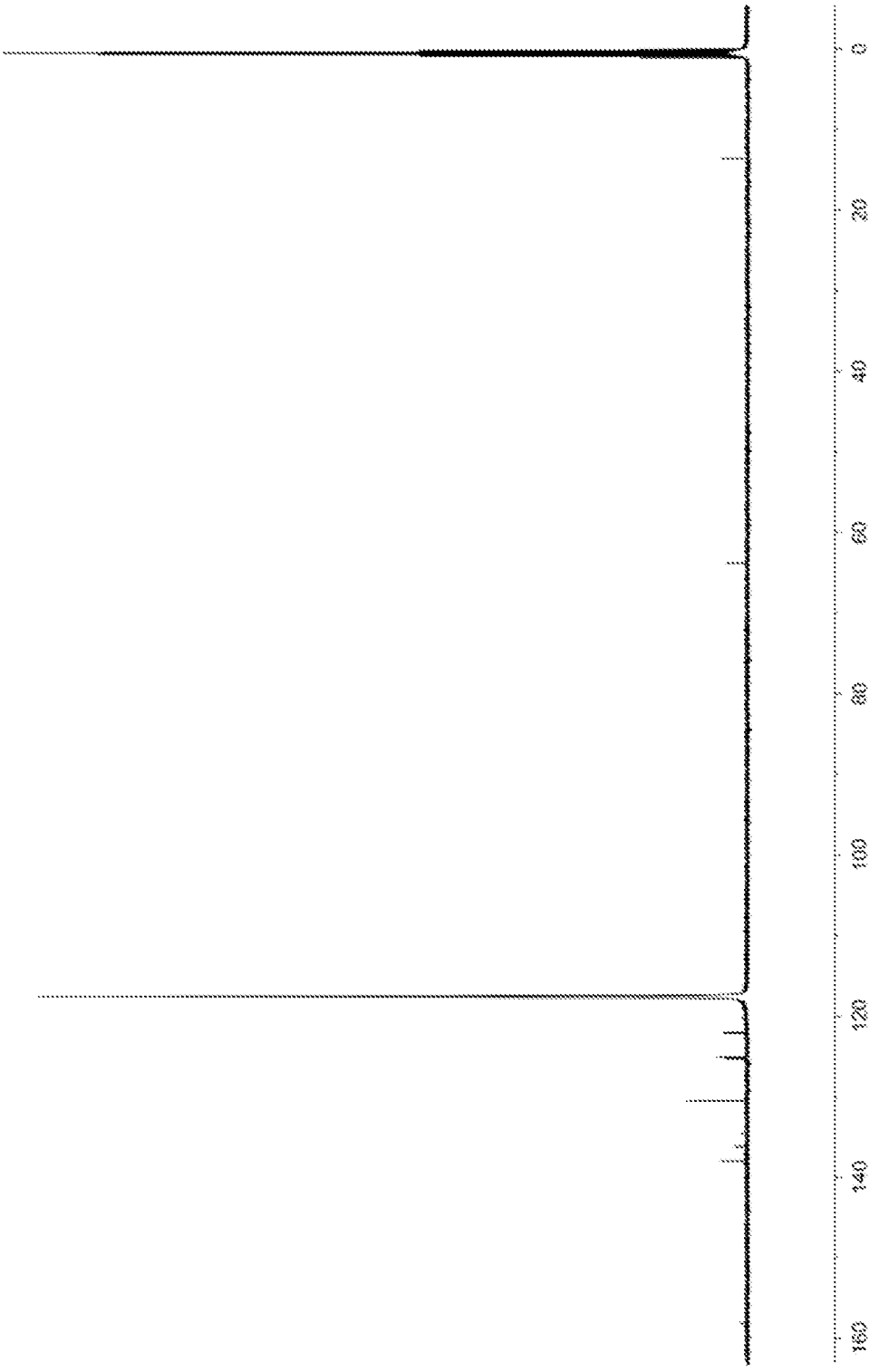


FIGURE 8

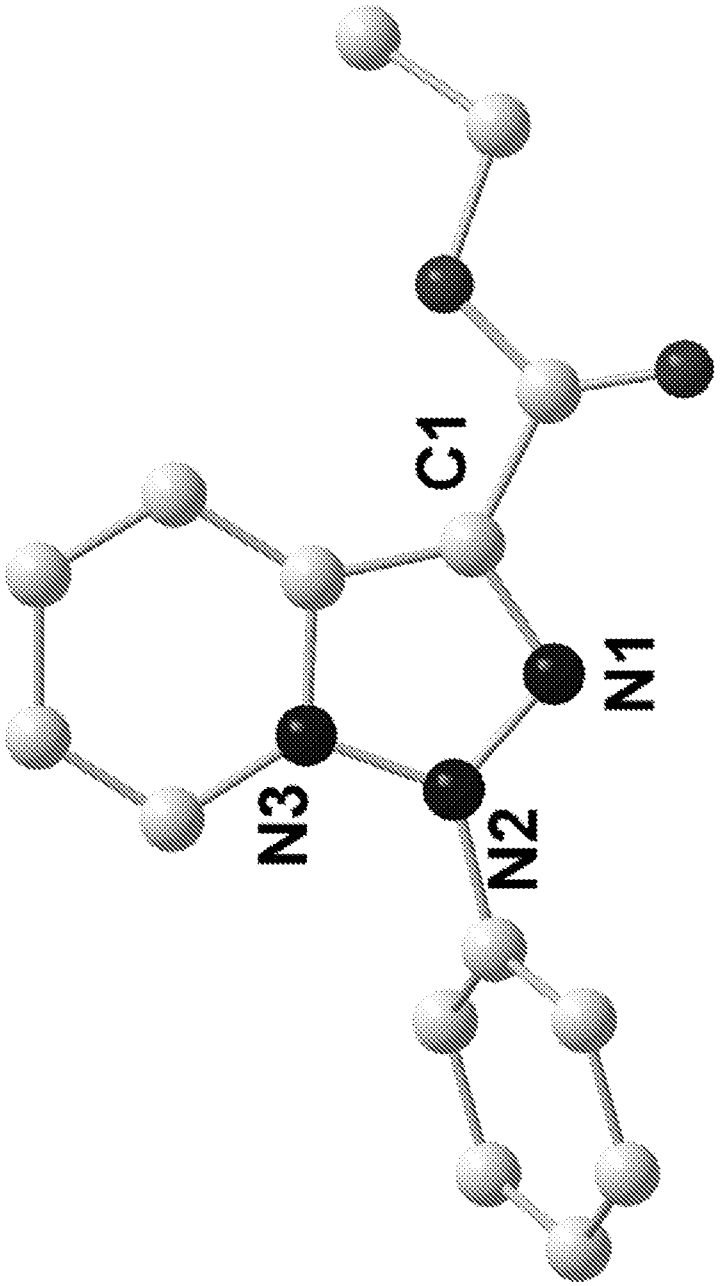


FIGURE 9

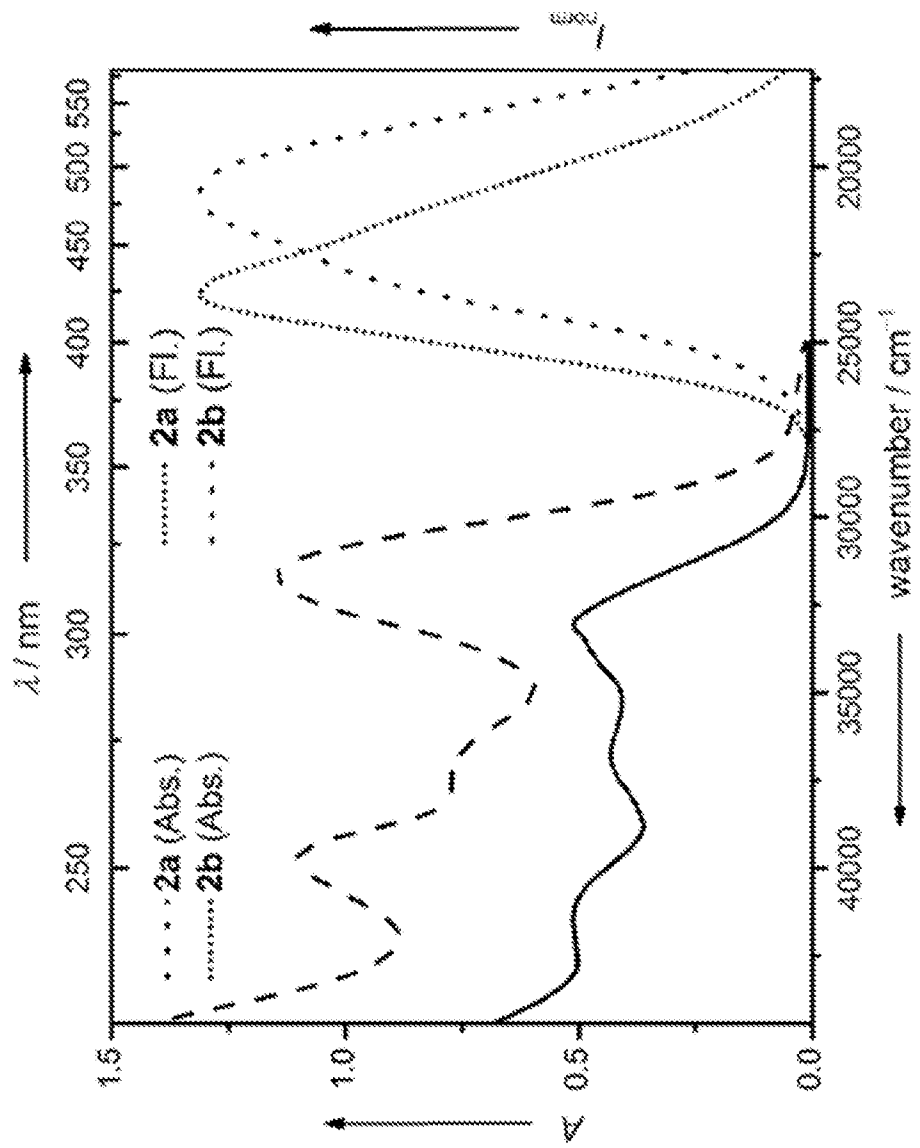

λ / nm
250
300
350
400
450
500
550
wavenumber / cm⁻¹
40000
35000
30000
25000
20000
A
1.5
1.0
0.5
0.0
I
2a (Fl.)
2b (Fl.)
2a (Abs.)
2b (Abs.)

FIGURE 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/069832

A. CLASSIFICATION OF SUBJECT MATTER

C09K ll/06(2006.01)i, H01L 51/50(2006.01)1

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)

C09K 11/06; C07D 233/60; H05B 33/14; H05B 33/22; C07D 233/58; C07D 403/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: triazolopyridinium, triazolopyridine, electroluminescent material, OLED

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2009-095012 Al (TECHNISCHE UNIVERSITAET DRESDEN) 06 August 2009 See Abstract and Claims, especially the general formula (I).	1-3,9-11,18-21 ,27-31
A	W0 2006-049013 Al (IDEMITSU KOSAN CO., LTD.) 11 May 2006 See Abstract and Claims.	1-3,9-11,18-21 ,27-31
A	WO 2005-029923 Al (FUJI PHOTO FILM CO. , LTD.) 31 March 2005 See Abstract and Claims.	1-3,9-11,18-21 ,27-31
PX	Xin Su et al. Water soluble triazolopyridiniums as tunable blue light emitters, Chem. Commun., 2013, 49, 4160-4162 (published online 26 Sep 2012) See the whole document.	1-3,9-11,18-21 ,27-31

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

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

Date of the actual completion of the international search	Date of mailing of the international search report
30 April 2013 (30.04.2013)	**30 April 2013 (30.04.2013)**

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-70 1, Republic of Korea Facsimile No. 82-42-472-7140	OH, Se Zu Telephone No. 82-42-481-5596

Form PCT/ISA/210 (second sheet) **(July** 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/069832

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: **8, 13, 26**
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

The claims 8, 13, 26 refer to unsearchable claims which do not comply with PCT Rule 6.4(a). Thus, it is not possible to make meaningful search regarding claims 8, 13, 26.

3. ☒ Claims Nos.: **4-7, 12, 14-17, 22-25**
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. Ill Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

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

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2012/069832

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009-095012 A1	06.08.2009	DE 112009000286 A5	28.10.2010
		EP 2254871 A1	01.12.2010
		US 2011-0105761 A1	05.05.2011
WO 2006-049013 A1	11.05.2006	CN 101052636 AO	10.10.2007
		EP 1808433 A1	18.07.2007
		EP 1808433 A4	15.04.2009
		JP 2006-131519 A	25.05.2006
		KR 10-2007-0073868 A	10.07.2007
		US 2009-0091240 A1	09.04.2009
WO 2005-029923 A1	31.03.2005	AT 535132 T	15.12.2011
		EP 1665897 A1	07.06.2006
		EP 1665897 A4	14.07.2010
		EP 1665897 B1	23.11.2011
		JP 2005-123168 A	12.05.2005
		KR 10-0990065 B1	26.10.2010
		KR 10-2006-0089203 A	08.08.2006
		US 2007-0099024 A1	03.05.2007
		US 8048535 B2	01.11.2011