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(54) **Title:** FLUORINATED COBALT REDOX MEDIATOR, METHOD FOR PRODUCING THE SAME, AND ITS USE IN DYE-SENSITIZED SOLAR CELL

(57) **Abstract:** The present invention provides a metal complex having the formula: (La)_n-M, wherein M is cobalt, La is fluorinated bidentate or fluorinated tridentate ligand, and n is 2 or 3. The fluorinated cobalt complex can be used as redox mediator in dye-sensitized solar cell.



Fluorinated cobalt redox mediator, method for producing the same, and its
use in dye-sensitized solar cell

TECHNICAL FIELD

This application claims priority to European or application No. 12185099.4 filed 19th September 2012, the whole content of this application being incorporated herein by reference for all purposes. The present invention relates to a metal complex comprising fluorinated polypyridine ligand, method for
5 producing the same, its use as redox mediator in photoelectric conversion device, particularly in dye-sensitized solar cell, and the dye-sensitized solar cells comprising the same.

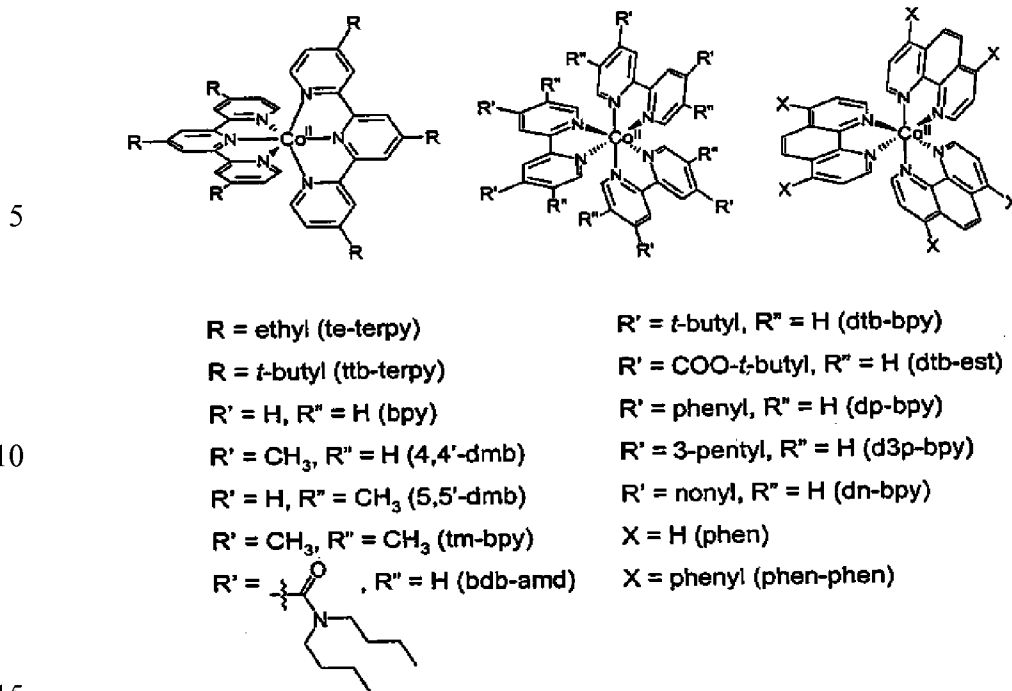
BACKGROUND OF THE INVENTION

10 Conventional solar cells convert light into electricity by exploiting the photovoltaic effect that exists at semiconductor junctions. In other words, the commercial solar cells absorb energy from visible light and convert excited charge carriers thereof to electric energy. At present, the main commercial solar cells are silicon-based solar cells. For the silicon-based solar cell, there are
15 shortcomings in that high energy costs for material processing is required and many problems to be addressed such as environmental burdens and cost and material supply limitations are involved. For an amorphous silicon solar cell, there are also shortcomings in that energy conversion efficiency decreases when used for a long time, due to deterioration in a short period.

20 One of the low-cost organic solar cells is a dye-sensitized solar cell (DSSC) which is formed based on a semiconductor sensitized by a dye to absorb incoming light to produce excited electrons, an electrode connected to the semiconductor, a counter electrode and an electrolyte usually comprising the triiodide/iodide (I_3^-/I^-) redox mediator.

25 The triiodide/iodide redox mediator has several drawbacks from both scientific and commercial point of views. US 7,019,138 B2 discloses certain cobalt complexes below as a candidate of alternative redox mediator.

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BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows the UV absorption spectra of the products according to examples 1 and 3 as well as comparative examples 1 and 2.

Figure 2 shows the cyclic voltammogram with the product according to comparative example 1.

Figure 3 shows the cyclic voltammogram with the product according to example 1.

DESCRIPTION OF THE INVENTION

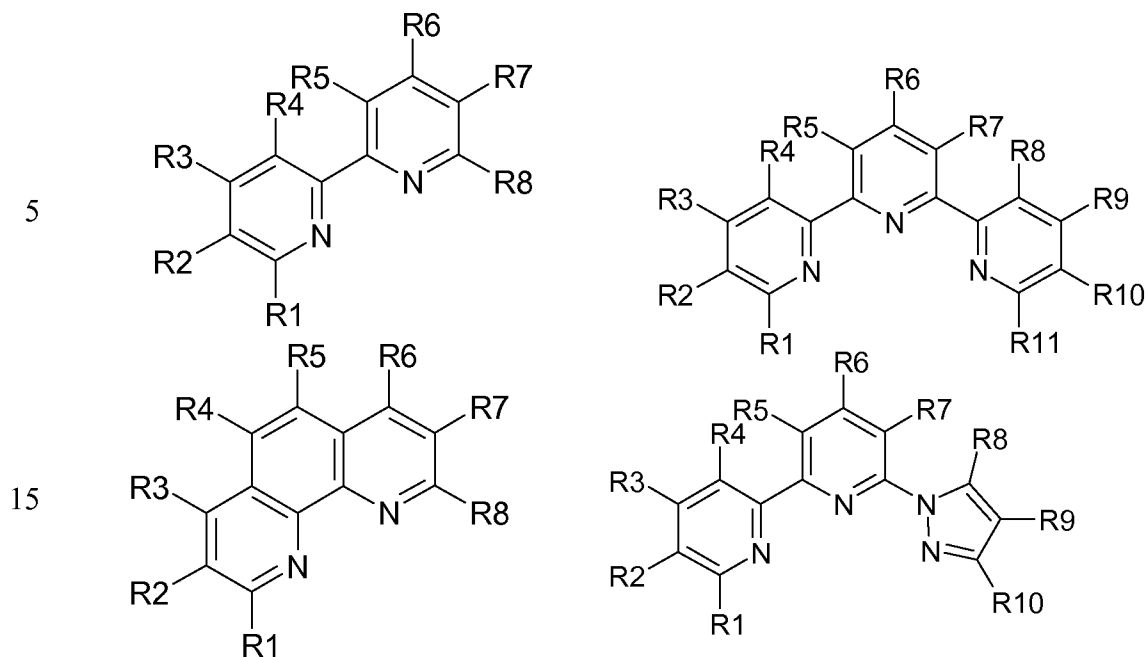
The purpose of the present invention is to provide a metal complex having advantages when used as redox mediator in photoelectric conversion device, especially in dye-sensitized solar cell.

The present invention therefore relates to a metal complex having the formula (I) below :



wherein M is cobalt, La is independently selected from the group consisting of the following bidentate and tridentate ligands, and n is 2 or 3 :

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wherein R1, R2, R3, R4, R5, R6, R7, R8, R9, R10 and R11 are independently selected from the group consisting of hydrogen, fluorine, alkyl groups, and fluorinated alkyl groups ; provided at least La comprises at least one fluorine atom. Preferably, R1, R2, R3, R4, R5, R6, R7, R8, R9, R10 and R11 are independently selected from the group consisting of hydrogen, fluorine, CH₃, and CF₃; provided at least La comprises at least one fluorine atom.

It has been surprisingly found that the metal complex according to the present invention provides more positive redox potential without having bulky substituent on the ligand. This is particularly advantageous as the bulky substituents cause retardation of the mobility. The positive shift of redox potential leads to larger photovoltage. Also, the metal complex according to the present invention allows easy fine tuning of the redox potential in accordance to HOMO level of the dye to be used by changing number and position of fluorides or fluorinated substituents on the ligand. Additionally, the metal complex according to the present invention is advantageous from its hydrophobicity and stable characteristics.

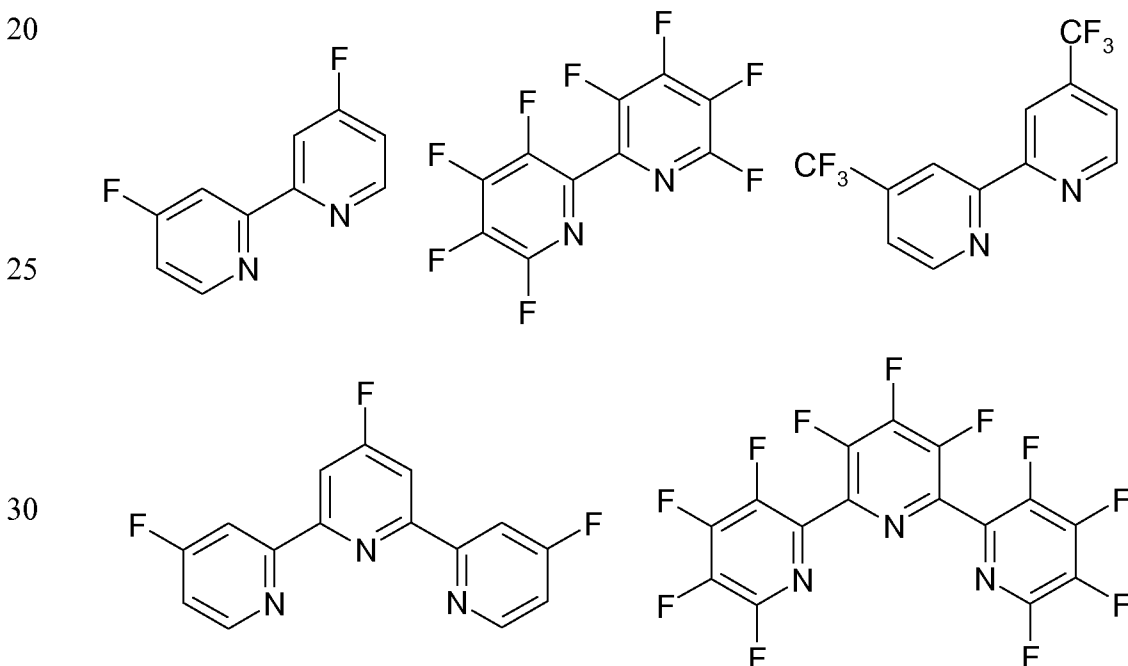
In the present invention, "redox mediator" is understood to denote in particular molecules or ions which mediate electron transfer from an electrode to an oxidized dye by their reduction-oxidation properties. More particularly, such redox mediators can be reversibly reduced at the electrode and reversibly oxidized by the oxidized dye.

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In the present invention, “alkyl groups” is understood to denote in particular a straight chain, branched chain, or cyclic hydrocarbon groups usually having from 1 to 20 carbon atoms, preferably having from 1 to 8 carbon atoms. Examples of alkyl groups include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, neopentyl, hexyl, cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. In sense of the present invention, the straight chain hydrocarbon groups having small number of carbon atoms are especially preferred, such as methyl and ethyl, further particularly methyl.

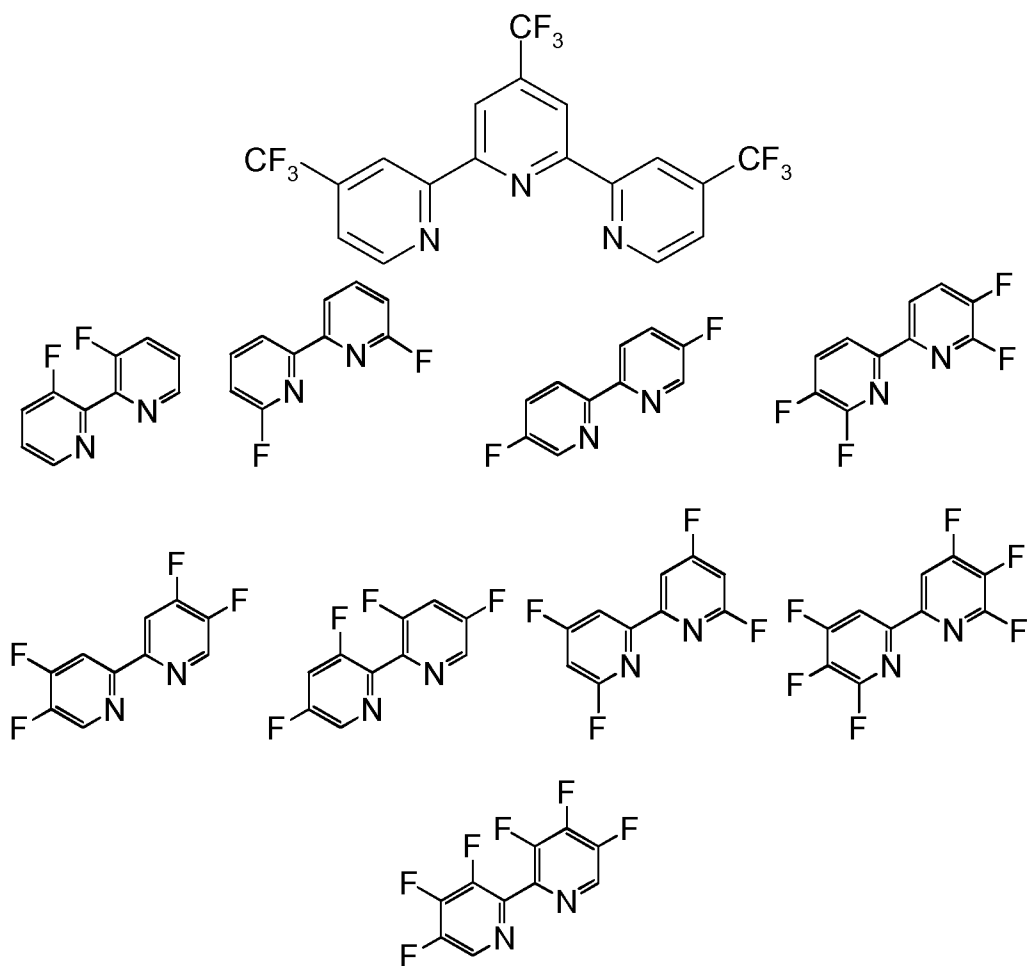
In the present invention, “fluorinated” is understood to denote in particular the fact that at least one of the hydrogen atoms of the respective chemical group has been replaced by a fluorine atom. If all of the hydrogen atoms have been replaced by fluorine atoms, the fluorinated chemical group is perfluorinated. For instance, “fluorinated alkyl groups” include (per)fluorinated alkyl groups such as (per)fluorinated methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *sec*-butyl or *tert*-butyl ; and for instance $-\text{CF}_3$, $-\text{C}_2\text{F}_5$, heptafluoroisopropyl ($-\text{CF}(\text{CF}_3)_2$), hexafluoroisopropyl ($-\text{CH}(\text{CF}_3)_2$) or $-\text{CF}_2(\text{CF}_2)_4\text{CF}_3$.

In one embodiment, La in the formula (I) is selected from polypyridines (for example, bi- and ter-pyridines) comprising at least one fluorine atom, preferably from the group consisting of the following ligands :

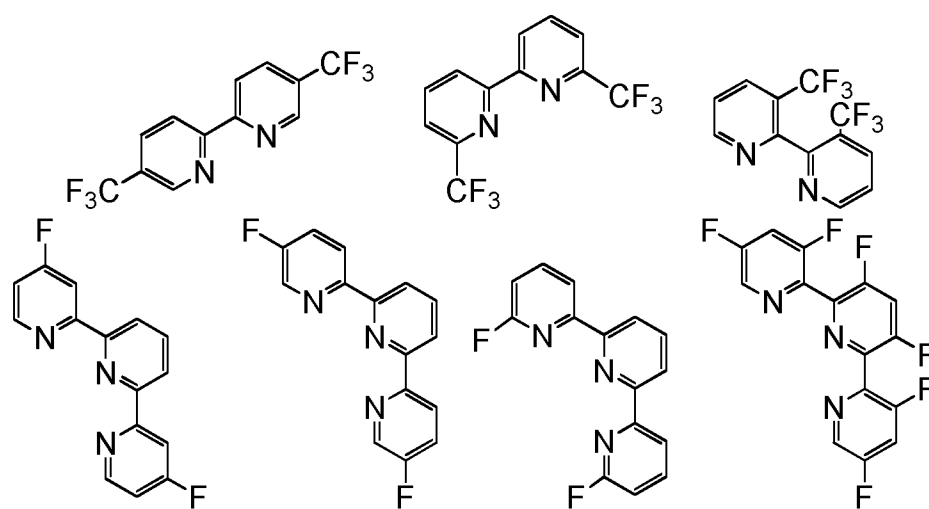


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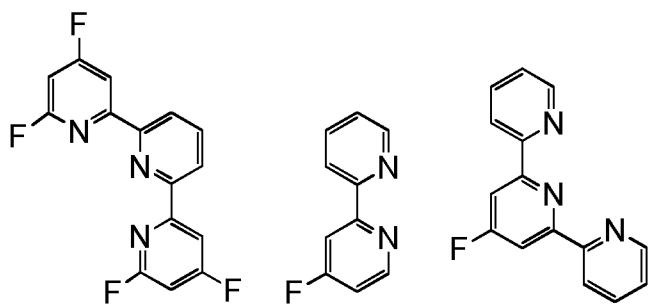
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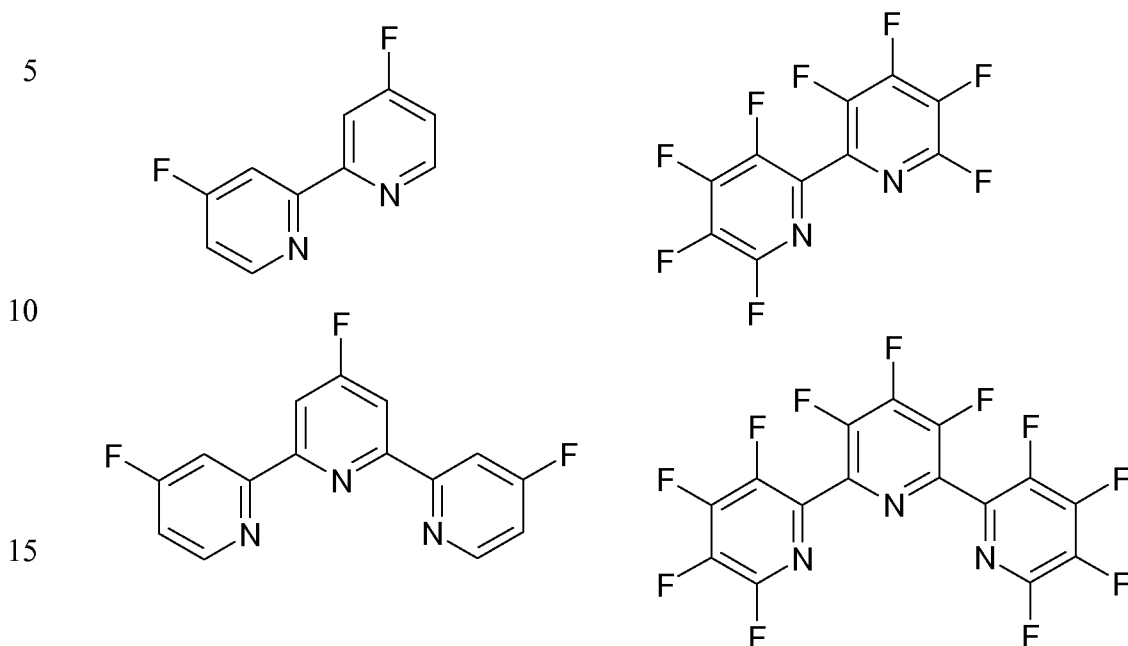
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More preferably, La in formula (I) is selected from the group consisting of the following ligands :

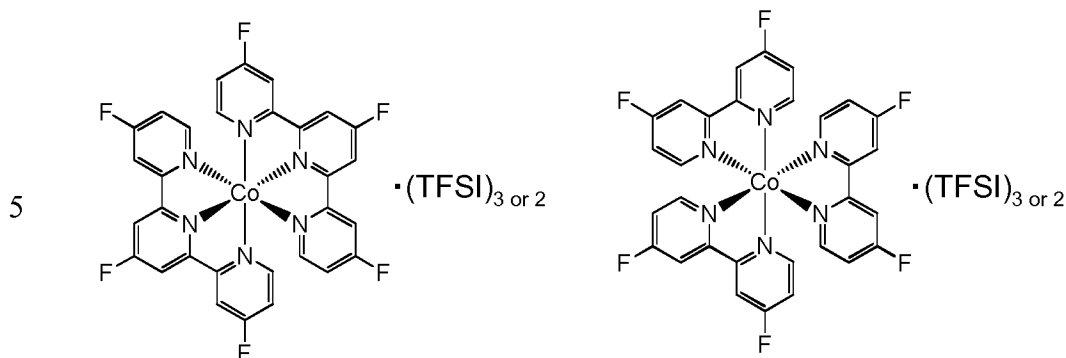


In another embodiment, the metal complex further comprises at least one counter-anion (X). Preferably, the counter-anion (X) is independently selected from monoanions. The number of the counter-anion can be two or three depending on the oxidation state of center metal, i.e. cobalt.

In a further embodiment, the counter-anion (X) is selected from the group consisting of Cl⁻, Br⁻, I⁻, CN⁻, NCO⁻, NCS⁻, NCSe⁻, amino groups, phosphate groups, PF₆⁻, borates such as [BF₄]⁻, tetracyanoborate ([B(CN)₄]⁻), [B(Ph)₄]⁻, [B(C₆F₅)₄]⁻, bis(trifluoromethanesulfonyl)imide (TFSI⁻), bis(fluorosulfonyl)imide (FSI⁻), and any combination thereof, preferably TFSI⁻.

Especially preferred metal complexes according to the present invention are as follows :

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10 Usually the two complexes, each comprising Co^{II} and Co^{III} ($= \text{Co}^{2+}$ and Co^{3+}), are used as a mixture when an electrolyte comprising the metal complex according to the present invention as redox mediator is formulated. In the sense of the present invention, Co^{II} is generally major portion.

15 The metal complexes according to the present invention described herein are suitable for use in photoelectric conversion device, particularly in dye-sensitized solar cell. Therefore, the present invention also relates to a use of the metal complex according to the present invention as redox mediator in photoelectric conversion device, in particular in dye-sensitized solar cell or organic photovoltaic device.

20 Another advantage of the fluorinated metal complexes according to the present invention is their versatility in regards to the dyes. The better performance in combination with conventional dyes and semiconductors, such as TiO_2 than the triiodide/iodide redox mediator or even other cobalt complexes is achievable by using the metal complexes according to the present invention.

25 Further, the present invention also concerns a use of cobalt complex having polypyridine ligand comprising at least one fluorine atom, as redox mediator in photoelectric conversion device, in particular in dye-sensitized solar cell.

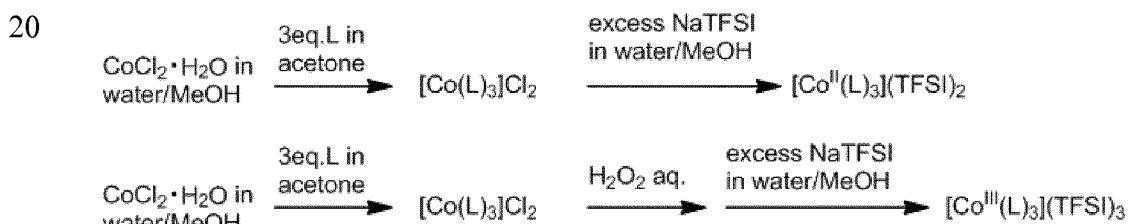
30 The basic element of a DSSC is generally a TiO_2 (titanium dioxide) nanoparticulate structure sensitized with dye molecules to form the core of a DSSC. Generally, the dye molecules can be metal complexes, such as ruthenium complexes, organic dyes having D- π -A structure (wherein D is donor group, π is bridge group and A is acceptor group), or macrocyclic dyes, such as porphyrin dyes and phthalocyanine dyes. The assembly of titanium dioxide nanoparticles is well connected to their neighbors. TiO_2 is the preferred material for the nanoparticles since its surface is highly resistant to the continued electron transfer. However, TiO_2 only absorbs a small fraction of the solar photons (those in the UV). The dye molecules attached to the semiconductor surface are used to

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harvest a great portion of the solar light. Another key component of the DSSC is an electrolyte which transports positive charge carriers from the sensitizing dye to the back contact of the device. Electrolytes containing the iodide/triiodide redox system are most commonly used. However, the iodide/triiodide redox system suffers from the disadvantages, such as large energy gap between the redox potential and HOMO energy level of oxidized dyes, low redox potential, corrosive characteristic to metals, and competition with the sensitizing dye in absorbing light.

In this context, it has been found that the metal complexes according to the present invention work in DSSC as redox mediator having improved characteristics, as set forth above, compared to traditional iodide/triiodide redox system and to non-fluorinated cobalt complexes. To this end, the metal complexes according to the present invention show improved absorption characteristics such as no significant absorption in the visible light region, improved UV absorption characteristics, e.g. improved UV absorption maxima. Furthermore, they show improved redox properties such as more positive redox potential.

The metal complexes according to the present invention can be prepared as exemplified in Scheme 1.



Scheme 1 : General synthetic scheme

In a first step, a solution of a suitable cobalt salt, preferably CoCl_2 , in a suitable solvent is stirred together with a solution of the corresponding ligand in the same or in another suitable solvent. The reaction is preferably performed at elevated temperatures, more preferably at a temperature from 40 to 60°C. Preferably, the CoCl_2 is dissolved in a 1:1 mixture of water and methanol. Also preferably, the ligand is dissolved in acetone.

If the desired complex is a complex comprising a Co(III) cation, an oxidation step can be performed subsequently, preferably in the presence of an oxidizing agent. Suitable oxidizing agents include O_2 , Br_2 , NOBF_4 or H_2O_2 , preferably Br_2 . Preferably, the oxidizing agent is added as a solution in a suitable solvent.

The counter ion X^- is introduced by subsequently stirring the reaction product from the first step or the reaction product from the oxidation step as a solution in a suitable solvent together with a suitable salt of the counter ion X^- . A preferred suitable salt is NaTFSI. The oxidation step is preferably performed at temperature from 15 to 25°C, more preferably the NaTFSI is dissolved in water/methanol (1:1).

The metal complexes according to the present invention are preferably isolated by precipitation.

The present invention further relates to a dye-sensitized solar cell (DSSC), which comprises the metal complex according to the present invention as redox mediator.

In a further specific embodiment, the DSSC according to the present invention further comprises $TiOF_2$ as semiconductor. $TiOF_2$ has the conduction band level at lower energy compared to TiO_2 which should improve the photo-induced electron transfer from the excited dye to the semiconductor. The $TiOF_2$ is preferably used in the form of $TiOF_2$ nanoparticles, in particular $TiOF_2$ particles having a mean primary particle size from 15 to 50 nm. The layer thickness is typically from 500 nm to 10 μm . The $TiOF_2$ may be used as the sole semiconductor in the DSSC semiconductor layer or may be combined in mixture with any other suitable semiconductor compound, for instance TiO_2 . Another possibility is to have at first a dense TiO_2 layer on the conducting glass followed by a nanoporous $TiOF_2$ layer. The fluorinated metal complexes according to the present invention can be used in combination with $TiOF_2$ used as semiconductor in dye sensitized solar cells.

The present invention also concerns a method for preparing the dye-sensitized solar cell, comprising :
a step of providing an electrode connected to dye-sensitized semiconductor and a counter electrode ; and
a step of providing an electrolyte ;
wherein said electrolyte comprises the metal complex according to the present invention as redox mediator.

While preferred embodiments of this invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit or teaching of this invention. The embodiments and examples described herein are exemplary only and are not limiting. Many variations and modifications of systems and methods are possible and are within

the scope of the invention. Accordingly, the scope of protection is not limited to the embodiments described herein, but is only limited by the claims that follow, the scope of which shall include all equivalents of the subject matter of the claims.

5 Examples

General Procedure for the preparation of $[\text{Co}(\text{L})_3](\text{TFSI})_2$

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ is dissolved in a mixture of water / MeOH. To this is added 3 equiv. L solution in acetone. The mixture is stirred at 50°C for 1 h, followed by addition of NaTFSI (excess) solution in water / MeOH. The mixture is stored
10 overnight at 5°C to aid precipitation. The resulting precipitate is collected by filtration, washed with water and MeOH, and dried *in vacuo*.

General Procedure for the preparation of $[\text{Co}(\text{L})_3](\text{TFSI})_3$

To a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in water / MeOH is added 3 equiv. L solution in acetone. After stirring for 10 minutes, an aqueous solution of H_2O_2 and HCl is
15 added. The mixture is stirred at 50°C for 1 h, followed by addition of NaTFSI (excess) solution in water / MeOH. The mixture is stored overnight at 5°C to aid precipitation. The resulting precipitate is collected by filtration, washed with water and MeOH, and dried *in vacuo*.

Example 1

20 Preparation of $[\text{Co}(\text{F-bpy})_3](\text{TFSI})_2$

0.5 g (2.11 mmol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in a mixture of water / MeOH (1:1, 20 ml). To this was added 3 equiv. 4,4'-difluoro-2,2'-bipyridine (1.25 g, 6.5 mmol) solution in acetone (20 ml). The mixture was stirred at 50°C for 3 h followed by addition of excess NaTFSI (4.3 g, 14.2 mmol) as a solution
25 in water / MeOH (1:1, 100 ml). The mixture was stored overnight at 5°C to aid precipitation. The resulting precipitate was collected by filtration, washed with water and MeOH, and dried *in vacuo* to yield the titled product (1.81 g, 1.5 mmol, 70 %). ^1H NMR (600 MHz, Acetone- d_6) δ 87.94(s, 6H), 78.67(s, 6H), 41.01(s, 6H).

30 Example 2

Preparation of $[\text{Co}(\text{CF}_3\text{-bpy})_3](\text{TFSI})_2$

1.0 g (4.22 mmol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in a mixture of water / MeOH (1:1, 30ml). To this was added 3 equiv. 4,4'-bis(trifluoromethyl)-2,2'-bipyridine (3.74 g, 12.8 mmol) as a solution in acetone (30 ml). The mixture
35 was stirred at 50°C for 3 h followed by addition of excess NaTFSI (8 g, 22.7 mmol) solution in water / MeOH (1:1, 100 ml). The mixture was stored

overnight at 5°C to aid precipitation. The resulting precipitate was collected by filtration, washed with water and MeOH, and dried *in vacuo* to yield the product (5.9 g, 3.95 mmol, 92 %). ¹H NMR (600 MHz, Acetone-d₆) δ 88.05(s, 6H), 80.92(s, 6H), 42.18(s, 6H).

5 Example 3

Preparation of [Co(F-bpy)₃](TFSI)₃

To a solution of CoCl₂·6 H₂O (0.5 g, 2.11 mmol) in a mixture of water / MeOH (1:1, 20 ml) was added 3 equiv. 4,4'-difluoro-2,2'-bipyridine (1.25 g, 6.50 mmol) solution in acetone (20 ml). The mixture was stirred at 50°C for 3 h.
10 After cooling to room temperature, bromine (0.5g, 3.13 mmol) was added as a solution in methanol (20 ml) while stirring. The mixture was stirred again at 50°C for 3 h. After cooling to room temperature, the solution was filtered to remove precipitate. Then the solvent was evaporated using a rotary evaporator under a vacuum and the residue was re-dissolved in methanol (50ml) and
15 filtered. To the filtrate was added excess NaTFSI (4.3 g, 14.2 mmol) as a solution in water / MeOH (1:1, 100 ml). The mixture was stored overnight at 5°C to aid precipitation. The precipitate was filtered, washed with water and MeOH and dried under a vacuum to give 2.00 g (1.35 mmol, 62 %) of the product. ¹H NMR (600 MHz, Acetone-d₆) δ 9.87(d, 6H), 8.07(t, 6H),
20 7.85(m, 6H).

Example 4

Preparation of [Co(CF₃-bpy)₃](TFSI)₃

To a solution of CoCl₂·6 H₂O (1.0 g, 4.22 mmol) in a mixture of water / MeOH (1:1, 30 ml) was added 3 equiv. 4,4'-bis(trifluoromethyl)-2,2'-bipyridine
25 (3.74 g, 12.80 mmol) as a solution in acetone (30 ml). The mixture was stirred at 50°C for 3 h. After cooling to room temperature, bromine (0.67g, 8.44 mmol) was added as a solution in methanol (20 ml) while stirring. The mixture was stirred again at 50°C for 3 h. After cooling to room temperature, the solution was filtered to remove any precipitate. Then the solvent was evaporated using a
30 rotary evaporator under a vacuum and the residue was re-dissolved in methanol (50 ml) and filtered. To the filtrate was added excess NaTFSI (8 g, 22.7 mmol) as a solution in water / MeOH (1:1, 100 ml). The mixture was stored overnight at 5°C to aid precipitation. The precipitated complex was filtered, washed with water and MeOH and dried under a vacuum to yield the product (5.2 g,
35 2.93 mmol, 68 %). ¹H NMR (600 MHz, Acetone-d₆) δ 9.78(s, 6H), 8.43(d, 6H), 8.27(d, 6H).

bpy = 2,2'-bipyridine and F-bpy = 4,4'-difluoro-2,2'-bipyridine.

Example 5

Preparation of 4,4'-bis(trifluoromethyl)-2,2'-bipyridine (CF₃-bpy)

A pressure vessel was charged with 120 g 2-bromo-4-(trifluoromethyl)pyridine (0.53 mol, 1 eq), 73.2 g potassium carbonate (0.53 mol, 1 eq), 85.2 g tetrabutylammonium bromide (0.26 mol, 0.5 eq) and 6 g palladium(II)acetate (0.027 mol, 0.05 eq). The reagents were suspended in 200 mL of a mixture composed of dimethylformamide, water and isopropyl alcohol at the ratio 2:1:3. The vessel was put under argon atmosphere, sealed and stirred at 80°C for 24 h. The reaction mixture was poured into water and extracted with MTBE. The combined organic layers were washed with water and brine, and the volatiles were removed *in vacuo*. The residue was purified by column chromatography on silica (ethyl acetate/hexane 1:20) to give 48 g product as a white solid (0.16 mol, 62 %). NMR (90 MHz, CDCl₃) δ 9.0 (d, 2H), 8.8 (s, 2H), 7.7 (d, 2H).

Example 6

Preparation of 4,4'-difluoro-2,2'-bipyridine (F-bpy)

A pressure vessel was charged with 12 g 2-bromo-4-fluoropyridine (68 mmol, 1 eq), 10.8 g tetrabutylammonium bromide (34 mmol, 0.5 eq), 9.3 g K₂CO₃ (68 mmol, 1 eq) and 0.76 g palladium(II)acetate (3.4 mmol, 0.05 eq). The mixture was suspended in 240 ml of a mixture composed of dimethylformamide, water and isopropyl alcohol at the ratio 2:1:3. The vessel was put under argon atmosphere and sealed. After stirring at 80°C for 3 d, another 0.1 eq palladium(II)acetate was added and the reaction was continued for another 12 d and then quenched with water. The mixture was extracted 3 times with a total of 500 ml ethyl acetate. Purification by column chromatography using ethyl acetate and hexanes 1:3 yielded 1.4 g of the product (7.3 mmol, 11 %) as a white solid with a purity of 99.8 % by HPLC. NMR (90 MHz, CDCl₃) δ 8.7 (dd, 2H), 8.2 (dd, 2H), 7.1 (m, 2H).

Example 7

4,4',4''-Tri(trifluoromethyl)-2,2:6',2''-terpyridine

Methyl 2-acetylnicotinate

To a stirred solution of methylisonicotinate (8 g, 0.058 mol, 1 eq) and paraldehyde (37.8 g, 0.29 mol, 4.9 eq) in acetonitrile at room temperature, iron sulfate heptahydrate (275 mg, 0.99 mmol, 0.017 eq), trifluoroacetic acid (7.31 g, 0.064 mol, 1.1 eq) and tert-butylhydroperoxide (70 % in H₂O, 10.5 g,

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0.116 mol, 2 eq) were added. The mixture was stirred at 85°C for 2 h. An additional 0.25 eq of each reagent was added and the reaction continued for 1 h. The solvent was removed *in vacuo* and the residue was taken up in 250 mL saturated aqueous sodium carbonate solution. The aqueous layer was extracted with toluene (3 x 100 mL). The combined organic fractions were washed with brine, dried over Na₂SO₄ and the solvent was removed *in vacuo*. The residue was then purified by silica gel column (300 g silica gel) and eluent EE/hexane 1:6 to get 4.7 g product (0.026 mol, 45 %).

Methyl 2-[3-(2-furyl)prop-2-enoyl]pyridine-4-carboxylate

10 A 20 mM KOH solution was prepared by dissolving 5.5 g KOH in 33.54 ml water and 167.7 ml methanol and cooled to 0°C. Freshly distilled furaldehyde (8.05 g, 83.8 mmol, 1 eq) was added thereto, allowing the mixture to react for 10 min. Methyl 2-acetylisonicotinate (15.0 g, 83.8 mmol, 1 eq) as prepared above was added and the reaction mixture was stirred for 3 h in the ice bath. A yellow precipitate formed. Subsequent filtration and washing with 50 ml cold methanol yielded 12.0 g of a residue (47 mmol, 56 %).

1-(2-(4-Methylcarboxyl)pyridinyl)carbonylpyridinium iodide

A mixture of methyl 2-acetylisonicotinate (15 g, 0.08mol, 1 eq), iodine (21.3 g, 0.08 mol, 1 eq) and pyridine (49.4 mL, 0.61 mol, 7.3 eq) was placed in an oil bath preheated to 130°C. The mixture solidified after 25 min and was then allowed to cool to room temperature. It was dissolved in MeCN/ H₂O 85:15 and preabsorbed on silica. The product was purified by column chromatography on silica (eluent MeCN/H₂O 85:15). The solvents were removed *in vacuo* and the product was recrystallized from hot MeOH twice to give 13.7 g of brown crystals (0.036 mol, 45 %).

Dimethyl 4'-furyl-2,2':6',2''-terpyridine-4,4''-dicarboxylate

1-(2-(4-Methylcarboxyl)pyridinyl)carbonylpyridinium iodide (9.2 g, 0.036 mol, 1 eq), methyl 2-[3-(2-furyl)prop-2-enoyl]pyridine-4-carboxylate (8.7 g, 0.034 mol, 1 eq) and ammonium acetate (17 g, 0.216 mol, 6 eq) were dissolved in 300 ml methanol. The mixture was warmed up to 50°C and stirred over night. Then it was diluted with 200 ml ethyl acetate and 200 ml H₂O and shaken vigorously, leading to precipitation. The precipitate was filtered off and dried, giving 6.1 g of a white solid (0.015 mol). The organic layer was washed with brine and sat. aqueous NaHCO₃ and dried over Na₂SO₄. The solvent was removed *in vacuo*. The residue was purified by silica gel column (400 g silica,

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MTBE/NH₃ in MeOH 10:0.2) to give an additional 0.7 g product (0.0017 mol), resulting in a total yield of 50 % (6.8 g, 0.017 mol).

4'-Furyl-2,2':6',2''-terpyridine-4,4''-dicarboxylic acid

Dimethyl 4'-furyl-2,2':6',2''-terpyridine-4,4''-dicarboxylate (6.5 g, 16 mmol, 5 1 eq) was dissolved in 260 ml of a mixture of THF and methanol (1:1).

Potassium hydroxide (2.6 g, 47 mmol, 3 eq) was dissolved in 65 ml water and added to the solution. The mixture was stirred at room temperature over night, while the product precipitated as a brown solid. It was filtered off, washed with methanol and dried *in vacuo*. The crude product was obtained in quantitative 10 yield (6.9 g) and used without further purification.

4,4',4''-Tricarboxy-2,2':6',2''-terpyridine

4'-furyl-2,2':6',2''-terpyridine-4,4''-dicarboxylic acid (6.7 g, 17 mmol, 1 eq) was dissolved in 270 ml water. Potassium permanganate (10.9 g, 69 mmol, 4 eq) was added and the pH was adjusted to 10 with dilute potassium hydroxide 15 solution. The reaction mixture was stirred over night at room temperature. Then the reaction was quenched by addition of aqueous sodium thiosulfate. Insoluble manganese dioxide was removed by passing the mixture through a bed of Celite[®], resulting in a clear, colourless solution. The pH was adjusted to 4 by addition of conc. hydrochloric acid, and the product precipitated as a white solid. The 20 precipitate was washed with water and ethanol and dried over phosphorus pentoxide. Residual water was removed by azeotropic distillation with toluene, giving 5.9 g product as a beige solid (16 mmol, 94 %).

4,4',4''-tri(trifluoromethyl)-2,2':6',2''-terpyridine

4,4',4''-tricarboxy-2,2':6',2''-terpyridine (0.5 g, 1.37 mmol) was provided in 25 a Hastelloy[®] C4 reactor under nitrogen flush. The reactor was evacuated using a water jet pump and cooled down to -70 °C in an iso-propanol/CO₂ bath. HF (5.2 g, 260 mmol) and SF₄ (4.2 g, 39 mmol) were added. The reactor was allowed to warm-up to room temperature and after that heated to 60°C. After 20 h the reactor was allowed to cool down to ambient temperature. The gas- 30 phase was purged off into a scrubber and residues of gas were disposed by evacuation of the reactor. After the reactor was opened, 50 ml of dichloromethane was added. The organic phase was carefully poured onto ice. The organic phase was separated and the aqueous phase was extracted with dichloromethane again. The combined organic phases were brought to pH 9 35 using a 10 % aqueous solution of NH₄OH. The organic phase was separated, washed with water and brine and dried over MgSO₄. The solvent was removed

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by vacuum distillation. The yield of the slight yellow solid was 0.16 g (26.7 %).

^1H NMR (500.50 MHz, CDCl_3 + 0.03 % TMS), δ : 7.65 ppm (d, 2H), 8.81 ppm (s, 4H), 8.93 ppm (d, 2H); ^{13}C NMR (125.85 MHz, CDCl_3 + 0.03 % TMS), δ : 117.04 ppm, 117.92 ppm, 120.14 ppm, 150.43 ppm, 155.85 ppm; ^{19}F NMR (470.94 MHz, CDCl_3 + 0.03 % TMS) δ : -64.73 ppm (s, 3F), -64.86 (s, 6F).

The ligand thus obtained is further converted into the corresponding Co^{2+} and Co^{3+} complexes analogously to the preparation as described in examples 1 and 2, respectively.

10 Comparative Example 1

Preparation of $[\text{Co}(\text{bpy})_3](\text{TFSI})_2$

5.0 g (21.1 mmol) $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ was dissolved in a mixture of water / MeOH (1:1, 50 ml). To this was added 3 equiv. 2,2'-bipyridine (bpy) (11.0 g, 70.5 mmol) as a solution in acetone (50 ml). The mixture was stirred at 50°C for 3 h followed by addition of excess NaTFSI (41.6 g, 137 mmol) as a solution in water / MeOH (1:1, 250 ml). The resulting precipitate was collected by filtration, washed with water and MeOH, and dried *in vacuo* to yield the product 18.2 g (16.7 mmol, 70 %). ^1H NMR (600 MHz, Acetone- d_6) δ 87.92(s, 6H), 83.78(s, 6H), 46.03(s, 6H), 14.66(s, 6H); ^{13}C NMR (600 MHz, Acetone- d_6) δ 180.3, 121.1, 118.9.

Comparative Example 2

Preparation of $[\text{Co}(\text{bpy})_3](\text{TFSI})_3$

To a solution of $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ (5.0 g, 21.1 mmol) in a mixture of water / MeOH (1:1, 50 ml) was added 3 equiv. 2,2'-bipyridine (11.0 g, 70.5 mmol) as a solution in acetone (50 ml). The mixture was stirred at 50°C for 3 h. After cooling to room temperature, bromine (3.37 g, 21.1 mmol) was added as a solution in methanol (50 ml) while stirring. The mixture was stirred again at 50°C for 3 h. After cooling to room temperature, the solution was filtered to remove any precipitate. Then the solvent was evaporated using a rotary evaporator under vacuum and the residue was re-dissolved in methanol (150 ml) and filtered. To the filtrate was added excess NaTFSI (41.6 g, 137 mmol) as a solution in water / MeOH (1:1, 250 ml). The precipitated complex was filtered, washed with water and MeOH and dried under vacuum to yield the product 19.7 g (14.4 mmol, 61 %). ^1H NMR (600 MHz, Acetone- d_6) δ 9.10(d, 6H), 8.68(m, 6H), 7.95(t, 6H), 7.89(t, 6H); ^{13}C NMR (600 MHz, Acetone- d_6) δ 156.2, 151.8, 144.1, 131.7, 127.4, 123.2, 121.1, 117.0.

Example 7**Cyclic Voltammetry**

The measurements were performed with a three-electrode potentiostat (Bio-Logic Science Instruments, Model VSP) in tetrahydrofuran, which was deoxygenated by purging with pre-purified nitrogen gas, with a scan rate of 10 mV/s at a temperature of 298 K. Cyclic voltammetry experiments for the cobalt complex used a 2 mM solution of $[\text{Co}(\text{bpy})_3](\text{TFSI})_2$ or $[\text{Co}(\text{F-bpy})_3](\text{TFSI})_2$, respectively, with 0.1 M tetra-butylammonium hexafluorophosphate (TBAPF_6) in acetonitrile. It was conducted with a three-electrode cell equipped with a glassy carbon (0.07 cm^2) disk as the working electrode, a platinum wire as the auxiliary electrode, and a Ag/Ag^+ electrode as the reference electrode in the acetonitrile, containing 0.1 M AgNO_3 and 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte. Potentials are reported vs. Ag/Ag^+ with reference to a ferrocene/ferrocenium (Fc/Fc^+) couple at $E^0 = +0.56$ vs the normal hydrogen electrode at 23°C in acetonitrile. The working electrode was polished with $0.03 \mu\text{m}$ aluminium on felt pads and treated ultrasonically for 1 min before each experiment.

Redox potentials :

$[\text{Co}(\text{bpy})_3](\text{TFSI})_2 = 0.56 \text{ V}$,

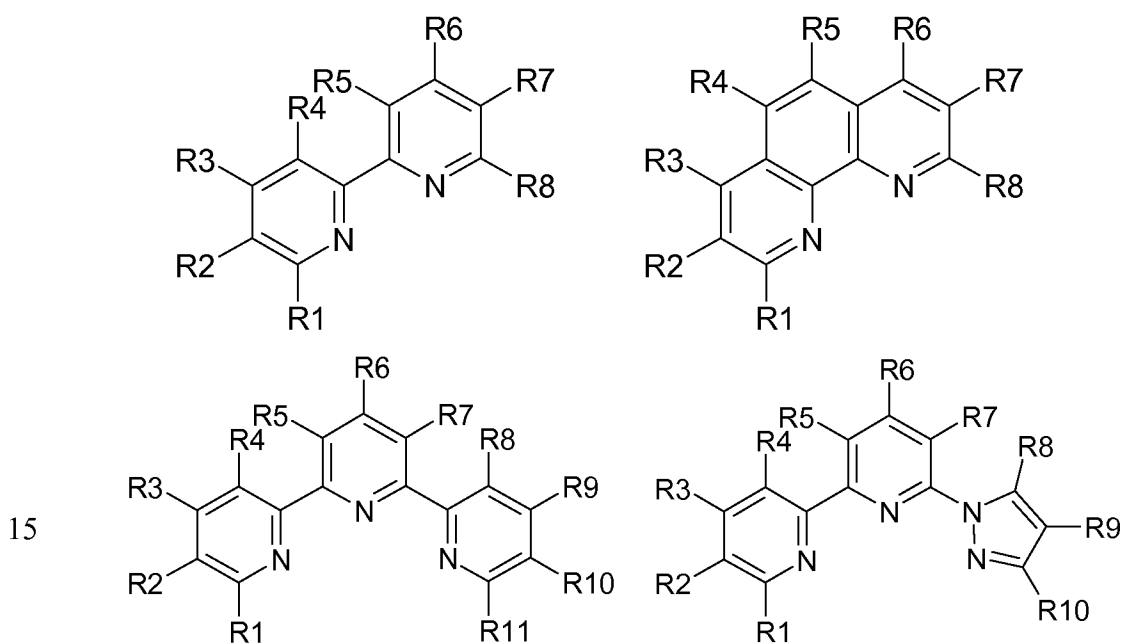
$[\text{Co}(\text{F-bpy})_3](\text{TFSI})_2 = 0.82 \text{ V}$.

CLAIMS

1. A metal complex having the formula (I) below :



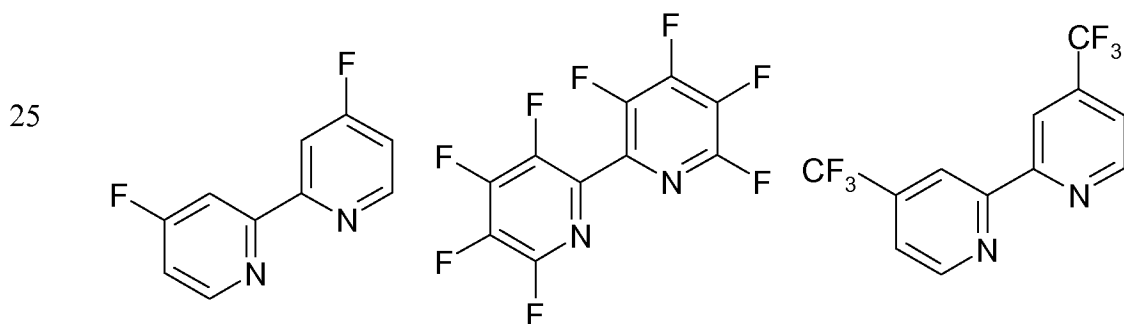
wherein M is cobalt, La is independently selected from the group consisting of the following bidentate and tridentate ligands, and n is 2 or 3 :



wherein R1, R2, R3, R4, R5, R6, R7, R8, R9, R10 and R11 are independently selected from the group consisting of hydrogen, fluorine, alkyl groups, in particular CH₃, and fluorinated alkyl groups, in particular CF₃ ; provided at least La comprises at least one fluorine atom.

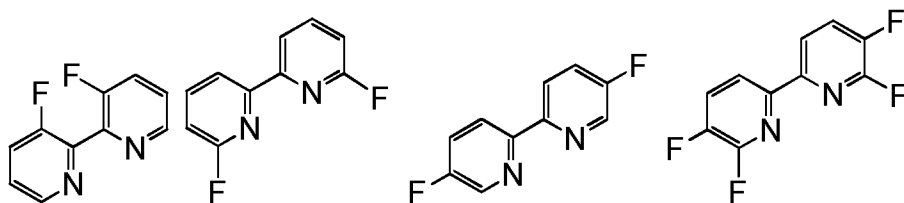
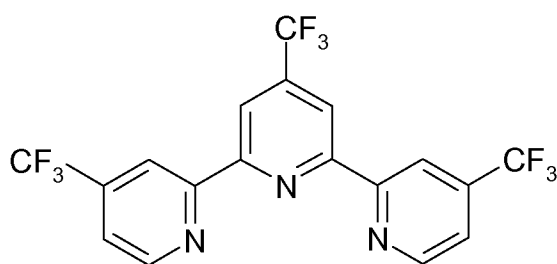
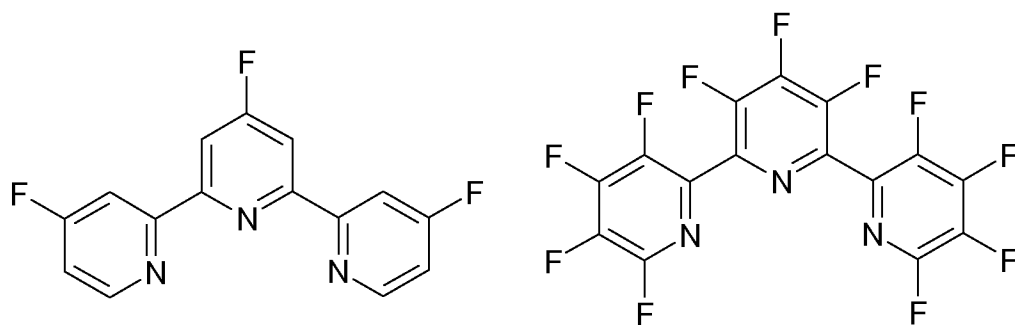
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2. The metal complex according to claim 1, wherein La is selected from the group consisting of the following ligands :

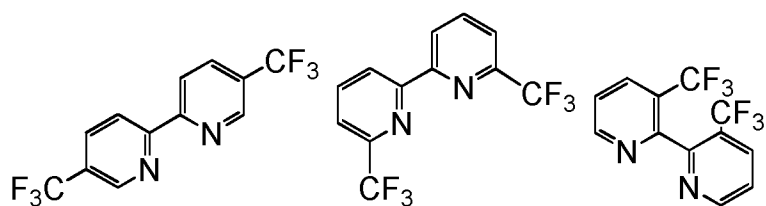
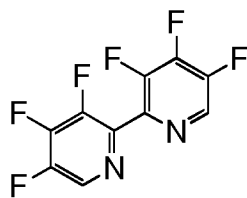
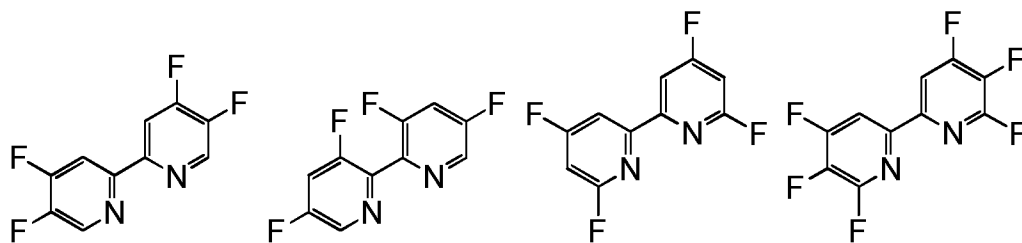


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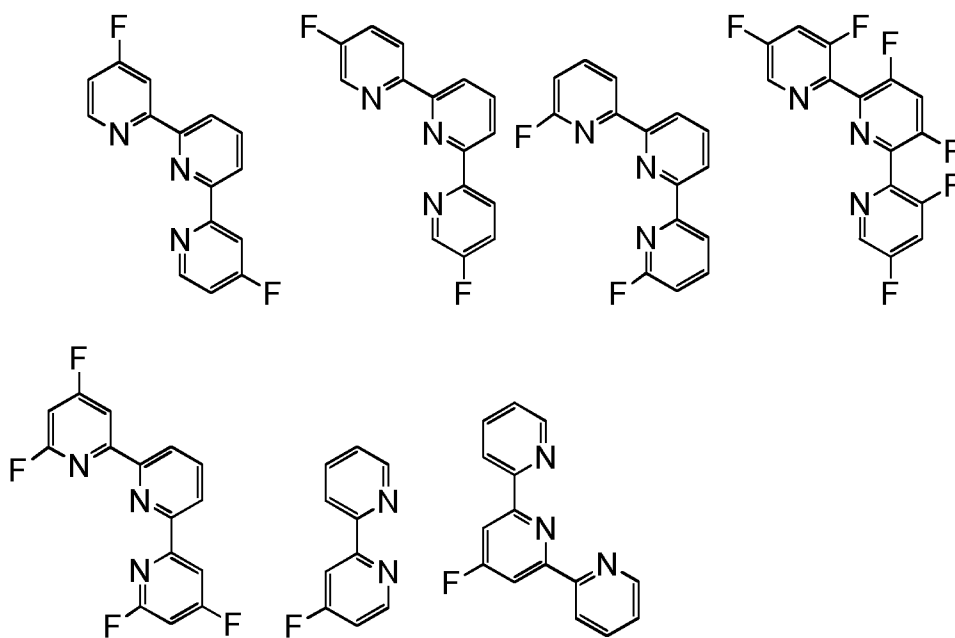
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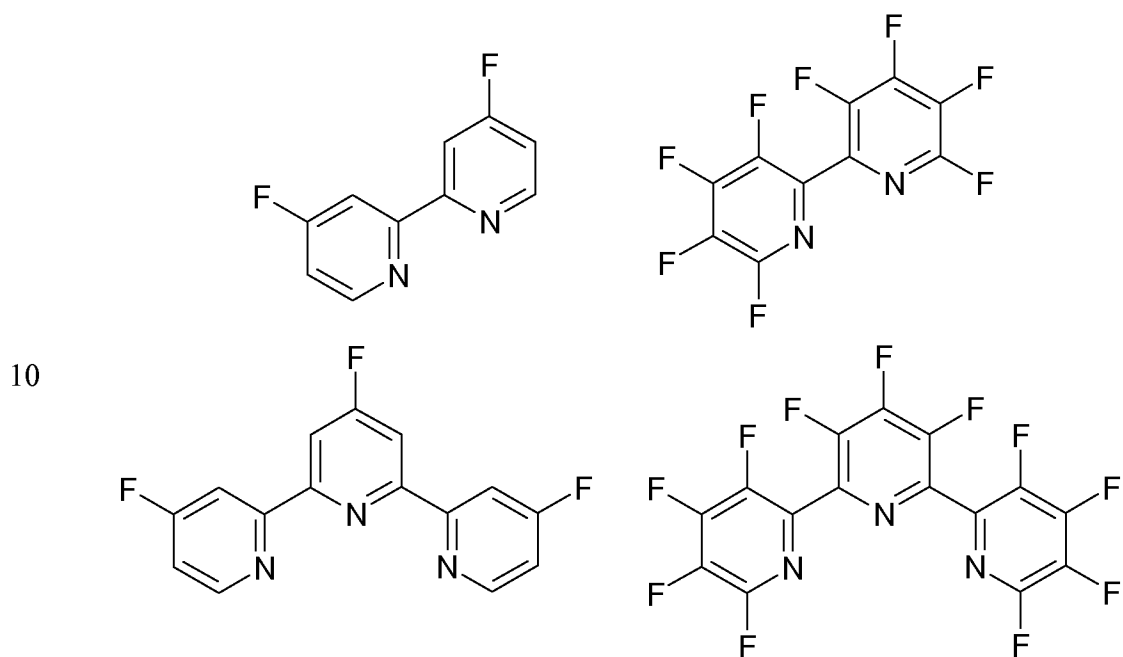
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3. The metal complex according to claim 1 or 2, wherein La is selected
5 from the group consisting of the following ligands :



4. The metal complex according to any one of claims 1 to 3, further
15 comprising at least one counter-anion (X).

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5. The metal complex according to claim 4, wherein the counter-anion is selected from the group consisting of Cl⁻, Br⁻, I⁻, CN⁻, NCO⁻, NCS⁻, NCSe⁻, amino groups, phosphate groups, PF₆⁻, borates such as [BF₄]⁻, tetracyanoborate ([B(CN)₄]⁻), [B(Ph)₄]⁻, [B(C₆F₅)₄]⁻, bis(trifluoromethanesulfonyl)imide (TFSI⁻), bis(fluorosulfonyl)imide (FSI⁻), and any combination thereof, preferably TFSI⁻.

6. Use of the metal complex according to any one of claims 1 to 5 as redox mediator in photoelectric conversion device, in particular in dye-sensitized solar cell or organic photovoltaic device.

7. A dye-sensitized solar cell comprising the metal complex according to any one of claims 1 to 5 as redox mediator.

8. The dye-sensitized solar cell according to claim 7, further comprising TiOF₂ as semiconductor.

9. A method for preparing the dye-sensitized solar cell according to claim 7 or 8, comprising :

a step of providing an electrode connected to dye-sensitized semiconductor and a counter electrode ; and

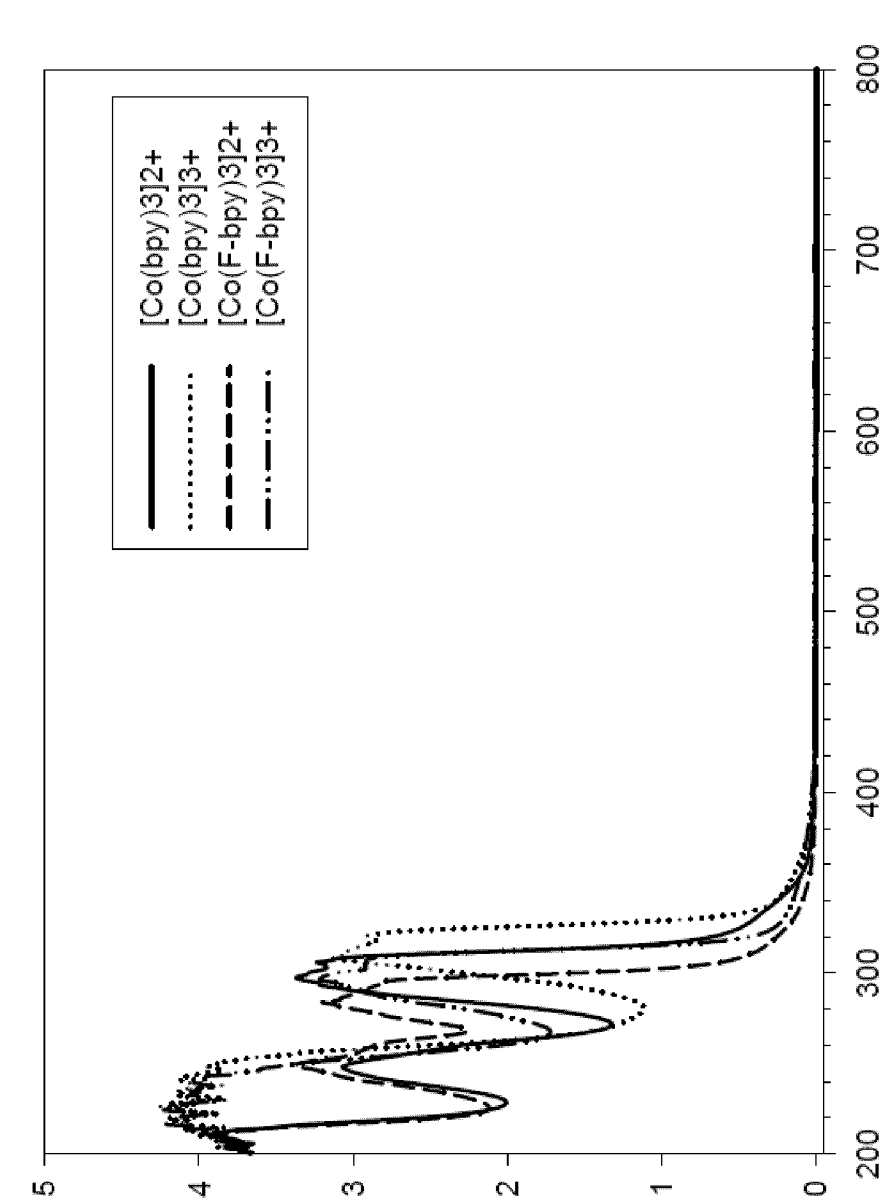
a step of providing an electrolyte ;

wherein said electrolyte comprises the metal complex according to any one of claims 1 to 5 as redox mediator.

10. Use of cobalt complex having polypyridine ligand comprising at least one fluorine atom, as redox mediator in photoelectric conversion device, in particular in dye-sensitized solar cell.

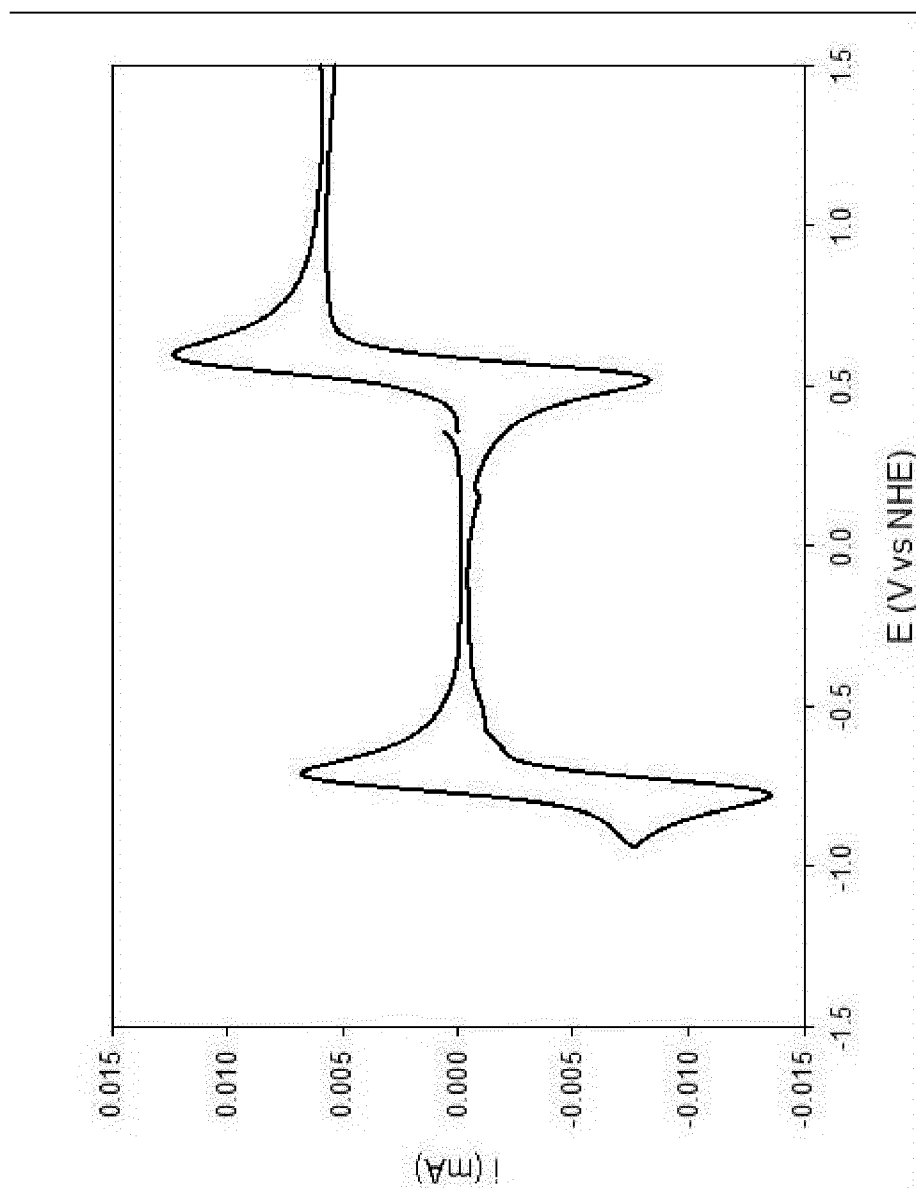
- 1 / 3 -

Figure 1



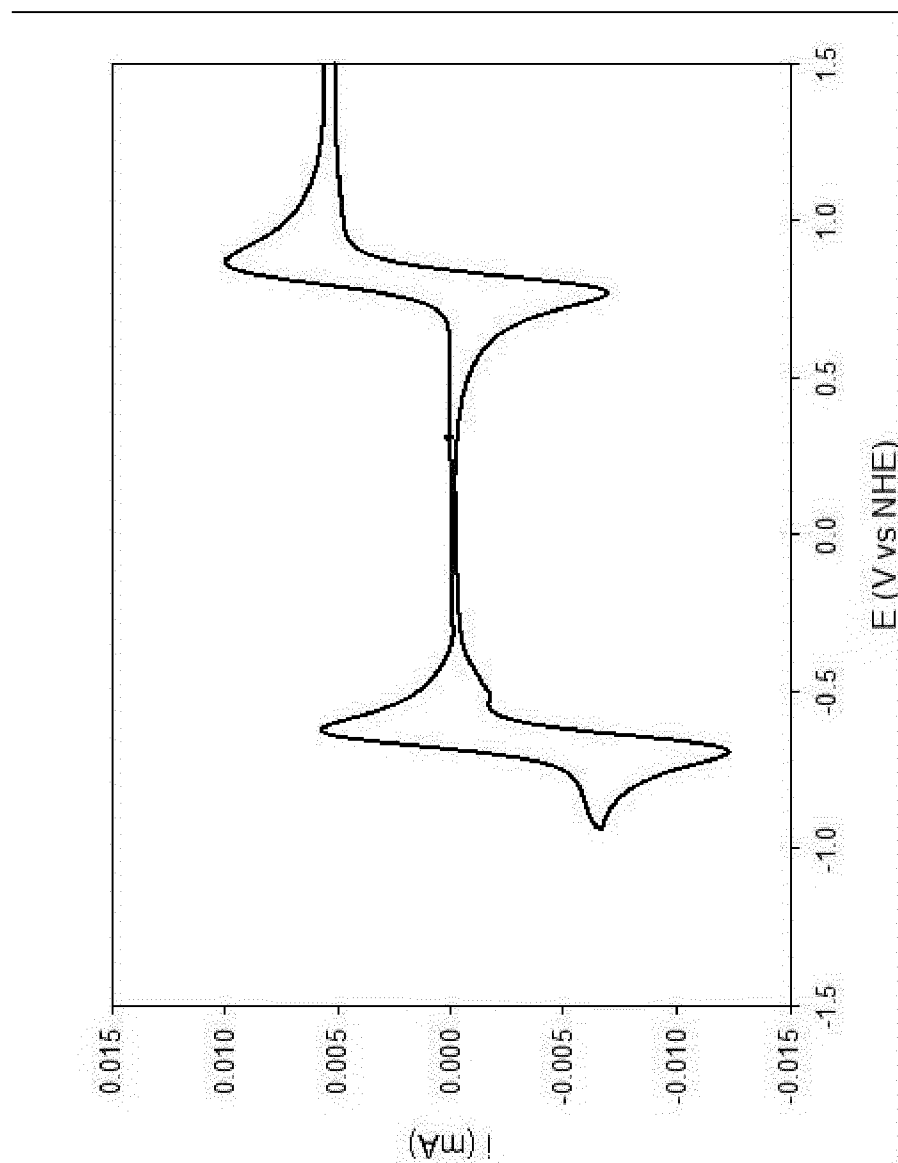
- 2 / 3 -

Figure 2



- 3 / 3 -

Figure 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/069300

A. CLASSIFICATION OF SUBJECT MATTER INV. C07D213/22 H01G9/20 ADD.											
According to International Patent Classification (IPC) or to both national classification and IPC											
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C07D H01G 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) EPO-Internal, WPI Data, CHEM ABS Data, BEILSTEIN Data											
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>QU F ET AL: "4-Fluoro-2,2'-bipyridine (fbpy) complexes of cobalt(II/III) and iron(II/III) and electron transfer in the Co(bpy)₃²⁺-Co(fbpy)₃³⁺ system", JOURNAL OF FLUORINE CHEMISTRY, ELSEVIER, NL, vol. 94, no. 1, 11 February 1999 (1999-02-11), pages 15-26, XP004159036, ISSN: 0022-1139, DOI: 10.1016/S0022-1139(98)00315-7</td> <td>1,2,4,5</td> </tr> <tr> <td>A</td> <td>page 24 - page 25; compounds Tris(4-fluoro-2,2'-bipyridine)cobalt(II/II I) ----- -/--</td> <td>3,6-10</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	QU F ET AL: "4-Fluoro-2,2'-bipyridine (fbpy) complexes of cobalt(II/III) and iron(II/III) and electron transfer in the Co(bpy) ₃ ²⁺ -Co(fbpy) ₃ ³⁺ system", JOURNAL OF FLUORINE CHEMISTRY, ELSEVIER, NL, vol. 94, no. 1, 11 February 1999 (1999-02-11), pages 15-26, XP004159036, ISSN: 0022-1139, DOI: 10.1016/S0022-1139(98)00315-7	1,2,4,5	A	page 24 - page 25; compounds Tris(4-fluoro-2,2'-bipyridine)cobalt(II/II I) ----- -/--	3,6-10
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A	page 24 - page 25; compounds Tris(4-fluoro-2,2'-bipyridine)cobalt(II/II I) ----- -/--	3,6-10									
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.											
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Date of the actual completion of the international search		Date of mailing of the international search report									
23 October 2013		31/10/2013									
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Jeanjean, Fabien									

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/069300

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/038508 A2 (UNIV COLORADO STATE RES FOUND [US]; UNIV FERRARA [IT]; ELLIOTT C MICHA) 8 May 2003 (2003-05-08) page 5, paragraph 27 page 27; claims 1, 3, 5, 8 page 28; claims 14, 18 page 29; claims 22, 23 page 18, line 25 - line 29 -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/069300

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 03038508	A2	08-05-2003	
		AU 2002357682 A1	12-05-2003
		US 2004267018 A1	30-12-2004
		WO 03038508 A2	08-05-2003
