

DOPANTS FOR SOLID-STATE DYE-SENSITIVE SOLAR CELLS

CROSS REFERENCE TO RELATED APPLICATIONS

[001] This application claims the benefit of priority under 35 U.S.C. §119(e) to United States Provisional Application No. 61/728,473 titled "A promising Co-based p-type dopant for spiro-OMeTAD in solid state dye sensitizer solar cells" filed on 20 November 2012 the entire disclosure of which is hereby incorporated by reference in its entirety for all purposes.

FIELD OF THE INVENTION

[002] The invention relates to new complexes that are useful as p-dopants. The present invention further relates to the use of the new complexes as p-dopants in hole-transporting-material (HTM). The invention further relates to HTM p-doped with the complex of the invention. The invention further relates to photo-electrochemical devices such as solar cells, in particular solid state dye sensitizer solar cells (ssDSC) that comprise the new complex of the invention.

BACKGROUND OF THE DISCLOSURE

[003] Chemical doping is an important strategy to alter the charge transport properties of both molecular and polymeric organic semiconductors, and finds application in organic electronic devices such as in solar cell.

[004] So far, solar cell market is still dominated by silicon-based solar cells. However, high production cost of silicon-based solar cells limits their growth in the market. Since the dye-sensitized solar cell (DSC) was invented by Grätzel in 1991 based on a nanocrystalline mesoporous TiO₂ film with ruthenium sensitizers and I⁻/I₃⁻ electrolyte system, it has emerged as one of the more promising solar cells due to its easy fabrication and low production cost in the manufacturing process. Even though, it still has some drawbacks: volatility and corrosive issues from the electrolyte system.

[005] Owing to the disadvantages of liquid-based DSC, solid-state dye-sensitized solar cells (ssDSC) have become another potential candidate solar cell design. In ssDSCs, a hole transporting material (HTM) acts as a charge transport medium which is similar to the role of conventional I⁻/I₃⁻ electrolyte in a liquid-based DSC. To date, the most commonly used HTM in ssDSC is still 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-

MeOTAD, Fig. 1) which was reported in the first ssDSC in 1998². Due to low conductivity in its pristine form, chemical doping is necessary to enhance the performance of spiro-MeOTAD as HTM in ssDSC. N(PhBr)₃SbCl₆ was first being used to dope the spiro-MeOTAD and exhibited an overall efficiency of 0.74 % in a Ru-based ssDSC.

[006] Recently, a new class of tris(2-(1*H*-pyrazol-1-yl)pyridine) cobalt(III) complex (FK102), Fig. 2 is used as p-type dopant in ssDSC sensitized with high molar extinction coefficient organic dye, Y123 (Fig. 4a), and a record high efficiency of 7.2 % was achieved³. The first oxidation potential of Spiro-MeOTAD in solution and FK102 dopant are 0.72 V and 1.06 V (vs. normal hydrogen electrode (NHE)), respectively. Thus, there is a driving force of around 350 mV for spiro-MeOTAD one-electron oxidation reaction.

[007] There is the need to provide further means to improve the conductivity of HTM that allow a more economical preparation of electrochemical devices such as solar cells, in particular ssDSC, and an efficient performance thereof.

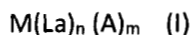
SUMMARY OF THE INVENTION

[008] The present invention addresses this need by providing new and improved p-dopants that improve the conductivity of HTM.

[009] The present invention provides new complexes of transition metal, in particular of cobalt, nickel, manganese, chromium and iron that are useful as p-dopants. In particular, the complexes are useful as p-dopants in HTM.

[0010] The complexes of the present invention have a high oxidation potential, which provides a high driving force for the one electron oxidation reaction in HTM, thereby improving the conductivity of the HTM.

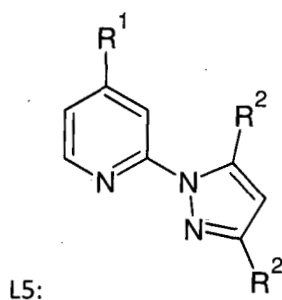
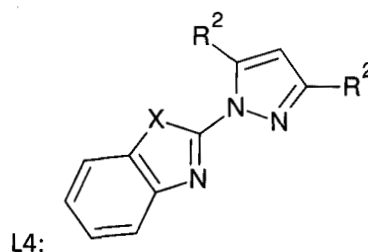
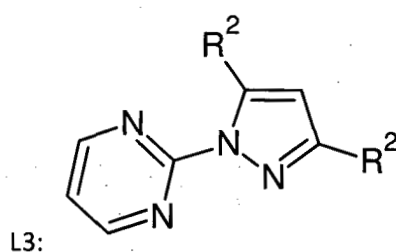
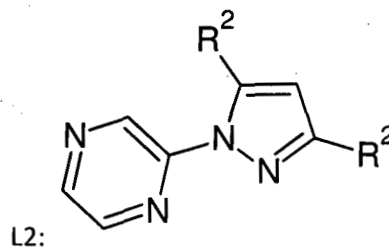
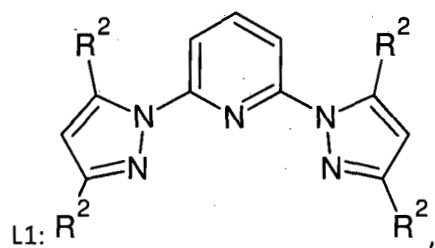
[0011] The present invention is therefore directed to a complex of formula (I)



wherein

M is Co, Ni, Cr, Mn and Fe preferably Co³⁺, Ni³⁺, Cr³⁺, Mn³⁺ and Fe³⁺,

La is independently a bi- or tri-dentate ligand selected from



wherein

R^1 is CF_3 or F

each R^2 is independently selected from H or CF_3

X is O or S,

n is an integer selected from 2 and 3,

A is a counter ion,

m is an integer selected from 0, 1, 2, or 3.

[0012] In a further aspect, the present invention provides a p-doped HTM comprising a HTM and a complex of formula (I). Preferably, the HMT is 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD).

[0013] In an aspect, the present invention provides a photo-electrochemical device comprising a complex of formula (I). Preferably the device is a solar cell, more preferably an ssDSC.

[0014] In an aspect, the present invention provides a photo-electrochemical device comprising a first and a second electrode having a layer between said first and second electrodes, said layer comprising a complex of formula (I). Preferably, the device is a solar cell, more preferably is an ssDSC.

[0015] In an aspect, the present invention provides a photo-electrochemical device comprising a first and a second electrode having a layer between said first and second electrodes, said layer comprising a p-doped HTM, said HTM comprising the complex of formula (I) as p-dopant. Preferably, the device is a solar cell, more preferably an ssDSC.

[0016] In an aspect the present invention provides a solar cell, more preferably an ssDSC, comprising the complex of formula (I).

[0017] In an aspect, the present invention provides the use of the complex of the invention as a p-dopant agent in an electrochemical device. Preferably, the device is a photo-electrochemical device, more preferably, the photochemical device is a solar cell, even more preferably an ssDSC.

[0018] In an aspect, the present invention provides the use of the complex of formula (I) as p-dopant for a HTM.

[0019] In an aspect, the present invention provides a method of preparing a p-doped HTM, the method comprising the step of providing an HTM, and, adding thereto the complex of formula (I).

[0020] In an aspect, the invention provides a method for increasing the conductivity of an HTM, the method comprising the step of adding to said HTM the complex of formula (I).

[0021] In an aspect, the present invention provides a method of preparing an electrochemical device, the method comprising the steps of providing a first and a second electrode and providing, between said first and second electrode, an HTM comprising the complex of formula (I).

DESCRIPTION OF THE DRAWINGS

[0022] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

[0023] Fig. 1 shows the chemical formula of the hole transporting material (HMT) 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD).

[0024] Fig. 2 shows the prior art complex FK102.

[0025] Fig. 3 shows the cationic component (MY) of the complex of the invention.

[0026] Fig. 4 (a), (b), (c), (d) and (e) show the chemical structures of (a) Y123, (b) D35 and (c) C220, (d) D-205 and (e) MK-2 organic sensitizers.

[0027] Fig. 5 shows the synthetic route for the preparation of 2,6-dipyrzolyipyridine ligand.

[0028] Fig. 6 shows the results of cyclic voltammetry of complex MY1.

[0029] Fig. 7 shows UV-Vis absorption spectra of spiro-MeOTAD solution in chlorobenzene with MY1 doping concentration of 0% (pristine spiro) 1.6 mole%, 2.1 mole%, 2.5 mole%, 3.0 mole%, 3.5 mole% and 6.0 mole%.

[0030] Fig. 8 shows spiro-MeOTAD to spiro-MeOTAD⁺ conversion yield using MY1 dopant.

[0031] Fig. 9 shows Current-voltage curves of non-doped, FK102 (1.6%) and MY1 (0.9%)-doped spiro-MeOTAD based devices measured under simulated AM1.5G (100 mWcm⁻²).

[0032] Fig. 10 depicts a schematic drawing of the device comprising Spiro-OMeTAD.

DETAILED DESCRIPTION

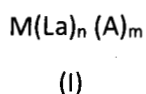
[0033] HMTs such as spiro 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD) (**Fig. 1**) act as charge transport medium in solid state dye sensitized solar cell (ssDSC). Due to the low conductivity of HMTs, such as spiro-MeOTAD, in their pristine form, chemical doping is necessary in order to enhance the performance of the HMT and ultimately of the solar cell.

[0034] Recently, a new class of tris(2-(1*H*-pyrazol-1-yl)pyridine) cobalt(III) complex (FK102, **Fig. 2**) is used as p-type dopant in ssDSC sensitized with high molar extinction coefficient organic dye, Y123 (**Fig. 4a**), and a record high efficiency of 7.2 % was achieved³. The first oxidation potential of spiro-MeOTAD in solution and of FK102 dopant are 0.72V and

1.06V (vs. NHE), respectively. Thus, there is a driving force of around 350mV for spiro-MeOTAD one-electron oxidation. The present inventors have found new complexes that provide a driving force greater than the driving force of FK102. Due to the large driving force for doping reaction, a high spiro-MeOTAD-to-spiro-MeOTAD⁺ conversion and a higher power conversion yield is achieved using an amount of p-dopant complex of formula (I) lower than the amount requires when FK102 is used.

[0035] The present inventors have measured the redox potential of the p-dopant of the invention "MY1" and found it to be 1.26 V vs. NHE, which is more positive of the first oxidation potential of spiro-MeOTAD (0.72 V vs. NHE) and greater than the redox potential of compound FK102 when measured under the same experimental conditions. Said difference provides a driving force of 540 mV for spiro-MeOTAD first electron oxidation reaction, which is greater than the driving force of about 350 mV of complex FK102 for spiro-MeOTAD one electro oxidation reaction. The greater driving force of the complexes of the invention results in a greater conductivity of the HTM.

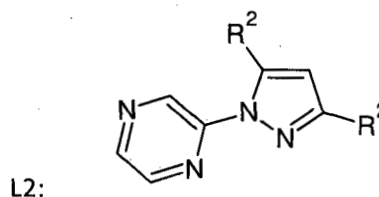
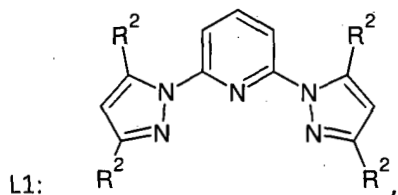
[0036] Hence, the present invention relates to a p-dopant complex of formula (I)

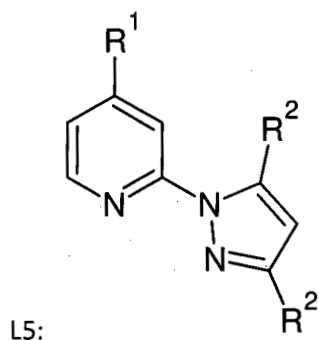
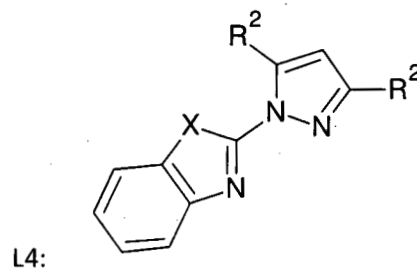
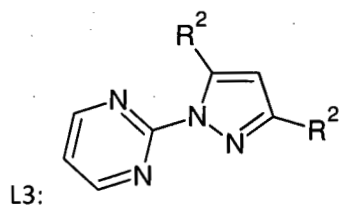


wherein

M is Co, Ni, Cr, Mn and Fe

La is independently a bi- or tri- dentate ligand selected from





wherein

R^1 is CF_3 or F;

each R^2 is independently selected from H or CF_3 ;

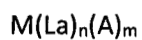
X is O or S;

n is an integer selected from 2 and 3;

A is a counter ion;

m is an integer selected from 0, 1, 2, or 3.

[0037] In an aspect the present invention relates to a complex of formula (I)

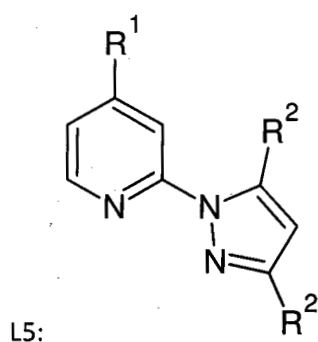
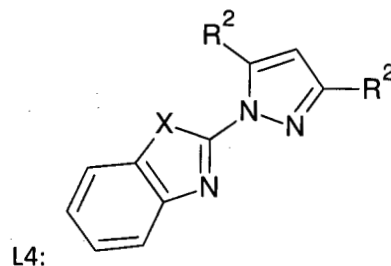
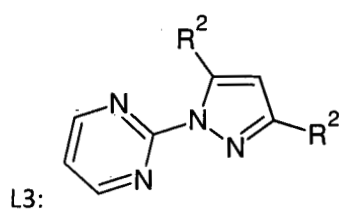
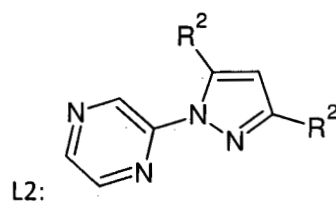
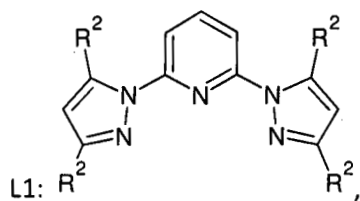


(I)

wherein

M is Co^{3+} , Ni^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} ;

La is independently a bi- or tri- dentate ligand selected from



wherein

R^1 is CF_3 or F;

each R^2 is independently selected from H or CF_3 ;

X is O or S;

n is an integer selected from 2 and 3;

A is a counter ion;

m is an integer selected from 0, 1, 2, or 3.

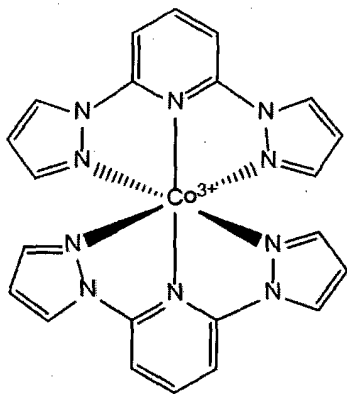
[0038] Preferably M is Co^{3+} or Ni^{3+} .

[0039] Preferably, A is bis(trifluoromethane)sulfonimide ($TfSI^-$), PF_6^- , BF_4^- , ClO_4^- or Trifluoromethanesulfonate (OTf^-). More preferably, A is $TfSI^-$.

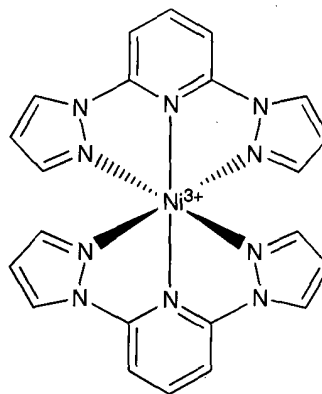
[0040] The value of "n" would depend on the ligand used. For example n=3 bidentate ligands or n=2 for tridentate ligands. Preferably, the ligand in a complex is the same ligand (for example (L1)₂, (L2)₃, (L4)₃, (L4)₃, (L5)₃).

[0041] The value of "m" would depend also on the counter ion A. Preferably, the value of m is such the net charge of the complex of formula (I) is 0. For example, if the charge of the counter ion has a (one) negative charge, such as TFSI⁻, PF₆⁻, BF₄⁻, ClO₄⁻, m is 3 to have a net 0 charge of the complex. Preferably, when the counter ion has a (one) negative charge m is 3. Preferably, A is PF₆⁻, TFSI⁻, BF₄⁻, ClO₄⁻ and m is 3. More preferably, A is TFSI⁻ and m is 3. TFSI⁻ may be chosen because it enhances solubility of the desired metal complexes, providing an additional advantage in case higher doping concentrations are required.

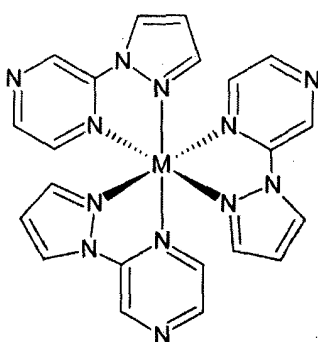
[0042] Preferably, M(La)_n of formula (I) is selected from:



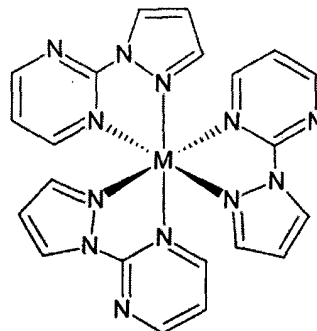
MY



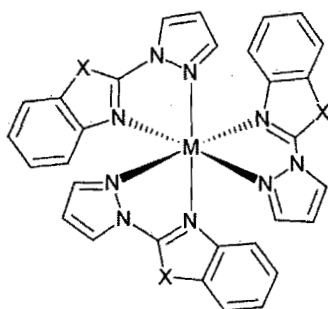
MY2



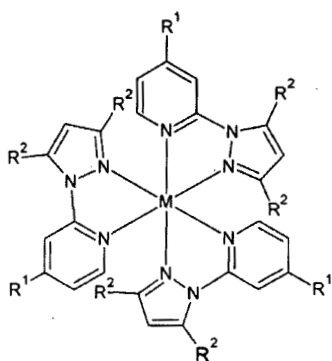
wherein M=Co³⁺ (MY3) or M=Ni³⁺ (MY4)



wherein M=Co³⁺ (MY5) or
M=Ni³⁺ (MY6)



wherein $X=S$ and $M=Co^{3+}$ (MY7) or
 $X=O$, $M=Co^{3+}$ (MY8) or
 $X=S$, $M=Ni^{3+}$ (MY9) or
 $X=O$, $M=Ni^{3+}$ (MY10)



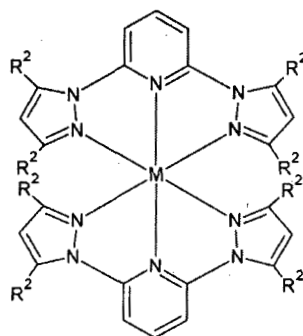
wherein

$R^1=F$ and $R^2=CF_3$ and $M=Co^{3+}$ (MY11)

$R^1=CF_3$ and $R^2=CF_3$ and $M=Co^{3+}$ (MY12)

$R^1=F$ and $R^2=CF_3$ and $M=Ni^{3+}$ (MY13)

$R^1=CF_3$ and $R^2=CF_3$ and $M=Ni^{3+}$ (MY14)



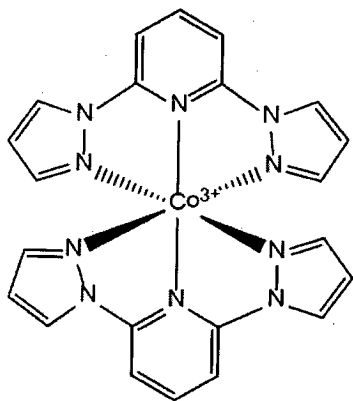
wherein

$R^2=CF_3$ and $M=Co^{3+}$ (MY15)

$R^2=CF_3$ and $M=Ni^{3+}$ (MY16)

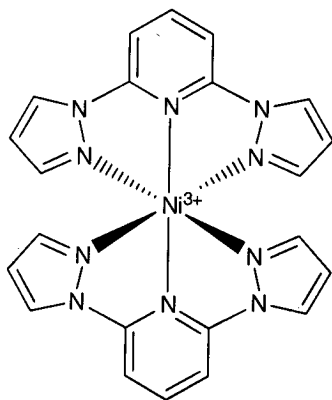
[0043] Hence, a preferred complex is a complex wherein in formula (I) $M(La)_n$ is MY, MY2, MY3, MY4, MY5, MY6, MY7, MY8, MY9, MY10, MY11, MY12, MY13, MY14, MY15 and MY16. A more preferred complex is a complex wherein in formula (I) $M(La)_n$ is MY, MY2, MY3, MY4, MY5, MY6, MY7, MY8, MY9, MY10, MY11, MY12, MY13, MY14, MY15 and MY16, A is $TFSl^-$ and m is 3.

[0044] Preferably, the complex of formula (I) is



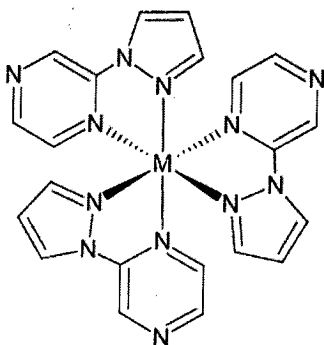
3TFSI^- .

[0045] Preferably, the complex of formula (I) is



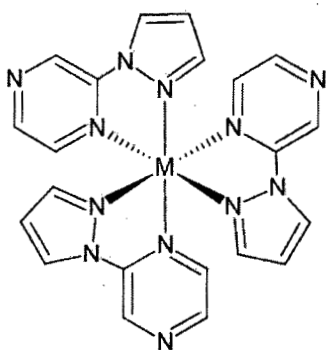
3TFSI^- .

[0046] Preferably, the complex of formula (I) is



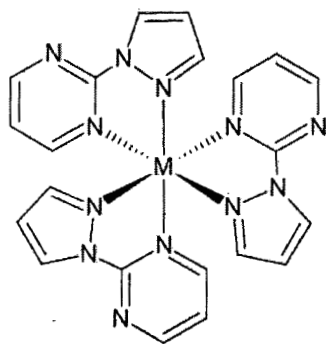
3TFSI^- wherein $\text{M}=\text{Co}^{3+}$.

[0047] Preferably, the complex of formula (I) is



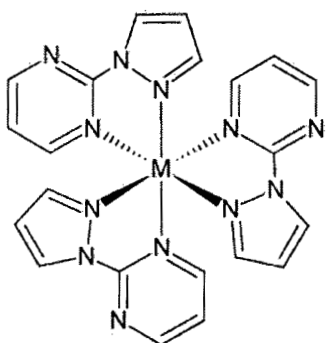
3TFSI⁻ wherein M=Ni³⁺.

[0048] Preferably, the complex of formula (I) is



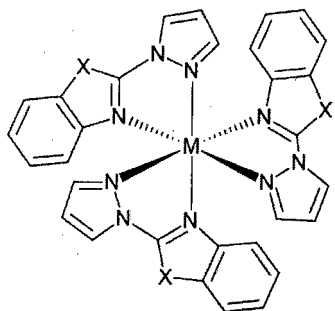
3TFSI⁻ wherein M=Co³⁺.

[0049] Preferably, the complex of formula (I) is



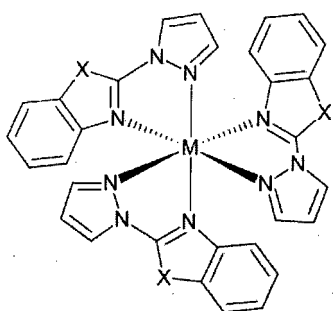
3TFSI⁻ wherein M=Ni³⁺.

[0050] Preferably, the complex of formula (I) is



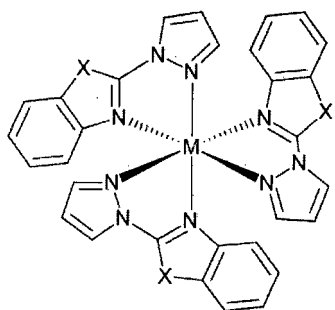
3TFSI⁻ wherein X=S and M= Co³⁺.

[0051] Preferably, the complex of formula (I) is



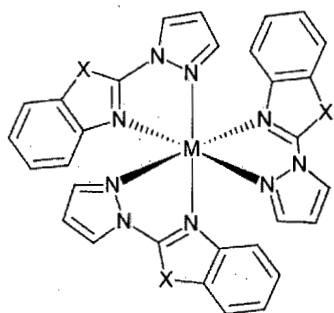
3TFSI⁻ wherein X=O, M= Co³⁺

[0052] Preferably, the complex of formula (I) is



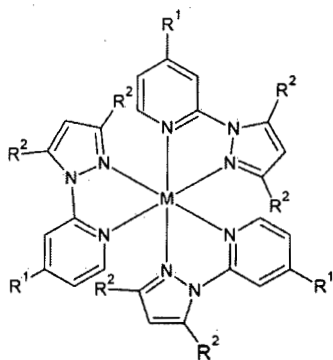
3TFSI⁻ X=S, M= Ni³⁺

[0053] Preferably, the complex of formula (I) is



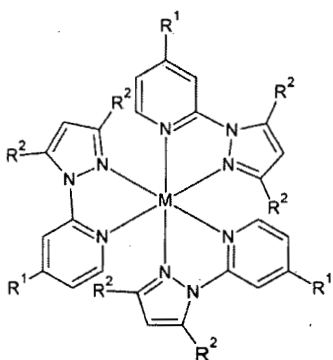
3TFSI⁻ X=O, M= Ni³⁺.

[0054] Preferably, the complex of formula (I) is



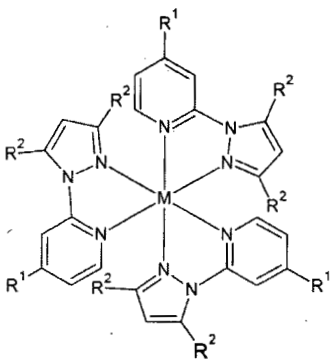
3TFSI⁻ wherein R¹=F and R²=CF₃ and M= Co³⁺.

[0055] Preferably, the complex of formula (I) is



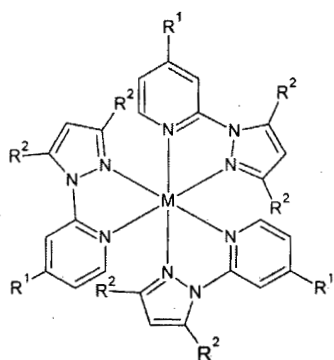
3TFSI⁻ wherein R¹= CF₃ and R²=CF₃ and M= Co³⁺.

[0056] Preferably, the complex of formula (I) is



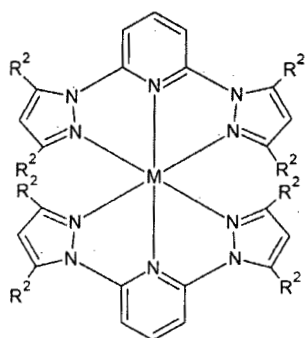
3TFSI⁻ wherein R¹= CF₃ and R²=CF₃ and M= Ni³⁺.

[0057] Preferably, the complex of formula (I) is



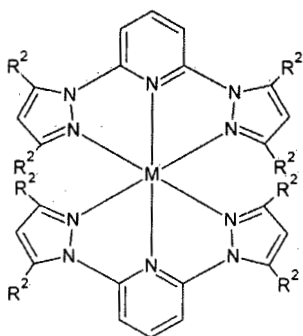
3TFSI⁻ wherein R¹=F and R²=CF₃ and M= Ni³⁺.

[0058] Preferably, the complex of formula (I) is



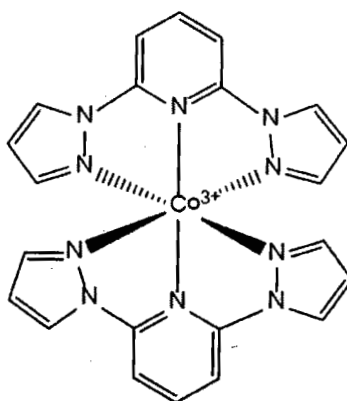
3TFSI⁻ wherein R₂=CF₃ and M= Co³⁺.

[0059] Preferably, the complex of formula (I) is



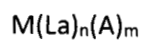
3TFSI⁻ wherein R₂=CF₃ and M= Ni³⁺.

[0060] The complex "MY1" of formula

3TFSI⁻

is a more preferred complex according to the invention.

[0061] In an aspect, the present invention is directed to a p dopant complex of formula (I):

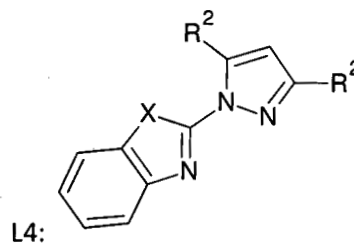
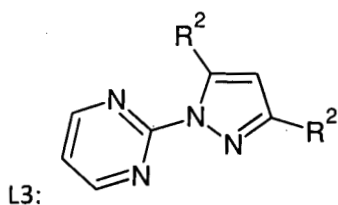
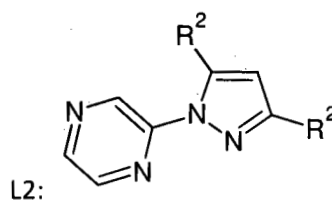
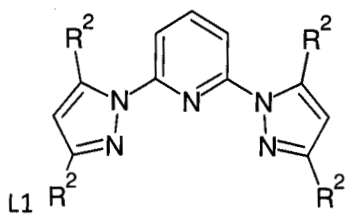


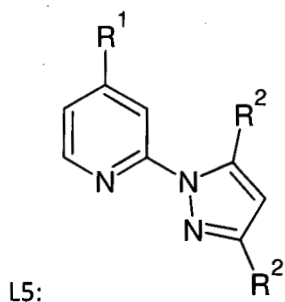
(I)

wherein

M is Co, Ni, Cr, Mn, Fe,

La is independently a bi- or tri- dentate ligand selected from





wherein R^1 is CF_3 or F

each R^2 is independently selected from H or CF_3 ;

X is O or S;

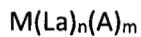
n is an integer selected from 2 and 3;

A is a counter ion;

m is an integer selected from 0, 1, 2, or 3;

with the proviso that the complex of formula (I) is not MY1.

[0062] In an aspect, the present invention is directed to a complex of formula (I),

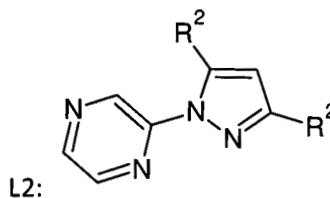
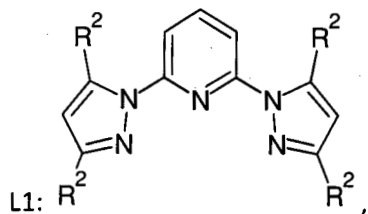


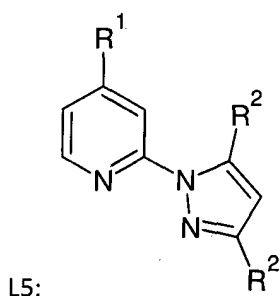
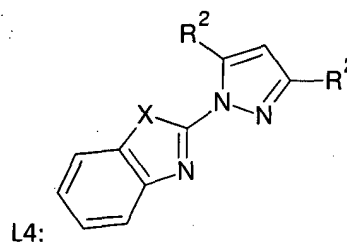
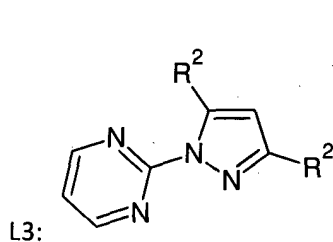
(I)

wherein

M is Co^{3+} , Ni^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} ;

La is independently a bi- or tri- dentate ligand selected from





wherein R^1 is CF_3 or F;

each R^2 is independently selected from H or CF_3 ;

X is O or S;

n is an integer selected from 2 and 3;

A is a counter ion;

m is an integer selected from 0, 1, 2, or 3;

with the proviso that the complex of formula (I) is not MY1.

[0063] As disclosed, the complex comprises one or more ligands, preferably two ligands or three ligands. Preferably the complex is made of 2 or 3 of same ligands. The inventors have first seen that introducing an additional pyrazole unit into the ligand framework is one of the ways to tune the redox potential of resultant complex more positively (MY and MY1). Therefore, they also investigated the doping ability by using Ni metal center (MY2). Further, the inventors coupled the pyrazole unit with different heterocycles instead of pyridine. Pyrazine (MY3 and MY4) and pyrimidine (MY5 and MY6) are two good candidates to couple with pyrazole and provide more positive redox potential of resultant Co^{3+} or Ni^{3+} complexes. Employing fused-ring heterocycles such as benzo-thiazole and benzoxazole moiety into ligand frameworks together with pyrazole is an additional way to tune the redox potential of the

dopant (MY7 to MY10). The presence of sulfur or oxygen atoms in the metal complexes brings different effect from nitrogen atoms in pyridine-based moiety. Similarly, electro-withdrawing substituents such as CF₃ in ortho position with respect to the "N" on the pyrazole ring have been seen to tune the redox potential leading to the complexes of the invention (MY11 to MY16).

[0064] The present invention is further directed to the use of the complexes as disclosed in the above embodiments as p-dopants. P-dopants are molecules, in particular complexes, that confer an excess of mobile electron hole to the material to be doped. The complex of the invention is preferably used as p-dopant in HTM. Preferred HTM according to the present invention is 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD).

[0065] The present invention is further directed to p-doped HTM comprising the complex of formula (I) of the invention. Preferably, the HTM according to the present invention is spiro-OMeTAD. The complex of the invention may be added to the HTM material at any suitable concentration. Preferred concentrations of the complex of the invention in the HTM range from 0.5 to 6.0% specifically 0.5 mole% to 6.0 mole%. The mole% calculation is based on the mole of HTM alone: i.e., $\text{mole\%} = (\text{mole of complex of formula (I)} / \text{mole of HTM}) \times 100$. More preferred concentrations range from 0.6% specifically 0.6 mole% to 2.5% specifically 2.5 mole%, even more preferred from 0.6% to 1.6%, specifically 0.6 mole% to 1.6 mole%, even further more preferred concentrations range from 0.7 to 0.9%, specifically 0.7 mole% to 0.9 mole%. Disclosed herein are also p-doped spiro-OMeTAD compositions comprising a complex wherein in formula (I) M(La)_n is MY, MY2, MY3, MY4, MY5, MY6, MY7, MY8, MY9, MY10, MY11, MY12, MY13, MY14, MY15 and MY16, A is TFSI⁻ and m is 3 at a concentration of 0.9%, specifically 0.9 mole%, 1.6% specifically 1.6 mole%, 2.1% specifically 2.1 mole%, 2.5% specifically 2.5 mole%, 3.0% specifically 3.0 mole%, 3.5% specifically 3.5 mole%, and 6.0% specifically 6.0 mole%. Disclosed herein are also p-doped spiro-OMeTAD compositions comprising MY1, at a concentration of 0.9%, specifically 0.9 mole%, 1.6%, specifically 1.6 mole%, 2.1%, specifically 2.1 mole%, 2.5% specifically 2.5 mole%, 3.0% specifically 3.0 mole%, 3.5% specifically 3.5 mole%, and 6.0% specifically 6.0 mole%. More preferably the concentration is of 0.9% specifically 0.9 mole%.

[0066] In fact, it has been found by the present inventors that the present complex has a high oxidative potential and provide a high driving force to the oxidation reaction in HTM.

Hence, low concentration of the complex can be used and yet achieve an effective conductivity of the HTM.

[0067] In another aspect, the present invention is directed to a photo-electro chemical device comprising the complex of formula (I) of the invention. Preferably, the photo-electro chemical device is a solar cell, more preferably a dye sensitized solar cell (DSC), even more preferably a solid state DSC (ssDSC). In the photo-electro chemical device of the invention, the complex of the invention is preferably comprised in a HTM. Hence, the HTM is a p-doped HTM doped with a complex of the invention. Hence, the photo-electro chemical device comprises a p-doped HTM comprising a complex of formula (I) of the invention. Preferably, the photochemical device comprises a p-doped HTM comprising the complex of formula (I) of the invention at a concentration ranging from 0.5% to 6.0% specifically 0.5 mole% to 6.0 mole%. More preferred concentrations range from 0.6% to 2.5% specifically 0.6 mole% to 2.5 mole%, even more preferred from 0.6% to 1.6% specifically 0.6 mole% to 1.6 mole%, and most preferred concentration ranges from 0.7 mole% to 0.9 mole%. Preferably, the p-doped HTM is spiro-OMeTAD and the preferred complex is a complex wherein in formula (I) $M(La)_n$ is MY, MY2, MY3, MY4, MY5, MY6, MY7, MY8, MY9, MY10, MY11, MY12, MY13, MY14, MY15 and MY16. A more preferred complex is complex wherein in formula (I) $M(La)_n$ is MY, MY2, MY3, MY4, MY5, MY6, MY7, MY8, MY9, MY10, MY11, MY12, MY13, MY14, MY15 and MY16 and A is TFSI⁻. Even more preferably, the dopant complex is MY1. Preferably, the concentration of MY1 in spiro-OMeTAD is of at a concentration of 0.9%, specifically 0.9 mole%, 1.6%, specifically 1.6 mole%, 2.1%, specifically 2.1 mole%, 2.5% specifically 2.5 mole%, 3.0% specifically 3.0 mole%, 3.5% specifically 3.5 mole%, and 6.0% specifically 6.0 mole%. More preferably, the concentration is of 0.9% specifically 0.9 mole%.

[0068] In another aspect, the present invention is directed to a photo-electro chemical device comprising the complex of formula (I) of the invention. Preferably, the photo-electro chemical device is a solar cell, more preferably a dye sensitized solar cell (DSC), even more preferably a solid state DSC (ssDSC). The complex of the invention is preferably comprised in a HTM. Hence, the HTM is a p-doped HTM doped with a complex of the invention. Preferably, the HTM is a p-doped HTM according to the invention. Hence, the photo-electro chemical device comprises a p-doped HTM comprising a complex of formula (I) of the invention. Preferably, the photochemical device comprises the p-doped HTM according to the invention comprising the complex of formula (I) of the invention. Preferably, the p-doped

HTM is spiro-OMeTAD and the preferred complex is a complex wherein $M(La)_n$ is MY, MY2, MY3, MY4, MY5, MY6, MY7, MY8, MY9, MY10, MY11, MY12, MY13, MY14, MY15 and MY16. More preferred complex is a complex wherein in formula (I) $M(La)_n$ is MY, MY2, MY3, MY4, MY5, MY6, MY7, MY8, MY9, MY10, MY11, MY12, MY13, MY14, MY15 or MY16, A is TFSI⁻ and m is 3. Even more preferably, the dopant complex is MY1. The concentration of the complex of formula (I) ranges from 0.5 mole% to 6.0 mole%, more preferably ranges from 0.5 mole% to 2.5 mole%; even more preferably the concentration ranges from 0.6 mole% to 1.6 mole%, even further more preferably the concentration ranges from 0.7 mole % to 0.9 mole%. Preferably, the concentration of MY1 in spiro-OMeTAD is of 0.9 mole% or of 1.6 mole% or of 2.1 mole% or of 2.5 mole%.

[0069] The photo-electro chemical device of the invention is preferably a DSC, even more preferably the DSC is selected from ssDSC. The dye/sensitizer is selected from the following dyes: triphenylamine-based organic dyes such as D35; metal free dyes such as Y123 and C220, the indoline dye D205 (2-((E)-5-(1,2,3,3a,4,8b-hexahydro-4-(4-(2,2-diphenylvinyl)phenyl)cyclopenta[b]indole-7-yl)methyl)-3-octyl-5-(3-carboxymethyl-4-oxo-thiazolidin-2-ylidene)rhodanine) and MK-2 (2-Cyano-3-[5'''-(9-ethyl-9H-carbazol-3-yl)-3',3'',3''',4-tetra-*n*-hexyl-[2,2',5',2'',5'',2''']-quater thiophen-5-yl] acrylic acid-CAS no. 1037440-21-3). Fig. 4 (a), (b), (c), (d) and (e) disclose the chemical formulae of these dyes.

[0070] The photo-electro chemical device of the invention comprises a first and a second electrode having a layer between said first and second electrodes, the layer comprising the complex of formula (I) as disclosed above. Preferred complex is a complex wherein $M(La)_n$ is MY, MY2, MY3, MY4, MY5, MY6, MY7, MY8, MY9, MY10, MY11, MY12, MY13, MY14, MY15 and MY16. More preferred complex is a complex wherein in formula (I) $M(La)_n$ is MY, MY2, MY3, MY4, MY5, MY6, MY7, MY8, MY9, MY10, MY11, MY12, MY13, MY14, MY15 and MY16 and A is TFSI⁻ and m is 3. An even more preferred complex is MY1.

[0071] In an aspect, the present invention is directed to a method for improving the conductivity of a HTM comprising doping the HTM with a complex of formula (I) of the invention. Preferably, the HTM is spiro-OMeTAD and the complex is a complex wherein $M(La)_n$ is MY, MY2, MY3, MY4, MY5, MY6, MY7, MY8, MY9, MY10, MY11, MY12, MY13, MY14, MY15 and MY16. A more preferred complex is complex wherein in formula (I) $M(La)_n$ is MY, MY2, MY3, MY4, MY5, MY6, MY7, MY8, MY9, MY10, MY11, MY12, MY13, MY14, MY15 and MY16, A is TFSI⁻ and m is 3. Even more preferably, the doped complex is MY1. Preferably,

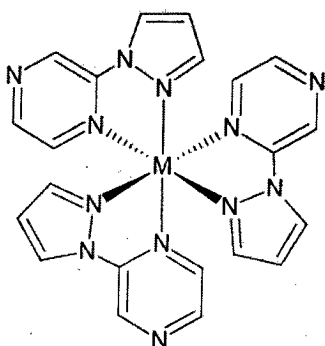
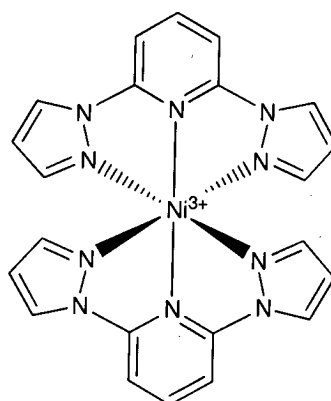
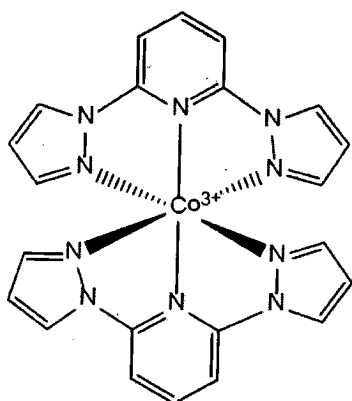
the complex of formula (I) is added to the HTM to have a final concentration ranging from 0.5 mole % to 6.0 mole %; more preferably to have a final concentration ranging from 0.6 mole % to 2.5 mole%, even more preferably from 0.6 mole% to 1.6 mole%, even further more preferably from 0.7 mole% to 0.9mole%. Preferably, the concentration of MY1 in spiro-OMeTAD is of 0.9%, specifically 0.9 mole %, 1.6%, specifically 1.6 mole %, 2.1%, specifically 2.1 mole %, 2.5% specifically 2.5 mole %, More preferably, MY1 is added to have p-doped-spiro-OMeTAD at 0.9 % specifically 0.9 mole %.

[0072] In a further aspect, the present invention is directed to a method for preparing a photochemical device comprising:

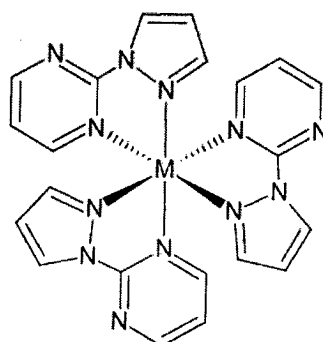
- a) providing a first and a second electrodes;
- b) providing between said first and second electrode an HTM comprising the complex of formula (I).

[0073] Preferably, the HTM is spiro-OMeTAD and the complex is a complex of formula (I) wherein $M(La)_n$ is MY, MY2, MY3, MY4, MY5, MY6, MY7, MY8, MY9, MY10, MY11, MY12, MY13, MY14, MY15 and MY16. A more preferred complex is a complex wherein in formula (I) $M(La)_n$ is MY, MY2, MY3, MY4, MY5, MY6, MY7, MY8, MY9, MY10, MY11, MY12, MY13, MY14, MY15 and MY16, A is TFSI⁻ and m is 3. Even more preferably, the dopant complex is MY1. Preferably, the complex of formula (I) is added to have a final concentration ranging from 0.5 mole% to 6.0 mole%; more preferably to have a final concentrations ranging from 0.6 mole% to 2.5 mole%, even more preferably from 0.6 mole% to 1.6 mole%, even further more preferably from 0.7 mole% to 0.9 mole%. Preferably, the concentration of MY1 in spiro-OMeTAD is of 0.9%, specifically 0.9 mole %, 1.6%, specifically 1.6 mole %, 2.1%, specifically 2.1 mole %, 2.5% specifically 2.5 mole %,.. More preferably, MY1 is added to have p-doped-spiro-OMeTAD at 0.9 % specifically at 0.9% mole%.

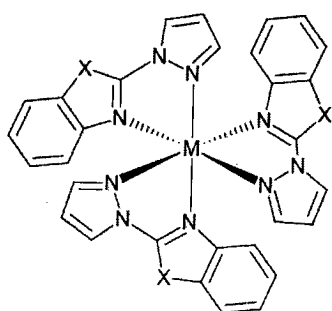
[0074] In an aspect the present invention is further directed to a complex selected from:



wherein $M = \text{Co}^{3+}$ or Ni^{3+}



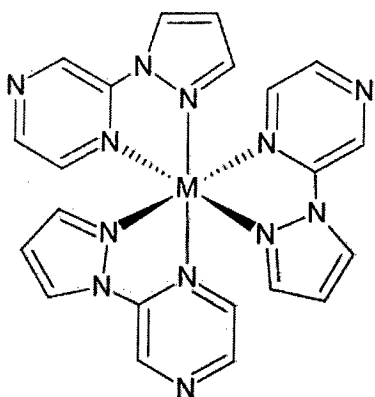
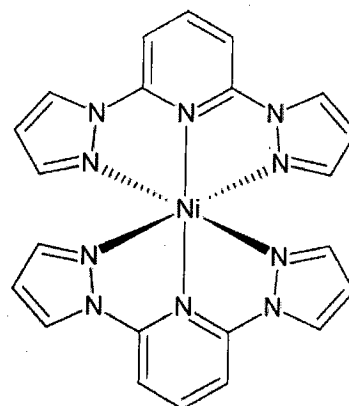
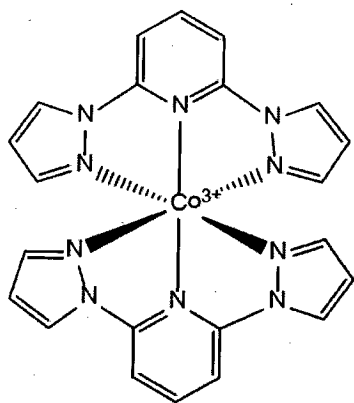
wherein $M = \text{Co}^{3+}$ or Ni^{3+}



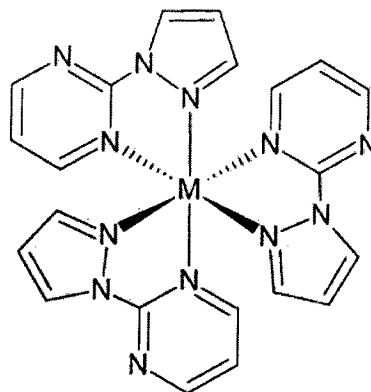
wherein

- X=S and $M = \text{Co}^{3+}$ or
- X=O, $M = \text{Co}^{3+}$ or
- X=S, $M = \text{Ni}^{3+}$ or
- X=O, $M = \text{Ni}^{3+}$.

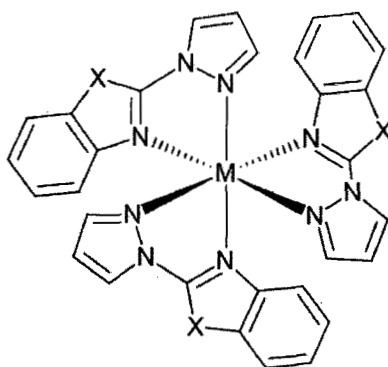
[0075] The present invention is further directed to a molecule selected from:



wherein M=Co or Ni



wherein M=Co or Ni



wherein X=S and M= Co or
 X=O, M= Co or
 X=S, M= Ni or
 X=O, M= Ni.

EXAMPLES

[0076] Incorporation of different heterocycles into the ligand framework is one of the strategies to tune the redox potential of the resultant metal complexes. In order to have more driving forces in spiro-OMeTAD oxidation reaction, a tridentate ligand having two pyrazole units incorporated to a pyridine moiety at 2,6-positions has been synthesized. The synthetic route of tridentate 2,6-bis(pyrazol-1-yl)pyridine (Ligand L) is shown in Figure 5. Herein, the use of a cobalt(III) complex (MY1) with even more positive redox potential than FK102 as p-type dopant for spiro-OMeTAD in ssDSC sensitized with triphenylamine-based organic dye, D35 (Figure 4b) is disclosed.

Example 1: Synthesis of complex MY1

a) Synthesis of 2,6-bis(pyrazol-1-yl)pyridine (ligand L1)

[0077] 2 g (0.029 mol) of pyrazole (Sigma Aldrich) and 3.96 g (0.035 mol) of potassium *tert*-butoxide (Sigma Aldrich) were mixed and 25 ml of DMSO was added into the mixture. The mixture was stirred at room temperature until dissolution. To this solution, 3.16 g (0.013 mol) of 2,6-dibromopyridine (Sigma Aldrich) was added and the solution turns to yellowish

brown. The mixture was heated to 110 °C for 4 days for complete reaction. The solution was cooled down to room temperature and precipitation of desired compound was induced by adding deionized water. The white precipitate formed was collected by filtration and washed thoroughly with deionized water to remove the excess pyrazole. The product was dried under vacuum and obtained in 89 % yield (2.51 g).

b) Synthesis of $\text{Co(L)}_2(\text{TFSI})_2$

[0078] To a solution of 250 mg (1.1 mmol) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich) in 20 ml MeOH, 444 mg (2.1 mmol) of ligand L was added. The solution was stirred at room temperature for 1 hour. Excess LiTFSI salt (Sigma Aldrich) was added to the solution and stirred for 30 mins. To this solution, deionized water was added to precipitate the cobalt complex. The compound was collected by filtration and washed thoroughly with deionized water and diethyl ether. The product was dried under vacuum and obtained in 75 % yield (1.09 g)

c) Synthesis of $\text{Co(L)}_2(\text{TFSI})_3$ (MY1)

[0079] 200 mg (0.19 mmol) of $\text{Co(L)}_2(\text{TFSI})_2$ was dissolved in 5 ml of MeCN and 67 mg (0.58 mmol) of NOBF_4 (Sigma Aldrich) was added to the solution. The solution was stirred at room temperature for 30 minutes and excess LiTFSI salt was added. The solution was allowed for another 30 minutes stirring and deionized water was added to precipitate the desired compound. The precipitate was collected by filtration and washed with deionized water and diethyl ether. The desired cobalt dopant, MY1, was dried under vacuum and obtained in 39 % yield (100 mg).

d) Solar cell device fabrication

[0080] Fluorine doped tin oxide (FTO) substrate was first immersed in 40 mM of TiCl_4 solution for 30 min at 70°C and then rinsed with deionized water and ethanol. A thin compact layer of TiO_2 (blocking layer) was deposited by aerosol spray-pyrolysis at 450°C. A 2.3 μm thick mesoporous TiO_2 film was screen-printed on the substrate and it was calcined at 500°C for 30 min. Then, the substrate was again immersed in 40 mM of TiCl_4 solution for 30 min at 70 °C, followed by sintering at 500 °C for 30 min. The films were dipped into ethanolic solution containing 0.2 mM D35 (Dyename) for 4 hours. Spiro-OMeTAD (2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)9,9'-spirobifluorene) solution was subsequently spin-coated

on top of mesoporous TiO_2 film loaded with D35 sensitizers. Gold counter electrode was deposited using thermal evaporation method. The cross-section of the device is shown in Fig.10.

Example 2: Photo electrochemical device results

[0081] The redox potential of the new spiro-OMeTAD dopant (**MY1**) is characterized by using cyclic voltammetry. The CV plot is given in Figure 6. The redox potential of the MY1 was found to be 1.26 V vs. NHE which is more positive compared to the first oxidation potential (0.72 V vs. NHE) of spiro-OMeTAD. There is more than 500 mV of driving for spiro-OMeTAD first electron oxidation reaction in order to enhance the conductivity from its pristine form in the device (Fig. 7)

[0082] The oxidation of pristine spiro-OMeTAD can be investigated via optical absorption measurement of doped spiro-OMeTAD solution. The UV-Vis absorption spectra of spiro-OMeTAD in chlorobenzene solution with different MY1 doping concentrations are shown in Fig. 7. With gradually increase of dopant concentrations, the appearance of absorption band at 523 nm is enhanced which is corresponded to the absorption of oxidized spiro species (spiro-OMeTAD⁺).

[0083] The conversion efficiency of spiro-OMeTAD by MY1 has been determined. The graph of mol % of spiro-OMeTAD⁺ against mol % of MY1 added is illustrated in Figure 7. Due to the large driving force (> 500 mV) for spiro-OMeTAD one-electron oxidation reaction, MY1 possesses high spiro-OMeTAD-to-spiro-OMeTAD⁺ conversion (~73 %) compared to that of FK102 which is around 65 %³. Therefore, the higher conversion yield from MY1 guarantees the enhanced conductivity of spiro-OMeTAD in the solid-state DSCs.

[0084] As aforementioned, non-doped spiro-OMeTAD is having an issue of low conductivity. By using MY1 dopant, spiro-OMeTAD is oxidized and radical cation of MeOTAD⁺ is formed. These free charge carriers increase the conductivity of spiro-OMeTAD and hence exhibited better photovoltaic performances. Solar cells using MY1-doped spiro-OMeTAD were fabricated together with the devices having non-doped and FK102-doped spiro-OMeTAD according to the process disclosed in Example 1 d). Fig. 10

[0085] *J-V* curves measured under simulated AM1.5G (100 mWcm⁻²) of these devices are illustrated in Figure 9 whereas the photovoltaic parameters are summarized in Table 1.

[0086] **Table 1.** Photovoltaic performances of DSCs (D35 as dye) using non-doped, FK102- and MY1-doped spiro-MeOTAD.

doping concentration	blank	FK102 1.6%	MY1 0.9%
J_{sc} (mAcm⁻²)	7.1	8.5	8.4
V_{oc} (mV)	977	929	933
FF	0.48	0.60	0.63
η (%)	3.4	4.7	4.9

[0087] FK102 has been shown its optimized performance at 1.6 mole% doping concentration². From Table 2, it can be noticed that 0.9% doping concentration of MY1 performs better than FK102 (1.6% doping concentration) in which 4.9 % of power conversion efficiency is achieved by using MY1 dopant. Owing to its more positive redox potential as compared to FK102 (1.26 V vs. 1.06 V), spiro-OMeTAD-to-spiro-OMeTAD⁺ conversion efficiency of MY1 is higher than FK102 (73% vs. 65%). Unlike the use of 1.6% doping concentration in FK102, high power conversion efficiency can also be accomplished by using lesser doping concentration (0.9% in MY1). The high spiro-OMeTAD conversion yield in MY1 allows less amount of dopant to be used in device which leads to reduced manufacturing cost.

[0088] The reduced form of dopant after oxidizing spiro-OMeTAD will remain in the device. It is actually behaved as impurity in device after spiro-OMeTAD doping reaction. The more dopant used, the more impurities remain in the device. The presence of the reduced form of dopant could affect the device performances as well as its long term stability. Therefore, it is advantageous to use minimal amount of dopant to achieve optimal solar cell performance as with the dopant of the present invention.

[0089] In summary, the experimental results show that MY1 is an excellent p-type dopant for spiro-OMeTAD in ssDSCs with high spiro-OMeTAD doping yield. With only 0.9% of MY1 doping concentration, a power conversion efficiency of 4.9% has been obtained. The power conversion of the obtained with the present is higher than that of using FK102 at a higher doping concentration of 1.6%. The feasibility of using minimal amount of dopant in achieving high efficiency ssDSCs could reduce the manufacturing cost as well as enhance the device long term stability. Lastly, MY1 with highly positive redox potential can be dopant for more kinds of HTMs as compared to FK102 in organic electronics and photovoltaic applications.

[0090] The invention has been described broadly and generically herein. Each of the narrower species and sub-generic groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

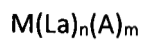
[0091] Other embodiments are within the following claims. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

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- [1] B. Oregan and M. Gratzel, *Nature* **1991**, 353, 737-740.
- [2] U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer and M. Gratzel, *Nature* **1998**, 395, 583-585.
- [3] J. Burschka, A. Dualeh, F. Kessler, E. Baranoff, N. L. Cevy-Ha, C. Y. Yi, M. K. Nazeeruddin and M. Gratzel, *Journal of the American Chemical Society* **2011**, 133, 18042-18045.

Claims

1. A complex of formula (I)

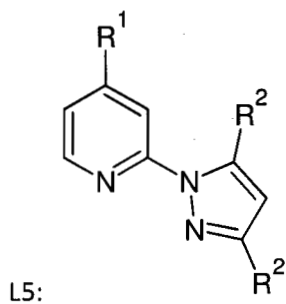
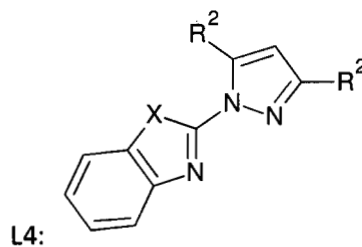
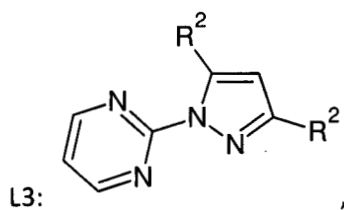
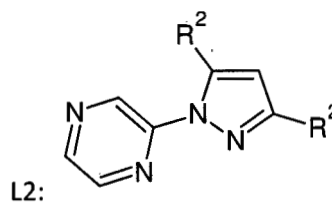
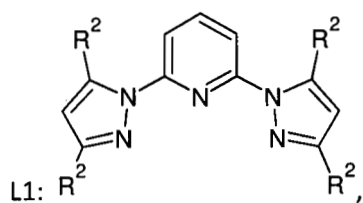


(I)

wherein

M is Co^{3+} , Ni^{3+} , Cr^{3+} , Mn^{3+} or Fe^{3+} ,

La is independently a bi- or tri-dentate ligand selected from



wherein

R^1 is CF_3 or F

each R^2 is independently selected from H or CF_3

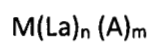
X is O or S,

n is an integer selected from 2 and 3,

A is a counter ion,

m is an integer selected from 0, 1, 2, or 3.

2. A p-dopant complex of formula (I)

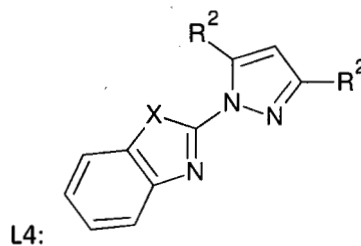
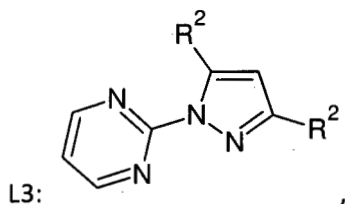
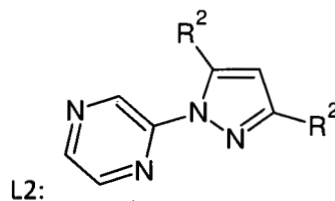
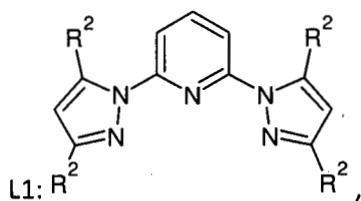


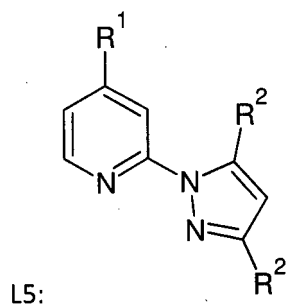
(I)

wherein

M is Co, Ni, Cr, Mn and Fe

La is independently a bi- or tri-dentate ligand selected from





wherein

R^1 is CF_3 or F

each R^2 is independently selected from H or CF_3

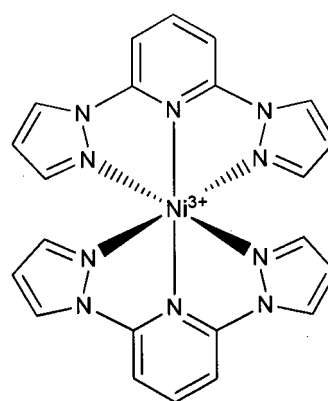
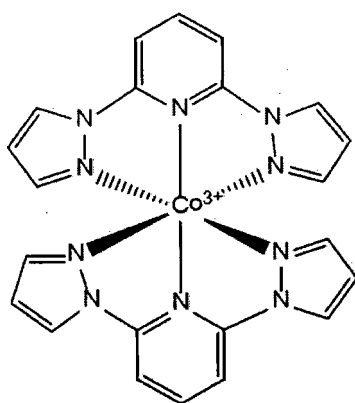
X is O or S,

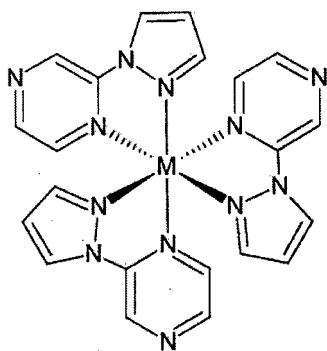
n is an integer selected from 2 and 3,

A is a counter ion,

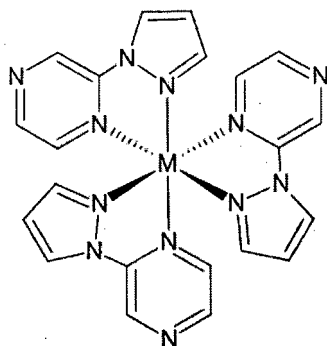
m is an integer selected from 0, 1, 2, or 3.

3. The complex according to anyone of claims 1 or 2 wherein M is Co^{3+} or Ni^{3+} .
4. The complex according to anyone of claims 1 or 2 or 3 wherein $M(La)_n$ is selected from:

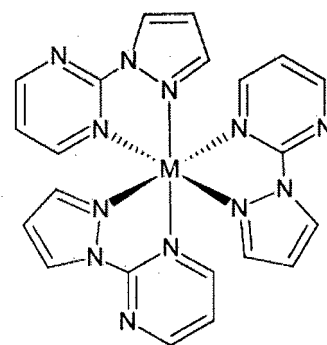




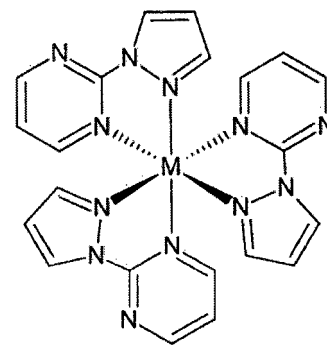
wherein $M = \text{Co}^{3+}$; or



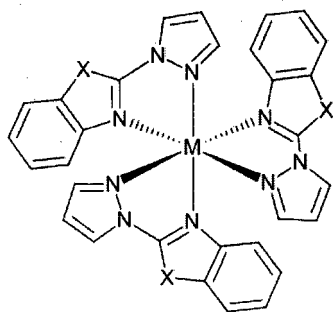
wherein $M = \text{Ni}^{3+}$; or



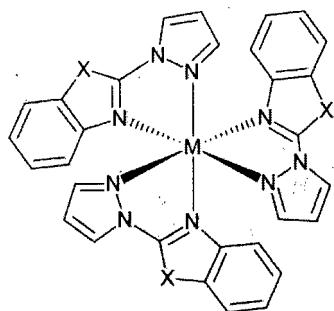
wherein $M = \text{Co}^{3+}$; or



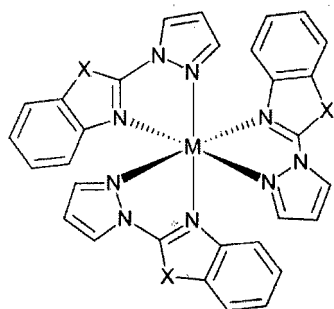
wherein $M = \text{Ni}^{3+}$; or



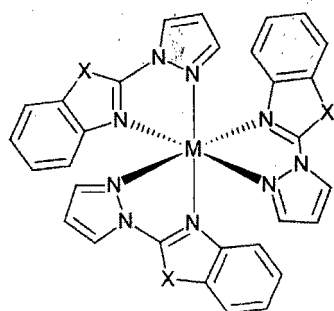
wherein $X=S$, $M=Co^{3+}$; or



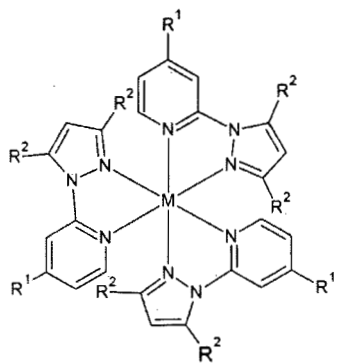
wherein $X=O$, $M=Co^{3+}$; or



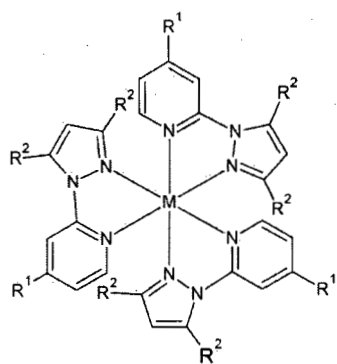
wherein $X=S$, $M=Ni^{3+}$ or



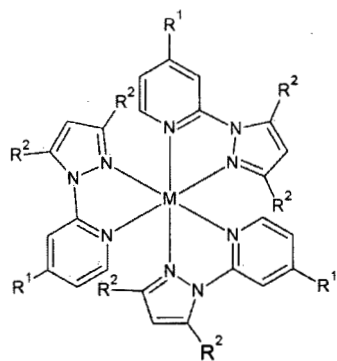
wherein $X=O$, $M=Ni^{3+}$; or



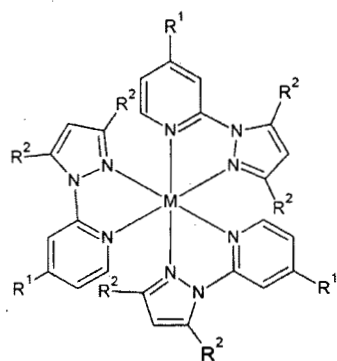
wherein $R^1 = F$ and $R^2 = CF_3$ and $M = Co^{3+}$ or



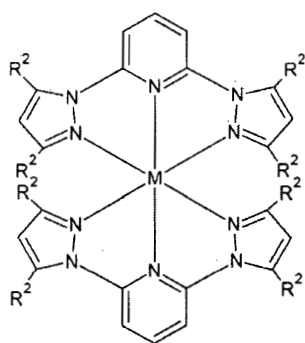
wherein $R^1 = CF_3$ and $R^2 = CF_3$ and $M = Co^{3+}$ or



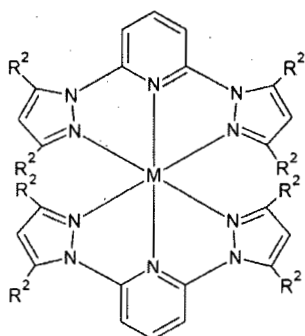
wherein $R^1 = F$ and $R^2 = CF_3$ and $M = Ni^{3+}$ or



wherein $R^1 = CF_3$ and $R^2 = CF_3$ and $M = Ni^{3+}$ or

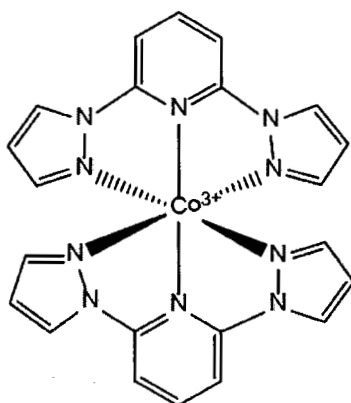


wherein $R^2 = CF_3$ and $M = Co^{3+}$ or



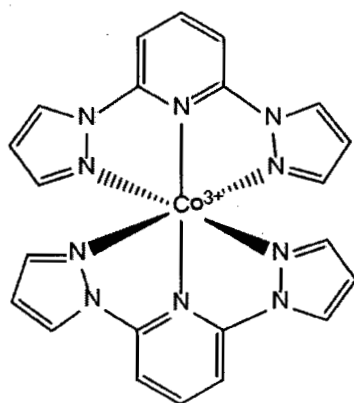
wherein $R^2 = CF_3$ and $M = Ni^{3+}$.

5. The complex according to anyone of claims 1 or 2 or 3 or 4 wherein the counter-ion A is selected from: PF_6^- , bis(trifluoromethane)sulfonimide ($TfSi^-$), BF_4^- , ClO_4^- , Trifluoromethanesulfonate (OTf^-).
6. The complex according to anyone of claims 1-5 wherein m is 3.
7. The complex according to anyone of claims 1 to 6 wherein A is $TfSi^-$ and m is 3.
8. The complex of anyone of claims 1 to 4 wherein m=0
9. The complex of formula

3TFSI⁻.

10. Use of the complex as defined in any of claims 1 to 9 as a p-dopant in hole-transporting material (HTM).
11. Use according to claim 10 wherein the hole transporting material is 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD).
12. A p-doped transporting material comprising a hole transporting material and the complex as defined in any of claims 1 to 9.
13. The p-doped hole transporting material according to claim 12 wherein the complex concentration (p-donor concentration) ranges from 0.5 mole % to 2.5 mole%.
14. The p-doped hole transporting material of anyone of claims 12-13 wherein the hole transporting material is spiro-OMeTAD.
15. The p-doped hole transporting material according to claim 14 wherein the complex is MY1 at a concentration of 0.9 % specifically 0.9 mole%, 1.6% specifically 1.6 mole%, 2.1 specifically 2.1 mole%.
16. A photo-electrochemical device comprising a complex as defined in any of claims 1 to 9.
17. A photo electrochemical device comprising p-doped hole transporting material as defined in anyone of claims 12-15.
18. The photo-electrochemical device according to claims 16-17 which is a solar cell, preferably a dye sensitized solar cell.
19. The photo-electrochemical device according to claims 16-18 wherein the dye is selected from D35, Y123, C220, D-250 and MK-2.

20. A photo-electrochemical device comprising a first and a second electrode having a layer between said first and second electrodes, the layer comprising the complex of any of claims 1 to 9.
21. A photo-electrochemical device comprising a first and a second electrode having a layer between said first and second electrodes, the layer comprising the p-doped hole transporting material of any of claims 12-15.
22. A method for improving the conductivity of a HTM comprising
- doping the HTM material with a complex of formula (I) as defined in any of claims 1-9.
23. A method for preparing a photochemical device comprising
- c) providing a first and a second electrodes;
 - d) providing between said first and second electrode an HTM comprising the complex of formula (I) as defined in any of claims 1-9.
24. A solid state dye sensitized solar cell (ssDSC) sensitized with D35 comprising spiro-OMeTAD doped with a complex of any of claims 1 to 9.
25. The ssDSC of claim 24 wherein the complex is

3TFSI⁻.