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(54) HETEROLEPTIC, DUAL TRIDENTATE RU(II) COMPLEXES AS SENSITIZERS FOR DYE-SENSITIZED SOLAR CELLS

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(57) **ABSTRACT**

Photosensitizers having a formula of RuL_1L_2 (1) are provided, wherein Ru is ruthenium; L_1 and L_2 are heterocyclic tridentate ligands. L_1 has a formula of (2), and L_2 has a formula of $G_1G_2G_3$ (3), wherein G_1 and G_3 are selected from the group consisting of formulae (4) to (7), and G_2 is selected from the group consisting of formulae (7) and (8). The abovementioned photosensitizers are suitable to be used as sensitizers for fabrication of high efficiency dye-sensitized solar cells.

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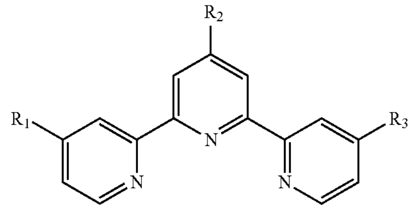

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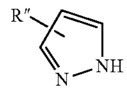

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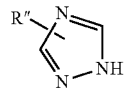

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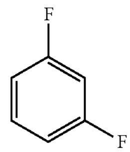

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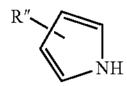

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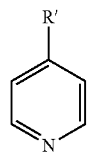
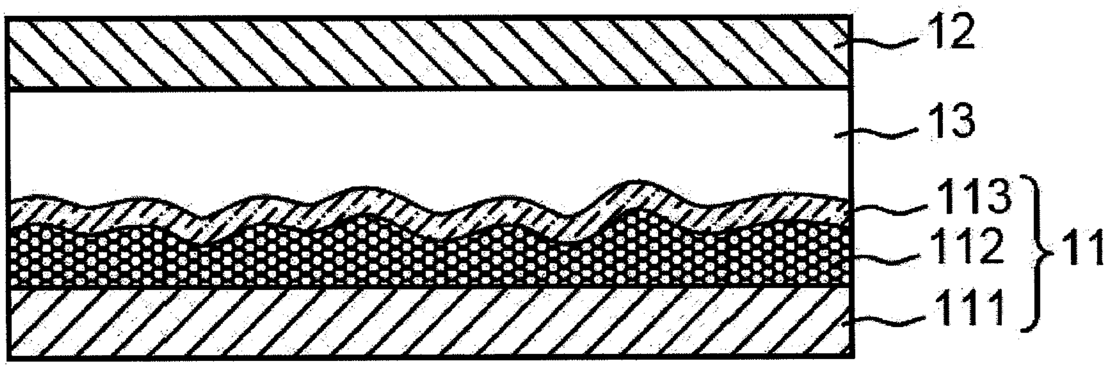




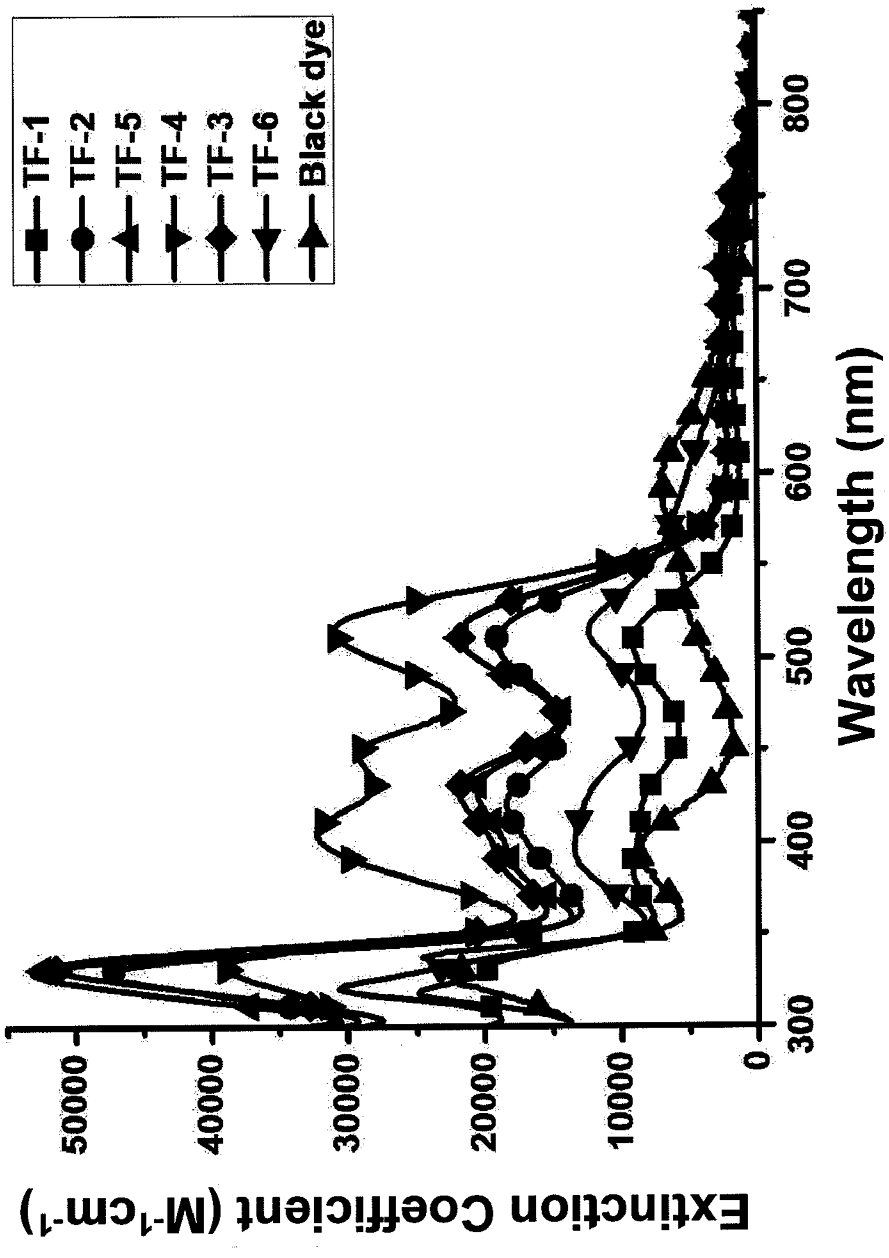

TF-1
TF-2
TF-5
TF-4
TF-3
TF-6
Black dye
Extinction Coefficient (M-1cm-1)
50000
40000
30000
20000
10000
0
300
400
500
600
700
800
Wavelength (nm)

Fig. 1

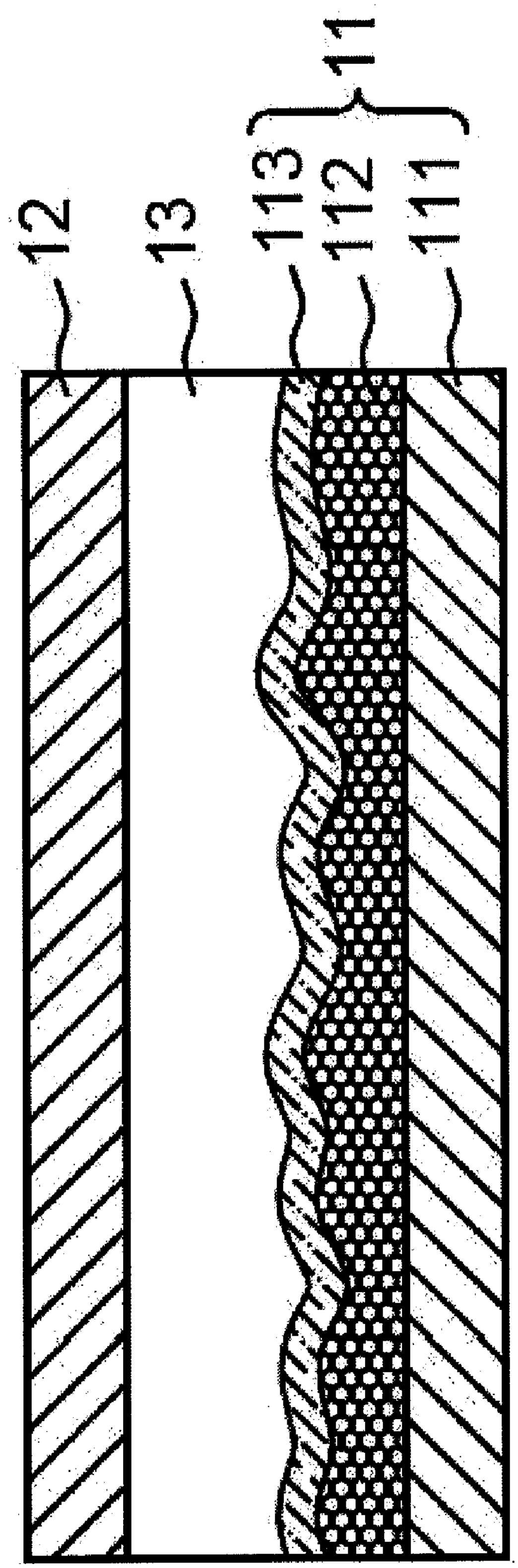


Fig. 2

HETEROLEPTIC, DUAL TRIDENTATE RU(II) COMPLEXES AS SENSITIZERS FOR DYE-SENSITIZED SOLAR CELLS

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to solar sensitizers using heteroleptic, dual tridentate Ru(II) complexes and dye-sensitized solar cells, particularly to sensitizers and dye-sensitized solar cells with better conversion efficiency.

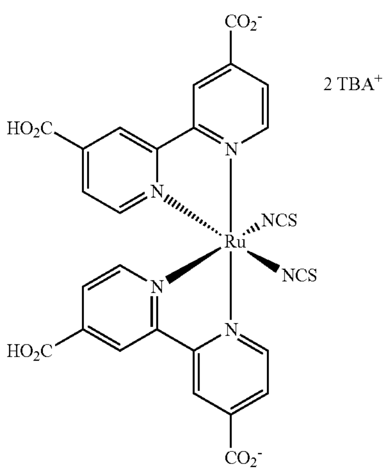
[0003] 2. Description of the Prior Art

[0004] Petrochemical fuel is a nonrenewable energy source and might possibly run out very soon. In addition, burning petrochemical fuel results in excessive CO_2 exhausts which not only pollute the atmosphere, but also become one of the primary causes of global warming. Therefore, searching for alternative energy supplies to reduce reliance on petrochemical fuels is a subject of great urgency.

[0005] During the development of green energy, it is found that solar energy is the cleanest, most abundant and requires neither mining nor refinement. Solar energy, therefore, becomes the most promising technology among the current development and search for new energy. The manufacturing process of a dye-sensitized solar cell (DSSC) is simple and the associated fabrication cost is also significantly lower than that of a silicon-based solar cell of prior arts. Therefore, DSSC has been regarded as one of the most notable solar cell technologies following silicon-based solar cells. Because the intrinsic properties of photosensitizers directly affect the photoelectric conversion efficiency of a DSSC, the photosensitizers therefore becomes one of key issues while conducting research on DSSCs.

[0006] A N719 dye and black dye (N749 dye) are photosensitizers commonly used at present, which comprises the structure shown in following formulae. However, the conventional N719 and N749 dyes possess two and three monodentate NCS^- (thiocyanate) ligands, which are considered to be the weakest coordination ligands of the whole molecule, and can be easily replaced by other donor fragments in the electrolyte solution of DSSCs. Therefore, replacing NCS^- ligands with other stronger coordinated chelates or chromophoric ligands would allow significant increase of efficiency and life-expectancy of DSSCs.

N719



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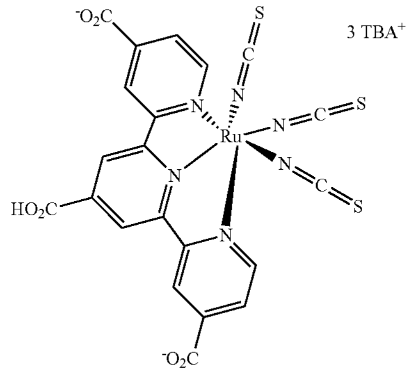
N749



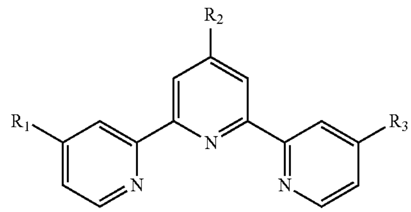
[0007] To sum up the foregoing descriptions, the photoelectric conversion efficiency of a DSSC is directly dependent on the inherent property of photosensitizer; therefore, developing photosensitizers with decent photoelectric conversion efficiency is an important goal to be achieved.

SUMMARY OF THE INVENTION

[0008] The present invention is directed to the design and preparation of photosensitizers having double-negative charged, tridentate ligands in substitution of three thiocyanates as observed in N749 for providing higher stability and better photoelectric conversion efficiency.

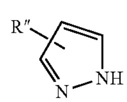
[0009] According to an embodiment, photosensitizers having a formula of RuL_1L_2 (1) are provided, wherein Ru is ruthenium; L_1 and L_2 are heterocyclic tridentate ligands. L_1 has a formula of (2),

(2)



and L_2 has a formula of $G_1G_2G_3$ (3), wherein G_1 and G_3 are selected from the group consisting of formulae (4) to (7), and G_2 is selected from the group consisting of formulae (7) and (8).

(4)



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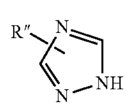

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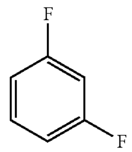

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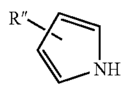

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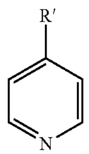


Each of R_1 to R_3 in L_1 is a member independently selected from the group consisting of hydrogen, a carboxyl group, a salt of a carboxyl group, a sulfonic acid group, a salt of a sulfonic acid group, a phosphoric acid group and a salt of a phosphoric acid group. Each of R' and R" in L_2 is a member independently selected from the group consisting of H, halo, cyano, trifluoromethyl, C_2-C_{10} fluorinated alkyl group, amino, C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{20} cycloalkyl, C_3-C_{20} cycloalkenyl, C_1-C_{20} heterocycloalkyl, C_1-C_{20} heterocycloalkenyl, aryl and heteroaryl.

[0010] The present invention is also directed to the fabrication of dye-sensitized solar cells, which have better photoelectric conversion efficiency and improved device efficiency and longer life-expectancy for DSSCs.

[0011] According to another embodiment, a DSSC comprises a first electrode (photoanode), a second electrode (cathode) and an electrolyte. The first electrode comprises a transparent conductive substrate and a porous membrane, wherein the porous membrane, disposed on a surface of the transparent conductive substrate, comprises a semiconductor material and is loaded with the aforementioned photosensitizers. The electrolyte is disposed between the porous membrane and the second electrode.

[0012] Other advantages of the present invention will become apparent from the following descriptions taken in conjunction with the accompanying drawings wherein certain embodiments of the present invention are set forth by way of illustration and examples.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The foregoing aspects and many of the accompanying advantages of this invention will become more readily appreciated as the same becomes better understood by reference to the following detailed descriptions, when taken in conjunction with the accompanying drawings, wherein:

[0014] FIG. **1** is a diagram illustrating absorption spectra of photosensitizers according to one preferred embodiment of the present invention and the conventional dye; and

[0015] FIG. **2** is a schematic diagram illustrating the structure of a dye-sensitized solar cell according to one embodiment of the present invention.

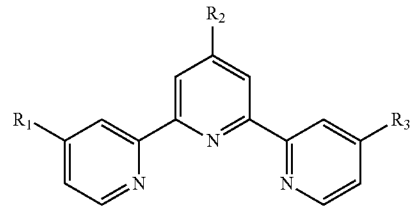
DESCRIPTION OF THE PREFERRED EMBODIMENT

[0016] Photosensitizers having a formula (1) are provided according to one embodiment of the present invention:

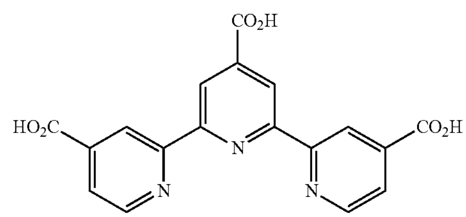
$$RuL_1L_2 \quad (1)$$

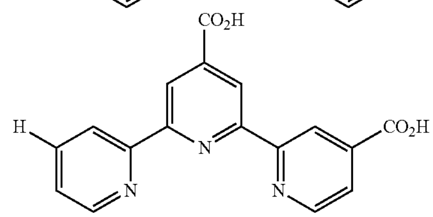
wherein Ru is ruthenium; L_1 and L_2 are heterocyclic tridentate ligands. L_1 is a 2,2';6',2"-terpyridine compound and has a formula of (2):

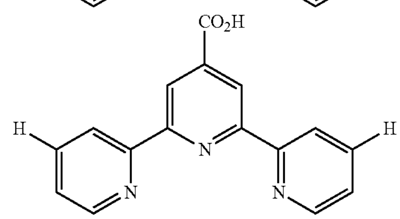
(2)

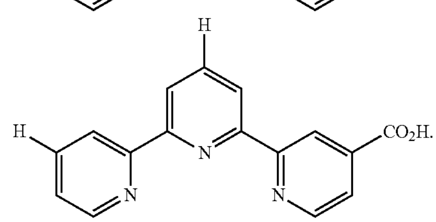


wherein R_1-R_3 is selected from the group consisting of hydrogen, a carboxyl group, a salt of a carboxyl group, a sulfonic acid group, a salt of a sulfonic acid group, a phosphoric acid group and a salt of a phosphoric acid group. The cation corresponding to the carboxylate, sulfonate and phosphate includes without limitation to an ammonium ion, a metal ion (such as alkali metal ion) and so on. For example, L_1 is represented by the following formulae:







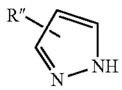


[0017] Preferably, L_1 is 4,4',4"-tricarboxy-2,2';6',2"-terpyridine.

[0018] L_2 has a formula (3):

$$G_1G_2G_3 \quad (3)$$

(4)



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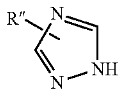

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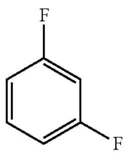

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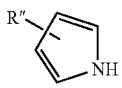

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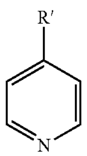
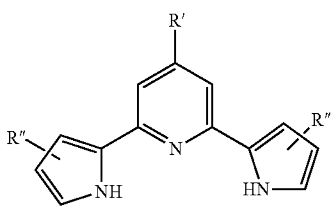


wherein G_1 and G_3 are selected from the group consisting of formulae (4) to (7), and G_2 is selected from the group consisting of formulae (7) and (8).

[0019] For example, L_2 is presented by formulae (9) to (14):

(9)



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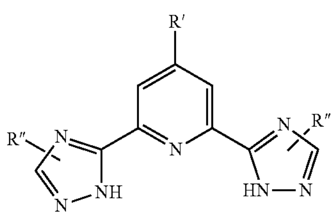

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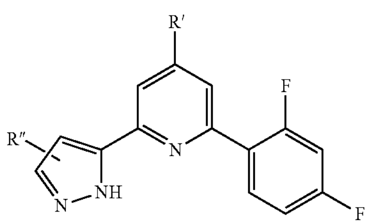

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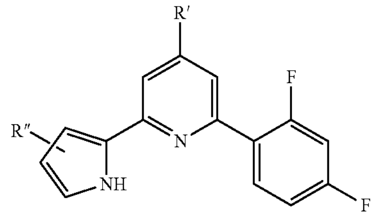

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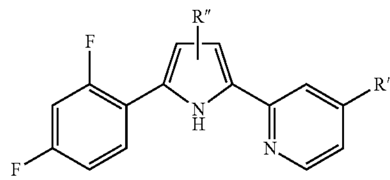

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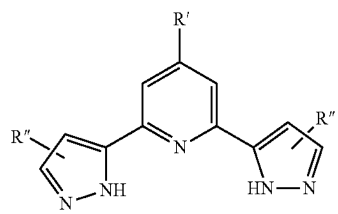


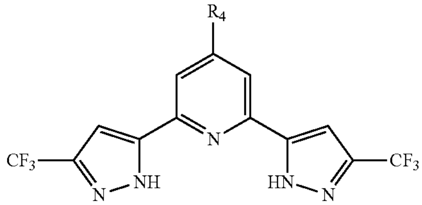
wherein each of R' and R" in L_2 is a member independently selected from the group consisting of H, halo, cyano, trifluoromethyl, C_2-C_{10} fluorinated alkyl group, amino, C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{20} cycloalkyl, C_3-C_{20} cycloalkenyl, C_1-C_{20} heterocycloalkyl, C_1-C_{20} heterocycloalkenyl, aryl and heteroaryl.

[0020] The term "aryl" refers to a hydrocarbon moiety having one or more aromatic rings. Examples of aryl moieties include phenyl (Ph), phenylene, naphthyl, naphthylene, pyrenyl, anthryl, and phenanthryl. The term "heteroaryl" refers to a moiety having one or more aromatic rings that contain at least one heteroatom (e.g., N, O, or S). Examples of heteroaryl moieties include furyl, furylene, fluorenyl, pyrrolyl, thienyl, oxazolyl, imidazolyl, thiazolyl, pyridyl, pyrimidinyl, quinazolinyl, quinolyl, isoquinolyl and indolyl.

[0021] Alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, heterocycloalkyl, heterocycloalkenyl, aryl, and heteroaryl mentioned herein include both substituted and unsubstituted moieties, unless specified otherwise. Possible substituents on cycloalkyl, cycloalkenyl, heterocycloalkyl, heterocycloalkenyl, aryl, and heteroaryl include, but are not limited to, C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{20} cycloalkyl, C_3-C_{20} cycloalkenyl, C_1-C_{20} heterocycloalkyl, C_1-C_{20} heterocycloalkenyl, C_1-C_{10} alkoxy, aryl, aryloxy, heteroaryl, heteroaryloxy, amino, C_1-C_{10} alkylamino, C_1-C_{20} dialkylamino, arylamino, diarylamino, C_1-C_{10} alkylsulfonamino, arylsulfonamino, C_1-C_{10} alkylimino, arylimino, C_1-C_{10} alkylsulfonimino, arylsulfonimino, hydroxyl, halo, thio, C_1-C_{10} alkylthio, arylthio, C_1-C_{10} alkylsulfonyl, arylsulfonyl, acylamino, aminoacyl, aminothioacyl, amido, amidino, guanidine, ureido, thioureido, cyano, nitro, nitroso, azido, acyl, thioacyl, acyloxy, carboxyl, and carboxylic ester. On the other hand, possible substituents on alkyl, alkenyl, or alkynyl include all of the above-recited substituents except C_1-C_{10} alkyl. Cycloalkyl, cycloalkenyl, heterocycloalkyl, heterocycloalkenyl, aryl, and heteroaryl can also be fused with each other.

[0022] Preferably, L_2 is presented by formula (15) or (16):

(15)



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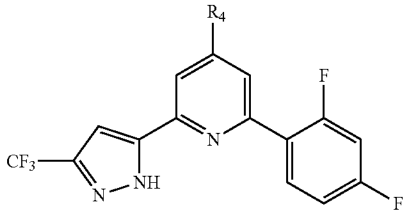
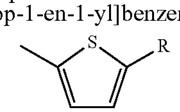
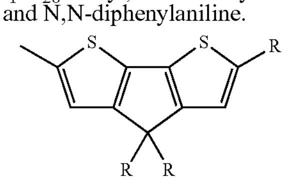
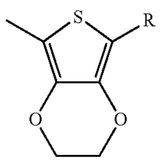


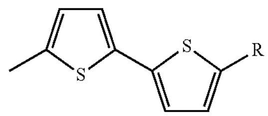
wherein R_4 is selected from the group consisting of H, halo, cyano, trifluoromethyl, C_2-C_{10} fluorinated alkyl group, amino, C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{20} cycloalkyl, C_3-C_{20} cycloalkenyl, C_1-C_{20} heterocycloalkyl, C_1-C_{20} heterocycloalkenyl, aryl and heteroaryl.

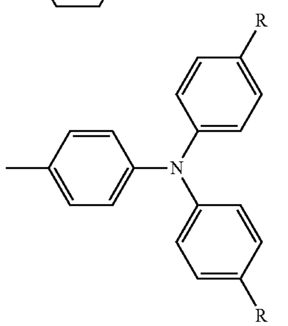
[0023] In one preferred embodiment, R_4 includes an aryl group or a heteroaryl group and is selected from the group consisting of thiophene, 5-(thiophen-2-yl)thiophene, thiophene-substituted C_1-C_{20} alkyl, 5-(thiophen-2-yl) thiophene-substituted C_1-C_{20} alkyl, 1-tert-butyl-4-[(1E)-prop-1-en-1-yl]benzene and N,N-diphenylaniline.

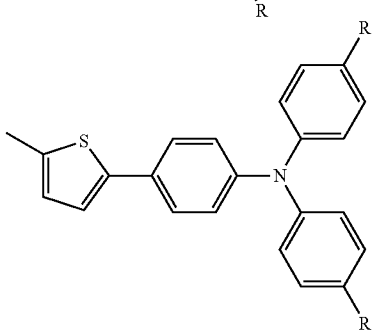












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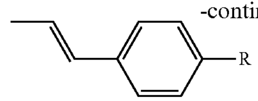
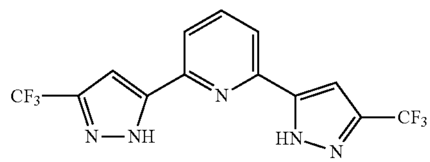


[0024] Herein, R is selected form the group consisting of H, halo, cyano, trifluoromethyl, C_2-C_{10} fluorinated alkyl group, amino, C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{20} cycloalkyl, C_3-C_{20} cycloalkenyl, C_1-C_{20} heterocycloalkyl, C_1-C_{20} heterocycloalkenyl, aryl and heteroaryl.

Example Ligands

[0025] The synthesis method and spectrum data for example ligand 1 having the tridentate ligand L_2 and represented by the formula (15), where R_4=H, is provided as following.

(15)

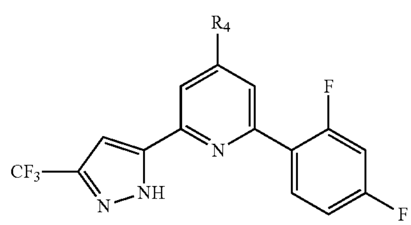


[0026] To a stirred suspension of NaOEt (1.25 g, 18.4 mmol) and THF (40 mL) at 0° C., a 30 mL THF solution of 2,6-diacetylpyridine (1 g, 6.1 mmol) and ethyl trifluoroacetate (2.18 mL, 18.4 mmol) were added in sequence. The mixture was heated at 80° C. for 12 h and then was neutralized with 2 M HCl until pH=5-6. After evaporating of THF, the residue was extracted with CH_2Cl_2 (3×80 mL). The combined extracts were washed with water, dried over anhydrous Na_2SO_4, and concentrated under vacuum to give the corresponding β-diketone compound. Without further purification, hydrazine monohydrate (98%, 2.9 mL, 59.9 mmol) was added into a 50 mL of EtOH solution of the aforementioned β-diketone reagent. The solution was reflux for 12 h and then the solvent was evaporated. The residue was redissolved in CH_2Cl_2 (100 mL), and the solution was washed with water, dried over anhydrous $MgSO_4$, and concentrated. Finally, the product was purified by silica gel column chromatography using a 3:1 mixture of hexane and ethyl acetate, giving the desired tridentate ligand as a white solid. Yield: 0.86 g, 40%.

[0027] Spectral data for formula (15): MS (EI), m/z 347 $(M)^+$. ^{1}H NMR (400 MHz, d-acetone, 298K): δ 13.68 (s, 2H), 8.08 (t, J_{HH}=8 Hz, 1H), 7.96 (d, J_{HH}=8 Hz, 2H), 7.40 (s, 2H).

[0028] The synthesis method and spectrum data for example ligand 2 having the tridentate ligand L_2 and represented by the formula (16), where R_4=H, is provided as following.

(16)



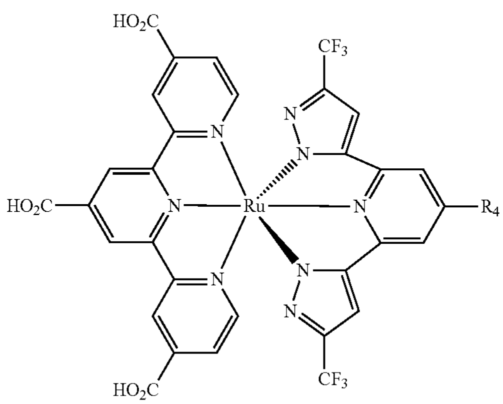
[0029] To a stirred suspension of NaOEt (0.77 g, 10.4 mmol) and THF (40 mL) at 0° C., a 30 mL THF solution of 1-(6-(2,4-difluorophenyl)pyridin-2-yl)ethanone (300 mg, 1.3 mmol) and ethyl trifluoroacetate (0.3 mL, 1.9 mmol) were added in sequence. The mixture was heated at 80° C. for 6 h and then was neutralized with 2 M HCl until pH=3. After evaporating of THF, the residue was extracted with CH_2Cl_2 (3×80 mL). The combined extracts were washed with water and concentrated under vacuum to give the corresponding β-diketone compound. Without further purification, hydrazine monohydrate (about 5 equiv.) was added into a 50 mL of EtOH solution of the aforementioned β-diketone reagent. The solution was reflux for 12 h and then the solvent was evaporated. The residue was redissolved in CH_2Cl_2 (100 mL), and the solution was washed with water, dried over anhydrous $MgSO_4$, and concentrated. Finally, the product was purified by silica gel column chromatography using a 3:1 mixture of hexane and ethyl acetate, giving the desired tridentate ligand as a white solid. Yield: 0.30 g, 72%.

[0030] Spectral data for formula (16): ^{1}H NMR ($CDCl_3$, 400 MHz, 298K): δ 11.40 (s, 1H), 8.00 (q, J_{HH}=8.4 Hz, 1H), 7.85 (t, J_{HH}=8.0 Hz, 1H), 7.73 (d, J_{HH}=8.4 Hz, 1H), 7.56 (d, J_{HH}=8.0 Hz, 1H), 7.03 (t, J_{HH}=8.0 Hz, 1H), 6.97 (s, 1H), 6.93 (t, J_{HH}=8.0 Hz, 1H).

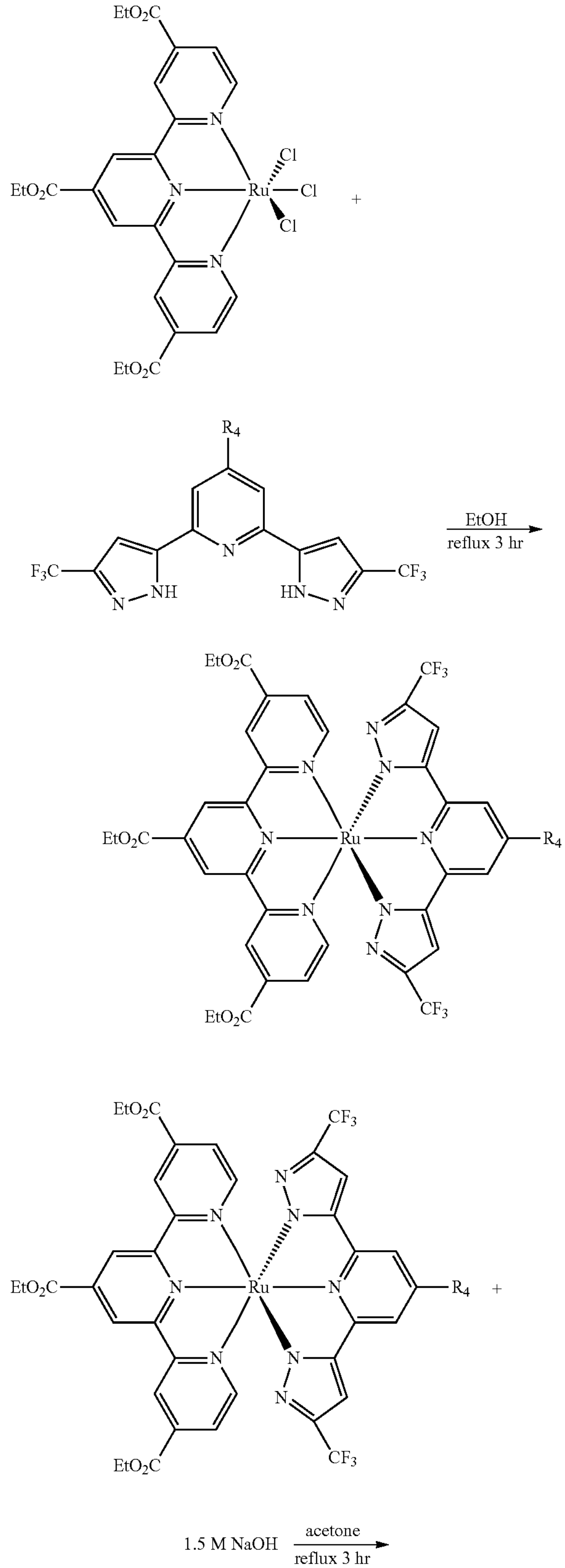
Example Ru(II) Complexes

[0031] In one embodiment, the Ru complex of the present invention is represented as formula (17).

(17)



[0032] A mixture of 2,6-bis(3-trifluoromethyl-1H-pyrazol-5-yl)pyridine (53 mg, 0.15 mmol), Ru(tectpy)Cl_3 (100 mg, 0.15 mmol) and 4-ethylmorpholine (0.05 mL, 0.39 mmol) in 30 mL of ethanol was heated at 80° C. for 3 h. After evaporating the solvent, the aqueous phase was separated and the residue was extracted with CH_2Cl_2 (3×25 mL). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate=1:1). After then, this solid was dissolved in a mixture of acetone (30 mL) and 1.5 M NaOH solution (1.8 mL). The solution was heated to 60° C. under N2 for 3 h. Finally, the solvent was removed, the solid was dissolved in 10 mL of H_2O and was titrated with 2 N HCl to pH 3 to afford a black precipitate. This black product was washed with CH_2Cl_2 and acetone, to yield the compound of formula (17).



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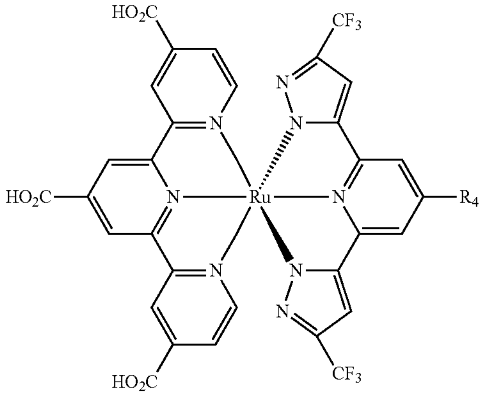
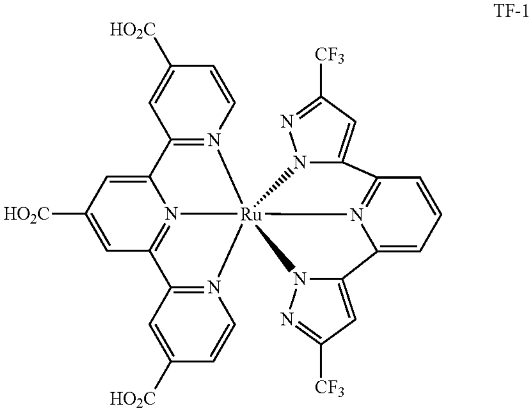


Example 1

TF-1

[0033]

TF-1



[0034] TF-1 is an example compound of formula (17), where R_4=H and was prepared according to the afore-mentioned procedure. Yield: 78% (60 mg, 0.07 mmol).

[0035] Spectrum data of TF-1: MS (FAB, ^{102}Ru): m/z 812 $(M+1)^+$. ^{1}H NMR (400 MHz, d_6-DMSO, 298K): δ 9.37 (s, 2H), 9.14 (s, 2H), 8.17 (t, J_{HH}=8.0 Hz, 1H), 8.06 (d, J_{HH}=8.0 Hz, 2H), 7.70 (d, J_{HH}=5.6 Hz, 2H), 7.59 (d, J_{HH}=5.6 Hz, 2H), 7.19 (s, 2H); ^{19}F NMR (376 MHz, d_6-DMSO, 298K): δ −58.44 (s, 3F; CF_3).

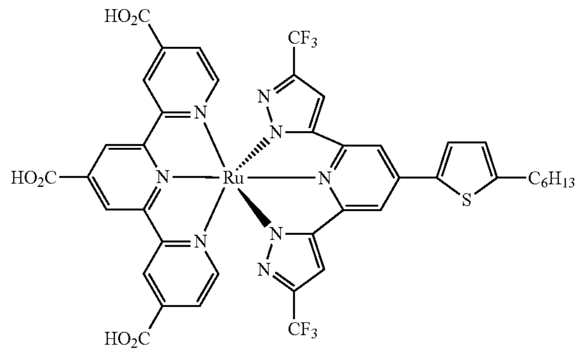
[0036] Anal. Calcd. for $C_{31}H_{16}F_6N8O_6Ru.3H_2O$: C, 43.01; N, 12.94; H, 2.56. Found: C, 43.22; N, 12.71; H, 2.51.

Example 2

TF-2

[0037]

TF-2



[0038] TF-2 is another example compound of formula (17), where R_4=2-hexylthiophene and was prepared according to the fore-mentioned procedure. Yield: 87% (264 mg, 0.27 mmol).

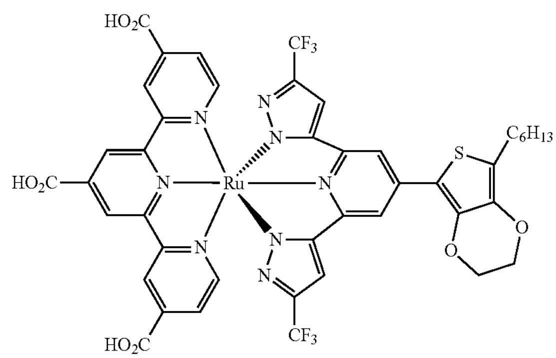
[0039] Spectral data of TF-2: MS (FAB, ^{102}Ru) m/z 978 $(M+1)^+$. ^{1}H NMR (400 MHz, d_6-DMSO, 298K): δ 9.36 (s, 2H), 9.14 (s, 2H), 8.34 (s, 2H), 7.96 (d, J_{HH}=4 Hz, 1H), 7.71~7.67 (m, 4H), 7.33 (s, 2H), 7.10 (d, J_{HH}=4 Hz, 1H), 2.95 (t, J_{HH}=8 Hz, 2H), 1.74 (quin, J_{HH}=8 Hz, 2H), 1.41~1.31 (m, 6H), 0.98 (t, J_{HH}=8 Hz, 3H). ^{19}F NMR (376 MHz, d_6-DMSO, 298K): δ −58.52 (s, 6F). Anal. Calcd. for $C_{41}H_{32}F_6N_8O_7RuS.H_2O$: C, 49.45; N, 11.25; H, 3.24. Found: C, 49.39; N, 11.14; H, 3.59.

Example 3

TF-3

[0040]

TF-3



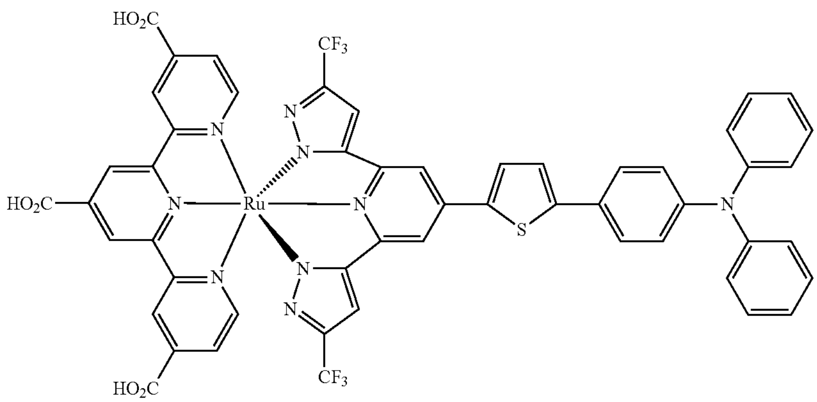
[0041] TF-3 is another example compound of formula (17), where R_4=5-hexyl-2H,3H-thieno[3,4-b][1,4]dioxine and was prepared according to the fore-mentioned procedure. Yield: 86% (48 mg, 0.05 mmol).

[0042] Spectral data of TF-3: MS (FAB, ^{102}Ru): m/z 1036 $(M+1)^+$. ^{1}H NMR (400 MHz, d_6-DMSO, 298K): δ 9.36 (s, 2H), 9.13 (s, 2H), 8.21 (s, 2H), 7.71~7.67 (m, 4H), 7.26 (s, 2H), 4.52 (t, J_{HH}=4 Hz, 2H), 4.38 (t, J_{HH}=4 Hz, 2H), 2.76 (t, J_{HH}=8 Hz, 2H), 1.66 (quin, J_{HH}=8 Hz, 2H), 1.40~1.31 (m, 6H), 0.89 (t, J_{HH}=8 Hz, 3H). ^{19}F NMR (376 MHz, d_6-DMSO, 298K): δ −58.41 (s, 6F).

Example 4

TF-4

[0043]



TF-4

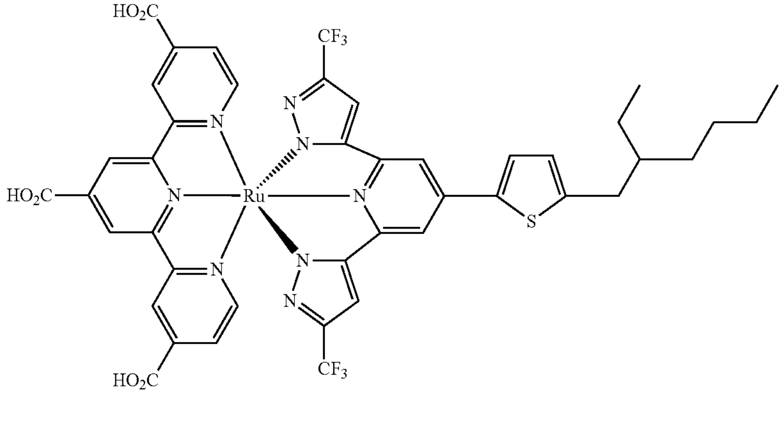
[0044] TF-4 is another example compound of formula (17), where R_4=N,N-diphenyl-4-(thiophen-2-yl)aniline and was prepared according to the fore-mentioned procedure. Yield: 51% (26 mg, 0.02 mmol).

[0045] Spectral data of TF-4: MS (FAB, ^{102}Ru): m/z 1137 $(M+1)^+$. ^{1}H NMR (400 MHz, d_6-DMSO, 298K): δ 9.36 (s, 2H), 9.14 (s, 2H), 8.43 (s, 2H), 8.14 (d, J_{HH}=4 Hz, 1H), 7.73~7.69 (m, 7H), 7.38~7.34 (m, 6H), 7.13~7.05 (m, 8H). ^{19}F NMR (376 MHz, d_6-DMSO, 298K): δ −58.47 (s, 6F).

Example 5

TF-5

[0046]



TF-5

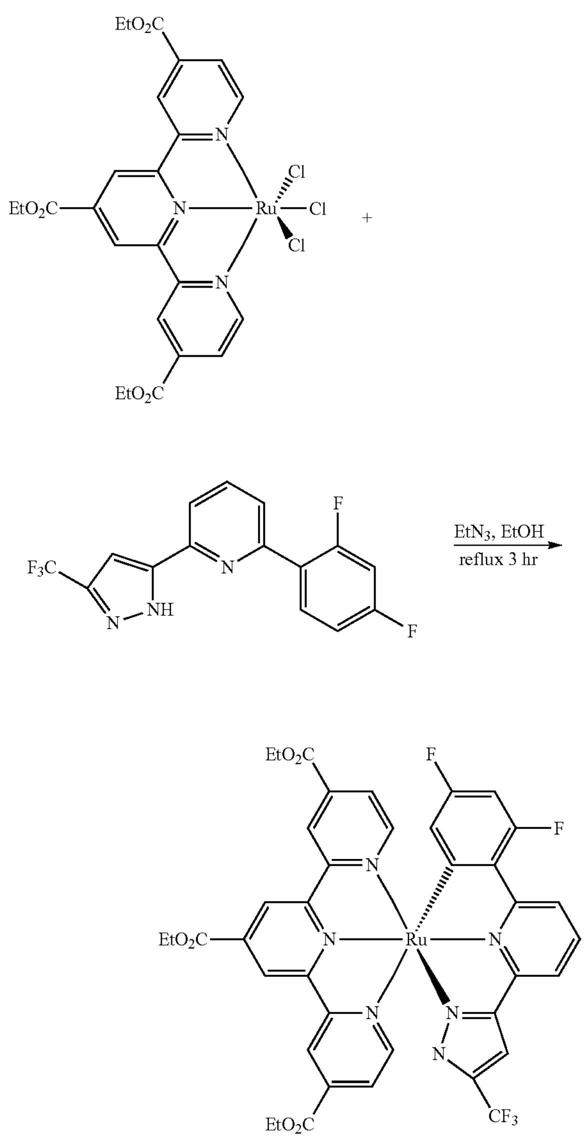
[0047] TF-5 is another example compound of formula (17), where R_4=2-(2-ethylhexyl)thiophene and was prepared according to the fore-mentioned procedure. Yield: 75% (62 mg, 0.06 mmol).

[0048] Spectral data of TF-5: MS (FAB, ^{102}Ru): m/z 1006 $(M+1)^+$. ^{1}H NMR (400 MHz, d_6-DMSO, 298K): δ 9.32 (s, 2H), 9.13 (s, 2H), 8.36 (s, 2H), 7.97 (d, J_{HH}=4.0 Hz, 1H), 7.72~7.69 (m, 4H), 7.35 (s, 2H), 7.09 (d, J_{HH}=4.0 Hz, 1H), 2.89 (d, J_{HH}=8.0 Hz, 2H), 1.67 (s, 1H), 1.41~1.30 (m, 8H), 0.95~0.88 (m, 6H); ^{19}F NMR (376 MHz, d_6-DMSO, 298K): δ −58.43 (s, 3F; CF_3).

Example 6

TF-6

[0049]



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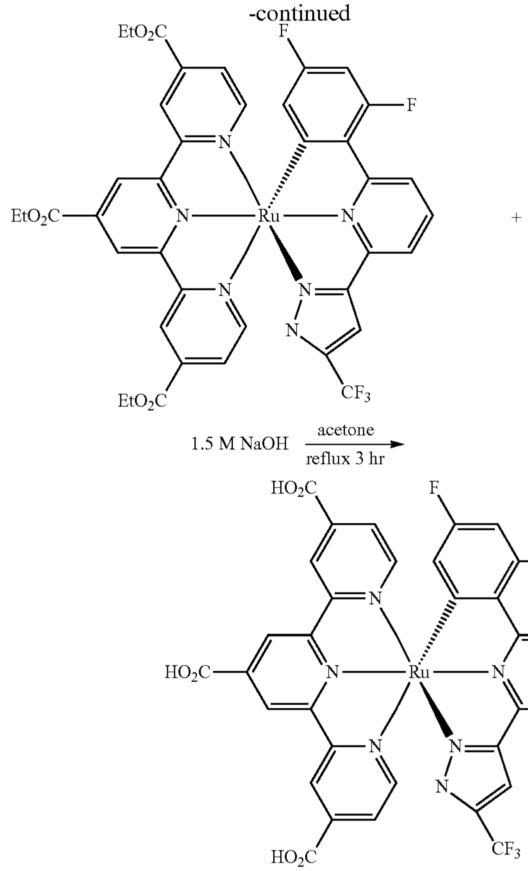


[0050] A mixture of (2-(2,4-Difluorophenyl)-6-(3-(trifluoromethyl)-1H-pyrazol-5-yl)pyridine) (21 mg, 0.06 mmol), Ru(tectpy)Cl_3 (40 mg, 0.06 mmol) and triethylamine (0.6 mL) in 25 mL of ethanol was heated at 90° C. for 3 h. After evaporating the solvent, the aqueous phase was separated and the residue was extracted with CH_2Cl_2 (3×25 mL). The crude product was purified by silica gel column chromatography (dichoromethane/ethyl acetate=10:1). After then, this solid was dissolved in a mixture of acetone (30 mL) and 1.5 M NaOH solution (1.8 mL). The solution was heated to 60° C. under N_2 for 3 h. Finally, the solvent was removed, the solid was dissolved in 10 mL of H_2O and was titrated with 2 N HCl to pH 3 to afford a black precipitate. This black product was washed with CH_2Cl_2 and ether. Yield: 24% (12 mg, 0.014 mmol),

[0051] Spectral data of TF-6: MS (FAB, ^{102}Ru): m/z 806 $(M+1)^+$. ^{1}H NMR (d_6-DMSO, 400 MHz, 298K) δ: 9.32 (s, 2H), 9.12 (s, 2H), 8.10 (s, 3H), 7.68 (d, J_{HH}=5.6 Hz, 2H), 7.62 (d, J_{HH}=5.2 Hz, 2H), 7.21 (s, 1H), 6.40 (t, J_{HF}=10.8 Hz, 1H), 4.65 (d, J_{HH}=7.2 Hz, 1H).

[0052] Referring to FIG. **1**, which is a diagram illustrating absorption spectra of photosensitizers of the formula (17) according to one preferred embodiment of the present invention and N749 (Black dye).

[0053] According to the spectra data illustrated in FIG. **1**, the photosensitizers, TF-2, TF-3 and TF-4 have better extinction coefficient in the range between 350 nm and 550 nm in comparison to N749.

[0054] Referring to FIG. **2**, a DSSC of an embodiment of the present invention comprises a first electrode **11** (photoanode), a second electrode **12** (cathode) and an electrolyte **13**. The first electrode **11** comprises a transparent conductive substrate **111** and a porous membrane **112**. The porous membrane **112**, disposed on a surface of the transparent conductive substrate **111**, is loaded with the aforementioned photosensitizers **113**. The porous membrane **112** comprises a semiconductor material, such as TiO_2. In one embodiment, the transparent conductive substrate **111** comprises F-doped SnO_2 glass (FTO glass). The electrolyte **13** is disposed between the porous membrane **112** and the second electrode **12**. The structures of the photosensitizers **113** are identical with the aforementioned photosensitizers; therefore, the detail description is omitted here.

[0055] The aforementioned photosensitizers TF-1~TF-6 are utilized to produce a DSSC of the present invention. The properties of DSSCs are illustrated in table 1, wherein the first electrode **11** comprises photosensitizers TF-1~TF-6, a porous membrane TiO_2 and FTO glass; the second electrode **12** comprises a Pt electrode, such as a general glass doped with metal Pt and other transparent conductive materials, e.g. carbon black or graphite; the electrolyte comprises a mixture consisting of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1M Lithium iodide (LiI), 0.1M I_2, and 0.5 M tert-butylpyridine in acetonitrile.

TABLE 1

Dye	V_{OC}, V	J_{SC}, mA · cm^{-2}	FF	η, %
TF-1	740	18.22	0.676	9.11
TF-2	790	20.00	0.665	10.51
TF-3	760	21.39	0.660	10.72
TF-4	770	20.27	0.675	10.55
TF-5	740	20.36	0.650	9.81
TF-6	770	10.17	0.692	5.42
N749	720	19.49	0.657	9.22

[0056] The DSSCs of the present invention have better photoelectric conversion efficiency as illustrated in Table 1. To be specific, the DSSCs of the present invention including photosensitizers TF-2, TF-3 and TF-4 respectively have better η of 10.51%, 10.72% and 10.55% than that of N749 (η=9.22%).

[0057] In addition, photosensitizers TF-2, TF-3, TF-4 and TF-5 are more efficient than N719, as confirmed by the better performance data such as higher efficiencies, including better V_{OC} and J_{SC} characteristics. In other words, the DSSCs of the present invention may include the first electrode prepared with the much thinner nanoporous TiO_2 layer so as to prevent the unnecessary reduction of V_{OC}. It has been reported that the V_{OC} is inversely proportional to the back recombination of injected electrons with the oxidized dye molecule or components in electrolyte. Moreover, usage of fewer amounts of photosensitizers can also reduce the overall cost of DSSC fabrication.

[0058] To sum up, the photosensitizers of the present invention, including heterocyclic tridentate ligands, are thiocyanate-free and have better photoelectric conversion efficiency η than devices fabricated employing the traditional N749 dye. Therefore, the DSSCs prepared with the photosensitizers of the present invention may provide better performance in overall battery efficiency.

[0059] While the invention can be subject to various modifications and alternative forms, a specific example thereof has been shown in the drawings and is herein described in detail. It should be understood, however, that the invention is not intended to be limited to the particular form disclosed, but on the contrary, the invention is intended to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the appended claims.

What is claimed is:

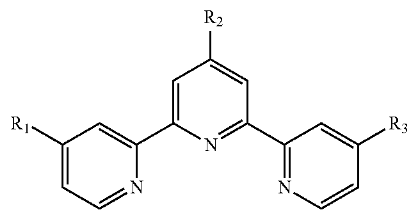
1. A heteroleptic, dual tridentate Ru(II) complex having a formula of (1):

$$RuL_1L_2 \quad (1)$$

, wherein Ru is ruthenium, L_1 and L_2 are heterocyclic tridentate ligands;

L_1 has a formula of (2):

(2)

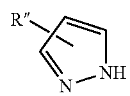


L_2 has a formula of (3):

$$G_1G_2G_3 \quad (3),$$

wherein G_1 and G_3 are selected from the group consisting of formulae (4) to (7), and G_2 is selected from the group consisting of formulae (7) and (8);

(4)



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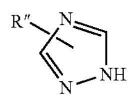

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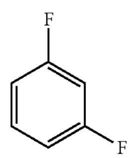

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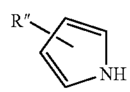

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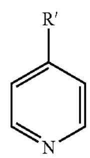


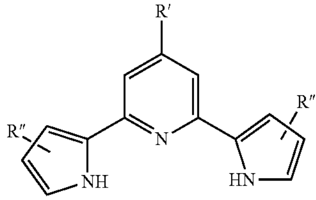
, wherein each of R_1 to R_3 in L_1 is a member independently selected from the group consisting of hydrogen, a carboxyl group, a salt of a carboxyl group, a sulfonic acid group, a salt of a sulfonic acid group, a phosphoric acid group and a salt of a phosphoric acid group; and

each of R' and R" in L_2 is a member independently selected from the group consisting of H, halo, cyano, trifluoromethyl, C_2-C_{10} fluorinated alkyl group, amino, C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{20} cycloalkyl, C_3-C_{20} cycloalkenyl, C_1-C_{20} heterocycloalkyl, C_1-C_{20} heterocycloalkenyl, aryl and heteroaryl.

2. The heteroleptic, dual tridentate Ru(II) complex as claimed in claim **1**, wherein L_1 is 4,4',4"-tricarboxy-2,2';6',2"-terpyridine.

3. The heteroleptic, dual tridentate Ru(II) complex as claimed in claim **1**, wherein L_2 is selected from the group consisting of formulae (9) to (14):

(9)



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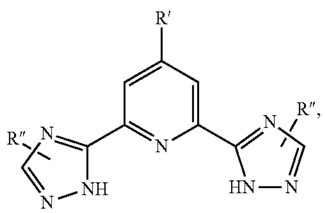

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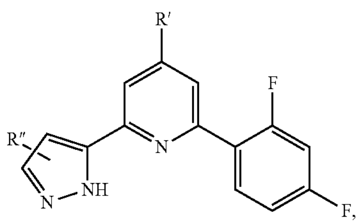

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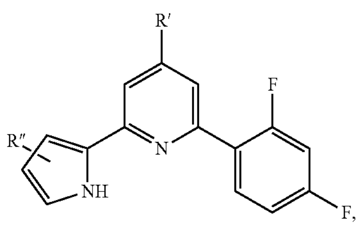

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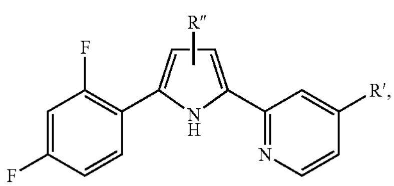

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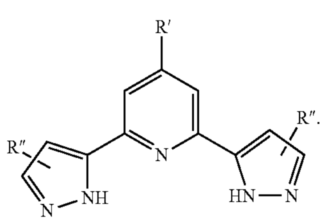
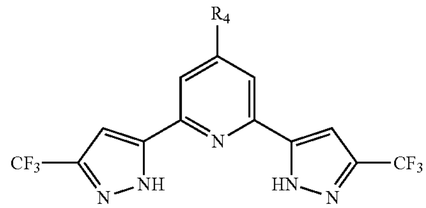


4. The heteroleptic, dual tridentate Ru(II) complex as claimed in claim **1**, wherein L_2 is selected from the group consisting of formulae (15) and (16):

(15)



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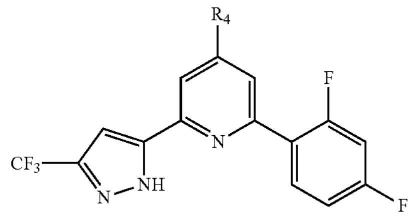
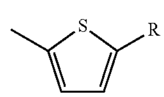
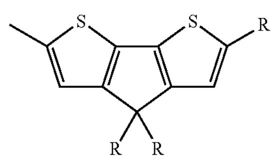


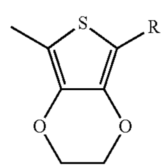
wherein R_4 is a member independently selected from the group consisting of H, halo, cyano, trifluoromethyl, C_2-C_{10} fluorinated alkyl group, amino, C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{20} cycloalkyl, C_3-C_{20} cycloalkenyl, C_1-C_{20} heterocycloalkyl, C_1-C_{20} heterocycloalkenyl, aryl and heteroaryl.

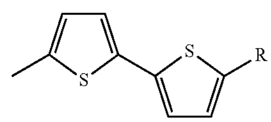
5. The heteroleptic, dual tridentate Ru(II) complex as claimed in claim **4**, wherein R_4 is heteroaryl or aryl.

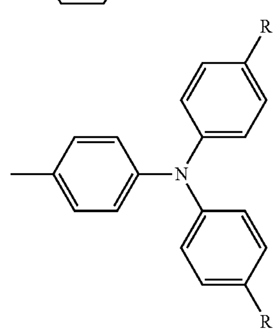
6. The heteroleptic, dual tridentate Ru(II) complex as claimed in claim **5**, wherein R_4 is selected from the group consisting of following formulae:











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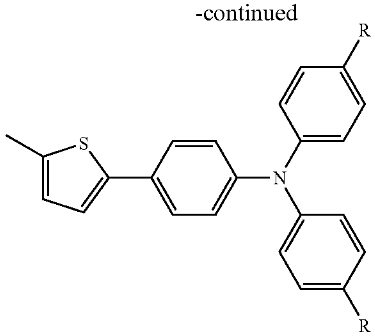
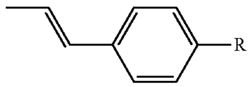




wherein R is a member independently selected from the group consisting of H, halo, cyano, trifluoromethyl, C_2-C_{10} fluorinated alkyl group, amino, C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{20} cycloalkyl, C_3-C_{20} cycloalkenyl, C_1-C_{20} heterocycloalkyl, C_1-C_{20} heterocycloalkenyl, aryl and heteroaryl.

7. A dye-sensitized solar cell comprising:

a first electrode comprising:

a transparent conductive substrate; and

a porous membrane comprising a semiconductor material, disposed on a surface of said transparent conductive substrate, and loaded with photosensitizers;

a second electrode; and

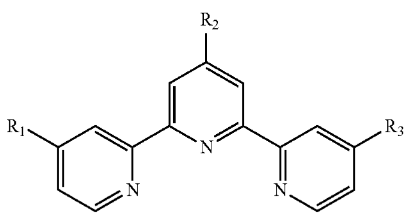
an electrolyte, disposed between said porous membrane and said second electrode, wherein said photosensitizers comprising a chemical formula represented by formula of (1):

RuL_1L_2 (1)

wherein Ru is ruthenium, L_1 and L_2 are heterocyclic tridentate ligands;

L_1 has a formula of (2)

(2)

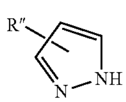


L_2 has a formula of (3)

$G_1G_2G_3$ (3)

wherein G_1 and G_3 are selected from the group consisting of formula (4) to (7), and G_2 is selected from the group consisting of formula (7) and (8);

(4)



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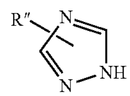
(5)



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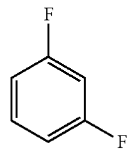
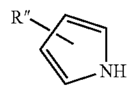
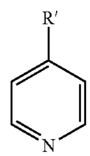


(7)



(8)



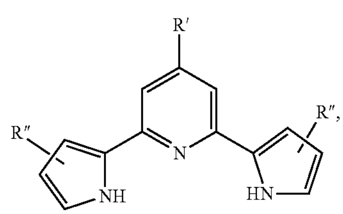
wherein each of R_1 to R_3 in L_1 is a member independently selected from the group consisting of hydrogen, a carboxyl group, a salt of a carboxyl group, a sulfonic acid group, a salt of a sulfonic acid group, a phosphoric acid group and a salt of a phosphoric acid group; and

each of R' and R" in L_2 is a member independently selected from the group consisting of H, halo, cyano, trifluoromethyl, C_2-C_{10} fluorinated alkyl group, amino, C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{20} cycloalkyl, C_3-C_{20} cycloalkenyl, C_1-C_{20} heterocycloalkyl, C_1-C_{20} heterocycloalkenyl, aryl and heteroaryl.

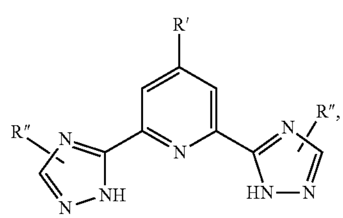
8. The dye-sensitized solar cell as claimed in claim **7**, wherein L_1 is 4,4',4"-tricarboxy-2,2';6',2"-terpyridine.

9. The dye-sensitized solar cell as claimed in claim **7**, wherein L_2 is selected from the group consisting of formulae (9) to (14):

(9)



(10)



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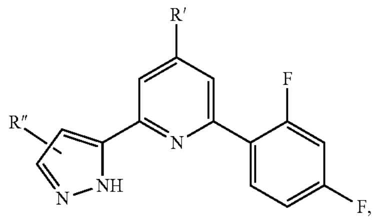
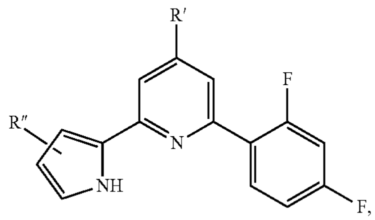
(11)



(12)



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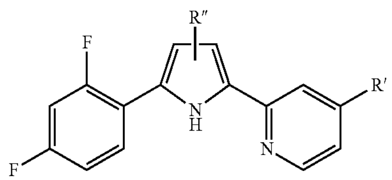
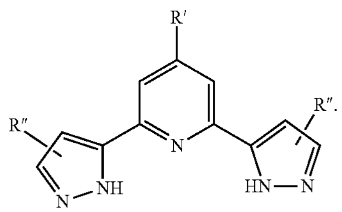


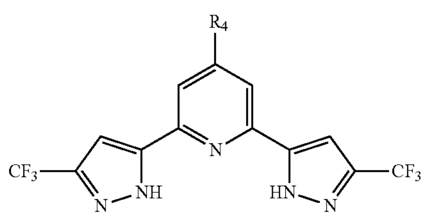
and

(14)

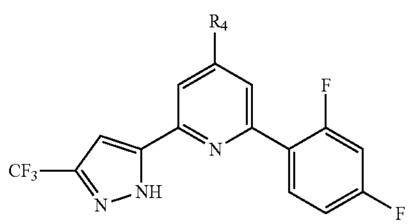


10. The dye-sensitized solar cell as claimed in claim **7**, wherein L_2 is selected from the group consisting of formulae (15) and (16):

(15)



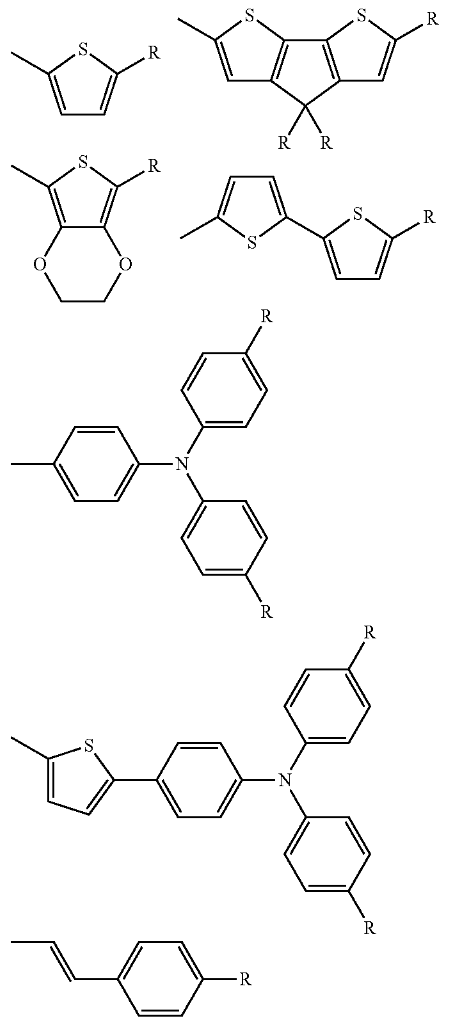
(16)



wherein R_4 is a member independently selected from the group consisting of H, halo, cyano, trifluoromethyl, C_2-C_{10} fluorinated alkyl group, amino, C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{20} cycloalkyl, C_3-C_{20} cycloalkenyl, C_1-C_{20} heterocycloalkyl, C_1-C_{20} heterocycloalkenyl, aryl and heteroaryl.

11. The dye-sensitized solar cell as claimed in claim **10**, wherein R_4 is heteroaryl or aryl.

12. The dye-sensitized solar cell as claimed in claim **11**, wherein R_4 is selected from the group consisting of following formulae:



wherein R is a member independently selected from the group consisting of H, halo, cyano, trifluoromethyl, C_2-C_{10} fluorinated alkyl group, amino, C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{20} cycloalkyl, C_3-C_{20} cycloalkenyl, C_1-C_{20} heterocycloalkyl, C_1-C_{20} heterocycloalkenyl, aryl and heteroaryl.

13. The dye-sensitized solar cell as claimed in claim **7**, wherein the material of said semiconductor comprises TiO_2.

14. The dye-sensitized solar cell as claimed in claim **7**, wherein said transparent conductive substrate comprises FTO glass.

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