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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C07F 15/00, 13/00, 15/02, C09B 57/10, H01G 9/20

A1

(11) International Publication Number: **WO 98/50393**

(43) International Publication Date: 12 November 1998 (12.11.98)

(21) International Application Number: PCT/IB98/00680

(22) International Filing Date: 7 May 1998 (07.05.98)

(30) Priority Data:
PCT/IB97/00518 7 May 1997 (07.05.97) WO
(34) Countries for which the regional or international application was filed: AU et al.

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(81) Designated States: AU, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: METAL COMPLEX PHOTOSENSITIZER AND PHOTOVOLTAIC CELL

(57) Abstract

A photosensitizer complex of formulae (Ia) MX_3L_t or (Ib) $MXYL_t$ in which M is a transition metal selected from ruthenium, osmium, iron, rhenium and technetium, preferably ruthenium or osmium; each X is a co–ligand independently selected from NCS^-, Cl^-, Br^-, I^-, CN^-, NCO^-, H_2O, NCN^{2-}, pyridine unsubstituted or substituted by at least one group selected from vinyl, primary, secondary or tertiary amine, OH and C_{1-30} alkyl, preferably NCS^-; and L_t is a tridentate ligand comprising heterocycles such as pyridine, thiophene, imidazole, pyrazole, triazole, carrying at least one carboxylic, phosphoric, hydoxamic acid or a chelating group. A photovoltaic cell comprising an electrically conductive layer deposited on a support to which at least one titanium dioxide layer has been applied and, as a photosensitizer applied to the titanium dioxide layer, a photosensitizer complex of formulae (Ia) or (Ib) as specified above.

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METAL COMPLEX PHOTOSENSITIZER AND PHOTOVOLTAIC CELL

The invention relates to a transition metal complex photosensitizer and to its use in a photovoltaic cell comprising a nanocrystalline titanium dioxide layer.

Transition metal complexes, commonly designated as "dyestuffs", useful as charge transfer photosensitizer for semiconductive titanium dioxide photoanode layers, in a photovoltaic cell, are already known. Such complexes consist of a light absorber and an anchoring group. The anchoring group allows the immobilization of the transition metal complex at the titanium dioxide layers and provides an electronic coupling between the light absorber and the titanium dioxide layers. The light absorber absorbs an incoming photon via a metal to ligand charge transfer, and injects an electron into the conduction band of titanium dioxide through the anchoring group. The oxidized complex is then regenerated by a redox mediator.

In such a process, it is crucial to guide the charge transfer toward the semiconductor titanium dioxide surface and to guarantee tight electronic overlap between the LUMO anchoring group and the vacant orbitals of titanium.

In particular, such complexes, as well as dye sensitized nanocrystalline titanium dioxide photovoltaic cells, are disclosed in the International Patent Applications published as PCT Publication No. WO 94/04497 and PCT Publication No WO 95/29924.

PCT Publication No. WO 94/04497 describes ruthenium complexes in which ruthenium is surrounded by at least one dicarboxy bipyridine ligand, the carboxy groups playing the role of anchoring groups. The best performing charge transfer photosensitizer employed for this application is cis-dithiocyanatobis(4,4'-dicarboxy-2,2'-bipyridine) ruthenium(II) complex. Using this complex in a nanocrystalline titanium dioxide photovoltaic cell has permitted to obtain a solar to electric power conversion efficiency of 10 % under standard spectral distribution of solar light emission AM 1.5, where the photosensitizer absorbs in the wavelength region from 400 to 650 nm. However, it has been found that in longer wavelength the incident photon to current conversion efficiency (IPCE) drops because of lack of spectral response of the photosensitizer.

PCT Publication No. WO 94/04497 describes other potent ruthenium complexes, being able to be immobilized at the titanium dioxide layers via at least one phosphonated group carried by polypyridine ligands. This particular anchoring group appeared to have a higher stability than the carboxy group on a wider pH range of 0 to 9, avoiding partial desorbtion of the complex. Unfortunately, the absorption spectrum upper limits of such complexes showed to be less than 600 nm.

The present invention aims at further improving the efficiency of solar to electric power conversion by providing a photosensitizer having an enhanced spectral response in the red and near infrared regions.

To that effect, according to the invention, there is provided a photosensitizer complex of formulae (Ia) or (Ib):

MX_3L_t (Ia); $MXYL_t$ (Ib);

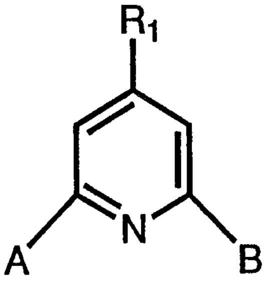
in which

M is a transition metal selected from ruthenium, osmium, iron, rhenium and technetium;

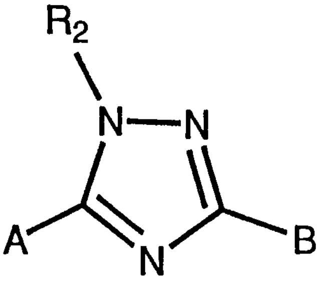
each X is a co-ligand independently selected from NCS^-, Cl^-, Br^-, I^-, CN^-, NCO^-, H_2O, NCN^{2-}, pyridine unsubstituted or substituted by at least one group selected from vinyl, primary, secondary or tertiary amine, OH and C_{1-30} alkyl;

Y is a co-ligand selected from o-phenanthroline, 2,2'-bipyridine, unsubstituted or substituted by at least one C_{1-30} alkyl; and

L_t is a tridentate ligand having a formula selected from the general formulae (IIa) and (IIb):



II a



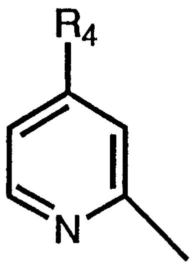
II b

wherein

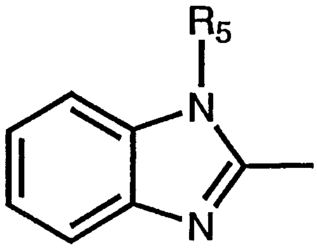
R_1 is selected from H, COOH, $PO(OH)_2$, $PO(OR_3)(OH)$, $PO(OR_3)_2$, CO(NHOH), pyrocatechol group, phenyl substituted by at least one of the groups selected from COOH, $PO(OH)_2$, $PO(OR_3)(OH)$, $PO(OR_3)_2$ and CO(NHOH); R_3 being selected from C_{1-30} alkyl and phenyl;

R_2 is selected from H, C_{1-30} alkyl and phenyl; and

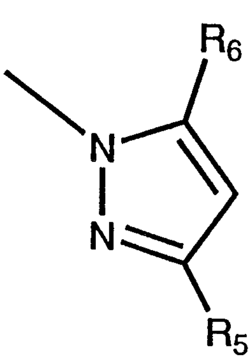
A and B are same or different groups independently selected from the groups of formulae (IIIa), (IIIb), (IIIc), (IIId), (IIIe) and (IIIf):



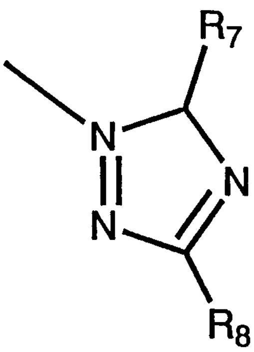
III a



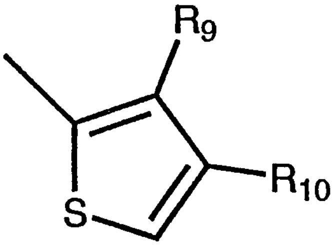
III b



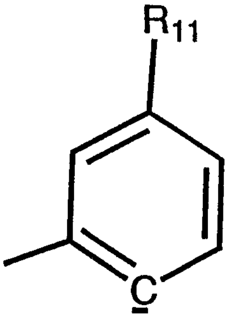
III c



III d



III e



III f

wherein

R_4 has the same meaning as R_1;

each R_5, R_6, R_7, R_8, R_9, R_{10} and R_{11} has the same meaning as R_2 and R_2, R_5, R_6, R_7, R_8, R_9, R_{10} and R_{11} being same as or different from each other;

with the proviso that at least one of the substituents R_1 and R_4 is different of H.

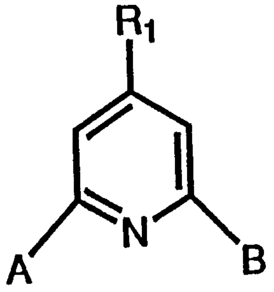
Preferably, when the photosensitizer complex corresponds to formula (Ia):

$$MX_3L_t \quad \text{(Ia)},$$

M is ruthenium or osmium;

each X is independently selected from NCS^- and CN^-; and

L_t has the formula (IIa):

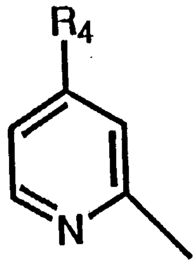


II a

wherein

R_1 is selected from H, COOH, $PO(OH)_2$, $PO(OR_3)(OH)$, $PO(OR_3)_2$, CO(NHOH), pyrocatechol group, phenyl substituted by at least one of the groups selected from COOH, $PO(OH)_2$, $PO(OR_3)(OH)$, $PO(OR_3)_2$ and CO(NHOH); R_3 being selected from C_{1-30} alkyl and phenyl;

A and B are same or different and have the formula (IIIa):



III a

wherein

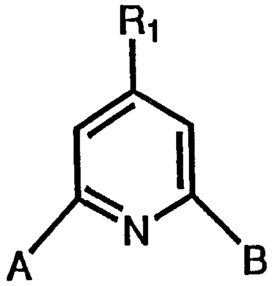
R_4 has the same meaning as R_1;

with the proviso that at least one of the substituents R_1 and R_4 is different of H.

More preferably, when the photosensitizer complex corresponds to formula (Ia):

$$MX_3L_t \quad (Ia),$$

M is ruthenium or osmium;
each X is independently selected from NCS^- and CN^-; and
L_t has the formula (IIa):



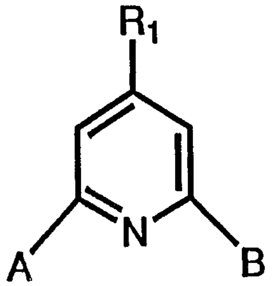
II a

wherein
R_1 is a phenyl substituted by at least one of the groups selected from COOH, $PO(OH)_2$, $PO(OR_3)(OH)$ and $PO(OR_3)_2$; R_3 being selected from C_{1-30} alkyl and phenyl; and
A and B are both 2-pyridyl.

More preferably, when the photosensitizer complex corresponds to formula (Ia):

$$MX_3L_t \quad (Ia),$$

M is ruthenium or osmium;
each X is independently selected from NCS^- and CN^-; and
L_t has the formula (IIa):



II a

wherein

R_1 is COOH; and

A and B are both 4-carboxy-2-pyridyl.

Preferably, when the photosensitizer complex corresponds to formula (Ib):

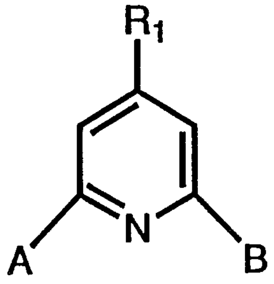
$$MXYL_t \quad \text{(Ib)},$$

M is ruthenium or osmium;

X is NCS^- or CN^-;

Y is selected from o-phenanthroline, 2,2'-bipyridine, unsubstituted or substituted by at least one C_{1-30} alkyl; and

L_t has the formula (IIa):



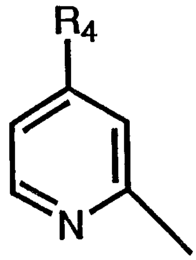
II a

wherein

R_1 is selected from H, pyrocatechol group, phenyl substituted by at least one of the groups selected from COOH, $PO(OH)_2$, $PO(OR_3)(OH)$, $PO(OR_3)_2$ and CO(NHOH);

R_3 being selected from C_{1-30} alkyl and phenyl;

A and B are same or different and have the formula (IIIa):



III a

wherein

R_4 is selected from H, COOH, $PO(OH)_2$, $PO(OR_3)(OH)$, $PO(OR_3)_2$, CO(NHOH), pyrocatechol group, phenyl substituted by at least one of the groups selected from COOH, $PO(OH)_2$, $PO(OR_3)(OH)$, $PO(OR_3)_2$ and CO(NHOH); R_3 being selected from H, C_{1-30} alkyl and phenyl;

with the proviso that at least one of the substituents R_1 and R_4 is different of H.

More preferably, when the photosensitizer complex corresponds to formula (Ib):

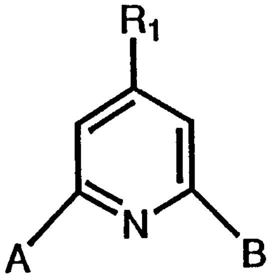
$$MXYL_t \quad (Ib),$$

M is ruthenium or osmium;

X is NCS^- or CN^-;

Y is 4,4'-dimethyl-2,2'-bipyridine; and

L_t has the formula (IIa):



II a

wherein

R_1 is a phenyl substituted by at least one of the groups selected from COOH, $PO(OH)_2$, $PO(OR_3)(OH)$ and $PO(OR_3)_2$; R_3 being selected from C_{1-30} alkyl and phenyl; and

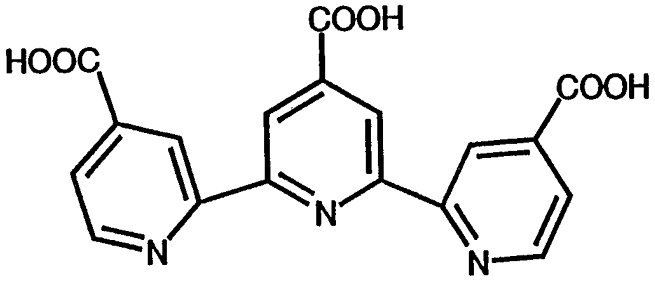
A and B are both 2-pyridyl.

The invention results from extensive research which have shown that the transition metal complex of formulae (Ia) and (Ib) has the unexpected property of exhibiting a substantially enhanced spectral response in the red and near infrared regions, in comparison with the prior art transition metal complexes.

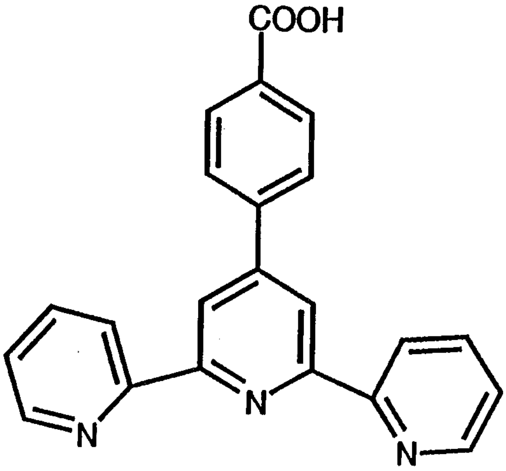
This property allows the use of the complex of formulae (Ia) or (Ib) as charge transfer photosensitizer for semiconductive titanium dioxide photoanode layers, in a photovoltaic cell with a very efficient panchromatic sensitization over the whole visible radiation spectrum, extending into the near infrared region up to 920 nm.

It appeared that the type of coordination around the transition metal, in particular ruthenium or osmium, and the nature of the ligand L_t and the co-ligands Y and/or X surrounding the metal are crucial for obtaining such spectral properties and the claimed combination of ligand and co-ligands has a favourable match to the solar spectrum for efficient energy conversion. This is particularly the case when the co-ligands X are the negatively charged species such as the cyanide anion or the thiocyanide anion and when the co-ligand Y is the electron-donor 4,4'-dimethyl-2,2'-bipyridine.

Among the potent tridentate ligands L_t, offering furthermore to the photosensitizer complex at least one anchoring group selected from carboxylate group [COOH], phosphonate group [$PO(OH)_2$, $PO(OR_3)(OH)$ or $PO(OR_3)_2$], hydroxamate group [CO(NHOH)] or chelating groups such as salicylate group [o-carboxyhydroxy-phenyl] or pyrocatechol group [o-dihydroxy-phenyl], the compounds having the following formulae contribute for the best to the increase of spectral properties of the photosensitizer:



(1)



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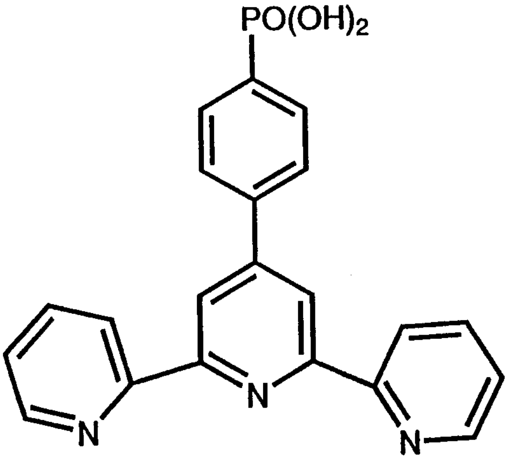

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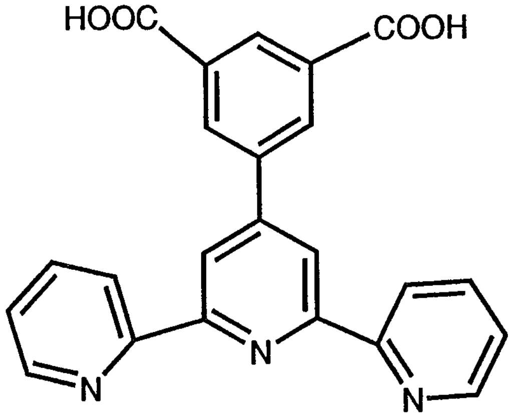

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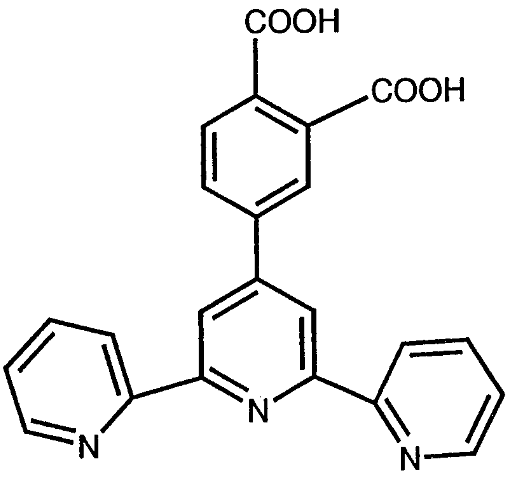

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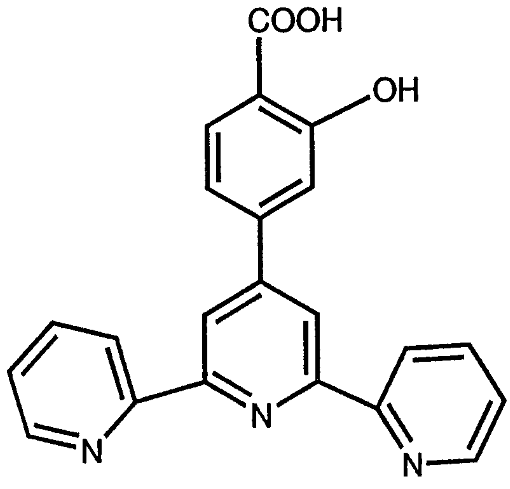

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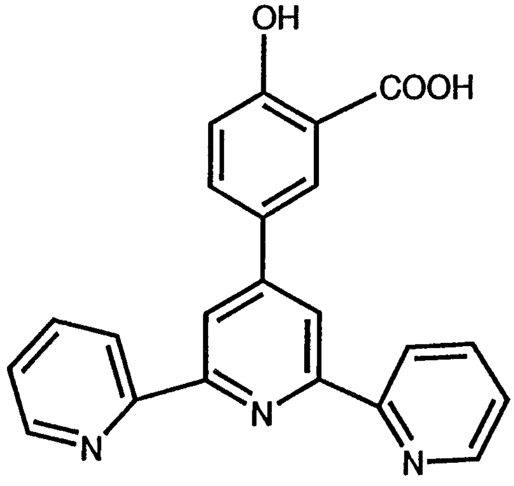

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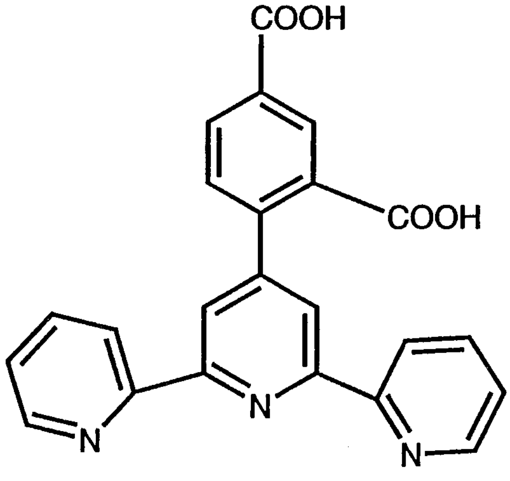

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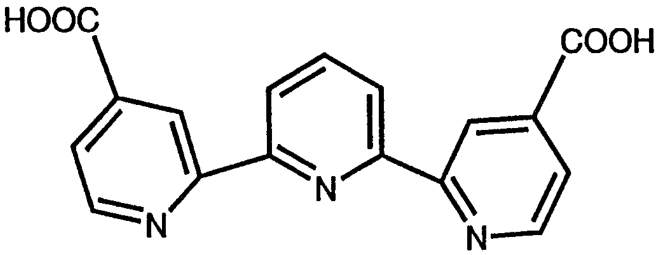


(9)

Still further according to the invention, there is provided a photovoltaic cell comprising an electrically conductive layer deposited on a support to which at least one titanium dioxide layer has been applied, characterized in that it comprises, as a photosensitizer applied to the titanium dioxide layer, a photosensitizer complex of formulae (Ia) or (Ib) as specified above.

The invention will now be illustrated by the following examples, with reference to the attached drawing, in which:

FIG. 1 is a schematic illustration of the layout and function of a photovoltaic cell comprising a photoanode provided with a nanostructured semiconductive titanium dioxide film having a transition metal complex of formulae (Ia) or (Ib) applied thereto as a charge transfer sensitizer,

FIG. 2 is a graph showing the photocurrent action spectrum of such a cell where the incident photon to current conversion efficiency (IPCE) is plotted as a function of wavelength, and

FIG. 3 is a graph, similar to the graph of FIG. 2, showing the respective photocurrent action spectra of a photovoltaic cell using the transition metal complex of formulae (Ia) or (Ib), in comparison with a similar cell using the cis-dithiocyanato-bis(4,4'-dicarboxy-2,2'-bipyridine) ruthenium(II) complex, of the prior art, as well as with two other similar cells using respectively two other prior art ruthenium complexes as a charge transfer photosensitizer for a semiconductive titanium dioxide photoanode layer, and with still another similar photovoltaic cell using no photosensitizer.

Example 1: Preparation of the complex trithiocyanato (4,4',4"-tricarboxy-2,2':6',2"-terpyridyl) ruthenium(II), i.e. the complex of formula $Ru(NCS)_3L_t$, wherein L_t is 4,4',4"-tricarboxy-2,2':6',2"-terpyridine

a) Preparation of 4,4',4"-trimethyl-2,2':6',2"-terpyridine:

4-Methyl-pyridine (900 mL, refluxed over and distilled fresh from KOH pellets) and palladium on charcoal (5%, 37 g) were heated on a bath at 170°C as long as the chemical equilibrium is reached. The reaction mixture was filtered hot, the catalyst was washed with hot toluene and the filtrate left to crystallise. The 4,4'-dimethyl-

2,2'-bipyridine crystals were filtered and washed with toluene. The mother liquors combined, concentrated to 1/3 of the volume and crystallised at 0°C. This second crop of bipyridine was treated as above, the mother liquor was evaporated to dryness under reduced pressure. The bipyridine and terpyridine components of the mother liquor were separated by careful multiple fractional sublimations at 0.02 mmHg, at bath temperatures 80 - 100°C (depending on the geometry of the apparatus). Under these conditions, the 4,4',4"-trimethyl-2,2':6',2"-terpyridine accumulates in the residue. The combined pure terpyridine fractions were sublimed twice at 0.02 mmHg at 120-140°C yielding 15g of off-white 4,4',4"-trimethyl-2,2':6',2"-terpyridine. (For some fractions column chromatography on silicagel with dichloromethane as eluent was used to get the highly pure 4,4',4"-trimethyl-2,2':6',2"-terpyridine.)
MS (70eV, chem.ionisation/NH3) m/e (rel.int.): 277(6.6, M+2), 276 (37.8; M+1), 275 (100.0; M), 274 (25.8), 260 (3.91, M-15), 247 (1.4, M-28), 233 (1.9, M-42), 183 (1.1, M-92), 92(4.58, M-183).
^{1}H-NMR ($CDCl_3$) δ ppm: 2.50 (6H, s), 2.58 (3H, s), 7.15 (2H, d), 8.26 (2H, s), 8.40 (2H, s), 8.55 (2H, d).

b) Preparation of 4,4',4"-tricarboxy-2,2';6',2"-terpyridine:

To an ice-cold solution of 4,4',4"-trimethyl-2,2':6',2"-terpyridine (0.32g; 1.16mmol) in sulfuric acid (4mL) chromium trioxide (1.05g; 10.5mmol) was added. Stirred for 4h at 75°C, poured to 50ml ice-water, then diluted with water (165ml) and the white precipitate was separated with in a centrifuge, washed until pH=7, and dried. Yielding 4,4',4"-tricarboxy-2,2':6',2"-terpyridine (0.15g; 41%) as a greenish white amorphous powder.
MS (70eV, chem.ionisation/NH3) m/e (rel.int.): 366 (12.22; M+1), 365 (12.57; M), 322 (16.44), 321 (55.11, M-44), 293 (4.05), 231 (1.34, M-3x44+3), 79 (100).
^{1}H-NMR (D_2O/NaOH) δ ppm: 7.52 (2H, d), 8.13 (2H, s), 8.31 (2H, s), 8.43 (2H, d)

c) Preparation of the tetrabutylammonium salt of trithiocyanato (4,4',4"-tricarboxy-2,2':6',2"-terpyridyl) ruthenium(II):

RuCl3.xH2O (60 mg, 0.23 mmol) and 4,4',4"-tricarboxy-2,2':6',2"-terpyridine (70 mg, 0.19 mmol) were added to a 100 mL three necked flask containing 30 mL of DMF and nitrogen bubbled through the mixture for 15 minutes. The mixture was protected from light by wrapping aluminium foil around the flask and then heated at

120°C for two hours. The brown-green solution was cooled slightly, 110°C, and excess KSCN (0.9 g, 9 mmol) dissolved in 5 mL of a 4:1 mixture of DMF/water added and heating continued for a further 70 hours at the same temperature under exclusion of light. The colour of the mixture changed for brown-green to green after this time. Base in the form of solid hydrated tetrabutylammonium hydroxide (TBAOH, 0.48 g) was then added and the mixture heated at 110°C for a further 24 hours. The reaction mixture was reduced to almost dryness on a rotary evaporator and a further 0.6 g of TBAOH added followed by ca. 100 mL of deionised water (the pH of the solution was ca. 11.7). The resulting purple solution was filtered to remove a small amount of insoluble material and the pH adjusted to 4 with dilute hydrochloric acid. A dark green precipitate formed immediately but the suspension was nevertheless refrigerated overnight prior to filtration to collect the product.
Yield: 192 mg (87 %) of the tetrabutylammonium salt of trithiocyanato (4,4',4"-tri-carboxy-2,2':6',2"-terpyridyl) ruthenium(II). Gel-permeation chromatography can be used to further purify the product.
Microanalyses: Found: C, 54.7; H, 7.0, N, 10.1. Calcd for $C_{53}H_{81}N_8O_6S_3Ru.2H_2O$: C, 54.9; H, 7.4, N 9.7
The UV - VIS absorption spectrum of the complex in ethanol shows an intense metal-to-ligand charge transfer band at 620 nm.
^1H NMR Spectrum (CD_3OD, ppm): 1.03 (t, 24H, $C\underline{H}_3$), 1.55 (q, 16H, $C\underline{H}_2CH_3$), 1.70 (m, 16H, $NCH_2C\underline{H}_2$), 3.28 (t, 16H, $NC\underline{H}_2$), 8.23 (dd, 2H, H-5, H-5'), 8.95 (d, 2H, H-3, H-3', s, 2H, H-3"), 9.17 (d, 2H, H-6, H-6').
^{13}C NMR Spectrum (CD_3OD, ppm): 13.95, 20.74, 24.83, 59.6, 122,12, 122.99, 129.89, 136.62, 138.16, 142.30, 154.86, 160.80, 162.19, 167.66.

Example 2: Preparation of the complex trithiocyanato (4'-(4-phenylphosphonate)-2,2':6',2"-terpyridyl) ruthenium(II), i.e. the complex of formula $Ru(NCS)_3L_t$, wherein L_t is 4'-(4-phenylphosphonate)-2,2':6',2"-terpyridine

a) Preparation of 4'-(4-phenylphosphonate)-2,2':6',2"-terpyridine:

This ligand was prepared following a described procedure (H. Toshikazu et al., Synthesis, 1981, 56)

b) Preparation of the tetrabutylammonium salt of trithiocyanato (4'-(4-phenyl-phosphonate)-2,2':6',2"-terpyridyl) ruthenium(II):

This complex was prepared by an analogous procedure to that described in Example 1.

The UV - VIS absorbtion spectrum of this complex in ethanol shows an intense metal-to-ligand charge transfer band at 580 nm.

Example 3: Preparation of the complex trithiocyanato (4'-(4-carboxyphenyl)-2,2':6',2"-terpyridyl) ruthenium(II), i.e. the complex of formula $Ru(NCS)_3L_t$, wherein L_t is 4'-(4-carboxyphenyl)-2,2':6',2"-terpyridine

a) Preparation of 4'-(4-carboxyphenyl)-2,2':6',2"-terpyridine:

This ligand was prepared by oxydation of the known 4'-(4-methylphenyl)-2,2':6',2"-terpyridine by an analogous procedure to that described in Example 1b.

b) Preparation of the tetrabutylammonium salt of trithiocyanato (4'-(4-carboxyphenyl)-2,2':6',2"-terpyridyl) ruthenium(II):

This complexe was prepared by an analogous procedure to that described in Example 1.
The UV - VIS absorbtion spectrum of this complex in ethanol shows an intense metal-to-ligand charge transfer band at 600 nm.

Example 4: Preparation of the complex tricyano (4,4',4"-tricarboxy-2,2':6',2"-terpyridyl) ruthenium(II), i.e. the complex of formula $Ru(NC)_3L_t$, wherein L_t is 4,4',4"-tricarboxy-2,2':6',2"-terpyridine

The tetrabutylammonium salt of this complexe was prepared by an analogous procedure to that described in Example 1.
The UV - VIS absorbtion spectrum of this complex in ethanol shows an intense metal-to-ligand charge transfer band at 540 nm.

Example 5: Preparation of the complex tricyano (4'-(4-phenylphosphonate)-2,2':6',2"-terpyridyl) ruthenium(II), i.e. the complex of formula $Ru(NC)_3L_t$, wherein L_t is 4'-(4-phenylphosphonate)-2,2':6',2"-terpyridine

The tetrabutylammonium salt of this complexe was prepared by an analogous procedure to that described in Example 1.
The UV - VIS absorbtion spectrum of this complex in ethanol shows an intense metal-to-ligand charge transfer band at 520 nm.

Example 6: Preparation of the complex tricyano (4'-(4-carboxyphenyl)-2,2':6',2"-terpyridyl) ruthenium(II), i.e. the complex of formula $Ru(NC)_3L_t$, wherein L_t is 4'-(4-carboxyphenyl)-2,2':6',2"-terpyridine

The tetrabutylammonium salt of this complexe was prepared by an analogous procedure to that described in Example 1.
The UV - VIS absorbtion spectrum of this complex in ethanol shows an intense metal-to-ligand charge transfer band at 530 nm.

Example 7: Preparation of the complex thiocyanato (4'-(4-phenylphosphonate)-2,2':6',2"-terpyridyl)(4,4'-dimethyl-2,2'-bipyridyl) ruthenium(II), i.e. the complex of formula Ru(NCS)YL$_t$, wherein L$_t$ is 4'-(4-phenylphosphonate)-2,2':6',2"-terpyridine and Y is 4,4'-dimethyl-2,2'-bipyridine

The synthesis and work-up of this reaction were performed under reduced light in order to avoid possible isomerization. $RuCl_2(dmso)_4$ (0.484 g) was dissolved into a 100 mL three necked flask containing 30 mL of DMF and nitrogen bubbled through the mixture for 15 minutes. To this solution was added (0.375 g) 4'-(4-phenyl-phosphonate)-2,2':6',2"-terpyridine. The reaction flask was protected from light by wrapping aluminium foil around the flask and then heated at 120°C for three hours. To this solution was added 4,4'-dimethyl-2,2'-bipyridine ligand (0.184 g), and refluxed under a nitrogen atmosphere for another 4 hours. The reaction mixture was cooled to 110°C, and excess KSCN (0.9 g, 9 mmol) dissolved in 5 mL of a 4:1 mixture of DMF/water added and heating continued for a further 5 hours at the same temperature under exclusion of light. The colour of the mixture changed after this time. Base in the form of solid hydrated tetrabutylammonium hydroxide (TBAOH, 0.48 g) was then added and the mixture heated at 110°C for a further 4 hours. The reaction mixture was reduced to almost dryness on a rotary evaporator and a further 0.6 g of TBAOH added followed by ca. 100 mL of deionised water (the pH of the solution was ca. 11.7). The resulting purple solution was filtered to remove a small amount of insoluble material and the pH adjusted to 2.5 with dilute hydrochloric acid. A dense precipitate formed immediately but the suspension was nevertheless refrigerated overnight prior to filtration to collect the product. After allowing it to cool to (25 °C) room temperature, it was filtered through a sintered (G-4) glass crucible and dried under vacuum. Yield 60% of the tetrabutylammonium salt of thiocyanato (4'-(4-phenylphosphonate)-2,2':6',2"-terpyridyl)(4,4'-dimethyl-2,2'-bipyridyl) ruthenium(II).
The UV - VIS absorption spectrum of this complex in ethanol shows an intense metal-to-ligand charge transfer band at 500 nm.

Example 8: Preparation of the complex thiocyanato (4'-(4-carboxyphenyl)-2,2':6',2"-terpyridyl)(4,4'-dimethyl-2,2'-bipyridyl) ruthenium(II), i.e. the complex of formula Ru(NCS)YL_t, wherein L_t is 4'-(4-carboxyphenyl)-2,2':6',2"-terpyridine and Y is 4,4'-dimethyl-2,2'-bipyridine

The tetrabutylammonium salt of this complexe was prepared by an analogous procedure to that described in Example 7.
The UV - VIS absorbtion spectrum of this complex in ethanol shows an intense metal-to-ligand charge transfer band at 510 nm.

Example 9: Preparation of the complex thiocyanato (4,4',4"-tricarboxy-2,2':6',2"-terpyridyl)(4,4'-dimethyl-2,2'-bipyridyl) ruthenium(II), i.e. the complex of formula Ru(NCS)YL_t, wherein L_t is 4,4',4"-tricarboxy-2,2':6',2"-terpyridine and Y is 4,4'-dimethyl-2,2'-bipyridine

The tetrabutylammonium salt of this complexe was prepared by an analogous procedure to that described in Example 7.
The UV - VIS absorbtion spectrum of this complex in ethanol shows an intense metal-to-ligand charge transfer band at 520 nm.

Example 10: Preparation of the complex cyano (4'-(4-phenylphosphonate)-2,2':6',2"-terpyridyl)(4,4'-dimethyl-2,2'-bipyridyl) ruthenium(II), i.e. the complex of formula Ru(NC)YL_t, wherein L_t is 4'-(4-phenylphosphonate)-2,2':6',2"-terpyridine and Y is 4,4'-dimethyl-2,2'-bipyridine

The tetrabutylammonium salt of this complexe was prepared by an analogous procedure to that described in Example 7.
The UV - VIS absorbtion spectrum of this complex in ethanol shows an intense metal-to-ligand charge transfer band at 500 nm.

Example 11: Preparation of the complex cyano (4'-(4-carboxyphenyl)-2,2':6',2"-terpyridyl)(4,4'-dimethyl-2,2'-bipyridyl) ruthenium(II), i.e. the complex of formula Ru(NC)YL_t, wherein L_t is 4'-(4-carboxyphenyl)-2,2':6',2"-terpyridine and Y is 4,4'-dimethyl-2,2'-bipyridine

The tetrabutylammonium salt of this complexe was prepared by an analogous procedure to that described in Example 7.
The UV - VIS absorbtion spectrum of this complex in ethanol shows an intense metal-to-ligand charge transfer band at 510 nm.

Example 12: Preparation of the complex cyano (4,4',4"-tricarboxy-2,2':6',2"-terpyridyl)(4,4'-dimethyl-2,2'-bipyridyl) ruthenium(II), i.e. the complex of formula Ru(NC)YL$_t$, wherein L$_t$ is 4,4',4"-tricarboxy-2,2':6',2"-terpyridine and Y is 4,4'-dimethyl-2,2'-bipyridine

The tetrabutylammonium salt of this complexe was prepared by an analogous procedure to that described in Example 7.
The UV - VIS absorbtion spectrum of this complex in ethanol shows an intense metal-to-ligand charge transfer band at 520 nm.

Example 13: Preparation of the complex cyano (4'-(4-carboxyphenyl)-2,2':6',2"-terpyridyl)(4,4'-dimethyl-2,2'-bipyridyl) osmium(II), i.e. the complex of formula Os(NC)YL$_t$, wherein L$_t$ is 4'-(4-carboxyphenyl)-2,2':6',2"-terpyridine and Y is 4,4'-dimethyl-2,2'-bipyridine

The tetrabutylammonium salt of this complexe was prepared by an analogous procedure to that described in Example 7 using NH_4OsCl_6 and ethyleneglycol as solvent.
The UV - VIS absorbtion spectrum of this complex in ethanol shows an intense metal-to-ligand charge transfer band at 510 nm, 650 nm and 700 nm.

Example 14: Preparation of the complex cyano (4,4',4"-tricarboxy-2,2':6',2"-terpyridyl)(4,4'-dimethyl-2,2'-bipyridyl) osmium(II), i.e. the complex of formula Os(NC)YL$_t$, wherein L$_t$ is 4,4',4"-tricarboxy-2,2':6',2"-terpyridine and Y is 4,4'-dimethyl-2,2'-bipyridine

The tetrabutylammonium salt of this complexe was prepared by an analogous procedure to that described in Example 13.
The UV - VIS absorbtion spectrum of this complex in ethanol shows an intense metal-to-ligand charge transfer band at 510 nm, 650 nm and 700nm.

Example 15: Preparation of the complex cyano (4'-(4-phenylphosphonate)-2,2':6',2"-terpyridyl)(4,4'-dimethyl-2,2'-bipyridyl) osmium(II), i.e. the complex of formula Os(NC)YL$_t$, wherein L$_t$ is 4'-(4-phenylphosphonate)-2,2':6',2"-terpyridine and Y is 4,4'-dimethyl-2,2'-bipyridine

The tetrabutylammonium salt of this complexe was prepared by an analogous procedure to that described in Example 13.
The UV - VIS absorbtion spectrum of this complex in ethanol shows an intense metal-to-ligand charge transfer band at 490 nm, 640 nm and 700nm.

Example 16: Preparation of the complex thiocyanato (4'-(4-phenylphosphonate)-2,2':6',2"-terpyridyl)(4,4'-dimethyl-2,2'-bipyridyl) osmium(II), i.e. the complex of formula Os(NCS)YL_t, wherein L_t is 4'-(4-phenylphosphonate)-2,2':6',2"-terpyridine and Y is 4,4'-dimethyl-2,2'-bipyridine

The tetrabutylammonium salt of this complexe was prepared by an analogous procedure to that described in Example 13.
The UV - VIS absorbtion spectrum of this complex in ethanol shows an intense metal-to-ligand charge transfer band at 510 nm, 650 nm and 700nm.

Application Exemple: A photovoltaic device shown in Figure 1 and based on the sensitization of a titanium dioxide film supported on conducting glass is fabricated as follows:

Nanocrystalline TiO_2 films were prepared by spreading a viscous dispersion of colloidal TiO_2 particles on a conducting glass support (Asahi TCO glass, fluorine-doped SnO_2 overlayer, transmission > 85% in the visible sheet resistance 7-8 Ω/square) with heating under air for 30 min at 450 °C. Two methods of preparation of colloidal TiO_2 dispersions were employed. Method A followed the procedure described earlier [O'Regan, B.; Grätzel, M. *Nature (London)* 1991, 353, 737], except that autoclaving was performed at 230 or 240 °C instead of 200 °C. After the colloid was spread on the conducting glass support and calcined, a few monolayers of TiO_2 were electrodeposited [Kavan, L.; O'Regan, B.; Kay, A.; Grätzel, M. *J. Electroanal. Chem.* 1993, 346, 291] onto the colloidal TiO_2 film from an aqueous Ti(III) solution followed by renewed annealing at 450 °C. This treatment was found to improve significantly the short-circuit photocurrent as well as the open-circuit voltage of the solar cell. A cross section of such a TiO_2 film obtained by scanning electron microscopy at two different magnifications confirms the presence of a three-layer structure, the lowest being the glass support followed by the 0,7-μm-thick fluorine-doped SnO_2 and the 10-μm-thick colloidal TiO_2 film. High resolution reveals the TiO_2 film to be composed of a three-dimensional network of interconnected particles having an average size of approximately 15 nm.

The second method for preparation of nanocrystalline films (Method B) employed commercial TiO_2 (P25, Degussa AG, Germany, a mixture of ca. 30% rutile and 70% anatase, BET surface area 55 m^2/g). This is produced by flame hydrolysis of $TiCl_4$ and consists of aggregated particles. Electron microscopy shows the mean size of primary particles to be about 25 nm. In order to break the aggregates into separate particles, the powder (12 g) was ground in a porcelain mortar with a small amount of water (4 mL) containing acetylacetone (0,4 mL) to prevent reaggregation of the particles. Other stabilizers such as acids, bases, or TiO_2 chelating agents were found to be suitable as well. After the powder had been dispersed by the high shear forces in the viscous paste, it was diluted by slow addition of water (16 mL) under continued grinding. Finally, a detergent (0,2 mL Triton X-100, Aldrich) was added to facilitate the spreading of the colloid on the substrate. The conducting TCO glass was covered on two parallel edges with adhesive tape (≈40-μm-thick) to control the thickness of the TiO_2 film and to provide noncoated areas for electrical contact. The colloid (5 μL/cm^2) was applied to one of the free edges of the conducting glass and distributed with a glass rod sliding over the tape-covered edges. After air drying, the electrode was fired for 30 min at 450-550 °C in air. The resulting film thickness was 12 μm but can be varied by changing the colloid concentration or the adhesive tape thickness.

The performance of the film as a sensitized photoanode was improved by further deposition of TiO_2 from aqueous $TiCl_4$ solution. A 2 M $TiCl_4$ stock solution was prepared [Kavan, L.; O'Regan, B.; Kay, A.; Grätzel, M. *J. Electroanal. Chem.* 1993, 346, 291] at 0 °C to prevent precipitation of TiO_2 due to the highly exothermic hydrolysis reaction. This stock solution was freshly diluted with water to 0,2 M $TiCl_4$ and applied onto the electrode (50 μL/cm^2). After being left overnight at room temperature in a closed chamber, the electrode was washed with distilled water. Immediately before being dipped into the dye solution, it was fired again for 30 min at 450-550 °C in air. Similarly to the electrodeposition from aqueous Ti(III) solution, this procedure results in the nucleation of nanometer-sized TiO_2 particles on the TiO_2 film, further increasing its active surface area. Furthermore, this treatment as well as the anodic deposition of TiO_2 from Ti(III) solution described above appears to lead to deposits having a very low impurity content. This is corroborated by the fact that the treatment becomes ineffective if the $TiCl_4$ solution is evaporated before firing instead of being washed off. Impurities in the $TiCl_4$, such as Fe^{3+}, are not deposited by hydrolysis from the acidic $TiCl_4$ solution due to the higher solubility of iron oxide compared to TiO_2. By contrast, evaporation of the $TiCl_4$ solution results in the deposition of impurities. The P25 powder contains up to 100 ppm of Fe_2O_3, which is known to interfere with electron injection from the excited dye. The $TiCl_4$ treatment covers this rather impure core with a thin layer of highly pure TiO_2, improving the injection efficiency and the blocking character of the semiconductor-electrolyte junction [Kavan, L.; O'Regan, B.; Kay, A.; Grätzel, M. *J. Electroanal. Chem.* 1993, 346, 291].

The above described treatment produces anatase films with a surface roughness factor of about 200 to 1000.

After cooling under a continuous argon flow, the glass sheet is immediately transferred to a $2x10^{-4}M$ solution in ethanol of the tetrabutylammonium salt of the ruthenium complex of Example 1, this solution further containing 40 mM of tauro-deoxycholic acid as a co-adsorbent. Prolonged exposure of the film to the open air prior to dye adsorption is avoided in order to prevent hydroxylation of the TiO_2 surface as the presence of hydroxyl groups at the electrode surface interferes with dye uptake. The adsorption of photosensitizer from the ethanolic solution is allowed to continue for 10 hours after which time the glass sheet is withdrawn and washed briefly with absolute ethanol. The TiO_2 layer on the sheet assumed a black colour owing to the photosensitizer coating.

A thus obtained black colored film, having a thickness of 12 mm, exhibited striking performance when tested in a photovoltaic cell in conjunction with a redox electrolyte containing a solution of 60% methoxypropionitrile, 40% acetonitrile, 0.5M 4-tert-butylpyridine, 0.1 M LiI, 0.6 M 1,2-dimethyl-3-propyl imidazoliumiodide and 0.1 M I_2. Figure 2 shows the photocurrent action spectrum of such a cell where the incident photon to current conversion efficiency (IPCE) is plotted as a function of the excitation wavelength. This was derived from the equation:

$$(1) \quad \text{IPCE}(\%) = \frac{[(1.24\text{x}10^3) \text{ x photocurrent density } (\mu A/cm^2)]}{[\text{wavelength (nm) x photon flux } (W/m^2)]}$$

From the overlap of the photocurrent action spectrum with solar emission the overall efficiency for the conversion of solar light to electricity η is calculated from the formula

$$(2) \quad \eta = 12 \text{ x OCV x FF}(\%)$$

where OCV is the open circuit voltage and FF is the fill factor of the photovoltaic cell.

For experimental verification of equation 2, a photovoltaic cell, as illustrated on FIG.1, is constructed, using the ruthenium complex of Example 1 (4) by way of photosensitizer loaded TiO_2 (5) film supported on a conducting glass (the working electrode) comprising a transparent conductive tin dioxide layer (6) and a glass substrate (7) as a photoanode. The cell has a sandwich-like configuration, the working electrode (4-7) being separated from the counter electrode (1,2) by a thin layer of electrolyte (3) having a thickness of ca. 20 microns. The counter-electrode comprises the conductive tin dioxide layer (2) deposited on a glass substrate (1) made also of Asahi conducting glass and is placed directly on top of the working electrode. A monomolecular transparent layer of platinum is deposited on to the conducting glass of the counter electrode (1,2) by electroplating from an aqueous hexachloroplatinate solution. The role of the platinum is to enhance the electrochemical reduction of iodine at the counter electrode. The transparent nature of the counterelectrode is an advantage for photovoltaic applications since it allows the harvesting of light from both the forward and the backward direction. Experiments are carried out with a high pressure Xenon lamp equipped with appropriate filters to simulate AM1,5 solar radiation. The intensity of the light is varied between 50 and 600 Watts per square meter and the open circuit voltage is 660 and 800mV, respectively. The fill factor defined as the maximum electric power output of the cell divided by the product of open circuit voltage and short circuit current is between 0.7 and 0.75V. The broad feature covering the entire visible spectrum and extending into the near IR region up to 920 nm is obtained, the IPCE value in the plateau region being about 80%. Taking the light losses in the conducting glass into account the efficiency of electric current generation is practically 100% over a broad wavelength range extending form 400 to 700 nm. The overlap integral of this curve with the standard global AM 1.5 solar emission spectrum yields a photocurrent density of 20m A/cm^2.

The comparison of the curves, shown on FIG. 3, illustrating, respectively:

- Curve 1: the photocurrent action spectrum of the above-described photovoltaic cell using the transition metal complex of formula (I) as a charge transfer photosensitizer;
- Curve 2: the photocurrent action spectrum of a similar photovoltaic cell using the prior art photosensitizer cis-dithiocyanatobis(4,4'-dicarboxy-2,2'-bipyridine) ruthenium(II) complex;
- Curve 3: the photocurrent action spectrum of another similar photovoltaic cell using a prior art photosensitizer having the formula, $RuL_2[Ru(bpy)_2(CN)_2]_2$, where bpy means bipyridyl, and L is 4,4'-dicarboxy-2,2'-bipyridine;

- Curve 4: the photocurrent action spectrum of still another similar photovoltaic cell using a prior art photosensitizer having the formula RuL_3, where L has the above-indicated meaning; and
- Curve 5: the photocurrent action spectrum of still another similar photovoltaic cell using no photosensitizer.

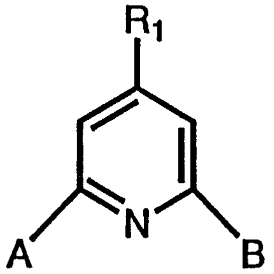
clearly demonstrates the superiority of the complex of formula (I), with regard to the spectral response in the red and near infrared regions, as well as the overall efficiency of panchromatic sensitization over the whole visible radiation spectrum.

Claims

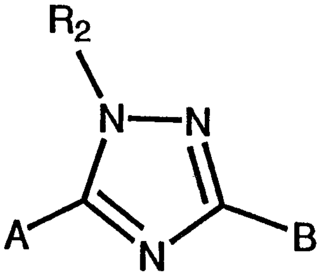
1. A photosensitizer complex of formulae (Ia) or (Ib):

MX_3L_t (Ia); $MXYL_t$ (Ib);

in which
M is a transition metal selected from ruthenium, osmium, iron, rhenium and technetium;
each X is a co-ligand independently selected from NCS^-, Cl^-, Br^-, I^-, CN^-, NCO^-, H_2O, NCN^{2-}, pyridine unsubstituted or substituted by at least one group selected from vinyl, primary, secondary or tertiary amine, OH and C_{1-30} alkyl;
Y is a co-ligand selected from o-phenanthroline, 2,2'-bipyridine, unsubstituted or substituted by at least one C_{1-30} alkyl; and
L_t is a tridentate ligand having a formula selected from the general formulae (IIa) and (IIb):

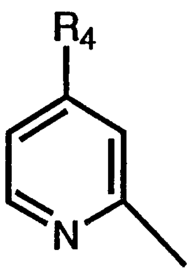


II a

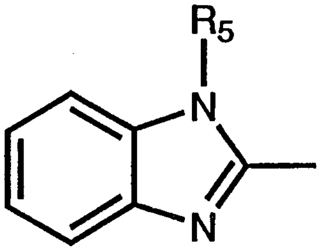


II b

wherein
R_1 is selected from H, COOH, $PO(OH)_2$, $PO(OR_3)(OH)$, $PO(OR_3)_2$, CO(NHOH), pyrocatechol group, phenyl substituted by at least one of the groups selected from COOH, $PO(OH)_2$, $PO(OR_3)(OH)$, $PO(OR_3)_2$ and CO(NHOH); R_3 being selected from C_{1-30} alkyl and phenyl;
R_2 is selected from H, C_{1-30} alkyl and phenyl; and
A and B are same or different groups independently selected from the groups of formulae (IIIa), (IIIb), (IIIc), (IIId), (IIIe) and (IIIf):



III a



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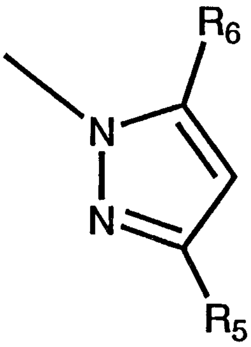
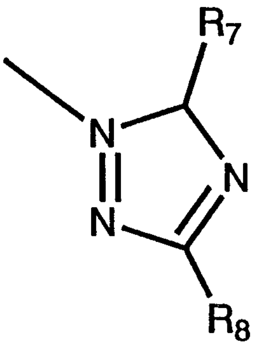
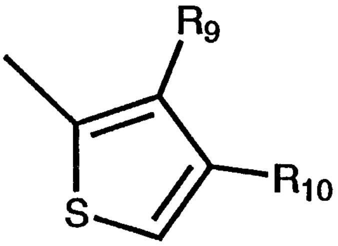


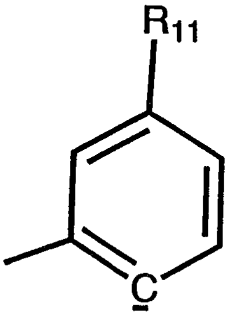
III c



III d



III e



III f

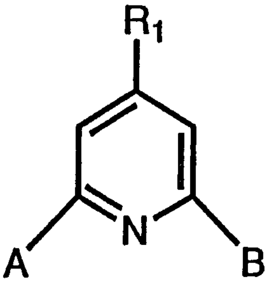
wherein

R_4 has the same meaning as R_1;

each R_5, R_6, R_7, R_8, R_9, R_{10} and R_{11} has the same meaning as R_2 and R_2, R_5, R_6, R_7, R_8, R_9, R_{10} and R_{11} being same as or different from each other;

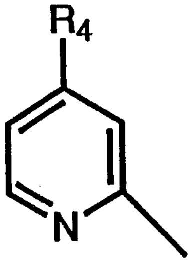
with the proviso that at least one of the substituents R_1 and R_4 is different of H.

2. A photosensitizer complex of formula (Ia), according to claim 1, characterized in that
M is ruthenium or osmium;
each X is independently selected from NCS^- and CN^-; and
L_t has the formula (IIa):



II a

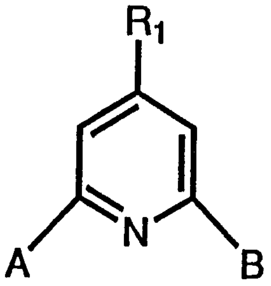
wherein
R_1 is selected from H, COOH, $PO(OH)_2$, $PO(OR_3)(OH)$, $PO(OR_3)_2$, CO(NHOH), pyrocatechol group, phenyl substituted by at least one of the groups selected from COOH, $PO(OH)_2$, $PO(OR_3)(OH)$, $PO(OR_3)_2$ and CO(NHOH); R_3 being selected from C_{1-30} alkyl and phenyl;
A and B are same or different and have the formula (IIIa):



III a

wherein
R_4 has the same meaning as R_1;
with the proviso that at least one of the substituents R_1 and R_4 is different of H.

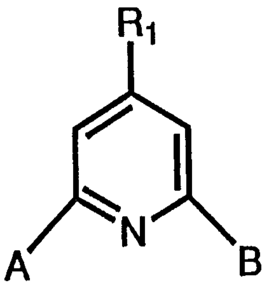
3. A photosensitizer complex of formula (Ia), according to claim 2, characterized in that
M is ruthenium or osmium;
each X is independently selected from NCS^- and CN^-; and
L_t has the formula (IIa):



II a

wherein
R_1 is a phenyl substituted by at least one of the groups selected from COOH, $PO(OH)_2$, $PO(OR_3)(OH)$ and $PO(OR_3)_2$; R_3 being selected from C_{1-30} alkyl and phenyl; and
A and B are both 2-pyridyl.

4. A photosensitizer complex of formula (Ia), according to claim 2, characterized in that
M is ruthenium or osmium;
each X is independently selected from NCS^- and CN^-; and
L_t has the formula (IIa):



II a

wherein

R_1 is COOH; and

A and B are both 4-carboxy-2-pyridyl.

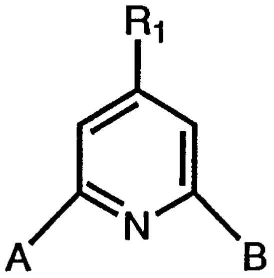
5. A photosensitizer complex of formula (Ib), according to claim 1, charaterized in that

M is ruthenium or osmium;

X is NCS^- or CN^-;

Y is selected from o-phenanthroline, 2,2'-bipyridine, unsubstituted or substituted by at least one C_{1-30} alkyl; and

L_t has the formula (IIa):



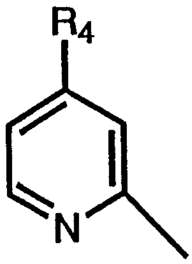
II a

wherein

R_1 is selected from H, pyrocatechol group, phenyl substituted by at least one of the groups selected from COOH, $PO(OH)_2$, $PO(OR_3)(OH)$, $PO(OR_3)_2$ and CO(NHOH);

R_3 being selected from C_{1-30} alkyl and phenyl;

A and B are same or different and have the formula (IIIa):



III a

wherein

R_4 is selected from H, COOH, $PO(OH)_2$, $PO(OR_3)(OH)$, $PO(OR_3)_2$, CO(NHOH), pyrocatechol group, phenyl substituted by at least one of the groups selected from COOH, $PO(OH)_2$, $PO(OR_3)(OH)$, $PO(OR_3)_2$ and CO(NHOH); R_3 being selected from C_{1-30} alkyl and phenyl;

with the proviso that at least one of the substituents R_1 and R_4 is different of H.

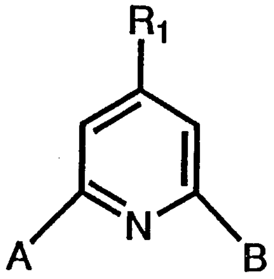
6. A photosensitizer complex of formula (Ib), according to claim 5, characterized in that

M is ruthenium or osmium;

X is NCS^- or CN^-;

Y is 4,4'-dimethyl-2,2'-bipyridine; and

L_t has the formula (IIa):



II a

wherein

R_1 is a phenyl substituted by at least one of the groups selected from COOH, $PO(OH)_2$, $PO(OR_3)(OH)$ and $PO(OR_3)_2$; R_3 being selected from C_{1-30} alkyl and phenyl; and

A and B are both 2-pyridyl.

7. A photovoltaic cell comprising an electrically conductive layer deposited on a support to which at least one titanium dioxide layer has been applied, characterized in that it comprises, as a photosensitizer applied to the titanium dioxide layer, a photosensitizer complex of formulae (Ia) or (Ib) as specified in claim 1.

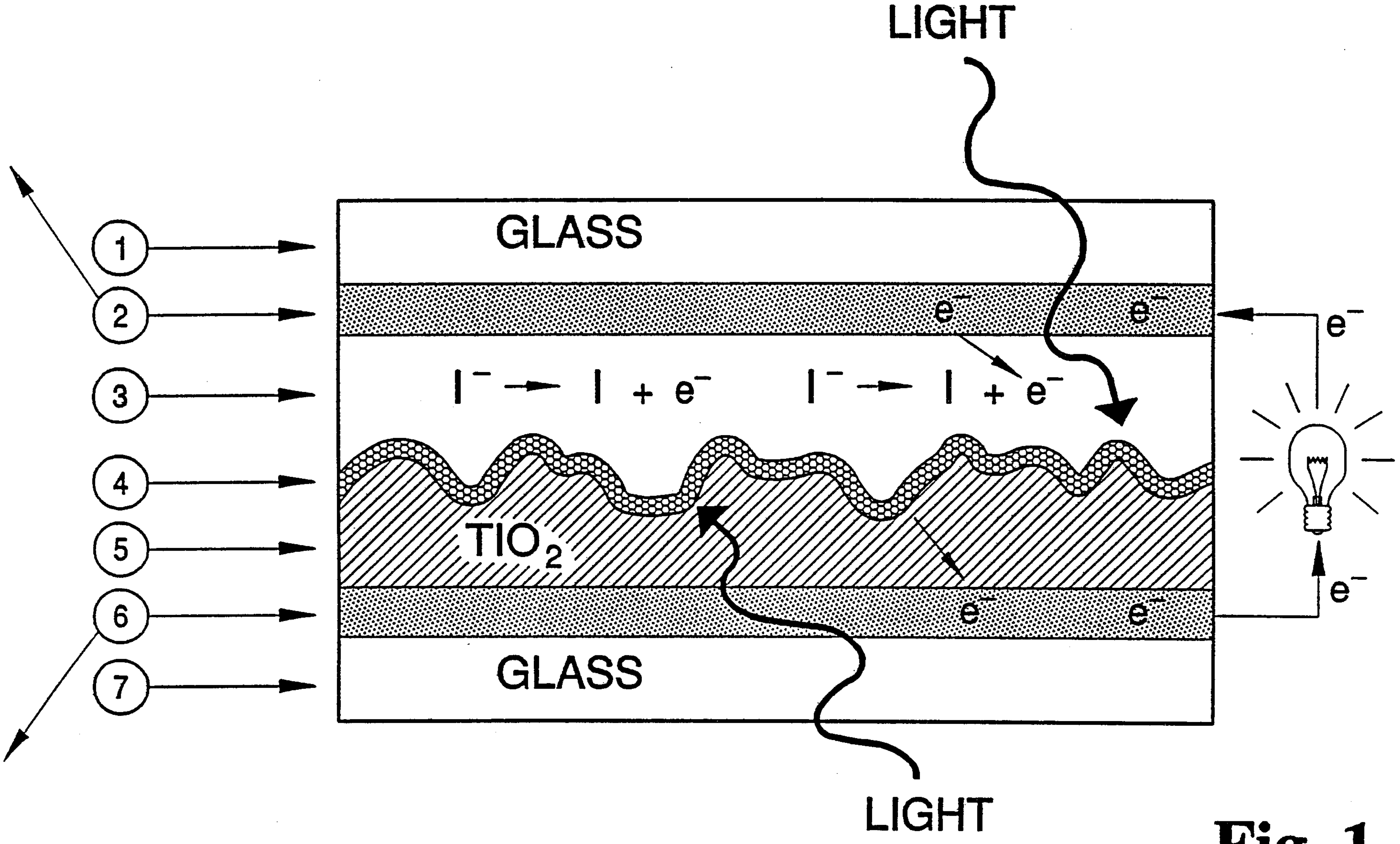


Fig. 1

FIG.2

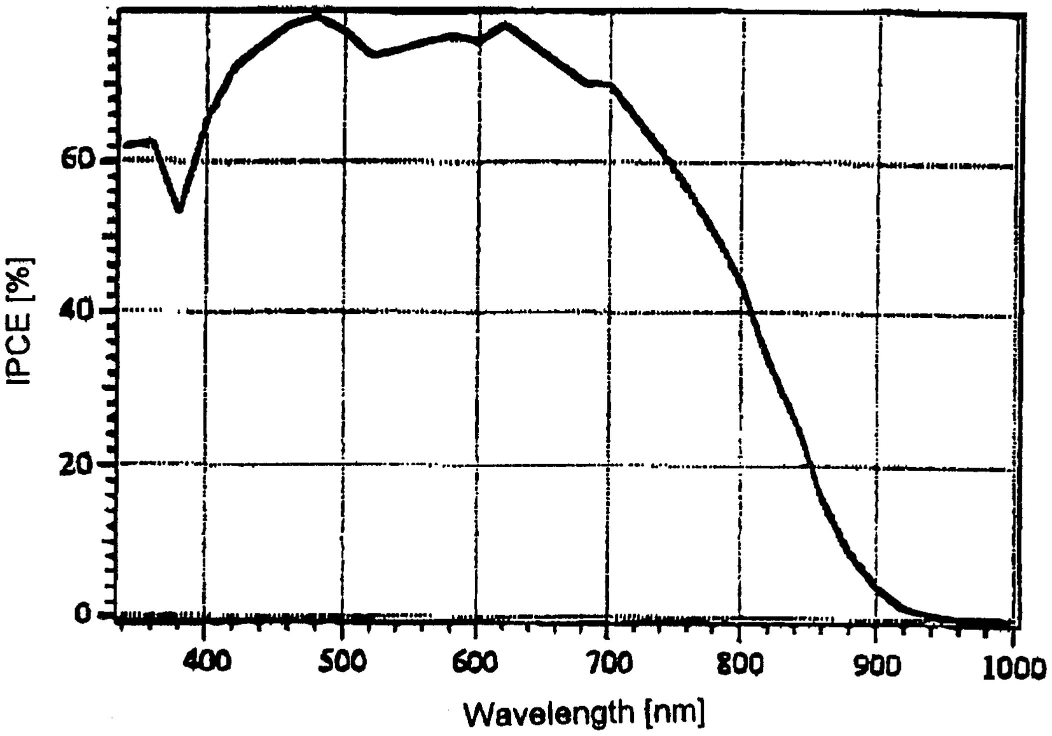
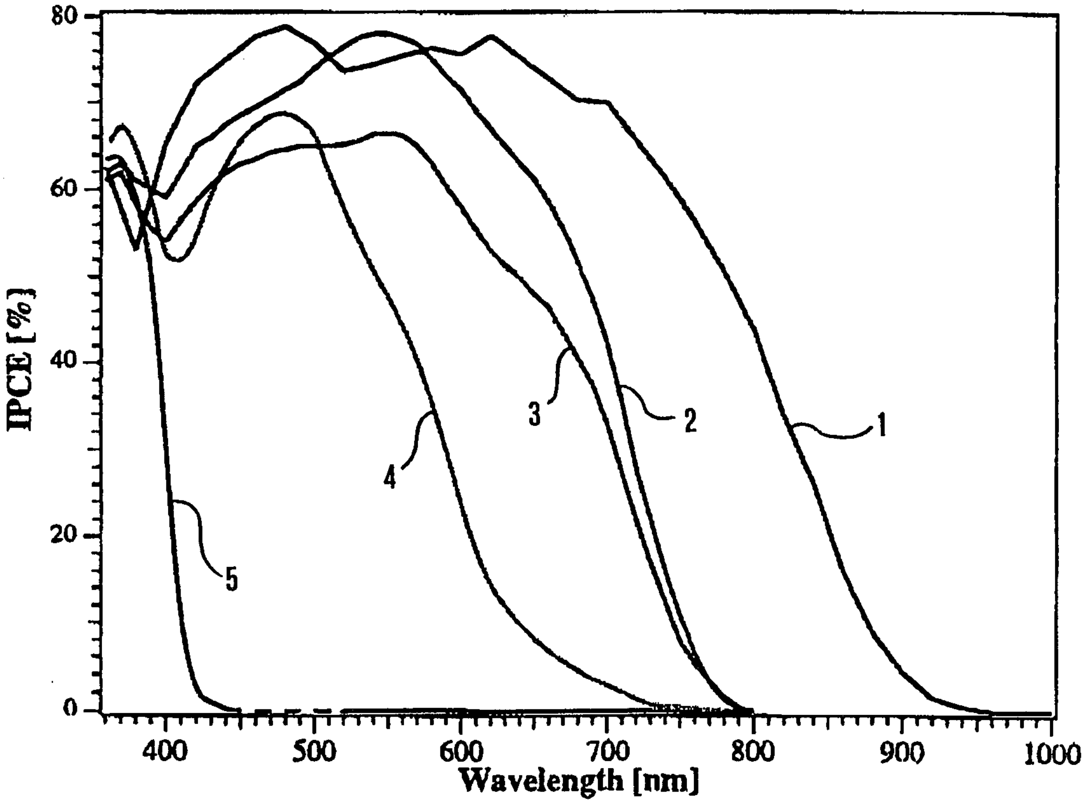


FIG.3


80
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40
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IPCE [%]
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Wavelength [nm]
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INTERNATIONAL SEARCH REPORT

Interi nal Application No
PCT/IB 98/00680

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07F15/00 C07F13/00 C07F15/02 C09B57/10 H01G9/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07F C09B H01G

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 29924 A (ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE) 9 November 1995 cited in the application see the whole document --- -/--	1,2,5-7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search 4 June 1998	Date of mailing of the international search report 22/06/1998
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Rinkel, L

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
P,X	CHEMICAL ABSTRACTS, vol. 128, no. 1, 5 January 1998 Columbus, Ohio, US; abstract no. 5683, ZAKEERUDDIN, S. M. ET AL: "Molecular Engineering of Photosensitizers for Nanocrystalline Solar Cells: Synthesis and Characterization of Ru Dyes Based on Phosphonated Terpyridines" XP002067002 see abstract & INORG. CHEM. (1997), 36(25), 5937-5946 CODEN: INOCAJ;ISSN: 0020-1669, 1997, ---	1,2,4-7
X	CHEMICAL ABSTRACTS, vol. 128, no. 11, 16 March 1998 Columbus, Ohio, US; abstract no. 130226, YANG, RONG ET AL: "Photoelectric performance study of nanocrystalling TiO2 film sensitized by phenylphosphonated polypyridyl ruthenium complex" XP002067003 see abstract & GANGUANG KEXUE YU GUANG HUAXUE (1997), 15(4), 293-296 CODEN: GKKHE9;ISSN: 1000-3231, 1997, ---	1,2,4-7
X	PECHY, PETER ET AL: "Preparation of phosphonated polypyridyl ligands to anchor transition-metal complexes on oxide surfaces: application for the conversion of light to electricity with nanocrystalline TiO2 films" J. CHEM. SOC., CHEM. COMMUN. (1995), (1), 65-6 CODEN: JCCCAT;ISSN: 0022-4936, 1995, XP002067001 see the whole document ---	1,2,5-7
X	CHEMICAL ABSTRACTS, vol. 128, no. 2, 12 January 1998 Columbus, Ohio, US; abstract no. 14844, FRANK, A. J. ET AL: "Photochemical solar cells based on dye-sensitization of nanocrystalline TiO2" XP002067004 see abstract & AIP CONF. PROC. (1997), 404(FUTURE GENERATION PHOTOVOLTAIC TECHNOLOGIES), 145-153 CODEN: APCPCS;ISSN: 0094-243X, 1997, --- -/--	1,2,4-7

INTERNATIONAL SEARCH REPORT

Interi nal Application No
PCT/IB 98/00680

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 04497 A (ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE) 3 March 1994 cited in the application see the whole document -----	1-7

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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