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(54) Title: ORGANIC DYE FOR A DYE SENSITIZED SOLAR CELL

(57) Abstract: An organic dye for a Dye Sensitized Solar Cell (DSSC) which comprises at least one electron acceptor unit and at least one π -conjugated unit. Said organic dye is particularly useful in a dye sensitized photoelectric conversion element which, in turn, may be used in a dye sensitized solar cell (DSSC).



ORGANIC DYE FOR A DYE SENSITIZED SOLAR CELL**DESCRIPTION**

The present invention relates to an organic dye for a dye sensitized solar cell (DSSC).

More in particular, the present invention relates to an organic dye for a dye sensitized solar cell (DSSC) which comprises at least one electron acceptor unit and at least one π -conjugated unit.

Said organic dye is particularly useful in a dye sensitized photoelectric conversion element which, in turn, may be used in a dye sensitized solar cell (DSSC).

Therefore, the present invention further relates to a dye sensitized photoelectric conversion element which comprises the organic dye mentioned above, as well as to a dye sensitized solar cell (DSSC) which comprises said photoelectric conversion element. Dye sensitized solar cells (DSSCs) were developed by Grätzel et al. in 1991 and have attracted a considerable amount of attention in recent years due to their high efficiency and the considerably more contained production cost compared to conventional silicon solar cells.

Dye sensitized solar cells (DSSCs) generally comprise four main components: an optically transparent electrode (anode); an organic or organometallic molecule, said dye or photosensitizer (hereinafter referred as dye), adsorbed on an oxide semiconductor, typically, on mesoporous nanocrystalline titanium dioxide (TiO_2); a liquid inorganic electrolyte or a solid organic hole transporting material; and a counter electrode (cathode). The dye is photochemically excited when it absorbs sunlight and its electrons thus pass into a higher energy orbital (LUMO or excited dye state) from which they are transferred to the conduction band of the oxide semiconductor [i.e. titanium dioxide (TiO_2)], leaving the molecules of dye in their oxidized form. Then, the electrons are collected on a transparent conductive layer, generally comprising fluorine doped tin

dioxide (SnO_2) (FTO) and, through an external electric circuit, they reach the counter electrode (cathode). The oxidized molecules of dye are regenerated as follows: through a platinum (Pt) catalyzed transfer, deposited on the cathode, the electrons activate a series of redox reactions through a redox pair which acts as an electrolyte (typically the iodide/triiodide pair), at the end of said reactions the redox pair in reduced form transfers an electron to the dye, which was still in the oxidized form, regenerating it and closing the cycle.

Further details on dye sensitized solar cells (DSSCs) may be found, for example, in: Kalyanasundaram K., *"Dye-Sensitized Solar Cells"* (2010), CRC Press Inc., 1st Edition; Elliott, C. M., *"Nature Chemistry"* (2011), Vol. 3, pg. 188-189; Hagfeldt A. et al., *"Chemical Reviews"* (2010), Vol. 110, pg. 6595-6663.

As dyes for dye sensitized solar cells (DSSCs), metallic complexes of ruthenium are widely used, which display high photoelectric conversion efficiency as described, for example, in Abbotto A. et al., *"Dalton Transaction"* (2011), Vol. 40, pg. 12421-12438. However, said metal complexes may have some drawbacks such as, for example, their poor chemical stability and high production cost due to the presence of metallic ruthenium (a rare and expensive element) as well as a synthesis that usually requires complicated purification steps.

It has recently been found that metal-free organic dyes that display excellent properties in terms of absorption efficiency, redox stability and intramolecular charge-transfer (CT) absorption, may be used for dye sensitized solar cells (DSSCs) as an alternative to expensive metallic ruthenium compounds.

Metal-free organic dyes generally comprise electron-donor units and electron-acceptor units connected by means of a π -conjugated unit. For most metal-free organic dyes, arylamide derivatives act as electron-donor units while cyanoacrylic acid or a rhodanine

residue act as electron-acceptor units, and they are connected by means of a π -conjugated unit such as, for example, a methanine unit or a thiophenic chain.

A large number of studies have been performed in relation to said metal-free organic dyes.

For example, Yen Y. - S. et al., in the article "Recent developments in molecule-based organic materials for dye-sensitized solar cells", *"Journal of Materials Chemistry"* (2012), Vol. 22, pg. 8734-8747, in addition to photosensitizers containing metal, such as metallic ruthenium and porphyrin complexes, also describe metal-free photosensitizers useful in dye sensitized solar cells (DSSCs).

Tan S. et al., in the article "Novel Carboxylated Oligothiophenes as Sensitizers in Photo-electric Conversion Systems", *"Chemistry - A European Journal"* (2005), Vol. 11, Issue 21, pg. 6272-6276, describe new carboxylate oligothiophenes with different thiophene units as photosensitizers in dye sensitized solar cells (DSSCs). Said article states that the introduction of the -COOH group into the thiophene molecules may lead to a movement towards the red of the UV-visible absorption, to an increase in the light collection efficiency and to an increase in the transport of the photo-induced charge through the formation of efficient covalent bonds at the surface of the substrate. It also states that dye sensitized solar cells (DSSCs) based on said oligothiophenes have excellent performance levels: in particular, under radiation of 100 mW/cm^2 , a short circuit current of 10.57 mA/cm^2 and a total photoelectric conversion efficiency (η) of 3.36% are obtained, when pentathiophene dicarboxylated acid is used as a sensitizer.

Tanaka K. et al., in the article "Development and Photovoltaic Performance of Oligothiophene-sensitized TiO_2 Solar Cells", *"Chemistry Letters"* (2006), Vol. 35, No. 6, pg. 592-593, describe new solar cells based on dye sensitized titanium dioxide (TiO_2) that use a variety of oligothiophene carboxylic acids. Said article states that said solar cells

show relatively high photovoltaic performance levels, i.e. a photoelectric conversion efficiency (η) ranging from 0.41% to 1.29%, which are largely dependent on the lengths of the chain of oligothiophenes and on the number of carboxylic groups.

Mishra A. et al., in the review "Metal-Free Organic Dyes for Dye-Sensitized Solar Cells: From Structure: Property Relationships to Design Rules", *"Angewandte Chemie"* (2009), Vol. 48, pg. 2474-2499, describe recent progress in the molecular design and technological aspects of metal-free organic dyes for application in dye sensitized solar cells (DSSCs). Special attention has been paid to the design principles of said organic dyes and to the effect of various electrolytic systems. Co-sensitization, an emerging technique for extending the absorption interval, is also described as a way of improving the performance of the device. Additionally, inverted organic dyes for photocathodes are also described, which constitute a relatively new approach for the production of tandem cells. Furthermore, special attention has been paid to the connection between the molecular structure and the physical characteristics of metal-free organic dyes in relation to their performance in dye sensitized solar cells (DSSCs).

Yang H. et al., in the article "Organic Dyes Incorporating the Dithieno[3,2-*b*:2',3'-*d*]thiophene Moiety for Efficient Dye-Sensitized Solar Cells", *"Organic Letters"* (2010), Vol. 12, No. 1, pg. 16-19, describe new dipolar compounds that incorporate dithieno[3,2-*b*:2',3'-*d*]thiophene units as electron-donor units, an oligothiophene as a conjugated spacer and 2-cyanoacrylic acid as an electron-acceptor unit. Said organic compounds, free from metals and from electron-donor units of the arylamine type are said to be used successfully as sensitizers of dye sensitized solar cells (DSSCs): in particular, under radiation of AM 1.5 G the photoelectric conversion efficiency (η) is ranging from 3.54% to 5.15%.

Sahu D. et al., in the article "Synthesis and applications of novel acceptor-donor-acceptor

organic dyes with dithienopyrrole- and fluorene-cores for dye-sensitized solar cells”, “*Tetrahedron*” (2011), Vol. 67, No. 2, pg. 303-311, describe new symmetrical organic dyes that include a fluorene or dithienopyrrole unit as an electron-donor unit, an oligothiophene as a conjugated spacer and two groups derived from 2-cyanoacrylic acid as electron-acceptor units. Said article states that dye sensitized solar cells (DSSCs) comprising said organic dyes, in particular in the case of dyes that include fluorene units, have a photoelectric conversion efficiency (η) of 4.73% under radiation of 100 mW/cm⁻² and a maximum incident photon-to-current efficiency (IPCE) of about 76% under simulated solar radiation of AM 1.5.

Warnan J. et al., in the article “Application of Poly(3-hexylthiophene) Functionalized with an Anchoring Group in Dye-sensitized Solar Cells”, “*Macromolecular Rapid Communication*” (2011), Vol. 32, DOI: 10.1002/marc.201100214, describe a series of poly(3-hexylthiophenes) functionalized with anchoring groups deriving from cyanoacetic acid (CA) or from rhodanine-3-acetic acid, which were synthesized and characterized. Dye sensitized solar cells (DSSCs) have also been produced, based on titanium dioxide (TiO₂) and their performance has been tested. Said article states that dye sensitized solar cells (DSSCs) comprising said poly(3-hexylthiophenes) show a photoelectric conversion efficiency (η) of 3.02% under radiation of 100 mW/cm⁻² and a maximum incident photon-to-current efficiency (IPCE) of about 50% under simulated solar radiation of AM 1.5. However, most of the organic dyes already known may have low photoelectric conversion efficiency (η) with respect to dyes based on metallic ruthenium complexes. Therefore, there are numerous and continuous attempts to develop new dye sensitized solar cells (DSSCs) having improved photoelectric conversion efficiency (η) compared to existing organic dyes.

For example, international patent applications WO 2013/160201 and WO 2015/049640,

in the name of the Applicant, describe organic dyes for dye sensitized solar cells (DSSCs) comprising at least one electron-acceptor group and at least one π -conjugated unit that are able to provide dye sensitized solar cells (DSSCs) having improved photoelectric conversion efficiency (η), i.e. photoelectric conversion efficiency (η) greater than or equal to 7.5%.

However, the aforementioned organic dyes may also have some drawbacks, in particular in relation to their long-term stability. In fact, it is known that one of the most important aspects to be resolved for considering the use of economically valid and commercially feasible dye sensitized solar cells (DSSCs) is the durability over time of their photovoltaic performance, which should be a number of years (for example, in building integration applications, even decades are talked about).

Despite numerous ongoing studies on the issue, the problem of the aforementioned long-term stability still appears to be an open matter as there are numerous aspects to be tackled for the purpose of improving it, such as:

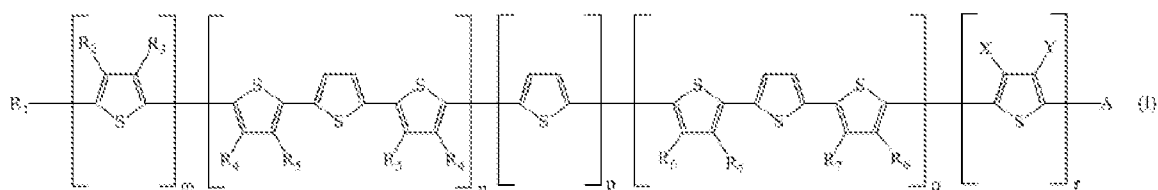
- the intrinsic photochemical stability of the dye absorbed on the titanium dioxide (TiO_2) electrode in interaction with the surrounding electrolyte;
- the chemical and photochemical stability of the electrolyte used;
- the stability of the platinum coating of the cathode in the electrolytic environment;
- the quality of the barrier properties of the sealant used both against the entry of oxygen and water present in the environment in which the dye sensitized solar cell (DSSC) is used, and against losses of electrolyte from the dye sensitized solar cell (DSSC) through sealing.

Therefore, the Applicant set out to solve the problem of finding an organic dye that may be stable over time and, therefore, provide dye sensitized solar cells (DSSCs) having greater durability over time, i.e. able to maintain their photovoltaic performance for longer

over time.

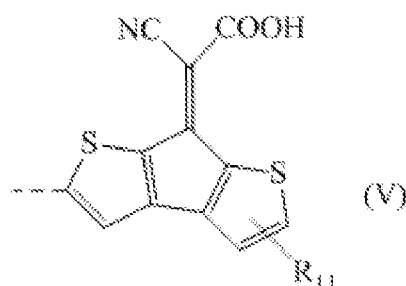
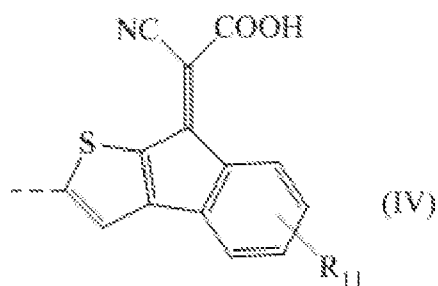
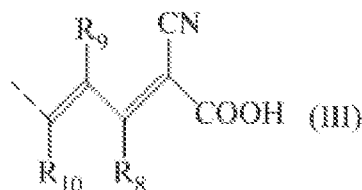
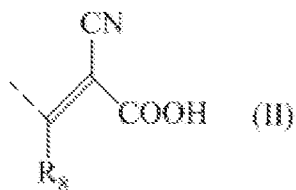
The Applicant has now found an organic dye comprising at least one electron-acceptor group and at least one π -conjugated unit having the specific general formula (I) (reported below) which is stable over time and, therefore, able to provide dye sensitized solar cells (DSSCs) having greater durability over time, i.e. able to maintain their photovoltaic performance for longer over time. Furthermore, said dye sensitized solar cells (DSSCs) also have good photoelectric conversion efficiency (η), Voc (open circuit photovoltage), FF (filling factor) and Jsc (short circuit photocurrent density) values.

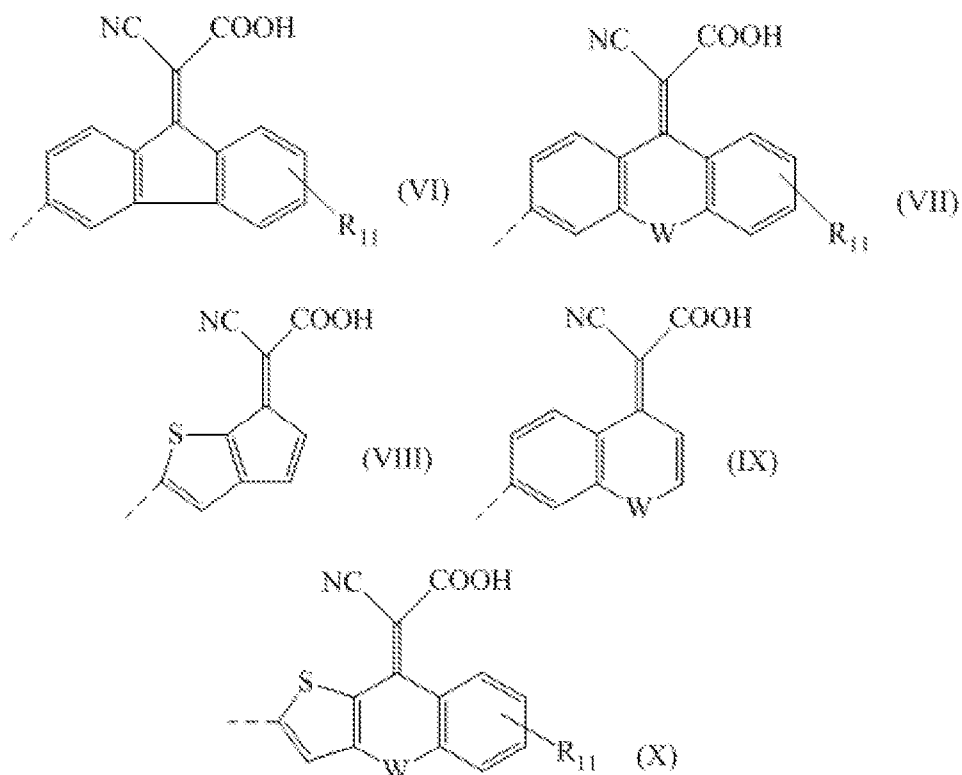
Therefore the subject matter of the present invention is an organic dye having general formula (I):



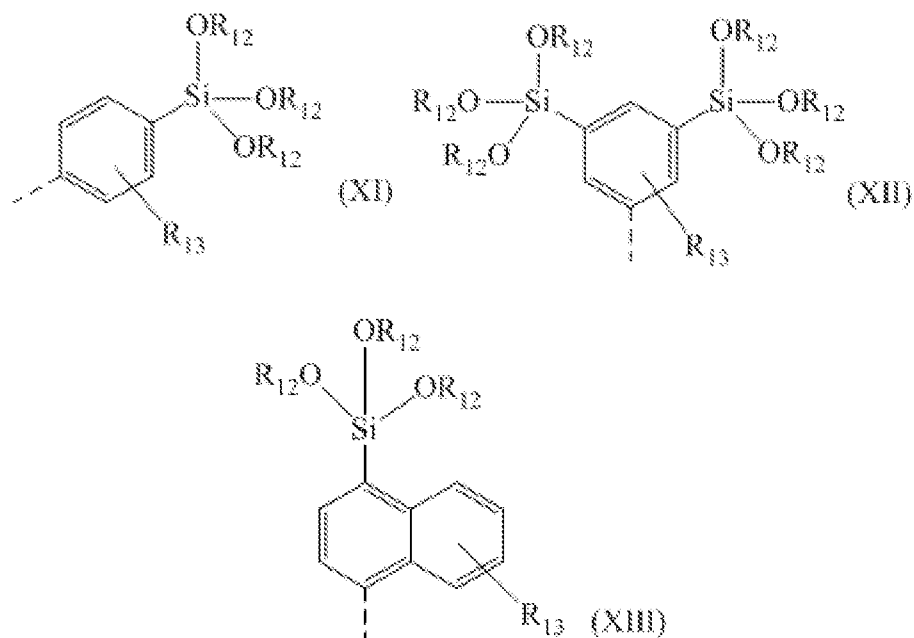
in which:

- A represents a -COOH group or a group having the general formula -Si(OR₁₂)₃ wherein R₁₂ has the meanings reported below; or it is selected from carboxycyanovinylene groups having the general formulae (II), (III), (IV), (V), (VI), (VII), (VIII), (IX), (X):





in which R_8 , R_9 , R_{10} and R_{11} , identical or different, represent a hydrogen atom, or are selected from linear or branched, C_1 - C_{20} alkyl groups, preferably C_2 - C_8 , W represents an oxygen atom or a sulfur atom; or it is selected from groups having the general formula (XI), (XII) or (XIII):



in which R_{12} represents a hydrogen atom, or is selected from linear or branched, saturated or unsaturated, C_1 - C_6 alkyl groups, preferably C_1 - C_2 , R_{13} represents a hydrogen atom or a halogen atom such as, for example, fluorine, chlorine, bromine, iodine, preferably fluorine, or is selected from linear or branched, saturated or unsaturated, C_1 - C_{16} alkyl groups, preferably C_1 - C_{12} , optionally containing one or more halogen atoms;

- R_1 represents a hydrogen atom; or is selected from: linear or branched, saturated or unsaturated C_1 - C_{20} alkyl groups, preferably C_4 - C_{20} , optionally containing heteroatoms, optionally substituted C_4 - C_{20} cycloalkyl groups, preferably C_4 - C_{12} , optionally substituted C_1 - C_{20} alkoxy or thioalkoxy groups, preferably C_1 - C_{10} , polyethylenoxyl groups having the general formula $R'-O-[-CH_2-CH_2-O]_m-$ in which R' represents a hydrogen atom, or is selected from linear or branched, C_1 - C_{20} alkyl groups, preferably C_1 - C_{12} , and m is an integer ranging from 1 to 20, preferably ranging from 2 to 10, optionally substituted C_6 - C_{24} aryloxy or thioaryloxy groups, preferably C_6 - C_{16} , optionally substituted C_6 - C_{24} aryl groups, preferably C_6 - C_{16} , tri-alkyl- or triaryl-silyl groups;
- R_2 , R_3 , R_4 , R_5 , R_6 and R_7 , identical or different, represent a hydrogen atom; or are selected from: linear or branched, saturated or unsaturated C_1 - C_{20} alkyl groups, preferably C_4 - C_{12} , optionally containing heteroatoms, optionally substituted C_4 - C_{20} cycloalkyl groups, preferably C_4 - C_{12} , trialkyl- or triaryl-silyl groups, with the proviso that at least one of R_4 and R_5 , or of R_6 and R_7 , is different from hydrogen;
- X represents a hydrogen atom, or a halogen atom such as fluorine, chlorine, bromine, iodine, preferably fluorine; or it is selected from: C_1 - C_{10} perfluoro- or perchloro-alkyl groups, preferably C_1 - C_8 , C_6 - C_{18} perfluoro- or perchloro-aryl groups,

preferably C₆-C₁₆;

- Y represents a hydrogen atom; or is selected from: linear or branched, saturated or unsaturated C₁-C₂₀ alkyl groups, preferably C₄-C₁₂, optionally containing heteroatoms, optionally substituted C₄-C₂₀ cycloalkyl groups, preferably C₄-C₁₂, trialkyl- or triaryl-silyl groups;

m, n, p and r, identical or different, are integers ranging from 0 to 5, preferably ranging from 0 to 2;

- q is an integer ranging from 1 to 5, preferably ranging from 1 to 2;

with the proviso that when r is 0, R₇ has the meanings of X and R₆ has the meanings of Y.

For the purpose of the present description and of the following claims, the definitions of the numeric ranges always include the extremes unless specified otherwise.

For the purpose of the present description and of the following claims, the term “which comprises” also includes the terms “which essentially consists of” or “which consists of”.

For the purpose of the present description and of the following claims, the term “C₁-C₂₀ alkyl groups”, “C₁-C₁₆ alkyl groups”, “C₁-C₆ alkyl groups”, means linear or branched, saturated or unsaturated, alkyl groups having from 1 to 20 carbon atoms, or from 1 to 16 carbon atoms, or from 1 to 6 carbon atoms, respectively. Specific examples of C₁-C₂₀ alkyl groups are: methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *iso*-butyl, *t*-butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-decyl, *n*-dodecyl, 2-ethylheptyl, 2-ethylhexyl, 2-butenyl, 2-pentenyl, 2-ethyl-3-hexenyl, 3-octenyl, 1-methyl-4-hexenyl, 2-butyl-3-hexenyl.

For the purpose of the present description and of the following claims, the term “C₁-C₂₀ alkyl groups optionally containing heteroatoms” means linear or branched alkyl groups having from 1 to 20 carbon atoms, in which at least one of the hydrogen atoms is substituted with a heteroatom selected from: halogens such as, for example, fluorine, chlorine, bromine, iodine, preferably fluorine; nitrogen, sulfur, oxygen. Specific examples

of C₁-C₂₀ alkyl groups optionally containing heteroatoms are: fluoro-methyl, difluoro-methyl, trifluoro-methyl, trichloro-methyl, 2,2,2-trifluoro-ethyl, 2,2,2-trichloro-ethyl, 2,2,3,3-tetrafluoro-propyl, 2,2,3,3,3-pentafluoro-propyl, perfluoro-pentyl, perfluoro-octyl, perfluoro-decyl, 4-oxymethylhexyl, 3-thiomethylpropyl, 2-oxyethylbutyl.

For the purpose of the present description and of the following claims, the term "C₁-C₁₆ alkyl groups optionally containing one or more halogen atoms" means linear or branched alkyl groups having from 1 to 16 carbon atoms, in which at least one of the hydrogen atoms is substituted with a halogen such as, for example, fluorine, chlorine, bromine, iodine, preferably fluorine. Specific examples of C₁-C₁₆ alkyl groups optionally containing one or more halogen atoms are: fluoro-methyl, difluoro-methyl, trifluoro-methyl, trichloro-methyl, 2,2,2-trifluoro-ethyl, 2,2,2-trichloro-ethyl, 2,2,3,3-tetrafluoro-propyl, 2,2,3,3,3-pentafluoro-propyl, perfluoro-pentyl, perfluoro-octyl, perfluoro-decyl.

For the purpose of the present description and of the following claims, the term "C₄-C₂₀ cycloalkyl groups" means cycloalkyl groups having from 4 to 20 carbon atoms. Said cycloalkyl groups may optionally be substituted with one or more groups, identical or different, selected from: halogen atoms; hydroxyl groups; C₁-C₁₂ alkyl groups; C₁-C₁₂ alkoxy groups; cyano groups; amino groups; nitro groups. Specific examples of cycloalkyl groups are: cyclopropyl, 2,2-difluoro-cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, methylcyclohexyl, methoxycyclohexyl, fluoro-cyclohexyl, phenylcyclohexyl, decalin, abietyl.

For the purpose of the present description and of the following claims, the term "alkoxy or thioalkoxy groups" means groups having one oxygen atom or one sulfur atom, respectively, joined to a C₁-C₂₀ alkyl group. Specific examples of alkoxy or thioalkoxy groups are: methoxy, ethoxy, propoxy, butoxy, *iso*-butoxy, 2-ethylsiloxy, thiomethoxy, thioethoxy, thiopropoxy, thiobutoxy, thio-*iso*-butoxy, 2-ethylthiohexyloxy.

For the purpose of the present description and of the following claims, the term “polyethyleneoxy groups” means groups having from 2 to 80 carbon atoms containing at least one oxyethylene unit. Specific examples of polyethyleneoxy groups are: methyloxy-ethyleneoxyl, methyloxy-diethyleneoxyl, 3-oxatetraoxyl, 3,6-dioxaheptyloxyl, 3,6,9-trioxadecyloxyl, 3,6,9,12-tetraoxahexadecyloxyl.

For the purpose of the present description and of the following claims, the term “aryloxy or thioaryloxy groups” means groups comprising one oxygen atom or one sulfur atom, respectively, joined to a C₆-C₂₄ aryl group. Said aryloxy or thioaryloxy groups may be optionally substituted with one or more groups, identical or different, selected from: halogen atoms such as, for example, fluorine, chlorine, bromine, preferably fluorine; hydroxyl groups, C₁-C₁₂ alkyl groups; C₁-C₁₂ alkoxy groups; C₁-C₁₂ thioalkoxy groups; C₃-C₂₄ trialkyl-silyl groups; cyano groups; amine groups; C₁-C₁₂ mono- or di-alkylamine groups; nitro groups. Specific examples of aryloxy or thioaryloxy groups are: phenoxyl, *para*-methylphenoxyl, *para*-fluorophenoxyl, *ortho*-butylphenoxyl, naphthyloxyl, anthracenoxyl, thiophenoxyl, *para*-methylthiophenoxyl, *para*-fluorothiophenoxyl, *ortho*-butylthiophenoxyl, naphthylthiooxyl, anthracenylthiooxyl.

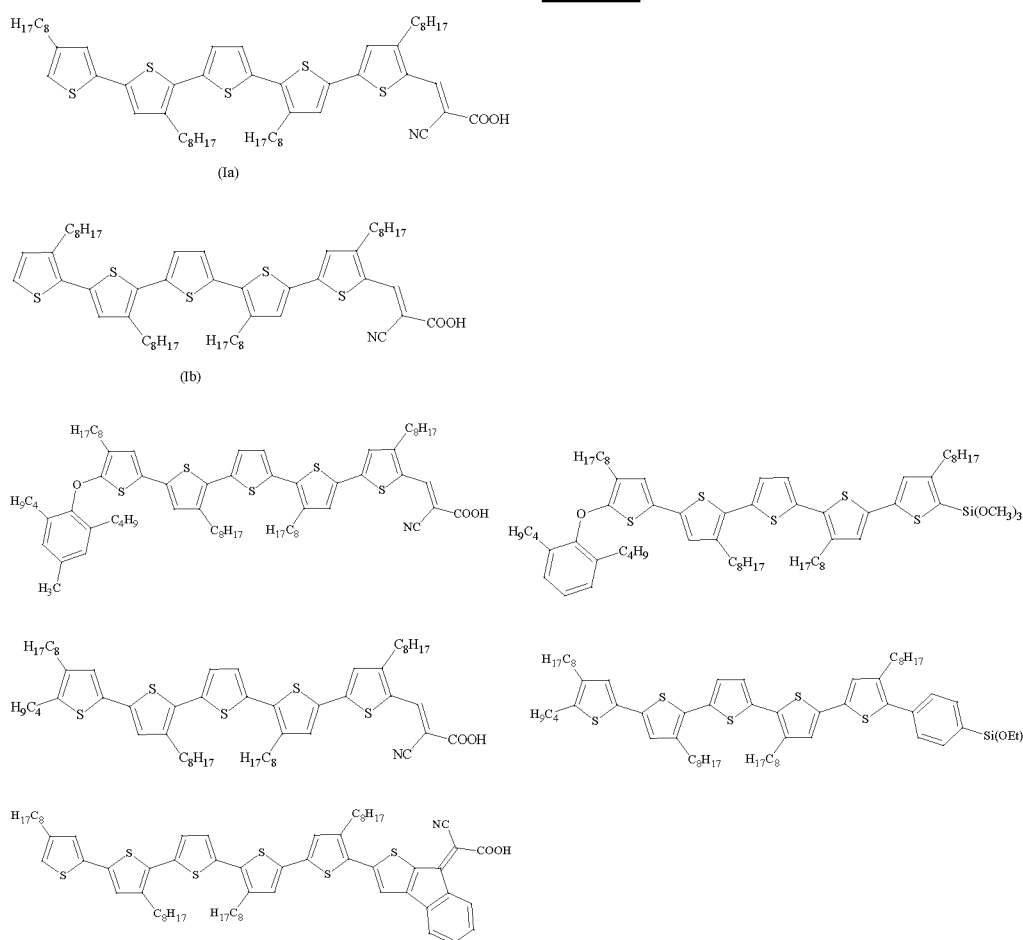
For the purpose of the present description and of the following claims, the term “C₆-C₂₄ aryl groups” means carbocyclic aromatic groups. Said aryl groups may optionally be substituted with one or more groups, identical or different, selected from: halogen atoms such as, for example, fluorine, chlorine, bromine, preferably fluorine; hydroxyl groups; C₁-C₁₂ alkyl groups; C₁-C₁₂ alkoxy groups; cyano groups; amino groups; nitro groups. Specific examples of aryl groups are: phenyl, methylphenyl, trimethylphenyl, methoxyphenyl, hydroxyphenyl, phenyloxyphenyl, fluorophenyl, pentafluorophenyl, chlorophenyl, bromophenyl, nitrophenyl, dimethylaminophenyl, naphthyl, phenylnaphthyl, phenanthrene, anthracene.

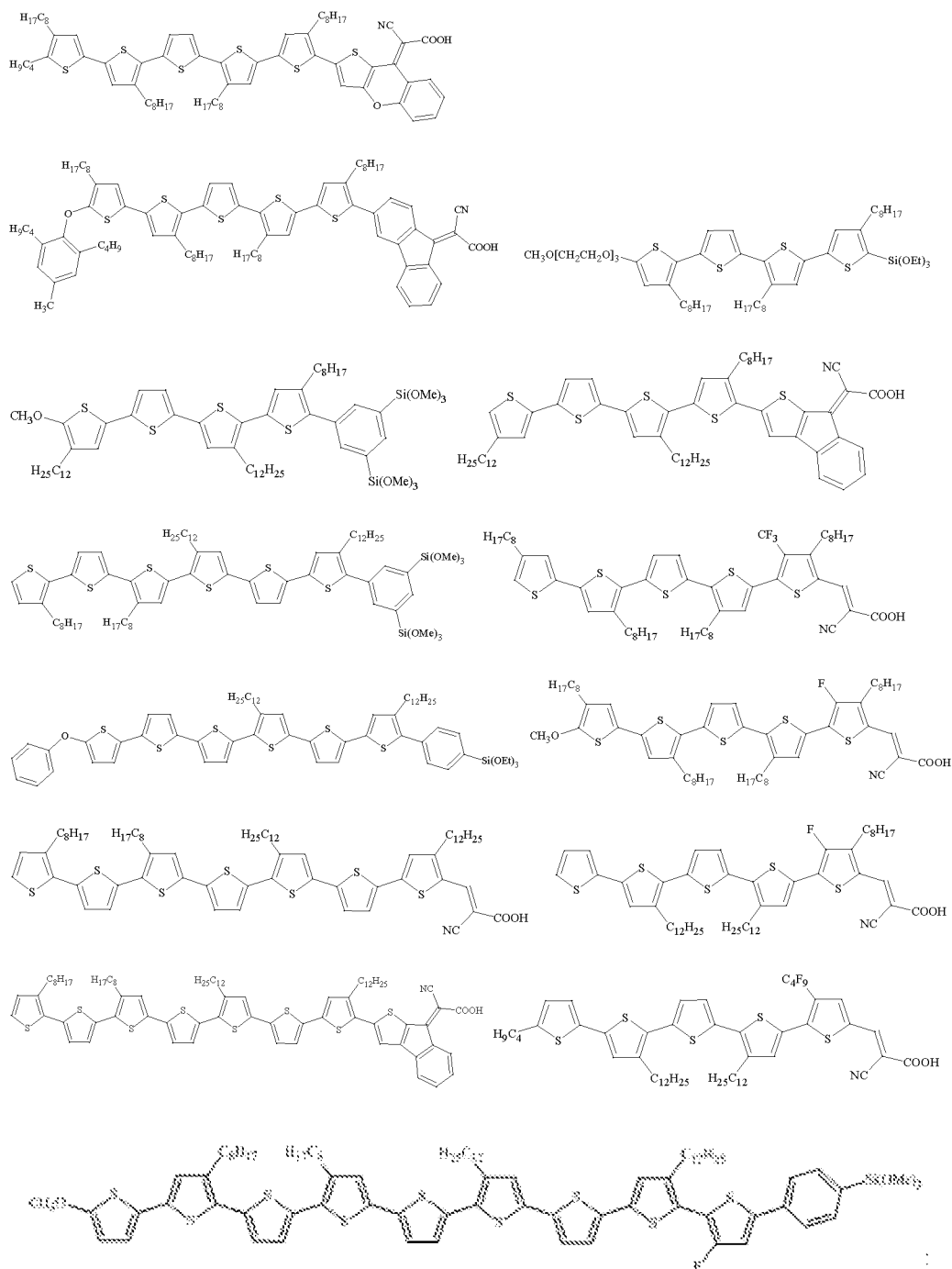
For the purpose of the present description and of the following claims, the term “trialkyl- or triaryl-silyl groups” means silane groups containing three C₁-C₁₂ alkyl groups, or three C₆-C₁₂ aryl groups. Specific examples of trialkyl- or triaryl-silyl groups are: trimethyl-silyl, triethyl-silyl, trihexyl-silyl, tridodecyl-silyl, dimethyldodecyl-silyl, triphenyl-silyl, methyldiphenyl-silyl, dimethylnaphtyl-silyl.

For the purpose of the present description and of the following claims, the term “perfluoro- or perchloro-alkyl groups” means C₁-C₈ alkyl groups in which all the hydrogen atoms are substituted with fluorine or chlorine atoms. Specific examples of perfluoro- or perchloro-alkyls are: trifluoro-methyl, pentafluoro-ethyl, heptafluoro-propyl, trichloro-methyl, pentachloro-ethyl, heptachloro-propyl, undecafluoro-pentyl.

Specific examples of compounds having general formula (I) are reported in Table 1.

Table 1





The organic dye having general formula (I) may be prepared through processes known in the state of the art, for example, through cross-coupling reaction catalyzed by palladium salts (e.g., a Suzuki-Miyaura reaction), as described, for example, by Martin R. et al. in the article "Palladium-Catalyzed Suzuki-Miyaura Cross-Coupling Reactions Employing Dialkylbiaryl Phosphine Ligands", *Account of Chemical Research* (2008), Vol. 41(11),

pg. 1461-1473; or through Vilsmaier-Heck formylation of thiophene groups, as described, for example, by Roquet S. et al., in the article "Triphenylamine-Thienylenevinylene Hybrid Systems with Internal Charge Transfer as Donor Materials for Heterojunction Solar Cells", *"Journal of American Chemical Society"* (2006), Vol. 128, No. 10, pg. 3459-3466; or through the reaction of formyl derivatives with cyano-acetic acid as described, for example, by Mikroyannidis J. A. et al., in the article "Triphenylamine- and benzo-thiadiazole-based dyes with multiple acceptors for application in dye-sensitized solar cells", *"Journal of Power Sources"* (2010), Vol. 195, Issue 9, pg. 3002-3010.

In accordance with a further aspect, the present invention further relates to a dye sensitized photoelectric conversion element which comprises at least one organic dye having general formula (I), said dye sensitized photoelectric conversion element being supported on oxide semiconductor particles.

The photoelectric conversion element in accordance with the present invention may be prepared through a process for the preparation of a dye sensitized photoelectric conversion element for dye sensitized solar cells (DSSCs) operating according to the prior art, except for the use of the organic dye having general formula (I).

Preferably, the photoelectric conversion element in accordance with the present invention is prepared by forming a thin film of an oxide semiconductor on a substrate and subsequently supporting at least one organic dye having general formula (I) on said thin film.

The substrate on which the thin film of oxide semiconductor is formed preferably has a conductive surface and is available commercially. Preferably, said substrate may be selected, for example, from: transparent polymers such as, for example, polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyethersulfone; or mixtures thereof. Preferably, said substrate may have a conductivity less than or equal to 1000 Ω ,

more preferably less than or equal to 100 Ω .

As an oxide semiconductor in the form of particles, a metal oxide is preferable.

Preferably, said oxide semiconductor may be selected, for example, from: titanium dioxide, tin oxide, zinc oxide, tungsten oxide, zirconium oxide, gallium oxide, indium oxide, yttrium oxide, niobium oxide, tantalum oxide, vanadium oxide, or mixtures thereof.

More preferably, titanium dioxide, tin oxide, zinc oxide, niobium oxide, indium oxide, or mixtures thereof, may be used; more preferably they are titanium dioxide, zinc oxide or tin oxide, or mixtures thereof; titanium dioxide is even more preferable.

Preferably, the particles of oxide semiconductor may have an average diameter ranging from 1 nm to 500 nm, more preferably ranging from 1 nm to 100 nm, and those having a large diameter and those having a small diameter may be mixed, or used in multi-layers.

The thin film of oxide semiconductor may be prepared through various known techniques such as: through spraying particles of oxide semiconductor to form a thin film directly on a substrate; through the electrical deposition of a thin film of oxide semiconductor particles using a substrate as the electrode; through the application of a dispersion or paste of oxide semiconductor particles, containing particles obtained through the hydrolysis of suitable precursors such as a halide or an alkoxide of a metal, on a substrate ("Doctor Blade" technique) and subsequent drying, hardening, or sintering. Preferably, the paste may be applied on a substrate: in this case, the dispersion may be obtained by dispersing the oxide semiconductor particles, with a particle diameter ranging from 1 nm to 200 nm, in a dispersing means through a method known in the prior art.

Any dispersing means may be used as long as it is able to disperse the particles of oxide semiconductor. Preferably, said dispersing means may be selected, for example, from: water, alcohols such as, for example, ethanol; ketones such as, for example, acetone, acetylacetone; hydrocarbons such as, for example, hexane; or mixtures thereof. Water is

preferable since it minimizes the variation in viscosity of the dispersion. Optionally, a dispersion stabilizer may be used for the purpose of stabilizing the dispersion of oxide semiconductor particles. Preferably, said dispersion stabilizer may be selected, for example, from acids such as, for example, acetic acid, hydrochloric acid, nitric acid, acrylic acid; ketones such as, for example, acetylacetone; glycols such as, for example, diethylene glycol, polyethylene glycol; alcohols such as, for example, ethyl alcohol, polyvinyl alcohol; or mixtures thereof.

The substrate on which the dispersion is applied may be sintered, and the sintering temperature may be greater than or equal to 100°C, preferably greater than or equal to 200°C. In any case, the upper limit of the sintering temperature may be the melting point or softening point of the substrate, commonly 900°C, preferably 600°C. It is possible for the sintering time not to be specifically limited, but it is preferably no more than 24 hours. The thickness of the thin film on the substrate may be ranging from 0.5 μm to 200 μm , preferably ranging from 1 μm to 50 μm . The thin film of oxide semiconductor may be subjected to a secondary treatment. For example, the thin film may be immersed in a solution of alkoxide, chloride, nitride, or sulfide, of the identical metal to the oxide semiconductor, and dried or re-sintered, hence improving the properties of the thin film. The metal alkoxide may be selected, for example, from: titanium ethoxide, titanium *iso*-propoxide, titanium *t*-butoxide, *n*-dibutyl-diethoxyl tin, or mixtures thereof. There are no specific limitations to the choice of solvent in which said metal alkoxide is dissolved; preferably, a solution in alcohol of said metal alkoxide may be used. The metal chloride may be selected, for example, from: titanium tetrachloride, tin tetrachloride, zinc chloride, or mixtures thereof. There are no specific limitations to the choice of solvent in which said metal chloride is dissolved, preferably, an aqueous solution of said metal chloride may be used. The thin film of oxide semiconductor thus obtained may be composed of oxide

semiconductor particles.

The method for supporting the organic dye on the oxide semiconductor particles in the form of a thin film is not limited to a specific method. For example, a substrate having a thin film of oxide semiconductor formed thereon may be immersed in a solution obtained by dissolving the organic dye having general formula (I) in a solvent able to dissolve it, or in a dispersion obtained by dispersing said organic dye having general formula (I). The concentration of the solution or of the dispersion may be determined in a suitable way. The immersion temperature may be ranging from -60°C to 100°C, preferably ranging from 0°C to 50°C, more preferably it is ambient temperature (25°C), and the immersion time may be ranging from about 1 minute to 7 days, preferably ranging from 1 hour to 26 hours. The solvent used to dissolve the organic dye may be selected, for example, from: methanol, ethanol, propanol, *iso*-propanol, acetonitrile, methoxypropionitrile, chloroform, dichloromethane, dimethylsulfoxide, *N,N*-dimethylformamide, acetone, tetrahydrofuran, 2-methyl-tetrahydrofuran, toluene, *n*-butanol, *iso*-butanol, *t*-butanol, or mixtures thereof. Usually, the concentration of the solution may be ranging from 1×10^{-6} M to 1 M, preferably ranging from 1×10^{-5} M to 1×10^{-1} M. In that way, a dye sensitized photoelectric conversion element may be obtained comprising oxide semiconductor particles on a thin dye sensitized film.

Optionally, the organic dye having general formula (I) may be mixed with other organic dyes or dyes based on metal complexes. Dyes based on metal complexes that may be mixed may include, although not specifically limited to, ruthenium bipyridine complexes either in neutral or ionic form such as, for example, zinc, copper, cobalt, nickel, iron, ruthenium, platinum, manganese; other metal-free organic dyes, which may be mixed may include phthalocyanine, porphyrin, cyanine, merocyanine, oxonols, triphenylmethane dyes, methine dyes such as the acrylate dyes described in European patent application

EP 1,311,001, xanthenes, azo, anthraquinone, perylene dyes [as described, for example, by Nazeeruddin M. K., in "*Journal of the American Chemical Society*" (1993), Vol. 115, pag. 6382-6390]. In the event that two or more types of organic dyes are used in combination, they may be absorbed in sequence on a thin layer of oxide semiconductor, or mixed, dissolved and absorbed.

For the purpose of preventing the aggregation of the organic dye on the thin layer of the oxide semiconductor, the organic dye having general formula (I) may optionally be mixed with an inclusion compound (co-adsorbent): the mixture obtained may be adsorbed on a thin layer of oxide semiconductor through methods known in the prior art. The inclusion compound may be selected, for example, from: cholic acids such as deoxycholic acid, dehydrodeoxycholic acid, kenodeoxycholic acid, cholic acid methyl ester, cholic acid sodium; polyethyleneoxides; crown ethers; cyclodextrins; calyxarenes; polyethyleneoxides; or mixtures thereof.

After the organic dye has been supported, the surface of a semiconductor electrode may be treated with a compound which may be selected from: amine compounds such as, for example, 4-*t*-butyl pyridine; alcohols such as, for example, methanol, ethanol, butanol, or mixtures thereof; organic acids such as, for example, acetic acid, propionic acid, or mixtures thereof; or mixtures thereof. For example, a substrate on which a thin film of oxide semiconductor particles has been formed combined with an organic dye may be immersed in a solution of an amine in ethanol.

According to a further aspect, the present invention also relates to a dye sensitized solar cell (DSSC) comprising the dye sensitized photoelectric conversion element disclosed above.

Said dye sensitized solar cell (DSSC) may be prepared by methods of the prior art relating to solar cells preparation using a photoelectric conversion element of the prior art,

except for the use of a dye sensitized photoelectric conversion element comprising oxide semiconductor particles where the organic dye having general formula (I) is supported.

The dye sensitized solar cell (DSSC) may comprise a photoelectric conversion element as the electrode (negative electrode) wherein the organic dye having general formula (I) is supported on the oxide semiconductor particles, a counter electrode (positive electrode), a redox electrolyte, a hole transporting material, or a p-type semiconductor compound.

Preferably, the dye sensitized solar cell (DSSC) according to the present invention may be prepared by depositing a titanium dioxide paste on a transparent conductive substrate; sintering the coated substrate to form a thin film of titanium dioxide; immersing the substrate having the titanium dioxide thin film formed thereon in a mixed solution in which the organic dye having general formula (I) is dissolved, so as to form a dye absorbed titanium dioxide film electrode; providing a second transparent conductive substrate having a counter electrode formed thereon; forming a hole penetrating the second transparent conductive substrate and the counter electrode; depositing a thermoplastic polymer film between the counter electrode and the dye absorbed titanium dioxide film electrode and heat pressing them to join the counter electrode and the titanium dioxide film electrode; injecting electrolyte into the thermoplastic polymer film placed between the counter electrode and the titanium dioxide film electrode through the hole; and, sealing the hole with suitable materials which may be selected, for example, from thermoplastic polymers.

The redox electrolyte, hole transporting material, or p-type semiconductor compound may be liquid (e.g. ionic liquid), or in coagulated form (gel and gel phase), or even solid. The liquid may be selected, for example, from those obtained by dissolving the redox electrolyte, a dissolved salt, the hole transporting material, or the p-type semiconductor in

a solvent, and a salt dissolved at ambient temperature. The coagulated form (gel and gel phase) may be selected, for example, from those obtained by including the redox electrolyte, a dissolved salt, the hole transporting material, or the p-type semiconductor in a polymer matrix or low molecular weight gellant. The solid may be selected, for example, from the redox electrolyte, a dissolved salt, the hole transporting material, or the p-type semiconductor compound.

The hole transporting material may be selected, for example, from: amine derivatives; conductive polymers such as, for example, polyacetylene, polyaniline, polythiophene; or discotic liquid crystal phases such as triphenylene. The p-type semiconductor may be selected, for example, from copper iodide (CuI), copper thiocyanate (CuSCN). As the counter electrode, those having conductivity and catalytic function on the reduction of the redox electrolyte may be preferably used, and, for example, those obtained by depositing platinum, carbon, rhodium, ruthenium, on a glass or a polymer film, or by applying conductive particles thereon, may be used.

The redox electrolyte used in the dye sensitized solar cell (DSSC) according to the present invention may include a halogen redox electrolyte comprising halogen compounds comprising a halogen ion as a counter ion and a halogen molecule; metal redox electrolytes such as ferrocyanide-ferricyanide or ferrocene-ferricyinium ion; metal complexes such as cobalt complexes; organic redox electrolytes such as, for example, alkylthio-alkyldisulfide, viologen dye, hydroquinone-quinone. Halogen redox electrolytes are preferred. As the halogen molecule comprised in the halogen redox electrolyte, an iodine molecule may be preferred. As the halogen compounds comprising a halogen ion as the counter ion, a halogenated metal salt such as lithium iodide (LiI), sodium iodide (NaI), potassium iodide (KI), cesium iodide (CsI), ammonium iodide [(NH₄)I], calcium diiodide (CaI₂), magnesium diiodide (MgI₂), barium diiodide (BaI₂), copper iodide (CuI),

copper diiodide (CuI_2), zinc diiodide (ZnI_2), or an organic ammonium halide such as, for example, tetraalkylammonium iodide, imidazolium iodide, pyridium iodide, or iodine (I_2), may be used.

In case the redox electrolyte is in the form of a solution, an electrochemically inert solvent may be used. For example, acetonitrile, propylenecarbonate, ethylenecarbonate, 3-methoxypropionitrile, methoxy-acetonitrile, valeronitrile, ethyleneglycol, propyleneglycol, diethyleneglycol, triethyleneglycol, butyrolactone, dimethoxyethane, dimethylcarbonate, 1,3-dioxolane, methylformate, 2-methyltetrahydrofuran, 3-methoxy-oxazolidin-2-on, sulforane, tetrahydrofuran, water, may be used. Acetonitrile, valeronitrile, propylenecarbonate, ethylenecarbonate, 3-methoxypropionitrile, ethyleglycol, 3-methoxy-oxazolidin-2-on, or butyrolactone, are preferred. Said solvents may be used alone or mixed together.

As a gel phase positive electrolyte, those obtained by including electrolyte or electrolyte solution in an oligomer or polymer matrix, or by including electrolyte or electrolyte solution in a starch gellant, may be used.

The concentration of the redox electrolyte may preferably range from 0.01% by weight to 99% by weight, and more preferably ranges from 0.1% by weight to 30% by weight, with respect to the total weight of the solution.

The dye sensitized solar cell (DSSC) according to the present invention may be obtained by arranging a photoelectric conversion element (negative electrode - anode) wherein the organic dye having general formula (I) is supported on oxide semiconductor particles on a substrate, and a counter electrode (positive electrode) opposite thereto, and inserting a redox electrolyte-containing solution therebetween.

The present invention will be further illustrated below by means of the following examples which are provided for purely indicative purposes and without any limitation of this

invention.

EXAMPLES

Reagents and materials

The reagents and materials used in the following examples, as well as the manufacturers thereof, have been reported below:

- 2-bromo-3-octyl-thiophene (Aldrich): used as it is;
- tetrahydrofuran anhydrous (THF) (Aldrich): used as it is;
- *n*-butyl lithium (2.5 M in hexane) (Aldrich): used as it is;
- 2-*iso*-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Aldrich): used as it is;
- sodium bicarbonate (NaHCO₃) (Aldrich): used in a saturated aqueous solution;
- 10% hydrochloric acid solution (HCl) (Aldrich): used as it is;
- ethyl acetate (Aldrich): used as it is;
- sodium chloride (NaCl) (Aldrich): used in a saturated aqueous solution;
- sodium sulfate anhydrous (Aldrich): used as it is;
- Celite[®] 545 (Aldrich): used as it is;
- hexane (Carlo Erba): used as it is;
- ethyl ether (Aldrich): used as it is;
- 2,5-dibromothiophene (Aldrich): used as it is;
- palladium acetate [Pd(OAc)₂] (Aldrich): used as it is;
- 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos) (Aldrich): used as it is;
- potassium phosphate (K₃PO₄) anhydrous (Aldrich): used as it is;
- Aliquat[®] 336 (Aldrich): used as it is;
- *N*-bromosuccinimide (Aldrich): used as it is;
- *N,N*-di-*iso*-propylamine anhydrous (Aldrich): used as it is;
- 3-octylthiophene (Aldrich): used as it is;

- dichloromethane (CH_2Cl_2) (Aldrich): used as it is;
- triethylamine (NEt_3) (Aldrich): used as it is;
- toluene anhydrous (Aldrich): used as it is;
- *N,N*-dimethylformamide (DMF) anhydrous (Aldrich): used as it is;
- 1,2-dichloroethane (1,2-DCE) anhydrous (Aldrich): used as it is;
- phosphorus oxychloride (POCl_3) (Aldrich): used as it is;
- sodium acetate (Aldrich): used in a 2M aqueous solution;
- glacial acetic acid (CH_3COOH) (Aldrich): used as it is;
- cyanoacetic acid ($\text{NC-CH}_2\text{-COOH}$) (Aldrich): used as it is;
- ammonium acetate ($\text{CH}_3\text{COONH}_4$) (Aldrich): used as it is;
- methanol (CH_3OH) (Carlo Erba): used as it is;
- ethanol (Carlo Erba): used as it is;
- titanium tetrachloride (Aldrich): used as it is;
- *N*-methyl-*N*-butylimidazolium iodide (Aldrich): used as it is;
- iodine (Carlo Erba): used as it is;
- lithium iodide (Aldrich): used as it is;
- guanidinium thiocyanate (Aldrich): used as it is;
- *t*-butylpyridine (Aldrich): used as it is;
- valeronitrile (Aldrich): used as it is;
- acetonitrile (Carlo Erba): used as it is.

In the following examples, the following characterization methods were used.

NMR Spectra

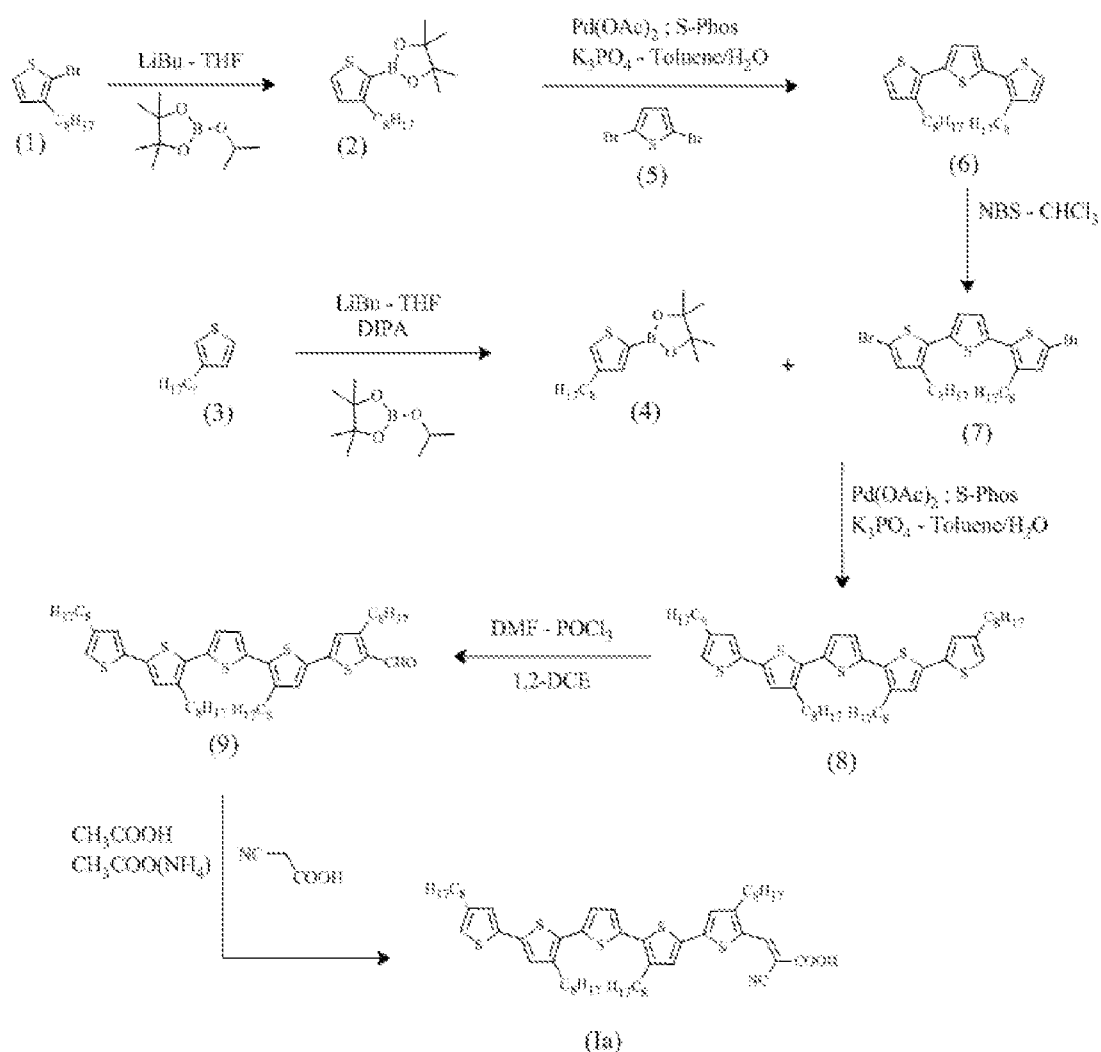
The NMR spectra of the compounds obtained were performed with an NMR Bruker Avance 400 spectrometer.

For that purpose, about 10 mg of the sample to be examined were dissolved in about 0.8

ml of a suitable deuterated solvent directly on the glass tube used for the measurement. The chemical shift scale was calibrated in relation to the signal of the tetramethylsilane adjusted to 0 ppm.

EXAMPLE 1

Synthesis of 2-cyano-3-(3''',4,4',4''''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-pentathiophene]-5-yl)acrylic acid having formula (Ia)



Synthesis of 4,4,5,5-tetramethyl-2-(3-octylthiophen-2-yl)-1,3,2-dioxaborolane having formula (2)

In a 250 ml three-neck flask equipped with a dropping funnel, an inert atmosphere was

created through nitrogen (N₂) insufflation. Subsequently, 5.0 g (18.16 mmol) of 2-bromo-3-octylthiophene having formula (1) and 90 ml of tetrahydrofuran (THF) anhydrous were added. The solution obtained was cooled to -78°C and 8.0 ml of *n*-butyl-lithium (LiBu) (2.5 M in hexane) were added slowly, over 15 minutes. The reaction mixture obtained was kept, under stirring, at -78°C, for a further 2 hours, at the end of which 6.76 g (36.32 mmol) of 2-*iso*-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were added, and subsequently heated, under stirring, slowly, over 1 hour, to ambient temperature (25°C). After 16 hours, under stirring, at ambient temperature (25°C), the reaction was stopped by adding 110 ml of a saturated aqueous solution of sodium bicarbonate (NaHCO₃) and the residual solvent was removed through distillation at reduced pressure. The residue obtained having pH ≈ 11, was brought to pH 8 through the addition of 13 ml of a 10% hydrochloric acid (HCl) solution, and then extracted with ethyl acetate (3 x 150 ml). The global organic phase (obtained by joining the three organic phases obtained from the extraction) was washed with a saturated aqueous solution of sodium chloride (NaCl) (3 x 100 ml) and subsequently anhydried on sodium sulfate anhydrous for 3 hours. The residual solvent was then removed through distillation at reduced pressure, obtaining a dark yellow oil, which was dissolved in 100 ml of ethyl acetate and filtered on Celite® 545: the residual solvent was removed again at reduced pressure obtaining a light yellow oil. Said light yellow oil was purified through chromatography on a silica gel column using a hexane/ethyl ether mixture (39/1 v/v) as eluent obtaining 3.68 g (yield 64%) of 4,4,5,5-tetramethyl-2-(3-octylthiophen-2-yl)-1,3,2-dioxaborolane having formula (2), as a colorless oil, which was characterized through ¹H-NMR (400 MHz, CDCl₃) obtaining the following spectrum: δ 7.48 (d, J ≈ 5 Hz, 1H), 7.01 (d, J ≈ 5 Hz, 1H), 2.88 (t, J = 7.5 Hz, 2H), 1.65-1.10 (m, 24H), 0.88 (t, J = 7.5 Hz, 3H) ppm; and through ¹³C-NMR (100 MHz, CDCl₃) obtaining the following spectrum: δ 154.7, 131.2, 130.3, 83.5, 31.9, 31.8, 30.1, 29.4, 29.3

(double signal), 24.8, 22.7, 14.1 ppm.

Synthesis of 3,3''-dioctyl-[2,2':5',2'']-terthiophene having formula (6)

In a 25 ml three-neck flask equipped with a magnetic stirrer and coolant, an inert atmosphere was created through nitrogen (N₂) insufflation. Subsequently, 0.35 g (1.45 mmoles) of 2,5-dibromothiophene having formula (5), 1.4 g (4.34 mmoles) of 4,4,5,5-tetramethyl-2-(3-octylthiophene-2-yl)-1,3,2-dioxaborolane having formula (2) obtained as described above, 6 ml of toluene anhydrous, 0.008 g (0.036 mmoles) of palladium acetate [Pd(OAc)₂], 0.03 g (0.073 mmoles) of 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos) and 0.092 g (4.34 mmoles) of potassium phosphate (K₃PO₄) anhydrous finely ground with a mortar and pestle were added, obtaining a light brown reaction mixture. Said reaction mixture was placed, under stirring, at ambient temperature (25°C), for 30 minutes, subsequently 1.5 ml of double distilled degassed water were added, immediately obtaining a dark brown color. Finally, 10 drops of Aliquat[®] 336 were added and the reaction mixture obtained was heated to 100°C, and maintained, under stirring, at said temperature, for 10 hours. After cooling to ambient temperature (25°C) and removing the residual solvent through distillation at reduced pressure, the residue obtained was diluted with water (60 ml) and extracted with hexane (3 x 60 ml). The global organic phase (obtained by joining the three organic phases obtained from the extraction) was washed with a saturated aqueous solution of sodium chloride (NaCl) (3 x 70 ml) and subsequently anhydriified on sodium sulfate anhydrous for 3 hours. The residual solvent was then removed by distillation at reduced pressure, obtaining a dark oil. Said dark oil was purified through chromatography on a silica gel column using hexane as eluent obtaining 0.56 g (yield 82%) of 3,3''-dioctyl-[2,2':5',2'']-terthiophene having formula (6), as yellow oil, which was characterized through ¹H-NMR (400 MHz, CDCl₃) obtaining the following spectrum: δ 7.18 (d, J= 5 Hz, 2H), 7.02 (s, 2H), 6.95 (d, J= 5 Hz, 2H), 2.78 (t, J=

7.5 Hz, 4H), 1.65 (quintet, $J = 7.5$ Hz, 4H), 1.45 – 1.15 (m, 20H), 0.87 (t, $J = 7.8$ Hz, 6H) ppm; and through ^{13}C -NMR (100 MHz, CDCl_3) obtaining the following spectrum: δ 139.7, 136.0, 130.4, 130.0, 126.0, 123.7, 31.9, 30.7, 29.6, 29.4, 29.3 (double signal), 22.7, 14.1 ppm.

Synthesis of 5,5''-dibromo-3,3''dioctyl-[2,2':5',2'']-terthiophene having formula (7)

1.16 g (2.45 mmoles) of 3,3''-dioctyl-[2,2':5',2'']-terthiophene having formula (6) obtained as described above and 15 ml of chloroform (CHCl_3) were placed into a 25 ml three-neck flask equipped with a magnetic stirrer. The solution obtained, kept under stirring, was cooled to 0°C and, subsequently, 0.92 g (5.15 mmoles) of *N*-bromosuccinimide (NBS) were added. The reaction mixture obtained was heated, under stirring, slowly, over 1 hour, to ambient temperature (25°C) and kept, under stirring, at said temperature, for 2 hours. At the end, the residual solvent was then removed by distillation at reduced pressure, obtaining a yellow oil. Said yellow oil was purified through "flash" chromatography on a silica gel column using hexane as eluent obtaining 139 g (yield 90%) of 5,5''-dibromo-3,3''-dioctyl-[2,2':5',2'']-terthiophene having formula (7), as light yellow oil, which was characterized through ^1H -NMR (400 MHz, CDCl_3) obtaining the following spectrum: δ 6.98 (s, 2H), 6.90 (s, 2H), 2.69 (t, $J = 8.0$ Hz, 4H), 1.60 (quintet, $J = 8.0$ Hz, 4H), 1.38 – 1.20 (m, 20H), 0.88 (t, $J = 7.0$ Hz, 6H) ppm; and through ^{13}C -NMR (100 MHz, CDCl_3) obtaining the following spectrum: δ 140.5, 135.2, 132.7, 131.6, 126.4, 110.7, 31.9, 30.6, 29.4 (double signal), 29.2 (double signal), 22.7, 14.1 ppm.

Synthesis of 4,4,5,5-tetramethyl-2-(4-octylthiophen-2-yl)-1,3,2-dioxaborolane having formula (4)

In a 50 ml three-neck flask, an inert atmosphere was created through nitrogen (N_2) insufflation. Subsequently, 1.3 g (12.0 mmoles) of *N,N*-di-*iso*-propylamine (DIPA) anhydrous and 5 ml of tetrahydrofuran (THF) anhydrous were added. The solution

obtained, kept under stirring, was cooled to 0°C and subsequently 4.8 ml of *n*-butyllithium (LiBu) (2.5 M in hexane) were added slowly, over 10 minutes. The reaction mixture obtained was kept, under stirring, at 0°C, for 30 minutes, subsequently, after cooling to -78°C, 2.0 g (10.0 mmoles) of 3-octylthiophene having formula (3) previously dissolved in 15 ml of tetrahydrofuran (THF) anhydrous were added slowly, over 15 minutes. The reaction mixture obtained was kept, under stirring, at -78°C, for 2 hours, at the end of which 2.3 g (12.00 mmol) of 2-*iso*-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were added: the whole was kept under stirring, at -78°C, for another 2 hours. Subsequently, the reaction mixture was heated slowly, over 1 hour, to ambient temperature (25°C) and kept, at said temperature, under stirring, for 16 hours, at the end of which 30 ml of a 10% hydrochloric acid (HCl) solution were added. The residual solvent was removed through distillation at reduced pressure and the residue obtained was extracted with hexane (3 x 70 ml). The global organic phase (obtained by joining the three organic phases obtained from the extraction) was washed with a saturated aqueous solution of sodium chloride (NaCl) (2 x 70 ml) and subsequently anhydried on sodium sulfate anhydrous for 3 hours. The residual solvent was removed by distillation at reduced pressure, obtaining a yellow oil. Said yellow oil was purified through chromatography on a silica gel column using a mixture of hexane/dichloromethane (8/2, v/v) as eluent, after pre-treating the silica with triethylamine (NEt₃), obtaining 1.46 g (yield 45%) of 4,4,5,5-tetramethyl-2-(4-octylthiophen-2-yl)-1,3,2-dioxaborolane having formula (4), as colorless oil, which was characterized through ¹H-NMR (400 MHz, CDCl₃) obtaining the following spectrum: δ 7.45 (s, 1H), 7.19 (s, 1H), 2.60 (t, J= 8.0 Hz, 2H), 1.59 (quintet, J= 8.0 Hz, 2H), 1.36 – 1.16 (m, 22H), 0.86 (t, J= 8.0 Hz, 3H) ppm.

Synthesis of 3''',4,4',4''''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene having formula (8)

In a 25 ml three-neck flask equipped with a magnetic stirrer and coolant, an inert atmosphere was created through nitrogen (N_2) insufflation. Subsequently, 0.63 g (1.0 mmoles) of 5,5''-dibromo-3,3''-dioctyl-2,2':5',2''-terthiophene having formula (7) obtained as described above, 0.97 g (3.0 mmoles) of 4,4,5,5-tetramethyl-2-(4-octylthiophen-2-yl)-1,3,2-dioxaborolane having formula (4) obtained as described above, 8 ml of toluene anhydrous were added. The reaction mixture obtained was kept, under stirring, at ambient temperature (25°C), for 30 minutes and, subsequently 0.007 g (0.03 mmoles) of palladium acetate $[Pd(OAc)_2]$, 0.025 g (0.06 mmoles) of 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos) and 0.62 g (3.0 mmoles) of potassium phosphate (K_3PO_4) anhydrous, finely ground with a mortar and pestle, were added, obtaining a dark orange reaction mixture. Subsequently, 2 ml of previously double distilled degassed water were added, immediately obtaining a dark brown color, finally 6 drops of Aliquat[®] 336 were added and the reaction mixture obtained was heated to 90°C, and maintained, under stirring, at said temperature, for 16 hours. After cooling to ambient temperature (25°C) and removing the residual solvent through distillation at reduced pressure, 30 ml of a 10% hydrochloric acid (HCl) solution were added to the residue obtained and the whole was extracted with hexane (3 x 50 ml). The global organic phase (obtained by joining the three organic phases obtained from the extraction) was washed with a saturated aqueous solution of sodium chloride (NaCl) (3 x 50 ml) and subsequently anhydridified on sodium sulfate anhydrous for 3 hours. The residual solvent was then removed by distillation at reduced pressure, obtaining a dark oil. Said dark oil was purified through chromatography on a silica gel column using a mixture of hexane/dichloromethane (95/5 v/v) as eluent obtaining 0.755 g (yield 88%) of 3''',4,4',4''''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene having formula (8), as dark oil, which was characterized through 1H -NMR (400 MHz, $CDCl_3$) obtaining the following spectrum: δ 7.06 (s, 2H), 7.00 (d, J = 4.0

Hz, 2H), 6.99 (s, 2H), 6.80 (d, J = 4.0 Hz, 2H) 2.76 (t, J = 8.0 Hz, 4H), 2.58 (t, J = 8.0 Hz, 4H), 1.71 - 1.59 (m, 8H), 1.45 - 1.20 (m, 40H), 0.93-0.83 (m, 12H) ppm; and through ^{13}C -NMR (100 MHz, CDCl_3) obtaining the following spectrum: δ 144.16, 140.17, 136.7, 135.8, 135.5, 129.10, 128.9, 126.9, 126.6, 124.72, 31.9, 30.5, 30.4, 29.5, 29.4, 29.3, 22.7, 14.1 ppm.

Synthesis of 3''',4,4',4''''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5-carbaldehyde having formula (9)

The Vilsmeier reactant was prepared in a 25 ml three-neck flask equipped with a magnetic stirrer and coolant, in which an inert atmosphere was created through nitrogen (N_2) insufflation, operating as follows.

0.063 g (0.85 mmoles) of *N,N*-dimethylformamide (DMF) anhydrous and 5.0 ml of 1,2-dichloroethane (1,2-DCE) anhydrous were placed in said flask: the solution obtained was cooled to 0°C and, maintaining the whole under stirring, 0.13 g (0.85 mmoles) of phosphorus oxychloride (POCl_3) were added. The reaction mixture obtained was heated to 40°C, maintained under stirring, at said temperature, for 1 hour, subsequently cooled, still under stirring, to ambient temperature (25°C) and immediately added, through a dropper funnel, to a solution, maintained at 0°C, of 0.70 g (0.81 mmoles) of 3''',4,4',4''''-tetraoctyl-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene having formula (8) obtained as described above in 5 ml of dichloromethane. The reaction mixture obtained was then heated to 40°C and kept at said temperature, under stirring, for 12 hours. After the cooling to ambient temperature, 10 ml of an aqueous solution of sodium acetate (2 M) were added: the whole was maintained, under stirring, at said temperature, for 2 hours, the residue obtained was extracted with dichloromethane (3 x 60 ml) and the global organic phase (obtained by uniting the three organic phases obtained from the extraction) was anhydriified on sodium sulfate anhydrous, for 3 hours. The residual solvent was then

removed by distillation at reduced pressure, obtaining a dark oil. Said dark oil was purified through chromatography on a silica gel column using a mixture of hexane/dichloromethane (1/1 v/v) as eluent obtaining 0.32 g (yield 44%) of 3''',4,4',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinguethiophene]-5-carbaldehyde having formula (9), which was characterized through $^1\text{H-NMR}$ (400 MHz, CDCl_3) obtaining the following spectrum: δ 9.99 (s, 1H), 7.18 (s, 1H), 7.11 (d, $J = 4.0$ Hz, 1H), 7.09 (d, $J = 4.0$ Hz, 1H), 7.04 (s, 1H), 7.01 (d, $J = 1.0$ Hz, 1H), 6.99 (s, 1H), 6.81 (d, $J = 4.0$ Hz, 1H), 2.92 (t, $J = 8.0$ Hz, 2H), 2.82 – 2.76 (m, two overlapped triplets, $J = 8.0$ Hz, 4H), 2.58 (t, $J = 8.0$ Hz, 2H), 1.75 – 1.6 (m, 8H) 1.45 - 1.20 (m, 40H), 0.95 – 0.85 (m, 12H) ppm; and through $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) obtaining the following spectrum: δ 181.5, 154.0, 145.8, 144.2, 140.7, 140.5, 136.6, 135.8, 134.9, 133.6, 132.3, 128.3, 126.0, 125.8, 31.9, 31.4, 30.5, 30.4, 29.6, 29.4, 29.3, 28.6, 22.7, 14.2, 14.0 ppm.

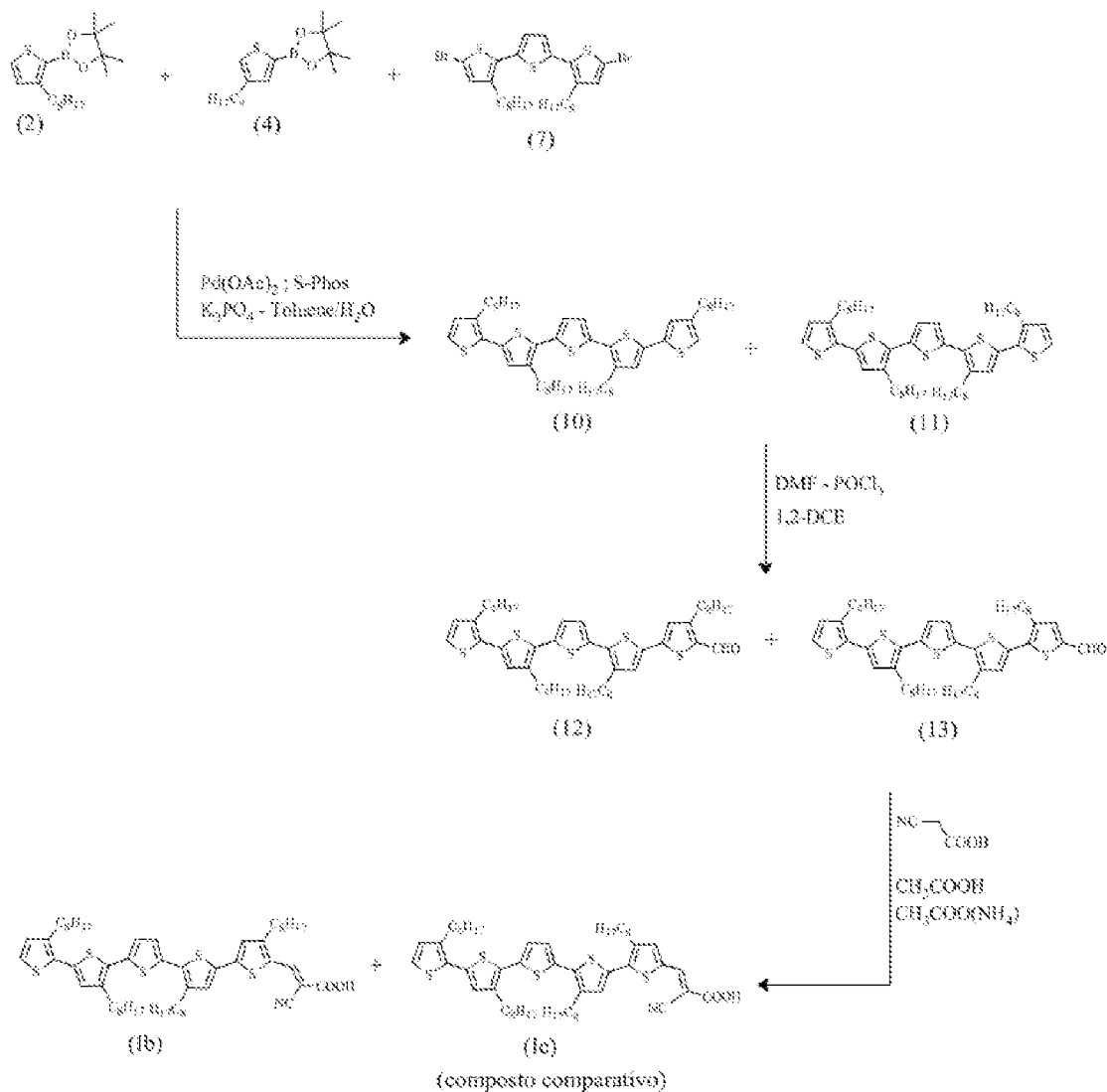
Synthesis of 2-cyano-3-(3''',4,4',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinguethiophen]-5-yl)acrylic acid having formula (Ia)

In a 50 ml two-neck flask, equipped with a magnetic stirrer and coolant, the following were placed in succession: 0.21 g (0.23 mmoles) of 3''',4,4',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinguethiophene]-5-carbaldehyde having formula (9) obtained as described above, 10 ml of glacial acetic acid (CH_3COOH), 0.64 g (7.5 mmoles) of cyanoacetic acid ($\text{NC-CH}_2\text{-COOH}$) and 0.38 g (5.0 mmoles) of ammonium acetate ($\text{CH}_3\text{COONH}_4$) and the reaction mixture was then heated to 110°C , under stirring, for 16 hours. After cooling to ambient temperature (25°C), the solid residue was recovered through filtration, washed, in succession, with a saturated aqueous solution of sodium bicarbonate (NaHCO_3) (3 x 10 ml), with distilled water (3 x 20 ml) and finally with methanol (CH_3OH) (3 x 10 ml) and subsequently purified by double crystallization using a dichloromethane/methanol mixture (1/10, v/v) obtaining 0.167 g (yield 94%) of 2-cyano-3-

(3''',4,4',4''''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophen]-5-yl)acrylic acid having formula (Ia) as a dark purple solid, which was characterized through $^1\text{H-NMR}$ (400 MHz, CDCl_3) obtaining the following spectrum: δ 8.40 (s, 1H), 7.24 (s, 1H), 7.11 (d, $J=4.0$ Hz), 7.07 – 7.05 (d, s overlapped, 2H), 7.00 (s, 1H), 6.98 (s, 1H), 6.80 (s, 1H), 2.83 – 2.70 (m, 6H), 2.58 (t, $J=7.6$ Hz, 2H), 1.75 – 1.58 (m, 8H), 1.48 – 1.20 (m, 40H), 0.93 – 0.85 (m, 12H) ppm; and through $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) obtaining the following spectrum: δ 168.5, 157.2, 146.9, 144.5, 144.1, 140.8, 140.4, 136.8, 136.5, 135.7, 134.6, 133.5, 132.7, 130.0, 128.9, 128.7, 126.3, 125.6, 125.0, 119.1, 116.2, 93.9, 77.3, 77.0, 76.7, 32.0, 31.2, 30.5, 29.7, 29.5, 29.4, 22.8, 14.2 ppm.

EXAMPLE 2

Synthesis of 2-cyano-3-(3''',3''''',4,4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-pentathiophene]-5-yl)acrylic acid having formula (Ib) and 2-cyano-3-(3,3''',3''''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-pentathiophene]-5-yl)acrylic acid having formula (Ic) (comparative compound)



Synthesis of 3''', 3''',4,4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene having formula (10) and of 3,3',3''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene having formula (11)

In a 250 ml three-neck flask equipped with a mechanical stirrer and coolant, an inert atmosphere was created through nitrogen (N_2) insufflation. Subsequently, 6.31 g (10.0 mmoles) of 5,5''-dibromo-3,3''-dioctyl-[2,2':5',2'']-terthiophene having formula (7), obtained as described in Example 1, 7.25 g (22.5 mmoles) of 4,4,5,5-tetramethyl-2-(3-octylthiophene-2-yl)-1,3,2-dioxaborolane having formula (2) obtained as described in Example 1, 2.42 g (7.5 mmoles) of 4,4,5,5-tetramethyl-2-(4-octylthiophen-2-yl)-1,3,2-

dioxaborolane having formula (4) obtained as described in Example 1, 60 ml toluene anhydrous, 0.067 g (0.30 mmoles) of palladium acetate [Pd(OAc)₂], 0.25 g (0.6 mmoles) of 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos) and 6.37 g (30.0 mmoles) of potassium phosphate (K₃PO₄) anhydrous, finely ground with a mortar and pestle, were added, obtaining a dark orange reaction mixture. 15 ml of previously double distilled degassed water were added to said reaction mixture, immediately obtaining a dark brown color, finally 60 drops of Aliquat[®] 336 were added and the reaction mixture obtained was heated to 90°C and maintained at said temperature, under stirring, for 8 hours. After cooling to ambient temperature (25°C) and removing the residual solvent through distillation at reduced pressure, the residue obtained was diluted with water (200 ml) and extracted with hexane (3 x 250 ml). The global organic phase (obtained by joining the three organic phases obtained from the extraction) was washed with a saturated aqueous solution of sodium chloride (NaCl) (3 x 200 ml) and anhydried on sodium sulfate anhydrous for 3 hours. The residual solvent was then removed by distillation at reduced pressure, obtaining a dark oil. Said dark oil was purified through chromatography on a silica gel column using hexane as eluent obtaining 6.74 g (yield 78%) of a mixture of 3''', 3''',4,4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene having formula (10) and of 3,3'',3''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene having formula (11), which were characterized through ¹H-NMR (400 MHz, CDCl₃) obtaining the following spectra:

- compound having formula (10): δ 7.26 – 7.22 (dd overlapped, J ≈ 5.0 Hz, 2H), 6.96 – 6.90 (m, 6H), 2.68 – 2.60 (m, 8H), 1.68 – 1.57 (m, 8H), 1.45 – 1.15 (m, 40H), 0.95 – 0.80 (m, 12H) ppm;
- compound having formula (11): δ 7.17 (d, J ≈ 5.0 Hz, 2H), 6.99 (s, 2H), 6.95 (s, 2H), 6.94 (d, J ≈ 5.0 Hz, 2H), 2.81 – 2.75 (m, 8H), 1.75 – 1.60 (m, 8H), 1.42 – 1.22 (m,

40H), 0.94 – 0.86 (m, 12H) ppm.

Synthesis of 5-formyl-3''', 3''', 4,4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene having formula (12) and of 5-formyl-3,3'',3''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene having formula (13)

In a 100 ml three-neck flask equipped with a magnetic stirrer and coolant, an inert atmosphere was created through nitrogen (N₂) insufflation. Subsequently, 6.50 g (7.5 mmoles) of a mixture of 3''', 3''', 4,4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene having formula (10) and of 3,3'',3''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene having formula (11), obtained as described above, 80 ml of 1,2-dichloroethane (1,2-DCE) anhydrous were added and the solution obtained was cooled to 0°C, under stirring. Subsequently, 0.58 g (7.9 mmoles) of *N,N*-dimethylformamide (DMF) anhydrous and 1.25 g (7.9 mmoles) of phosphorus oxychloride (POCl₃) were added to said solution: the reaction mixture obtained was then heated to 70°C and kept at said temperature, under stirring, for 16 hours. After cooling to ambient temperature (25°C) 100 ml of an aqueous solution of sodium acetate (2M) were added and the reaction mixture was kept, under stirring, at said temperature, for 2 hours. The residual solvent was then removed through distillation at reduced pressure and the residue obtained was extracted with dichloromethane (3 x 100 ml). The global organic phase (obtained by joining the three organic phases obtained from the extraction) was anhydriified on sodium sulfate anhydrous for 3 hours. The residual solvent was then removed by distillation at reduced pressure, obtaining a dark oil. Said dark oil was purified through chromatography on a silica gel column using a mixture of hexane/dichloromethane (1/1; v/v) as eluent, obtaining 3.9 g (yield 50%) of a mixture of 5-formyl-3''', 3''', 4,4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene having formula (12) and of 5-formyl-3,3'',3''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene having formula (13)

which were characterized through ^1H -NMR (400 MHz, CDCl_3) obtaining the following spectrum: δ 9.99 (s, 0.26H, [12]), 9.83 (s, 1H, [13]), 7.26 ([12]), 7.17 (d, $J \approx 5.0$ Hz, 1H, [13]), 7.13 (s, 1H, [13]), 7.12 (s, 1H, [13]), 7.10 (d, $J \approx 5.0$ Hz, 1H, [13]), 7.04 (s, [12]), 6.96 (s, 1H, [13]), 6.93 (d, $J \approx 5.0$ Hz, 1H, [13]), 2.95 – 2.73 (m, $\approx 9\text{H}$, [12+13]), 1.74 – 1.60 (m, $\approx 9\text{H}$, [12+13]), 1.47 – 1.20 (m, $\approx 45\text{H}$, [12+13]), 0.93 – 0.83 (m, $\approx 14\text{H}$, [12+13]) ppm {[12]: compound having formula (12); [13]: compound having formula (13)}.

Synthesis of 2-cyano-3-(3''',3''',4,4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene-5-yl)acrylic acid and 2-cyano-3-(3,3'',3''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene-5-yl)acrylic acid having formula (Ic) (comparative compound)

3.30 g (3.71 mmoles) of a mixture of 5-formyl-3''',3''',4,4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene having formula (12) and of 5-formyl-3,3'',3''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene having formula (13) obtained as described above, 50 ml of glacial acetic acid (CH_3COOH), 9.47 g (111.3 mmoles) of cyanoacetic acid ($\text{NC-CH}_2\text{-COOH}$) and 5.72 g (74.2 mmoles) of ammonium acetate ($\text{CH}_3\text{COONH}_4$) were placed in a 100 ml flask equipped with a magnetic stirrer and coolant and the reaction mixture was then heated to 110°C , under stirring, for 16 hours. After cooling to ambient temperature (25°C) a dark solid was obtained which was recovered by filtration and washed, in succession, with a saturated aqueous solution of sodium bicarbonate (NaHCO_3) (3 x 50 ml), with distilled water (3 x 70 ml) and finally with methanol (CH_3OH) (3 x 30 ml). The residue obtained was purified by double crystallization using a mixture of dichloromethane/methanol (20/150, v/v) obtaining 3.10 g (yield 87%) of a dark purple solid corresponding to a mixture of 2-cyano-3-(3''',3''',4,4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene-5-yl)acrylic acid having formula (Ib) and 2-cyano-3-(3,3'',3''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene-5-yl)acrylic acid having formula (Ic) (comparative compound). Said mixture was subjected

to separation through chromatography on a silica gel column using a mixture of dichloromethane/methanol (85/15, v/v) as eluent obtaining 0.71 g of 2-cyano-3-(3'',3''',4,4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene-5-yl)acrylic acid having formula (Ib) and 1.76 g of 2-cyano-3-(3,3'',3''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''']-quinquethiophene-5-yl)acrylic acid having formula (Ic) (comparative compound).

The compound having formula (Ib) was characterized through $^1\text{H-NMR}$ (400 MHz, CDCl_3) obtaining the following spectrum: δ 8.41 (s, 1H), 7.27 (s, 1H) 7.17 (d, $J = 5.0$ Hz, 1H), 7.14 – 7.07 (m, 3H), 6.97 – 6.90 (s,d overlapped, $J = 5.0$ Hz, 2H), 2.85 – 2.75 (m, 8H), 1.75 – 1.60 (m, 8H), 1.48 – 1.20 (m, 40H), 0.92 – 0.80 (m, 12H) ppm.

The compound having formula (Ic) (comparative compound) was characterized through $^1\text{H-NMR}$ (400 MHz, CDCl_3) obtaining the following spectrum: δ 8.26 (s, 1H), 7.62 (s, 1H), 7.22 (s, 1H), 7.17 (d, $J = 5.0$ Hz, 1H), 7.15 (d, $J = 5.0$ Hz, 1H), 7.11 (d, $J = 5.0$ Hz, 1H), 2.89 – 2.74 (m, 8H), 1.76 – 1.60 (m, 8H), 1.49 – 1.21 (m, 40H) 0.91 – 0.83 (m, 12H) ppm.

EXAMPLE 3

Preparation of a dye sensitized solar cell (DSSC)

Titanium dioxide (TiO_2) electrodes were prepared through deposition ("Doctor Blade" technique) of a colloidal paste containing particles of titanium dioxide (TiO_2) having a size of 20 nm (TiO_2 Paste DSL 18NR-T - Dyesol) on FTO conductive glass (Hartford Glass Co., TEC 8, having a thickness of 2.3 mm and a sheet resistance of $6 \Omega/\text{cm}^2$ - $9 \Omega/\text{cm}^2$), previously cleaned with water and ethanol, treated with a plasma cleaner, at 100°C , for 10 minutes, immersed in an aqueous solution of titanium tetrachloride (TiCl_4) prepared fresh (4.5×10^{-2} M), at 70°C , for 30 minutes, and finally washed with ethanol.

After a first drying at 125°C , for 15 minutes, a reflecting diffusion layer containing titanium dioxide particles sized >100 nm (TiO_2) (Ti-Nanoxide R/SP - Solaronix), was deposited ("Doctor Blade" technique) on the first layer of titanium dioxide (TiO_2) and sintered up to

500°C, for 30 minutes. The glass coated with titanium dioxide (TiO₂) was cooled to ambient temperature (25°C) and immersed again in a freshly prepared aqueous solution of titanium tetrachloride (TiCl₄) (4.5×10^{-2} M), at 70°C, for 30 minutes, finally washed with ethanol and sintered at 500°C, for 30 minutes, obtaining a titanium dioxide (TiO₂) electrode having a uniform thickness of 12 µm.

After sintering, the glass coated with the titanium dioxide (TiO₂) film was cooled to about 80°C - 100°C and immediately immersed in a solution of dichloromethane (CH₂Cl₂) (5×10^{-4} M) of the compound having formula (Ia) obtained as described in Example 1, at ambient temperature (25°C), for 24 hours. The glass covered in colored titania was washed with ethanol and dried at ambient temperature (25°C), under a flow of nitrogen (N₂).

A Surlyn spacer having a thickness of 50 µm (TPS 065093-50 - Dyesol) was used to seal the photoanode obtained as described above and the counter-electrode comprising platinized FTO glass (Hartford Glass Co., TEC 8, having a thickness of 2.3 mm and a sheet resistance of $6 \Omega/\text{cm}^2$ - $9 \Omega/\text{cm}^2$), subsequently the cell was filled with the electrolyte solution having the following composition: *N*-methyl-*N*-butyl imidazolium iodide (0.6 M), iodine (0.04 M), lithium iodide (LiI) (0.025 M), guanidine-thiocyanate (0.05 M) and *t*-butylpyridine (0.28 M), in a 15:85 (v/v) mixture of valeronitrile and acetonitrile.

The photovoltaic performance of the cell was measured, after applying above the active area thereof an opaque black mask of adhesive card having a $4 \times 4 \text{ mm}^2$ square hole, with a solar simulator (Abet 2000) equipped with a 300 W xenon light source, the light intensity was calibrated with a standard silica solar cell ("VLSI Standard" SRC-1000-RTD-KGS), the current/voltage characteristics were obtained by applying an external voltage to the cell and by measuring the photocurrent generated with a digital multimeter "Keithley 2602A" (3A DC, 10A Pulse). The following results were obtained:

- Voc (open circuit photovoltage) = 0.670 V;
- FF (Fill Factor) = 75.2%;
- Jsc (short circuit current density) = 11.93 mA/cm²;
- η (photoelectric conversion efficiency) = 6.01%.

EXAMPLE 4

Preparation of a dye sensitized solar cell (DSSC)

With the same procedure described in Example 3 a dye sensitized solar cell (DSSC) was prepared using the compound having formula (Ib) obtained as described in Example 2.

The photovoltaic performance of the cell was measured as described in Example 3. The following results were obtained:

- Voc (open circuit photovoltage) = 0.641 V;
- FF (Fill Factor) = 74.2%;
- Jsc (short circuit current density) = 11.56 mA/cm²;
- η (photoelectric conversion efficiency) = 5.50%.

EXAMPLE 5

Preparation of a dye sensitized solar cell (DSSC)

With the same procedure described in Example 3 a dye sensitized solar cell (DSSC) was prepared using the compound having formula (Ic) (comparative compound) obtained as described in Example 2. The photovoltaic performance of the cell was measured as described in Example 3. The following results were obtained:

- Voc (open circuit photovoltage) = 0.664 V;
- FF (Fill Factor) = 75.0%;
- Jsc (short circuit current density) = 12.83 mA/cm²;
- η (photoelectric conversion efficiency) = 6.39%.

EXAMPLE 6

Procedure for the accelerated aging of a dye sensitized solar cell (DSSC)

The dye sensitized solar cell (DSSC), obtained as described in Example 3, was placed inside an accelerated aging device, Solarbox Mod. 1500: the whole was maintained at a constant temperature of 65°C and under a Xenon lamp regulated to obtain light intensity of 0.5 sun. The photovoltaic performance of the cell was measured as described in Example 3 at pre-established time intervals (hours): said time intervals [Time (h)] and the result obtained are reported in Table 1 and in Figure 1 [the x coordinate indicates the time in hours (h); the y coordinate indicates the photoelectric conversion efficiency (η) in (%)].

EXAMPLE 7Procedure for the accelerated aging of a dye sensitized solar cell (DSSC)

The dye sensitized solar cell (DSSC), obtained as described in Example 4, was placed inside an accelerated aging device, Solarbox Mod. 1500: the whole was maintained at a constant temperature of 65°C and under a Xenon lamp regulated to obtain light intensity of 0.5 sun. The photovoltaic performance of the cell was measured as described in Example 3 at pre-established time intervals (hours): said time intervals [Time (h)] and the result obtained are reported in Table 1 and in Figure 1 [the x coordinate indicates the time in hours (h); the y coordinate indicates the photoelectric conversion efficiency (η) in (%)].

EXAMPLE 8 (comparative)Procedure for the accelerated aging of a dye sensitized solar cell (DSSC)

The dye sensitized solar cell (DSSC), obtained as described in Example 5, was placed inside an accelerated aging device, Solarbox Mod. 1500: the whole was maintained at a constant temperature of 65 °C and under a Xenon lamp regulated to obtain light intensity of 0.5 sun. The photovoltaic performance of the cell was measured as described in Example 3 at pre-established time intervals (hours): said time intervals [Time (h)] and the result obtained are reported in Table 1 and in Figure 1 [the x coordinate indicates the time

in hours (h); the y coordinate indicates the photoelectric conversion efficiency (η) in (%)].

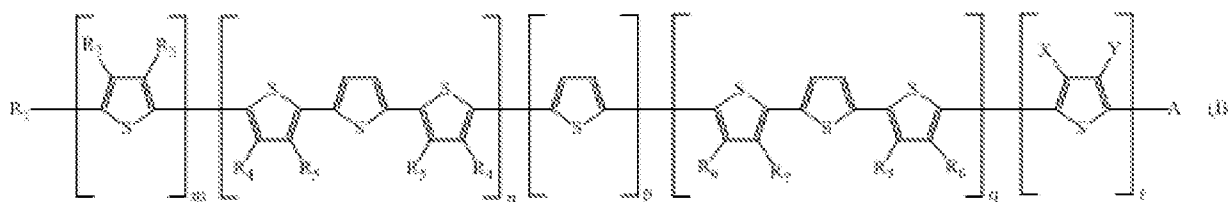
TABLE 1

EXAMPLE	TIME (h)	η (%)	FF	Voc (V)	Jsc (mA/cm ²)
6	0	6.01	75.2	0.670	11.93
6	4	5.83	72.7	0.648	12.38
6	24	5.19	69.9	0.588	12.67
6	48	4.28	64.7	0.550	12.03
7	0	5.50	74.2	0.641	11.56
7	4	5.57	71.9	0.632	12.25
7	24	4.95	69.9	0.573	12.36
7	48	4.17	67.1	0.540	11.51
8 (comparative)	0	6.39	75.0	0.664	12.83
8 (comparative)	4	2.18	61.9	0.590	5.97
8 (comparative)	24	1.97	67.3	0.495	5.93
8 (comparative)	48	1.69	62.2	0.446	6.10

From the data reported in Table 1, it is clear that the dye sensitized solar cells (DSSCs) comprising the organic dye according to the present invention (Example 6 and Example 7), are able to maintain good performance over time, particularly in terms of photoelectric conversion efficiency (η), with respect to the dye sensitized solar cell (DSSC) comprising the comparative organic dye [Example 8 (comparative)].

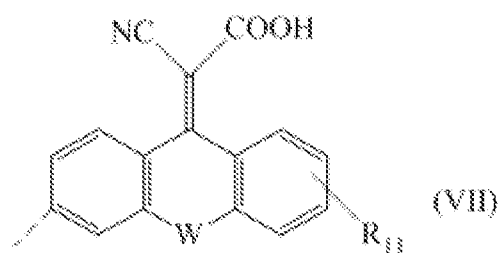
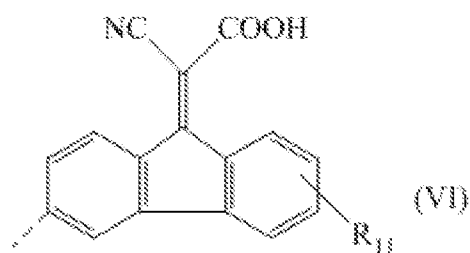
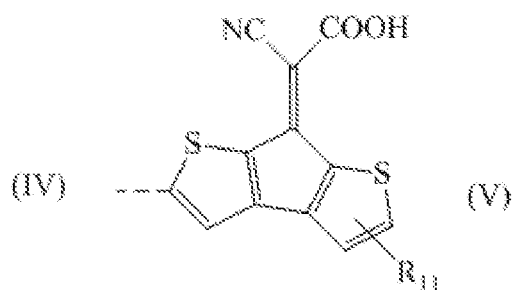
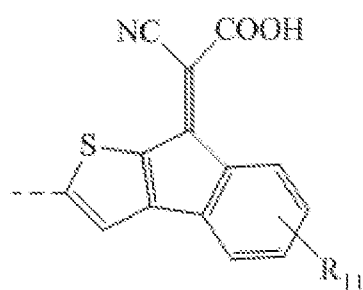
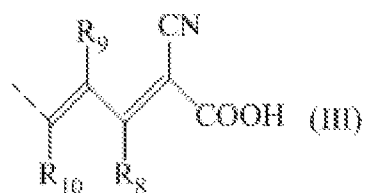
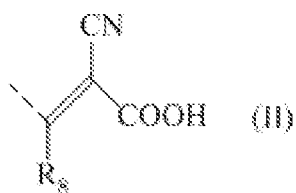
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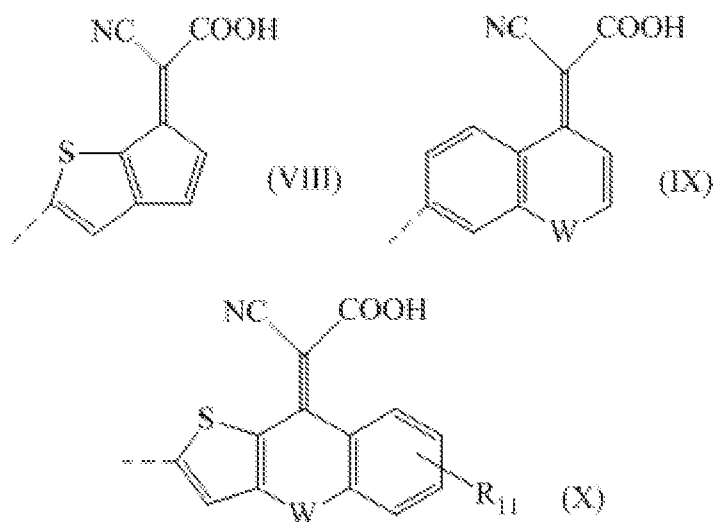
1. Organic dye having the general formula (I):



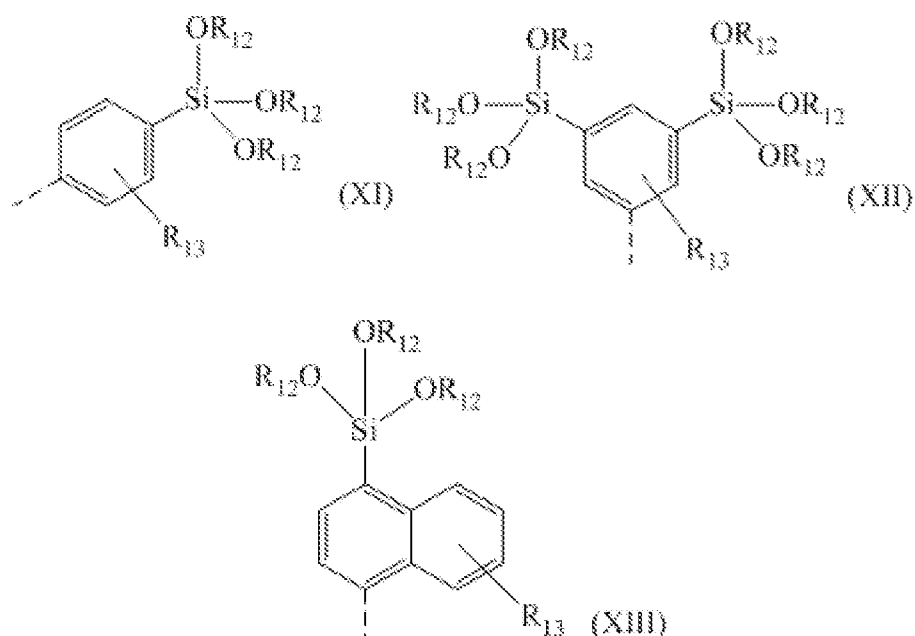
in which:

- A represents a -COOH group or a group having the general formula -Si(OR₁₂)₃ wherein R₁₂ has the meanings reported below; or it is selected from carboxycyanovinylene groups having the general formulae (II), (III), (IV), (V), (VI), (VII), (VIII), (IX), (X):





in which R₈, R₉, R₁₀ and R₁₁, identical or different, represent a hydrogen atom, or are selected from linear or branched, C₁-C₂₀ alkyl groups, preferably C₂-C₈, W represents an oxygen atom or a sulfur atom; or it is selected from groups having the general formula (XI), (XII) or (XIII):



in which R₁₂ represents a hydrogen atom, or is selected from linear or branched, saturated or unsaturated, C₁-C₆ alkyl groups, preferably C₁-C₂, R₁₃

represents a hydrogen atom or a halogen atom such as fluorine, chlorine, bromine, iodine, preferably fluorine, or is selected from linear or branched, saturated or unsaturated, C₁-C₁₆ alkyl groups, preferably C₁-C₁₂, optionally containing one or more halogen atoms;

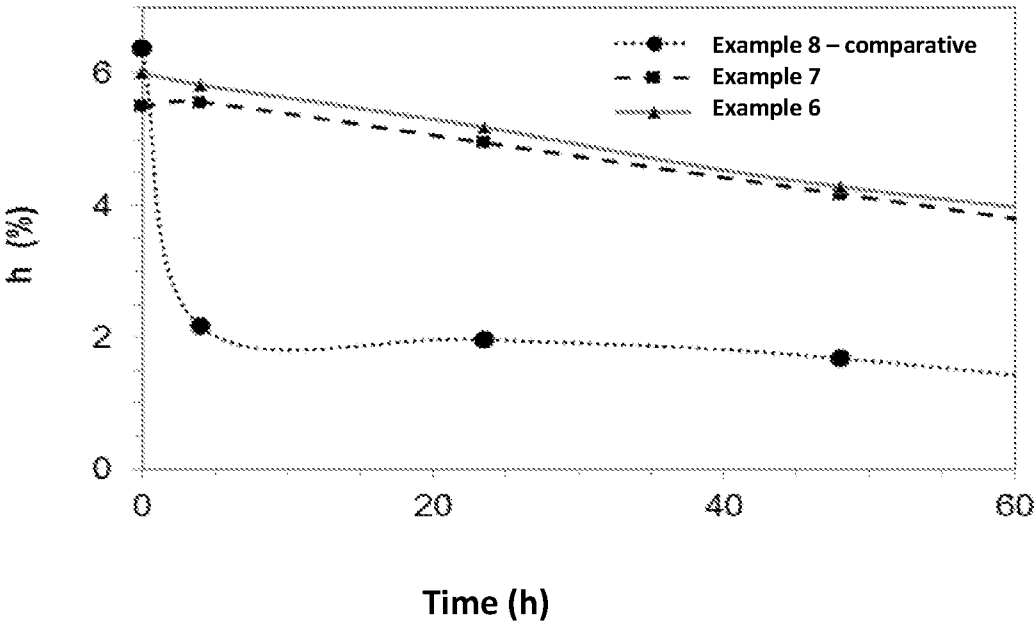
- R₁ represents a hydrogen atom; or is selected from: linear or branched, saturated or unsaturated C₁-C₂₀ alkyl groups, preferably C₄-C₂₀, optionally containing heteroatoms, optionally substituted C₄-C₂₀ cycloalkyl groups, preferably C₄-C₁₂, optionally substituted C₁-C₂₀ alkoxy or thioalkoxy groups, preferably C₁-C₁₀, polyethylenoxyl groups having the general formula R'-O-[-CH₂-CH₂-O]_m- in which R' represents a hydrogen atom, or is selected from linear or branched, C₁-C₂₀ alkyl groups, preferably C₁-C₁₂, and m is an integer ranging from 1 to 20, preferably ranging from 2 to 10, optionally substituted C₆-C₂₄ aryloxy or thioaryloxy groups, preferably C₆-C₁₆, optionally substituted C₆-C₂₄ aryl groups, preferably C₆-C₁₆, trialkyl- or triaryl-silyl groups;
- R₂, R₃, R₄, R₅, R₆ and R₇, identical or different, represent a hydrogen atom; or are selected from: linear or branched, saturated or unsaturated C₁-C₂₀ alkyl groups, preferably C₄-C₁₂, optionally containing heteroatoms, optionally substituted C₄-C₂₀ cycloalkyl groups, preferably C₄-C₁₂, trialkyl- or triaryl-silyl groups, with the proviso that at least one of R₄ and R₅, or R₆ and R₇, is different from hydrogen;
- X represents a hydrogen atom, or a halogen atom such as fluorine, chlorine, bromine, iodine, preferably fluorine; or it is selected from: C₁-C₁₀ perfluoro- or perchloro-alkyl groups, preferably C₁-C₈, C₆-C₁₈ perfluoro- or perchloro-aryl groups, preferably C₆-C₁₆;
- Y represents a hydrogen atom; or is selected from: linear or branched,

saturated or unsaturated C₁-C₂₀ alkyl groups, preferably C₄-C₁₂, optionally containing heteroatoms, optionally substituted C₄-C₂₀ cycloalkyl groups, preferably C₄-C₁₂, trialkyl- or triaryl-silyl groups;

- m, n, p and r, identical or different, are integers ranging from 0 to 5, preferably ranging from 0 to 2;
- q is an integer ranging from 1 to 5, preferably ranging from 1 to 2;

with the proviso that when r is 0, R₇ has the meanings of X and R₆ has the meanings of Y.

2. Dye sensitized photoelectric conversion element which comprises at least one organic dye having general formula (I) according to claim 1, said dye sensitized photoelectric conversion element being supported on oxide semiconductor particles.
3. Dye Sensitized Solar Cell (DSSC), which includes the dye sensitized photoelectric conversion element according to claim 2.



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/052839

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09B69/00 C09B23/10 C09B57/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09B

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DORA DEMETER ET AL: "Linearly [pi]-conjugated oligothiophenes as simple metal-free sensitizers for dye-sensitized solar cells", JOURNAL OF MATERIALS CHEMISTRY C: MATERIALS FOR OPTICAL AND ELECTRONIC DEVICES, vol. 3, no. 29, 3 July 2015 (2015-07-03), pages 7756-7761, XP055334245, UK ISSN: 2050-7526, DOI: 10.1039/C5TC01183C page 7757; figure 1 ----- -/-	1-3



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

3 August 2017

Date of mailing of the international search report

10/08/2017

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Ketterer, Michael

INTERNATIONAL SEARCH REPORT

International application No

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A	US 2010/174095 A1 (KOUMURA NAGATOSHI [JP] ET AL) 8 July 2010 (2010-07-08) examples	1-3
A	WO 2013/160201 A1 (ENI SPA [IT]; CENTRE NAT RECH SCIENT [FR]) 31 October 2013 (2013-10-31) cited in the application examples	1-3
A	GUANGRUI HE ET AL: "Impact of dye end groups on acceptor-donor-acceptor type molecules for solution-processed photovoltaic cells", JOURNAL OF MATERIALS CHEMISTRY, vol. 22, no. 18, 14 March 2012 (2012-03-14), pages 9173-9180, XP055113291, ISSN: 0959-9428, DOI: 10.1039/c2jm30194f page 9173; compounds DTDMP7T, DCA07T -/--	1-3

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/052839

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	WO 2013/030737 A1 (PIANETA S R L [IT]; CAPUTO GIUSEPPE [IT]) 7 March 2013 (2013-03-07) page 25; compound GC12 page 26; compounds GC14-GC16 page 31; compound GC29 claims	1-3

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International application No

PCT/IB2017/052839

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