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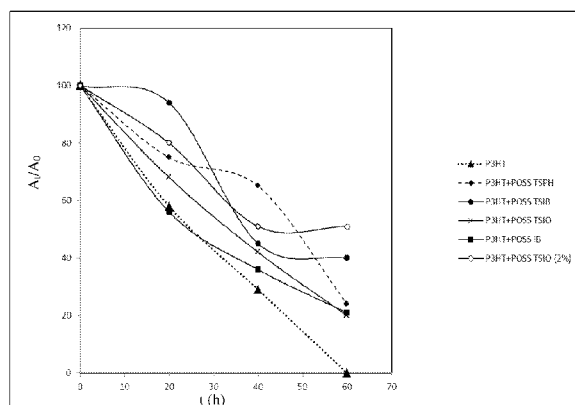
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[Continued on next page]

## (54) Title: STABILIZED PHOTOACTIVE COMPOSITION AND USE THEREOF



**Figure 2** - Accelerated aging in a Solar box 3000 of the films (average thickness of the film equal to 0.5  $\mu\text{m}$ ) of: P3HT obtained from solution A; P3HT + POSS TSPH obtained from solution E; P3HT + POSS TSIB obtained from solution G; P3HT + POSS TSIO obtained from solution H; P3HT + POSS IB obtained from solution I; P3HT + POSS TSIO obtained from solution L.

(57) Abstract: Stabilized photoactive composition comprising: - at least one photoactive organic polymer; - at least one UV stabilizer selected from polyhedral oligomeric silsesquioxanes - POSS. Said stabilized photoactive composition can be advantageously used in the construction of photovoltaic devices (or solar devices) such as, for example, photovoltaic cells (or solar cells), photovoltaic modules (or solar modules) on both rigid and flexible supports.



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## STABILIZED PHOTOACTIVE COMPOSITION AND USE THEREOF

The present invention relates to a stabilized  
5 photoactive composition.

More specifically, the present invention relates to  
a stabilized photoactive composition comprising at  
least one photoactive organic polymer and at least one  
UV stabilizer selected from polyhedral oligomeric  
10 silsesquioxanes (POSS).

The present invention also relates to the use of  
said stabilized photoactive composition in the  
construction of photovoltaic devices (or solar devices)  
such as, for example, photovoltaic cells (or solar  
15 cells), photovoltaic modules (or solar modules) on both  
rigid and flexible supports.

Photovoltaic devices (or solar devices) are  
devices capable of converting the energy of a light  
radiation into electric energy. At present, most  
20 photovoltaic devices (or solar devices) which can be  
used for practical applications exploit the physico-  
chemical properties of photoactive materials of the  
inorganic type, in particular high-purity crystalline  
silicon. As a result of the high production costs of  
25 silicon, scientific research, however, has been  
orienting its efforts towards the development of  
alternative materials of the organic type having a  
polymeric structure [so-called "polymer photovoltaic  
cells (or solar cells)]. Unlike high-purity crystalline  
30 silicon, in fact, organic polymers are characterized by  
a relatively easy synthesis and control of the opto-

electronic properties, a low production cost, a reduced weight of the relative photovoltaic device (or solar device), and also allow the recycling of said polymer at the end of the life cycle of the photovoltaic device  
5 (or solar device) in which it is used.

The functioning of organic photovoltaic devices (or solar devices) such as, for example, organic photovoltaic cells (or solar cells), is based on the combined use of an electron-acceptor compound and an  
10 electron-donor compound. In the state of the art, the most widely-used electron-acceptor compounds in organic photovoltaic devices (or solar devices) are fullerene derivatives, in particular [6,6]-phenyl-C<sub>61</sub>-methyl butyrate ([60]PCBM) or phenyl-C<sub>71</sub>-methyl butyrate  
15 ([70]PCBM), which have reached the greatest efficiencies when mixed with electron-donor compounds selected from  $\pi$ -conjugated polymers such as, for example, polythiophenes ( $\eta > 5\%$ ), polycarbazoles ( $\eta > 6\%$ ), derivatives of poly(thienothiophene)-  
20 benzodithiophene (PTB) ( $\eta > 8\%$ ).

It is known that photovoltaic devices (or solar devices), in particular photovoltaic cells (or solar cells), photovoltaic modules (or solar modules) are normally assembled outside, on roofs or in wide-open  
25 spaces, in order to allow them to be exposed to sunlight as much as possible.

It is also known that, as the presence of light, oxygen and/or humidity negatively influences the performances of said photovoltaic devices (or solar  
30 devices), various strategies can be adopted for increasing their useful lifetime such as, for example:

- encapsulation with polymers having high oxygen and/or humidity barrier properties or, preferably, having ultra-high oxygen and/or humidity barrier properties, in the form of mono- or multi-layer film, preferably multi-layer;
- encapsulation by means of the so-called "active packaging" (of the getter type) wherein an adsorbing agent of the chemical or physical type included in the "package" neutralizes the effect of the oxygen and humidity;
- use of stabilizers which can be mixed with the photoactive organic polymer so as to make it stable to light and/or oxygen, in particular.

American patent application US 2007/0295390, for example, describes a device comprising a solar cell individually encapsulated, wherein the solar cell includes at least one protective layer coupled with at least one surface of the solar cell, the protective layer having a chemical composition suitable for substantially preventing contact between the solar cell and humidity; wherein the light passes through the protective layer so as to reach the absorbing layer of the solar cell; wherein the protective layer substantially comprises inorganic material. The above-mentioned protective layer is said to be capable of improving the protection to the external environment of solar cells, in particular thin film solar cells.

International patent application WO 2006/093936 describes a composition which can be used for encapsulating photovoltaic cells, comprising: (a) a

polymeric encapsulating agent [e.g., an ionomer, an ethylene-vinyl acetate (EVA) copolymer, or a block copolymer (Kraton G1726)]; (b) Cyasorb UV-1164 as stabilizer to UV rays ("UV stabilizer"); and (c) a  
5 sterically hindered amine as light stabilizer; wherein said UV stabilizer is present in the composition in a quantity ranging from about 0.2% by weight to about 1.0% by weight and the light stabilizer is present in a quantity ranging from about 0.3% by weight to about  
10 0.6% by weight. The above composition is said to have an improved photothermal and photochemical stability.

International patent application WO 2012/017048 in the name of the Applicant, describes a stabilized photoactive composition comprising:

- 15 - at least one photoactive organic polymer;
- at least one light stabilizer selected from the sterically hindered amines;
- at least one UV stabilizer selected from triazines, benzooxazinones, benzotriazoles, benzophenones,  
20 benzoates, formamidines, cinnamates or propenoates, aromatic propanediones, benzoimidazoles, cycloaliphatic ketones, formanilides including oxamides, cyanoacrylates, benzopyranones, salicylates, or mixtures thereof.

25 It is said that the above stabilized photoactive composition can be advantageously used in the construction of photovoltaic devices (or solar devices) such as, for example, photovoltaic cells (or solar cells), photovoltaic modules (or solar modules) on both  
30 rigid and flexible supports.

The encapsulation of said photovoltaic devices (or

solar devices), however, in particular in the case of photovoltaic devices (or solar devices) on flexible support, requires the use of specific polymers having particular barrier properties with respect to oxygen  
5 and/or humidity (e.g., polymers having very low permeability values) and therefore an increase in production costs which, particularly in the case of polymer photovoltaic devices (or solar devices), generally having a low conversion efficiency of solar  
10 radiation (ranging from about 3% to about 7%), would make their production cost even more disadvantageous.

The Applicant has therefore considered the problem of obtaining photovoltaic devices (or solar devices) stable to the action of light, oxygen, humidity,  
15 avoiding the use of polymers having ultra-high barrier properties with respect to oxygen and/or humidity (e.g., polymers having very low permeability values).

The Applicant has now found that the addition of at least one UV stabilizer selected from polyhedral  
20 oligomeric silsesquioxanes (POSS) to photoactive organic polymers which can be used in the construction of photovoltaic devices (or solar devices), is capable of stabilizing said polymers. The use of the polymers thus stabilized can avoid the use of polymers having  
25 ultra-high barrier properties with respect to oxygen and/or water vapour (e.g., polymers having very low permeability values).

An object of the present invention therefore relates to a stabilized photoactive composition  
30 comprising:

- at least one organic photoactive polymer;

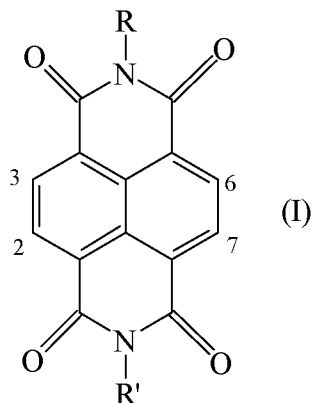
- at least one UV stabilizer selected from polyhedral oligomeric silsesquioxanes (POSS).

For the aim of the present description and of the following claims, the definitions of the numerical  
5 intervals always include the extremes, unless otherwise specified.

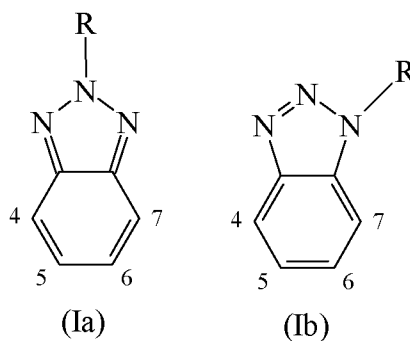
For the aim of the present description and of the following claims, the term "comprising" also includes the terms "which essentially consists of" or "which  
10 consists of".

According to a preferred embodiment of the present invention, said photoactive organic polymer can be selected from:

- (a) polythiophenes such as, for example, poly(3-hexylthiophene) (P3HT), poly(3-octylthiophene), poly(3,4-ethylenedioxythiophene), or mixtures thereof;  
15
- (b) polyphenylenevinylenes such as, for example, poly(2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylenevinylene, poly(paraphenylenevinylene),  
20 { (poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene]-alt-(vinylene)) } (MDMO-PPV), or mixtures thereof;
- (c) alternating conjugated copolymers comprising:  
25
  - naphthalene diimide units (A) having general formula ( I ):



- wherein R and R', equal to or different from each other, are selected from linear or branched, preferably branched, alkyl groups containing from 1 to 36 carbon atoms, preferably from 4 to 24 carbon atoms, more preferably from 6 to 18 carbon atoms, or from aryl groups, preferably phenyl groups, said aryl groups being optionally substituted with alkyl radicals having from 1 to 24 carbon atoms, preferably from 4 to 18 carbon atoms;
- at least one conjugated electron-donor structural unit (B), wherein the unit (A) is connected to the unit (B), in the alternating copolymer, in any of the positions 2, 3, 6 or 7;
- (d) alternating or statistic conjugated copolymers comprising:
- at least one benzotriazole unit (B) having general formula (Ia) or (Ib)

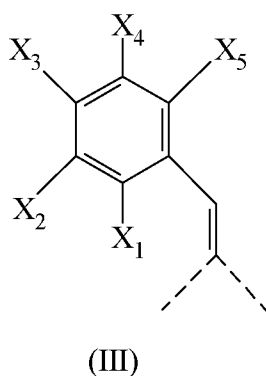


wherein the group R is selected from alkyl groups, aryl groups, acyl groups, thioacyl groups, said alkyl, aryl, acyl and thioacyl groups being optionally substituted;

- at least one conjugated structural unit (A), wherein each unit (B) is connected to at least one unit (A) in any of the positions 4, 5, 6, or 7, preferably in positions 4 or 7;

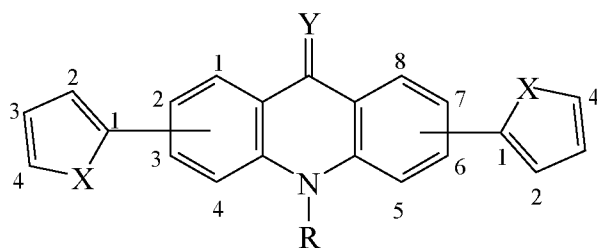
(e) alternating  $\pi$ -conjugated polymers comprising:

- at least one fluoroarylvinyldiene electron-acceptor unit (A) having general formula (III):



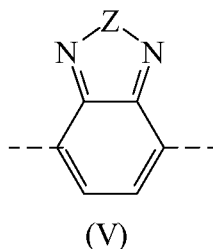
wherein the substituents  $X_1$ - $X_5$ , equal to or different from each other, are selected from hydrogen, fluorine, or from alkyl groups containing from 1 to 12 carbon atoms,

- preferably from 1 to 4 carbon atoms, and with the proviso that at least one, preferably at least two, more preferably at least three, of the substituents  $X_1-X_5$  is fluorine, or a  $-CF_2R$  group, wherein R is selected from hydrogen, fluorine, or from hydrocarbon groups having from 1 to 10 carbon atoms, said hydrocarbon groups being optionally fluorinated;
- at least one conjugated electron-donor structural unit (B) connected to the unit (A) in the points indicated by the dashed lines in general formula (III);
- (f) copolymers based on acridone units comprising:
- one monomeric unit (A) having general formula (IV):



(IV)

- wherein X is selected from sulfur, selenium; Y is selected from oxygen, sulfur, or from  $-NR'$  groups; R and  $R'$ , equal to or different from each other, are organic substituents having from 1 to 24 carbon atoms selected from alkyl groups, aryl groups, said alkyl groups being optionally substituted, acyl groups, thioacyl groups;
- at least one monomeric unit (B) having general formula (V):



wherein Z is selected from O, S, Se, or from  
 -NR'' groups wherein R'' is an organic  
 substituent having from 1 to 24 carbon atoms  
 selected from alkyl groups, aryl groups, said  
 alkyl and aryl groups being optionally  
 substituted, acyl groups, thioacyl groups;  
 said monomeric unit (B) being connected to any  
 available position of a heteroaromatic side-  
 ring of unit (A), through one of the two  
 positions indicated by the dashed lines in  
 general formula (V);

(g) alternating conjugated copolymers comprising  
 benzothiadiazole units such as, for example,  
 PCDTBT {poly[N-9''-heptadecanyl-2,7-carbazole-  
 alt-5,5-(4',7'-di-2-thienyl-2',1',3'-  
 benzothiadiazaole]}}, PCPDTBT {poly [2,6-(4,4-  
 bis-(2-ethylhexyl)-4*H*-cyclopenta [2,1-b;3,4-  
 b']-dithiophene)-alt-4,7-(2,1,3-  
 benzothiadiazaole)]};

(h) alternating conjugated copolymers comprising  
 thieno[3,4-b]pyrazidine units;

(i) alternating conjugated copolymers comprising  
 quinoxaline units;

(l) alternating conjugated copolymers comprising  
 silole monomeric units such as copolymers of  
 9,9-dialkyl-9-silafluorene;

(m) alternating conjugated copolymers comprising condensed thiophene units such as, for example, copolymers of thieno[3,4-b]thiophene and of benzo[1,2-b:4,5-b']dithiophene;

5 or mixtures thereof.

Further details relating to alternating conjugated copolymers (c) comprising naphthalene diimide units (A) and at least one conjugated electron-donor structural unit (B) and to the process for their preparation, can  
10 be found, for example, in international patent application WO 2010/006698 in the name of the Applicant.

Further details relating to alternating or random conjugated copolymers (d) comprising at least one  
15 benzotriazole unit (B) and at least one conjugated structural unit (A) and to the process for their preparation, can be found, for example, in international patent application WO 2010/046114 in the name of the Applicant.

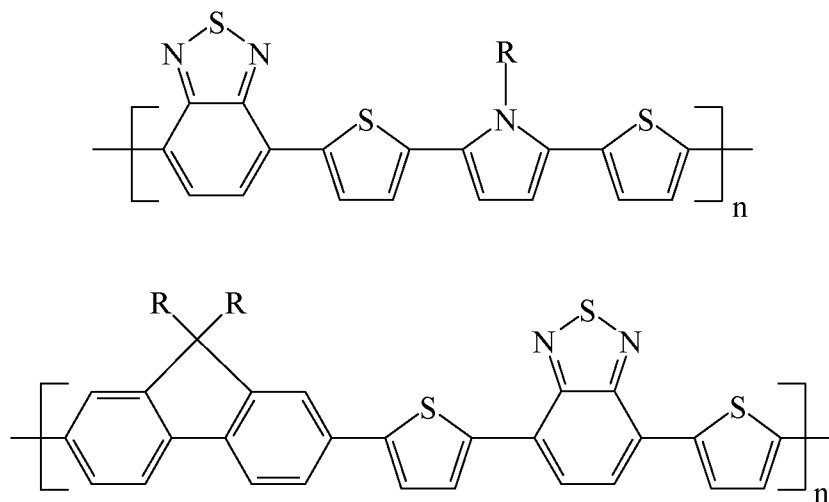
20 Further details relating to  $\pi$ -conjugated alternating polymers (e) comprising at least one fluoroarylvinylidene electron-acceptor unit (A) and at least one conjugated electron-donor structural unit (B) and to the process for their preparation can be found,  
25 for example, in international patent application WO 2011/066954 in the name of the Applicant.

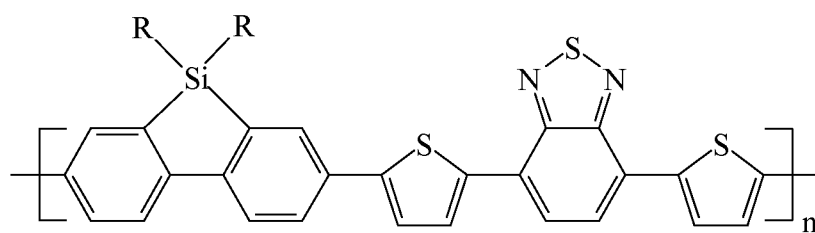
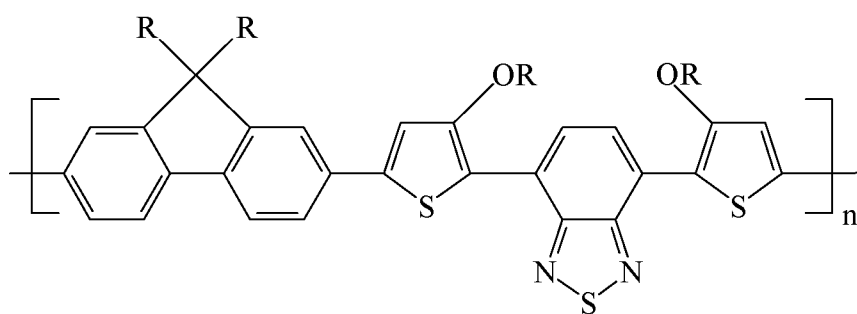
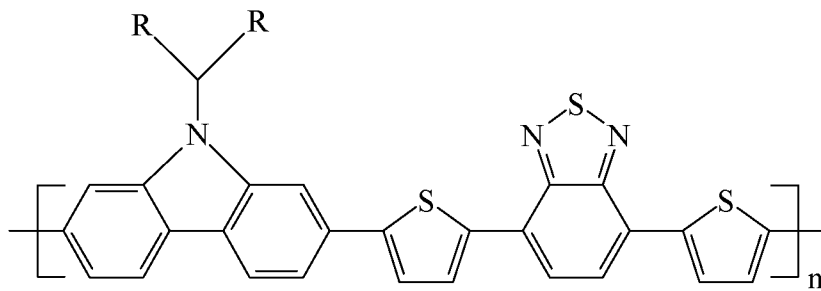
Further details relating to copolymers based on acridone units (f) comprising a monomeric unit (A) and at least one monomeric unit (B) and to the process for  
30 their preparation can be found for example, in international patent application WO 2011/072876 in the

name of the Applicant.

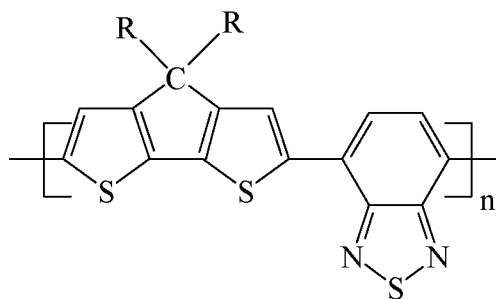
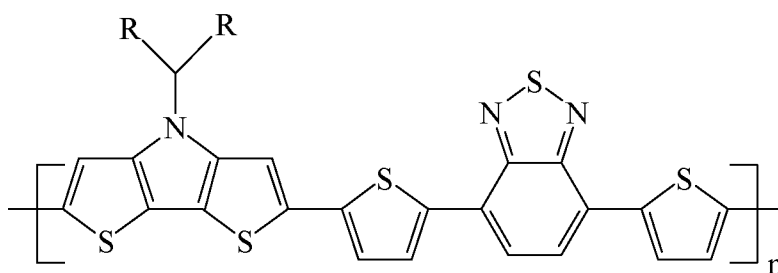
Further details relating to alternating conjugated copolymers comprising benzothiadiazole units (g), alternating conjugated copolymers comprising  
 5 thieno[3,4-b]pyrazine units (h), alternating conjugated copolymers comprising quinoxaline units (i), alternating conjugated copolymers comprising silole monomeric units (l), alternating conjugated copolymers comprising condensed thiophene units (m), can be found,  
 10 for example, in "Accounts of Chemical Research" (2009), Vol. 42, No. 11, pages 1709-1718, "Development of Novel Conjugated Donor Polymers for High-Efficiency Bulk-Heterojunction Photovoltaic Device" (Chen et al.).

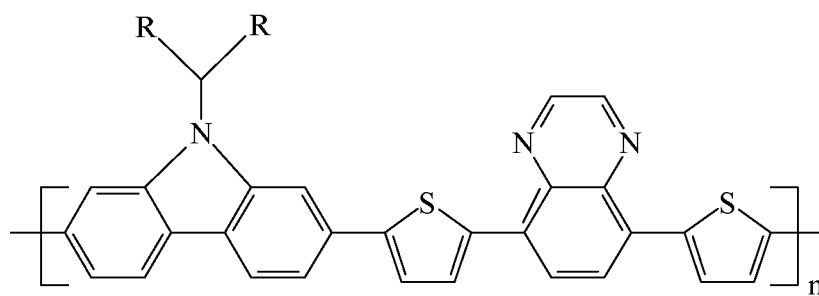
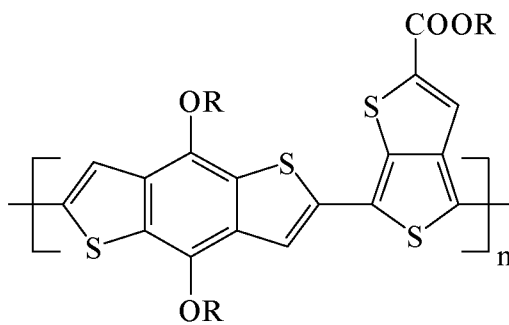
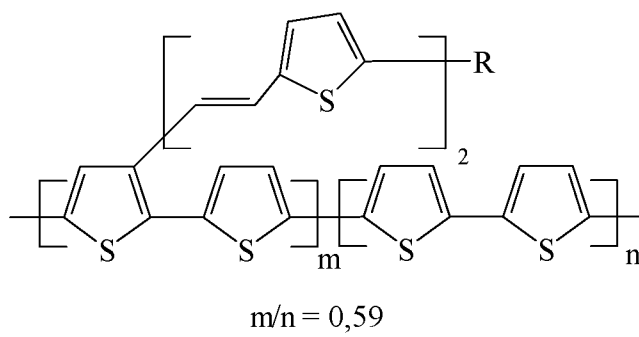
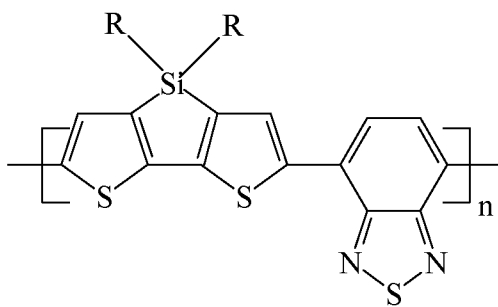
According to a further preferred embodiment of the  
 15 present invention, said photoactive organic polymer can be selected from poly(3-hexylthiophene) (P3HT); or from polymers having the following general formulae:

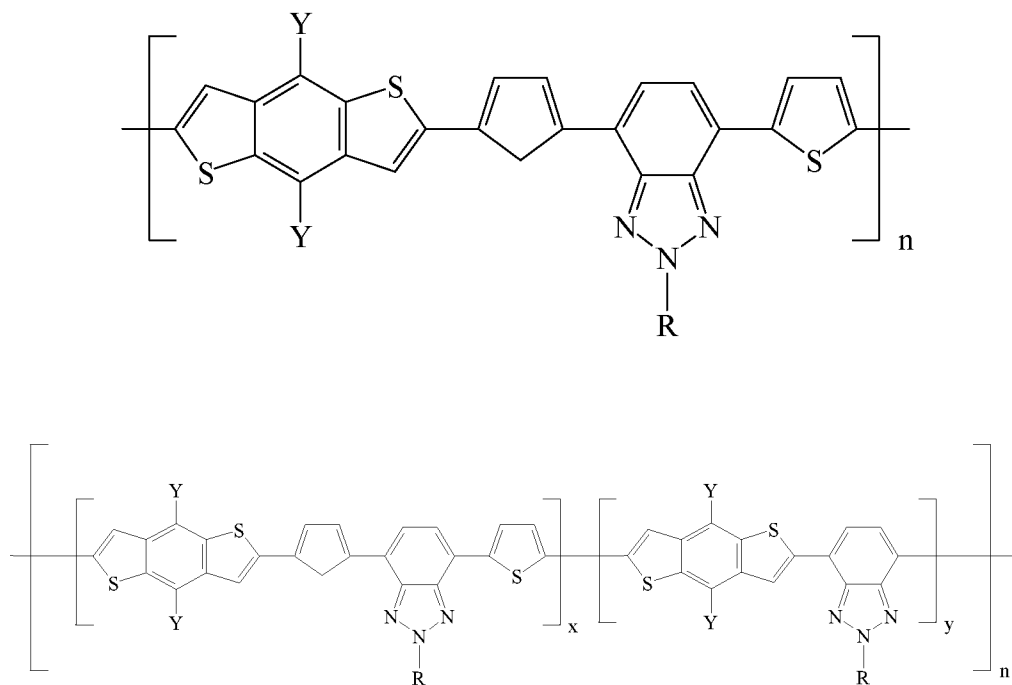




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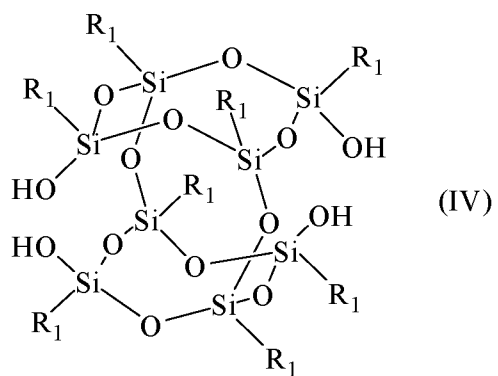
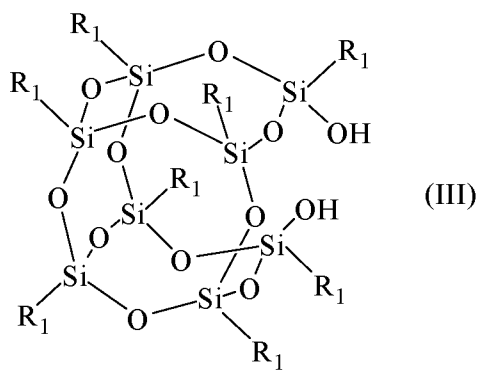
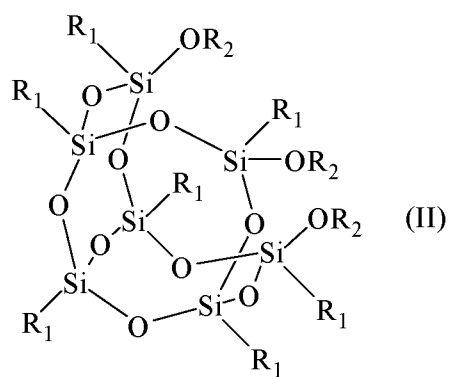
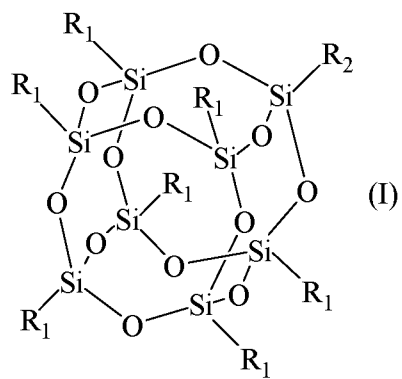


5 wherein R, equal to or different from each other, are selected from linear or branched C<sub>1</sub>-C<sub>20</sub>, preferably C<sub>6</sub>-C<sub>15</sub>, alkyl groups, Y, equal to or different from each other, are selected from -R or -OR groups, wherein R has the same meanings reported above, n and p are  
 10 integers ranging from 2 to 500, preferably from 5 to 100, extremes included, x+y = 1, x > 0.1 and y > 0.1; or mixtures thereof.

Poly(3-hexylthiophene) (P3HT) is preferred.

The polyhedral oligomeric silsesquioxanes (POSS)  
 15 can be represented by the general formula (R<sub>1</sub>)<sub>n</sub>(Si<sub>n</sub>O<sub>1.5n</sub>) wherein R<sub>1</sub> has the meanings reported hereunder and n is 6, 7, 8, 10, preferably 8.

According to a preferred embodiment of the present invention, said polyhedral oligomeric silsesquioxanes  
 20 (POSS) can be selected from those having general formula (I), (II), (III), (IV):



wherein:

- $R_1$  is a hydrogen atom, or is selected from linear or branched, preferably branched,  $C_1$ - $C_{20}$ , preferably  $C_3$ - $C_{12}$ , alkyl groups, optionally substituted with one or more halogen atoms such as, for example, chlorine, fluorine, bromine, iodine, preferably chlorine, fluorine, bromine;  $C_3$ - $C_8$  cycloalkyl groups; aryl groups; alkyl or aryl or N-alkylaryl- or cycloalkyl-amine groups; epoxy groups; carboxyl groups; amide groups; (meth)acrylate groups; olefinic groups; siloloxane groups having general formula  $-O-Si(R_3)_2R_4$  wherein  $R_3$  is selected from linear or branched  $C_1$ - $C_{20}$ , preferably  $C_3$ - $C_{12}$ , alkyl groups, and  $R_4$  is a hydrogen atom, or is selected from linear or branched  $C_1$ - $C_{20}$ , preferably  $C_3$ - $C_{12}$ , alkyl groups, alkenyl or cycloalkenyl groups, alkyl or cycloalkyl groups containing one or more oxygen atoms and/or one or more hydroxyl groups; polyethyleneglycol groups having general formula  $-CH_2-CH_2-(O-CH_2-CH_2)_n-O-CHR_5R_6$  wherein  $n$  is an integer ranging from 1 to 20, preferably from 1 to 14, and  $R_5$  and  $R_6$ , each independently, are a hydrogen atom, or are selected from linear or branched, preferably branched,  $C_1$ - $C_{20}$ , preferably  $C_3$ - $C_{12}$ , alkyl groups, optionally substituted with one or more halogen atoms such as, for example, chlorine, fluorine, bromine, iodine, preferably chlorine, fluorine, bromine;  $C_3$ - $C_8$  cycloalkyl groups; groups having general formula  $-O^{\ominus}N^+(R_7)_4$  wherein  $R_7$  is selected from linear or branched  $C_1$ - $C_{20}$ , preferably  $C_3$ - $C_{12}$ , alkyl groups;

- R<sub>2</sub> can be the same as R<sub>1</sub>, or is selected from linear or branched, preferably branched, C<sub>1</sub>-C<sub>20</sub>, preferably C<sub>3</sub>-C<sub>12</sub>, alkyl groups, optionally substituted with one or more cyano groups; mercapto-alkyl groups, hydroxyalkyloxy-(aryloxy-sulfonic acids)-alkyl groups; diol groups; imide-groups; norbornenyl groups;
- or in general formula (II), R<sub>2</sub> can be an alkaline metal, preferably lithium.

10       The term "C<sub>1</sub>-C<sub>20</sub> alkyl groups" indicates saturated aliphatic hydrocarbon radicals containing from 1 to 20 carbon atoms, linear or branched. Said alkyl groups can be optionally substituted with one or more halogen atoms, such as, for example, chlorine, fluorine, bromine, iodine, preferably chlorine, fluorine, bromine, or with one or more cyano groups. Specific examples of said C<sub>1</sub>-C<sub>20</sub> alkyl groups, optionally substituted, are: methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, *iso*-propyl, *iso*-butyl, *t*-butyl, neopentyl, 2-ethyleptyl, 2-ethylexyl, *iso*-octyl, trifluoropropyl, chloropropyl, dibromoethyl.

25       The term "C<sub>3</sub>-C<sub>8</sub> cycloalkyl groups" indicates cycloaliphatic hydrocarbon radicals containing from 3 to 8 carbon atoms. Specific examples of said C<sub>3</sub>-C<sub>8</sub> cycloalkyl groups are: cyclopropyl, cyclobutyl, cyclohexyl.

30       The term "aryl groups" indicates aromatic radicals containing 6, 10 or 14 carbon atoms in the conjugated aromatic system. Said aryl groups can optionally be substituted with one or more halogen atoms such as, for example, chlorine, fluorine, bromine, iodine,

preferably chlorine, or with one or more alkyl groups substituted with one or more halogen atoms. Specific examples of said aryl groups are benzyl, chlorobenzyl, chlorobenzylethyl, phenyl, naphthyl, phenylnaphthyl, anthracenyl.

The term "epoxy groups" indicates alkyl or cycloalkyl groups having from 2 to 12 carbon atoms and an epoxy group, and optionally containing one or more silicon atoms. Specific examples of epoxy groups are: epoxycyclohexyl, glycidyloxyethyl, glycidyloxypropyl, dimethylsilyloxyglycidyloxypropyl, dimethylsilyloxy-epoxycyclohexyl.

The term "olefinic groups" indicates alkyl or cycloalkyl groups containing at least one carbon-carbon double bond, said groups being optionally substituted with alkyl groups or alkoxy-silyl-oxy groups having from 2 to 10 carbon atoms. Specific examples of olefinic groups are: allyl, vinyl, dimethyl-silyloxy-cyclohexenyl, dimethyl-silyloxy-vinyl.

Specific examples of "siloloxane groups having general formula  $-O-Si(R_3)_2R_4$ " are: trimethylsilyloxyl, triethylsilyloxyl, tri-*iso*-propylsilyloxyl, dimethyl-*tert*-butylsilyloxyl, dimethylphenyloxyl, dimethylethyl-silyloxyl.

The term "alkenyl or cycloalkenyl groups" indicates unsaturated aliphatic or cycloaliphatic hydrocarbon radicals. Specific examples of alkenyl or cycloalkenyl groups are: ethenyl, propenyl, butenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl.

The term "alkyl- or aryl- or N-alkylaryl or cycloalkyl-amine groups" indicates alkyl-amino, aryl-

amino or cycloalkyl-amino groups having from 3 to 12 carbon atoms. Specific examples of said amine groups are: 3-aminopropyl, 3-(2-aminoethyl)aminopropyl, para-aminophenyl, meta-aminophenyl, N-phenylaminopropyl, N-methylaminopropyl.

The term "diol groups" indicates alkyl or cycloalkyl groups having from 3 to 12 carbon atoms and at least two oxygen atoms. Specific examples of said diol groups are: 3-(2,2-bis(hydroxymethyl)-butoxy)propyl)dimethylsiloxyl, 2-(cyclohexyl-3,4-diol)-ethyl, 3-(2,3-dihydroxypropyl)oxy)propyl.

The term "imide groups" indicates a residue obtained by removing a hydrogen atom bound to the nitrogen atom of an acidic amide, said residue having from 4 to 20 carbon atoms. Specific examples of acid imide groups are: maleimide, propyl-maleimide.

The term "(meth)acrylate groups" indicates acrylate or methacrylate groups having from 2 to 10 carbon atoms. Specific examples of (meth)acrylate groups are: ethyl(meth)acrylate, propyl(meth)acrylate.

The term "norbornene groups" indicates an unsaturated bicyclic group containing 7 carbon atoms, said group being optionally substituted with alkyl or alkoxy-silyl-oxyl or dialkylsilyl groups, having from 2 to 10 carbon atoms. Specific examples of norbornene groups are propylnorbornene, dimethylsilyl-oxyethylnorbornene.

The term "hydroxyalkyloxy-(aryloxy-sulfonic acids)-alkyl groups" indicates groups having formula  $-R_8-SO_2-OH$  wherein  $R_8$  is an aryl or heteroaryl group. A specific examples of sulfonic groups is 3-(3-(4-phenoxy-2-

hydroxypropoxy)propyl)dimethylsiloxy sulfonic acid.

The term "mercapto-alkyl groups" indicates groups having formula  $-R_{10}-SH$  wherein  $R_{10}$  is an alkyl group having from 1 to 20 carbon atoms. A specific example of  
5 thiol group is 3-mercaptopropyl.

The term "amide groups" indicates an organic group containing a nitrogen atom and a  $-COOH$  carboxyl group. Specific examples of amide groups are monoamide of maleic acid, monoamide of fumaric acid.

10 According to a preferred embodiment of the present invention, said polyhedral oligomeric silsesquioxanes (POSS) are selected from those having general formula (I) wherein  $R_1$  and  $R_2$ , the same as each other, are *iso*-butyl.

15 According to a further preferred embodiment of the present invention, said polyhedral oligomeric silsesquioxanes (POSS) are selected from those having general formula (II) wherein  $R_1$  is *iso*-butyl and  $R_2$  is hydroxyl.

20 According to a further preferred embodiment of the present invention, said polyhedral oligomeric silsesquioxanes (POSS) are selected from those having general formula (II) wherein  $R_1$  is *iso*-octyl and  $R_2$  is hydroxyl.

25 Polyhedral oligomeric silsesquioxanes (POSS) which can be advantageously used for the aim of the present invention, are, for example, the compounds known with the trade-name of OctaIsobutyl POSS<sup>®</sup> (MS0825), Isooctyl POSS<sup>®</sup> Cage Mixture (MS0805), TriSilanolIsobutyl POSS<sup>®</sup>  
30 (S01450), TriSilanolIsooctyl POSS<sup>®</sup> (S01455), TriSilanolPhenyl POSS<sup>®</sup> (S01458), of Hybrid Plastics.

According to a preferred embodiment of the present invention, said UV stabilizer can be present in the stabilized photoactive composition in a quantity ranging from 0.05% by weight to 3% by weight, preferably from 0.08% by weight to 2.5% by weight with respect to the total weight of said photoactive organic polymer.

According to a preferred embodiment of the present invention, said stabilized photoactive composition can comprise at least one fullerene ( $C_x$ ) wherein  $x$  represents an integer ranging from 50 to 250, preferably ranging from 60 to 90, and is more preferably 60, 70, 84, or a derivative thereof.

For the aim of the present description and of the following claims the term "fullerene" indicates a compound (e.g., a molecule) including a three-dimensional carbon skeleton, having a plurality of carbon atoms. The carbon skeleton of said fullerene generally forms a closed shell, which can have, for example, a spherical or semi-spherical form. Alternatively, the carbon skeleton can form a not completely closed structure, such as, for example, a tubular structure. Each carbon atom of said fullerene is generally bound to three adjacent carbon atoms, forming a tetrahedral network.

According to a preferred embodiment of the present invention, said fullerene is selected from derivatives of fullerene ( $C_{60}$  or  $C_{70}$ ), preferably [6,6]-phenyl- $C_{61}$ -methyl butyrate ([60]PCBM), phenyl- $C_{71}$ -methyl butyrate ([70]PCBM).

According to a preferred embodiment of the present

invention, the weight ratio between said fullerene and said photoactive organic polymer can range from 1:4 to 4:1, preferably from 1:2 to 2:1.

According to a further embodiment of the present invention said stabilized photoactive composition can comprise at least one carbon nanotube.

According to a further embodiment of the present invention, the weight ratio between said carbon nanotube and said photoactive organic polymer can range from 1:6 to 3:1, preferably from 1:3 to 2:1.

According to a further embodiment of the present invention, said stabilized photoactive composition can comprise at least one antioxidant.

According to a further embodiment of the present invention, said antioxidant can be selected from: 2',3-bis[3,5-di-t-butyl-4-hydroxyphenyl]propionyl]propionohydrazide [Irganox<sup>®</sup> MD 1024 (Ciba Specialty Chemicals)], triethyleneglycol bis-3-(t-butyl-4-hydroxy-5-methylphenyl)propionate [Irganox<sup>®</sup> 245 (Ciba Specialty Chemicals)], pentaerythritol tetrakis[3-(3,5-di-t-butyl-4-hydroxyhydroxyphenyl)]propionate [Irganox<sup>®</sup> 1010 (Ciba Specialty Chemicals)], octadecyl-3,5-di-t-butyl-4-hydroxyhydrocinnamate [Irganox<sup>®</sup> 1076 (Ciba Specialty Chemicals)], branched alkyl esters C<sub>7</sub>-C<sub>9</sub> of 3,5-di-t-4-hydroxyhydrocinnamic acid [Irganox<sup>®</sup> 1135 (Ciba Specialty Chemicals)], reaction product between N-phenylbenzeneamine and 2,4,4-trimethylpentene [Irganox<sup>®</sup> 5057 (Ciba Specialty Chemicals)], 1,3,5-tris-(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione [Cyanox<sup>®</sup> 1790 (Cytec Industries)], aryl phosphonite [Sandostab<sup>®</sup> P-EPQ

(Clariant Corp.)], tris-(2,4-di-t-butyl-phenyl)phosphite [Irgafos<sup>®</sup> 168 (Ciba Specialty Chemicals)], mixture of 1,3,5-tris-(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, tris-(2,4-di-t-butyl-phenyl)-phosphite 1:2 [Cyanox<sup>®</sup> 2777 (Cytec Industries)], or mixtures thereof.

Other antioxidants belonging to the group of sterically hindered phenols, which can be advantageously used for the aim of the present invention are: 2,6-di-t-butyl-4-methylphenol, 2,6-di-t-butyl-4-nonyl-phenol, 2,2'-methylene-bis-(4-methyl-6-t-butyl-phenol), 4,4'-butylidene-bis-(2-t-butyl-5-methyl-phenol), 4,4'-thio-bis-(2-t-butyl-5-methyl-phenol), 2,2'-thio-bis(6-t-butyl-4-methyl-phenol), 2,5-di-t-amyl-hydroquinone, polymeric sterically hindered phenols, tris-(3,5-di-t-butyl-4-hydroxybenzyl) isocyanurate, 2,2'-thiodiethyl bis-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, 1,1,3-tris-(2'-methyl-4'-hydroxy-5'-t-butyl-phenyl)butane, 2,2'-methylene-bis-6-(1-methylcyclohexyl)-para-cresol, 2,4-dimethyl-6-(1-methylcyclohexyl)-phenol, N,N'-hexamethylene bis-(3,5-di-t-butyl-4-hydroxy-hydrocinnamide), or mixtures thereof.

Other antioxidants belonging to the group of phosphites, which can be advantageously used for the aim of the present invention are: tris-(2,4-di-t-butyl-phenyl)phosphite, tris-(2,4-di-t-butyl-phenyl)phosphite plus distearyl-3,3-thiodipropionate (about 3% by weight with respect to the weight of the phosphite), bis-(2,4-di-t-butyl-phenyl) pentaerythritol-diphosphite,

tetrakis-(2,4-di-t-butyl-phenyl)-4,4'-biphenylene-  
diphosphonite, tris-(p-nonylphenyl)phosphite,  
diisodecyl-phenyl-phosphite, diphenyl-isodecyl-  
phosphite, triisodecyl-phosphite, trilauryl-phosphite,  
5 or mixtures thereof.

According to a further embodiment of the present invention, said antioxidant can be present in the stabilized photoactive composition in a quantity ranging from 0.005% by weight to 3% by weight,  
10 preferably from 0.05% by weight to 1% by weight, with respect to the total weight of said photoactive organic polymer.

According to a further embodiment of the present invention, said stabilized photoactive composition can  
15 optionally comprise at least one sterically hindered amine, such as, for example, Cyasorb® UV-3529 (Cytec Industries), Cyasorb® UV-3346 (Cytec Industries).

According to a further embodiment of the present invention, said sterically hindered amine can be  
20 present in the stabilized photoactive composition in a quantity ranging from 0% by weight to 3% by weight, preferably from 0.05% by weight to 1% by weight, with respect to the total weight of said photoactive organic polymer.

25 Said stabilized photoactive composition can be advantageously used in the construction of photovoltaic devices (or solar devices) such as, for example, photovoltaic cells (or solar cells) photovoltaic modules (or solar modules).

30 A further object of the present invention therefore relates to the use of said stabilized photoactive

composition in the construction of photovoltaic devices (or solar devices) such as, for example, photovoltaic cells (or solar cells), photovoltaic modules (or solar modules).

5        A further object of the present invention also relates to a photovoltaic device (or solar device) comprising the stabilized photoactive composition described above.

Some illustrative and non-limiting examples are provided hereunder for a better understanding of the present invention and for its practical embodiment.

#### EXAMPLE 1

Five different solutions were prepared:

- 15        - solution A: 15 mg of poly(3-hexylthiophene) (P3HT) (Aldrich, regioregular) were dissolved in 1 ml of 1,2-dichlorobenzene (four solutions A were prepared);
- 20        - solution B: 1.5 mg of TriSilanolPhenyl POSS<sup>®</sup> (S01458) (Hybrid Plastics) (POSS TSPH) were dissolved in 1 ml of 1,2-dichlorobenzene;
- 20        - solution C: 1.5 mg of TriSilanolIsobutyl POSS<sup>®</sup> (S01450) (Hybrid Plastics) (POSS TSIB) were dissolved in 1 ml of 1,2-dichlorobenzene;
- 25        - solution D: 1.5 mg of TriSilanolIsooctyl POSS<sup>®</sup> (S01455) (Hybrid Plastics) (POSS TSIO) were dissolved in 1 ml of 1,2-dichlorobenzene;
- 25        - solution E: 1.5 mg of OctaIsobutyl POSS<sup>®</sup> (MS0825) (Hybrid Plastics) (POSS IB) were dissolved in 1 ml of 1,2-dichlorobenzene.

30        990  $\mu$ l of solution A and 10  $\mu$ l of solution B were subsequently mixed, obtaining a solution in 1,2-

dichlorobenzene of poly(3-hexylthiophene) and TriSilanolPhenyl POSS<sup>®</sup> (S01458) [0.1% by weight with respect to the weight of poly(3-hexylthiophene)] (solution F).

5           990  $\mu$ l of solution A and 10  $\mu$ l of solution C were also mixed, obtaining a solution in 1,2-dichlorobenzene of poly(3-hexylthiophene) and TriSilanolIsobutyl POSS<sup>®</sup> (S01450) [0.1% by weight with respect to the weight of poly(3-hexylthiophene)] (solution G).

10           Furthermore, 990  $\mu$ l of solution A and 10  $\mu$ l of solution D were mixed, obtaining a solution in 1,2-dichlorobenzene of poly(3-hexylthiophene) and TriSilanolIsooctyl POSS<sup>®</sup> (S01455) [0.1% by weight with respect to the weight of poly(3-hexylthiophene)]  
15           (solution H).

          990  $\mu$ l of solution A and 10  $\mu$ l of solution E were also mixed, obtaining a solution in 1,2-dichlorobenzene of poly(3-hexylthiophene) and OctaIsobutyl POSS<sup>®</sup> (MS0825) [0.1% by weight with respect to the weight of  
20           poly(3-hexylthiophene)] (solution I).

          Furthermore, 800  $\mu$ l of solution A, 165  $\mu$ l of solution D and 35  $\mu$ l of 1,2-dichlorobenzene were mixed, obtaining a solution in 1,2-dichlorobenzene of poly(3-hexylthiophene) and TriSilanolIsooctyl POSS<sup>®</sup> (S01455)  
25           [2% by weight with respect to the weight of poly(3-hexylthiophene)] (solution L).

          Films were prepared from solutions F-L by means of spin-coating deposition (Spin Coater WS 400 6NPlite of Laurell Technologies) on an inert glass support,  
30           operating at 100 rpm, for 15 seconds, and subsequently at 500 rpm, for a further 15 seconds, in the air, at

room temperature (25°C), using 0.2 ml of each of the solutions F-L for each film.

The films obtained from the above solutions F-L, after evaporation of the solvent, proved to have an  
5 average thickness equal to about 0.5  $\mu\text{m}$  (the thickness was measured with a Dektak 150 Surface Profiler of Veeco Metrology).

For comparative purposes, proceeding analogously with spin-coating deposition (Spin Coater WS 400  
10 6NPlite of Laurell Technologies) on an inert glass support, a film was prepared from solution A operating at 100 rpm, for 15 seconds, and subsequently at 500 rpm, for a further 15 seconds, in the air, at room temperature (25°C), using 0.2 ml of solution A.

15 The film of poly(3-hexylthiophene) (P3HT) obtained from the above solution A, after evaporation of the solvent, proved to have an average thickness equal to about 0.5  $\mu\text{m}$  (the thickness was measured with a Dektak 150 Surface Profiler of Veeco Metrology).

20 The films obtained as described above were simultaneously subjected to accelerated aging in a Solar box3000e, equipped with an air-cooled Xenon lamp and with a UV SX05 Outdoor filter of CO.FO.ME.GRA, operating at 60°C, with an irradiance equal to 550 W/m<sup>2</sup>,  
25 over a range of 290 nm - 800 nm. Three samples were used for each of the solutions reported above, and the values of the absorbance variations in relation to the aging time are the average of the three single values obtained.

30 The degradation of the poly(3-hexylthiophene) (P3HT) was monitored by means of UV-Vis transmission

spectrophotometry, collecting the films to be analyzed at pre-established time intervals from the Solar box3000e.

The UV-Vis absorption spectra (290 nm - 800 nm) were recorded with a Perkin Elmer  $\lambda$  950 double-beam UV-Vis-NIR spectrophotometer and double monochromator, with a bandwidth of 2.0 nm and step of 1 nm.

In the films subjected to accelerated aging, the UV-Vis absorption spectrophotometry allowed the decrease in absorbance in the visible region to be monitored, as reported in Figure 1 [the absorbance (A) is reported in the ordinate, the wave-length ( $\lambda$ ) in nm is reported in the abscissa] indicating the lesser conjugation extension of the system following degradation of the polymeric backbone, i.e. backbone of poly(3-hexylthiophene) (P3HT).

The decrease in absorbance in the visible region was also monitored by means of UV-Vis absorption spectrophotometry as reported in Figure 2 [the ratio between the absorbance at time t ( $A_t$ ) and the absorbance at time 0 ( $A_0$ ) is reported in the ordinate, the time (t) in hours (h) is reported in the abscissa] of the film comprising poly(3-hexylthiophene) (P3HT) alone obtained from solution A, as also that of the films comprising the photoactive compositions object of the present invention, i.e. the films obtained from solutions F-L. Three samples were used for each of said solutions, and the values in the absorbance variations in relation to the aging time are the average of the three single values obtained. In particular, the absorbance values ( $A_t$ ) and ( $A_0$ ) reported in Figure 2, are the average of

the absorbance values measured for the above three samples, at time t and at time zero respectively, for the peaks at 520 nm, 540 nm and 600 nm.

The results reported in Figure 2 show that, in these particularly thin films, after 60 hours of accelerated aging in a Solar Box, the poly(3-hexylthiophene) (P3HT) film obtained from the above solution A is almost completely degraded (P3HT), whereas the films comprising the stabilized photoactive compositions object of the present invention, i.e. the films obtained from the above solutions H and G still have a relative absorbance equal to: about 20% and about 40% (film obtained from the above solution I), about 35% (film obtained from the above solution F), about 50% (film obtained from the above solution L), of the initial value of the respective non-aged films.

#### EXAMPLE 2

Two different solutions were prepared:

- solution A1: 15 mg of poly(3-hexylthiophene) (P3HT) (Aldrich, regioregular) and 12 mg of fullerene (C60) (PCBM) (purity > 99.5%; Aldrich), were dissolved in 1 ml of 1,2-dichlorobenzene;
- solution B1: 1.5 mg of TriSilanolIsobutyl POSS<sup>®</sup> (S01450) (Hybrid Plastics) (POSS TSIB) were dissolved in 1 ml of 1,2-dichlorobenzene.

990 µl of solution A1 and 10 µl of solution B1 were subsequently mixed, obtaining a solution in 1,2-dichlorobenzene of poly(3-hexylthiophene), fullerene (C60) and TriSilanolIsobutyl POSS<sup>®</sup> (S01450) [0.1% by weight with respect to the weight of poly(3-hexylthiophene)] (solution C1).

800  $\mu$ l of solution A1, 165  $\mu$ l of solution B1 and 35  $\mu$ l of 1,2-dichlorobenzene were also mixed, obtaining a solution in 1,2-dichlorobenzene of poly(3-hexylthiophene), fullerene (C60) and TriSilanolIsobutyl POSS<sup>®</sup> (S01450) [2% by weight with respect to the weight of poly(3-hexylthiophene)] (solution D1).

Films were prepared from solutions C1-D1 by means of spin-coating deposition (Spin Coater WS 400 6NPlite of Laurell Technologies) on an inert glass support, operating at 100 rpm, for 15 seconds, and subsequently at 500 rpm, for a further 15 seconds, in the air, at room temperature (25°C), using 0.2 ml of each of the solutions C1-D1 for each film.

The films obtained from the above solutions C1-D1, after evaporation of the solvent, proved to have an average thickness equal to about 0.5  $\mu$ m (the thickness was measured with a Dektak 150 Surface Profiler of Veeco Metrology).

For comparative purposes, proceeding analogously with spin-coating deposition (Spin Coater WS 400 6NPlite of Laurell Technologies) on an inert glass support, a film was prepared from solution A1 operating at 100 rpm, for 15 seconds, and subsequently at 500 rpm, for a further 15 seconds, in the air, at room temperature (25°C), using 0.2 ml of solution A1.

The film of poly(3-hexylthiophene) (P3HT) obtained from the above solution A1, after evaporation of the solvent, proved to have an average thickness equal to about 0.5  $\mu$ m (the thickness was measured with a Dektak 150 Surface Profiler of Veeco Metrology).

The films obtained as described above were

simultaneously subjected to accelerated aging in a Solar box3000e, equipped with an air-cooled Xenon lamp and with a UV SX05 Outdoor filter of CO.FO.ME.GRA, operating at 60°C, with an irradiance equal to 550 W/m<sup>2</sup>,  
5 over a range of 290 nm - 800 nm.

The decrease in absorbance in the visible region was monitored by means of UV-Vis absorption spectrophotometry, as reported in Figure 3 [the ratio between the absorbance at time t ( $A_t$ ) and the absorbance  
10 at time 0 ( $A_0$ ) is reported in the ordinate, the time (t) in hours (h) is reported in the abscissa] of the film comprising poly(3-hexylthiophene) (P3HT) alone obtained from solution A1 as also that of the films comprising the photoactive compositions object of the present  
15 invention, i.e. the films obtained from solutions C1-D1. Three samples were used for each of these solutions, and the values in the absorbance variations in relation to the aging time are the average of the three single values obtained. In particular, the  
20 absorbance values ( $A_t$ ) and ( $A_0$ ) reported in Figure 3, are the average of the absorbance values measured for the above three samples, at time t and at time zero respectively, for the peaks at 520 nm, 540 nm and 600 nm.

25 The results reported in Figure 3 show that, in these particularly thin films, after about 650 hours of accelerated aging in a Solar Box, the film of poly(3-hexylthiophene) (P3HT) and fullerene (C60) obtained from the above solution A1 still has a relative  
30 absorbance equal to about 25% of the initial value of the respective non-aged film, whereas the films

comprising the stabilized photoactive compositions  
object of the present invention, i.e. the films  
obtained from the above solutions C1 and D1, have a  
relative absorbance equal to: about 38% (film obtained  
5 from the above solution C1), about 38% (film obtained  
from the above solution D1), of the initial value of  
the respective non-aged films.

## CLAIMS

1. A stabilized photoactive composition comprising:

- at least one photoactive organic polymer;
- at least one UV stabilizer selected from

5 polyhedral oligomeric silsesquioxanes (POSS).

2. The stabilized photoactive composition according to claim 1, wherein said photoactive organic polymer is selected from:

(a) polythiophenes such as poly(3-hexylthiophene)

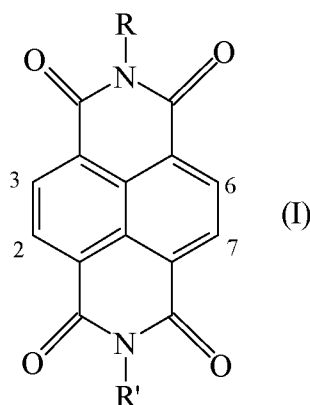
10 (P3HT), poly(3-octylthiophene), poly(3,4-ethylenedioxythiophene), or mixtures thereof;

(b) polyphenylenevinylenes such as poly(2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene,

15 poly(paraphenylenevinylene), {(poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene]-alt-(vinylene)} (MDMO-PPV), or mixtures thereof;

(c) alternating conjugated polymers comprising:

- naphthalene diimide units (A) having general formula (I):



20

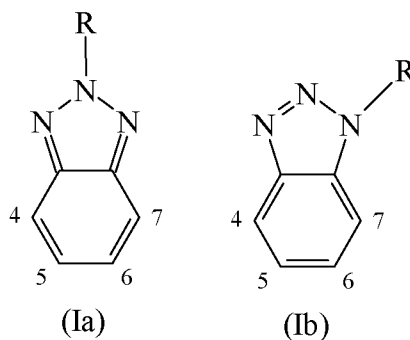
wherein R and R', equal to or different from each other, are selected from linear or branched alkyl groups containing from 1 to 36 carbon atoms, or from aryl groups, said aryl groups

being optionally substituted with alkyl radicals having from 1 to 24 carbon atoms;

- at least one conjugated electron-donor structural unit (B), in which the unit (A) is connected to the unit (B), in the alternating copolymer, in any of the positions 2, 3, 6 or 7;

(d) alternating or statistic conjugated copolymers comprising:

- at least one benzotriazole unit (B) having general formula (Ia) or (Ib)

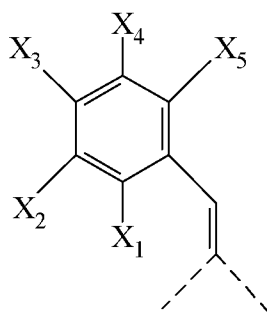


wherein the group R is selected from alkyl groups, aryl groups, acyl groups, thioacyl groups, said alkyl, aryl, acyl and thioacyl groups being optionally substituted;

- at least one conjugated structural unit (A) wherein each unit (B) is connected to at least one unit (A) in any of the positions 4, 5, 6 or 7;

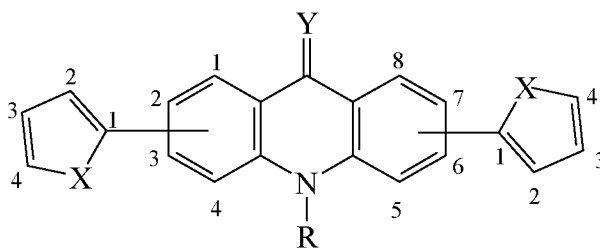
(e) alternating  $\pi$ -conjugated polymers comprising:

- at least one fluoroarylvinylidene electron-acceptor unit (A) having general formula (III):



(III)

- wherein the substituents  $X_1$ - $X_5$ , equal to or different from each other, are selected from hydrogen, fluorine, or from alkyl groups containing from 1 to 12 carbon atoms, and on the condition that at least one of the substituents  $X_1$ - $X_5$  is fluorine, or a  $-CF_2R$  group, wherein R is selected from hydrogen, fluorine, or hydrocarbon groups having from 1 to 10 carbon atoms, said hydrocarbon groups being optionally fluorinated;
- at least one conjugated electron-donor structural unit (B) connected to unit (A) in the points indicated by the dashed lines in general formula (III);
- (f) copolymers based on acridon units comprising:
- one monomeric unit (A) having general formula (IV):

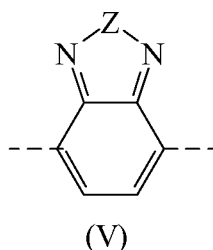


(IV)

wherein X is selected from sulfur, selenium; Y

is selected from oxygen, sulfur, or from -NR' groups; R and R', equal to or different from each other, are organic substituents having from 1 to 24 carbon atoms selected from alkyl groups, aryl groups, said alkyl groups being optionally substituted, acyl groups, thioacyl groups;

- at least one monomeric unit (B) having general formula (V):



wherein Z is selected from O, S, Se or from -NR'' groups wherein R'' is an organic substituent having from 1 to 24 carbon atoms selected from alkyl groups, aryl groups, said alkyl and aryl groups being optionally substituted, acyl groups, thioacyl groups; said monomeric unit (B) being connected to any available position of a heteroaromatic side-ring of unit (A), through one of the two positions indicated by the dashed lines in general formula (V);

(g) alternating conjugated copolymers comprising benzothiadiazole units such as PCDTBT {poly[N-9''-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazaole]}}, PCPDTBT {poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazaole)]};

(h) alternating conjugated copolymers comprising

thieno[3,4-b]pyrazidine units;

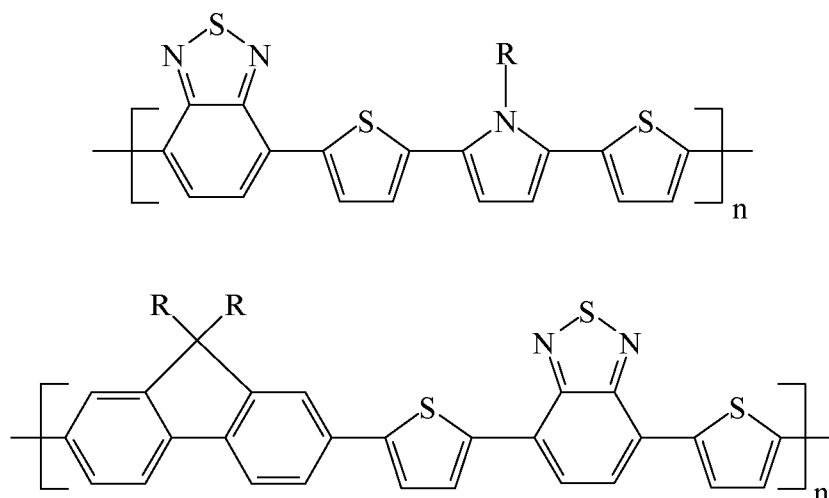
(i) alternating conjugated copolymers comprising quinoxaline units;

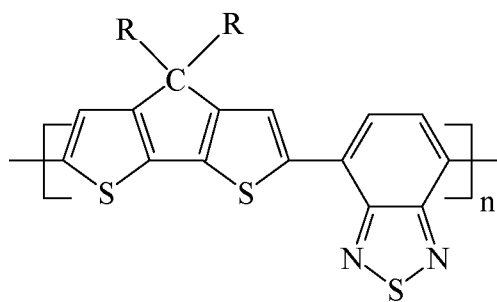
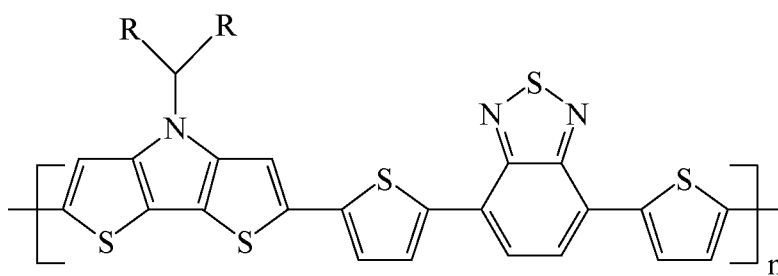
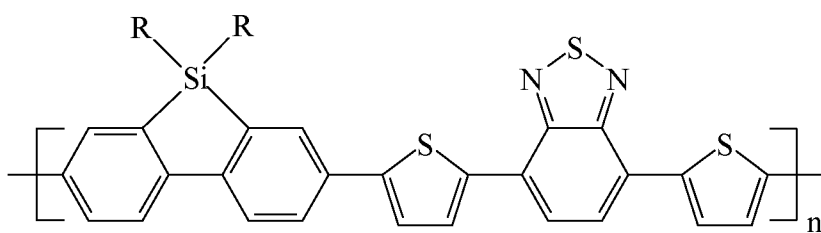
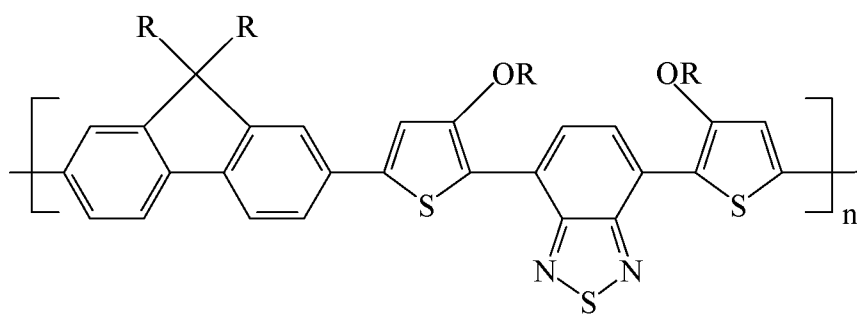
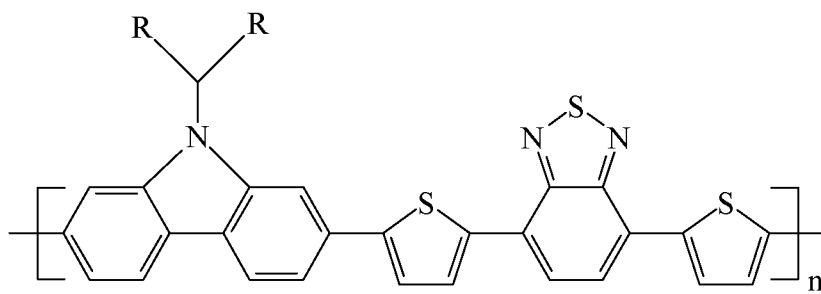
5 (l) alternating conjugated copolymers comprising silole monomeric units such as copolymers of 9,9-dialkyl-9-silafluorene;

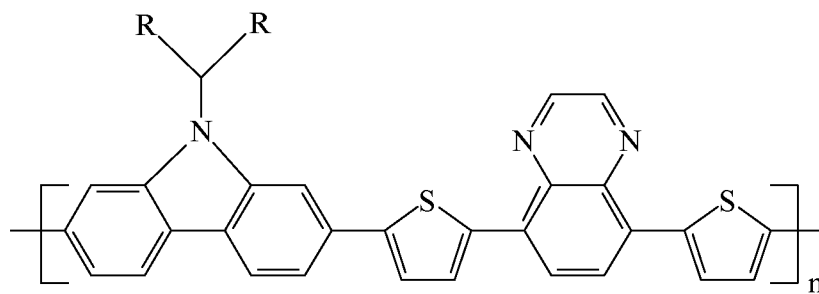
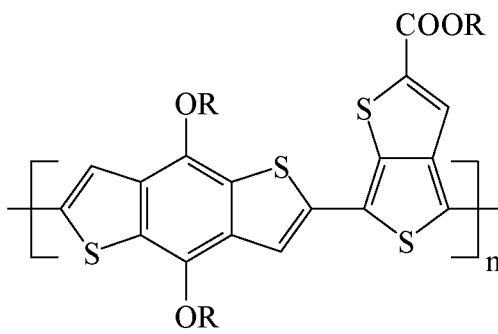
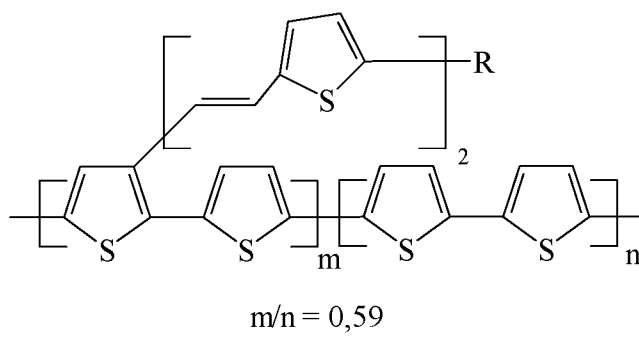
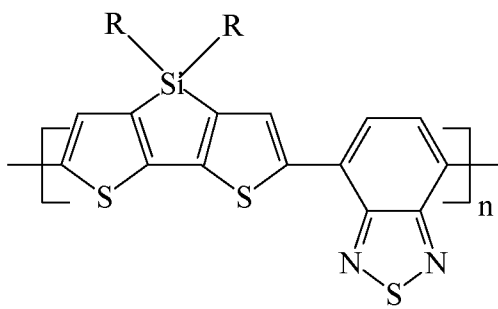
(m) alternating conjugated copolymers comprising condensed thiophene units such as copolymers of thieno[3,4-b]thiophene and benzo[1,2-b:4,5-b']dithiophene;

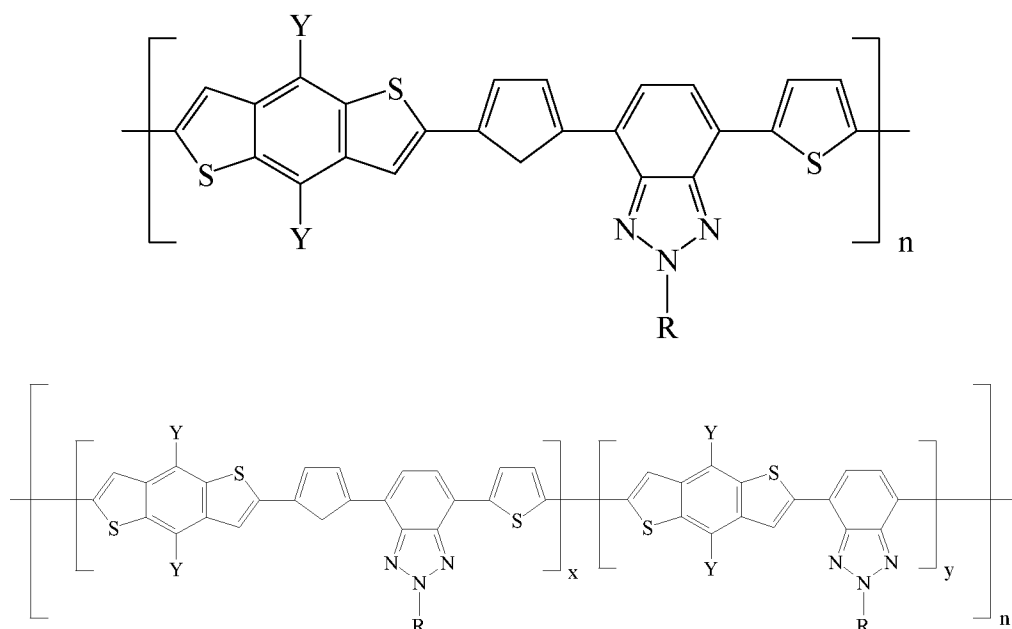
or mixtures thereof.

3. The stabilized photoactive composition according to claim 1 or 2, wherein said photoactive organic polymer is selected from poly(3-hexylthiophene); or  
15 from polymers having the following general formulae:





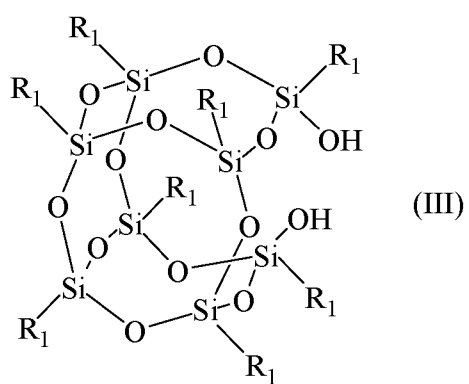
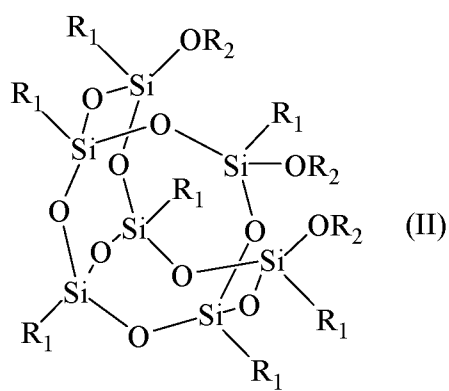
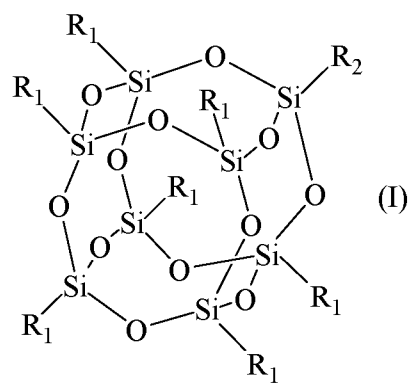


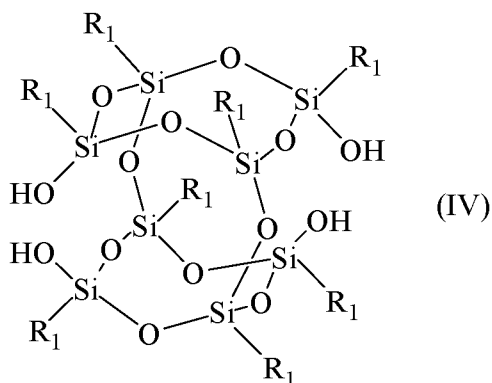


wherein R, equal to or different from each other, are  
 5 selected from linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl groups, Y,  
 equal to or different from each other, are selected  
 from -R or -OR groups, wherein R has the same meanings  
 reported above, n and p are integers ranging from 2 to  
 500, extremes included, x+y = 1, x > 0.1 and y > 0.1; or  
 10 mixtures thereof.

4. The stabilized photoactive composition according  
 to claim 3, wherein said photoactive organic polymer is  
 poly(3-hexylthiophene) (P3HT).

5. The stabilized photoactive composition according  
 15 to any of the previous claims, wherein said polyhedral  
 oligomeric silsesquioxanes (POSS) are selected from  
 those having general formula (I), (II), (III), (IV):





wherein:

- R<sub>1</sub> is a hydrogen atom, or is selected from linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl groups, optionally substituted with one or more halogen atoms such as chlorine, fluorine, bromine, iodine; C<sub>3</sub>-C<sub>8</sub> cycloalkyl groups; aryl groups; alkyl or aryl or N-alkylaryl- or cycloalkylamine groups; epoxy groups; carboxyl groups; amide groups; (meth)acrylate groups; olefin groups; siloloxane groups having general formula -O-Si(R<sub>3</sub>)<sub>2</sub>R<sub>4</sub> wherein R<sub>3</sub> is selected from linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl groups and R<sub>4</sub> is a hydrogen atom, or is selected from linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl groups, alkenyl or cycloalkenyl groups, alkyl or cycloalkyl groups containing one or more oxygen atom and/or one or more hydroxyl groups; polyethylene glycol groups having general formula -CH<sub>2</sub>-CH<sub>2</sub>-(O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>n</sub>-O-CHR<sub>5</sub>R<sub>6</sub> wherein n is an integer ranging from 1 to 20, and R<sub>5</sub> and R<sub>6</sub>, each independently, are a hydrogen atom, or are selected from linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl groups, optionally substituted with one or more halogen atoms such as chlorine, fluorine, bromine, iodine; C<sub>3</sub>-C<sub>8</sub> cycloalkyl groups; groups having general

formula  $-O^-N^+(R_7)_4$  wherein  $R_7$  is selected from linear or branched  $C_1$ - $C_{20}$  alkyl groups;

- $R_2$  can be the same as  $R_1$ , or is selected from linear or branched  $C_1$ - $C_{20}$  alkyl groups, optionally substituted with one or more cyano groups; mercapto-alkyl groups, hydroxyalkyloxy-(aryloxy-sulfonic acids)-alkyl groups; diol groups; imide-groups; norbornenyl groups;
- or in general formula (II),  $R_2$  can be an alkaline metal, preferably lithium.

6. The stabilized photoactive composition according to claim 5, wherein said polyhedral oligomeric silsesquioxanes (POSS) are selected from those having general formula (I) wherein  $R_1$  and  $R_2$ , the same as each other, are *iso*-butyl.

7. The stabilized photoactive composition according to claim 5, wherein said polyhedral oligomeric silsesquioxanes (POSS) are selected from those having general formula (II) wherein  $R_1$  is *iso*-butyl and  $R_2$  is hydroxyl.

8. The stabilized photoactive composition according to claim 5, wherein said polyhedral oligomeric silsesquioxanes (POSS) are selected from those having general formula (II) wherein  $R_1$  is *iso*-octyl and  $R_2$  is hydroxyl.

9. The stabilized photoactive composition according to any of the previous claims, wherein said UV stabilizer is present in the stabilized photoactive composition in an amount ranging from 0.05% by weight to 3% by weight with respect to the total weight of the photoactive organic polymer.

10. The stabilized photoactive composition according to any of the previous claims, wherein said stabilized photoactive composition comprises at least one fullerene ( $C_x$ ) wherein x represents an integer ranging from 50 to 250.

11. The stabilized photoactive composition according to claim 10, wherein said fullerene is selected from derivatives of fullerene ( $C_{60}$  or  $C_{70}$ ), preferably [6,6]-phenyl- $C_{61}$ -methylbutyrate([60]PCBM), phenyl- $C_{71}$ -methylbutyrate ([70]PCBM).

12. The stabilized photoactive composition according to claim 10 or 11, wherein the weight ratio between said fullerene and said photoactive organic polymer ranges from 1:4 to 4:1.

13. The stabilized photoactive composition according to any of the previous claims, wherein said photoactive stabilized composition comprises at least one carbon nanotube.

14. The stabilized photoactive composition according to claim 13, wherein the weight ratio between said carbon nanotube and said photoactive organic polymer ranges from 1:6 to 3:1.

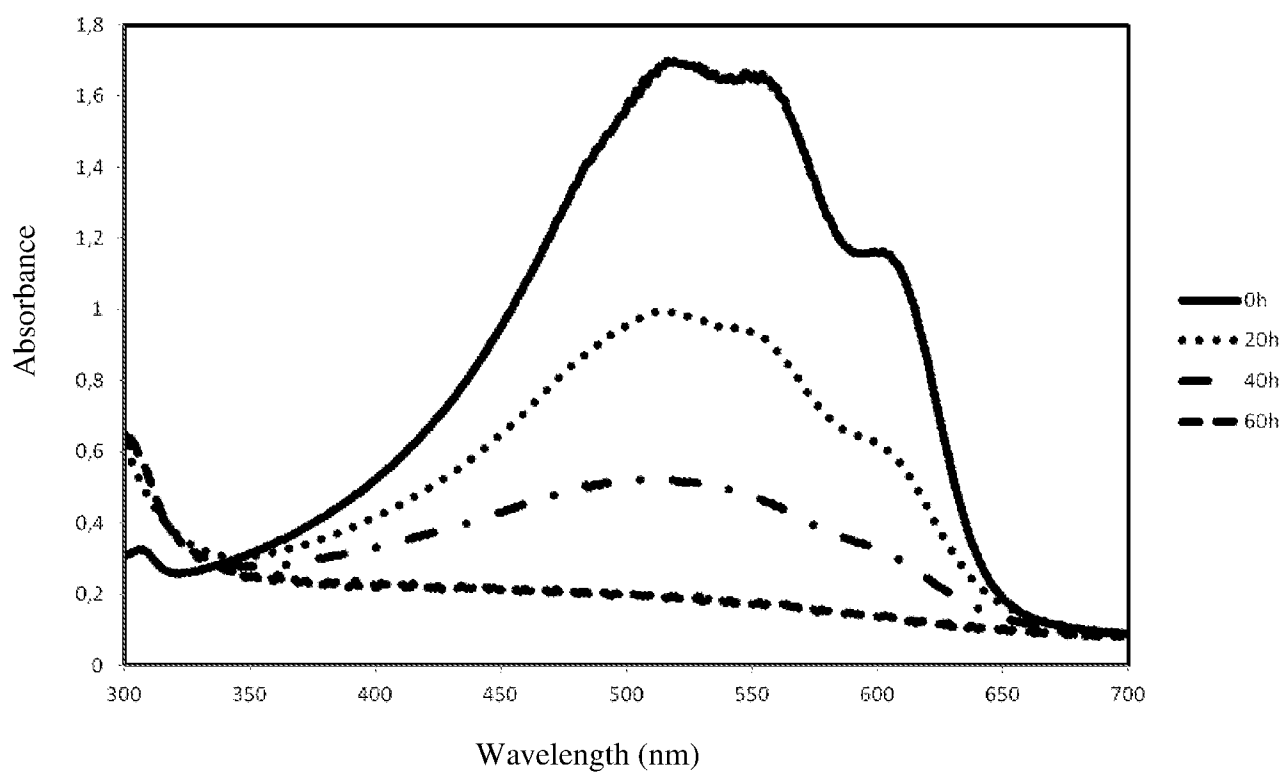
15. The stabilized photoactive composition according to any of the previous claims, wherein said stabilized photoactive composition comprises at least one antioxidant.

16. The stabilized photoactive composition according to claim 15, wherein said antioxidant is present in the stabilized photoactive composition in an amount ranging from 0.005% by weight to 3% by weight with respect to the total weight of said photoactive organic polymer.

17. The stabilized photoactive composition according to any of the previous claims, wherein said stabilized photoactive composition comprises at least one sterically hindered amine.
- 5 18. The stabilized photoactive composition according to claim 17, wherein said sterically hindered amine is present in the stabilized photoactive composition in an amount ranging from 0% by weight to 3% by weight with respect to the total weight of said photoactive organic  
10 polymer.
19. Use of the stabilized photoactive composition according to any of the previous claims in the construction of photovoltaic devices (or solar devices) such as photovoltaic cells (or solar cells),  
15 photovoltaic modules (or solar modules).
20. A photovoltaic device (or solar device) comprising the stabilized photoactive composition according to any of the claims from 1 to 18.

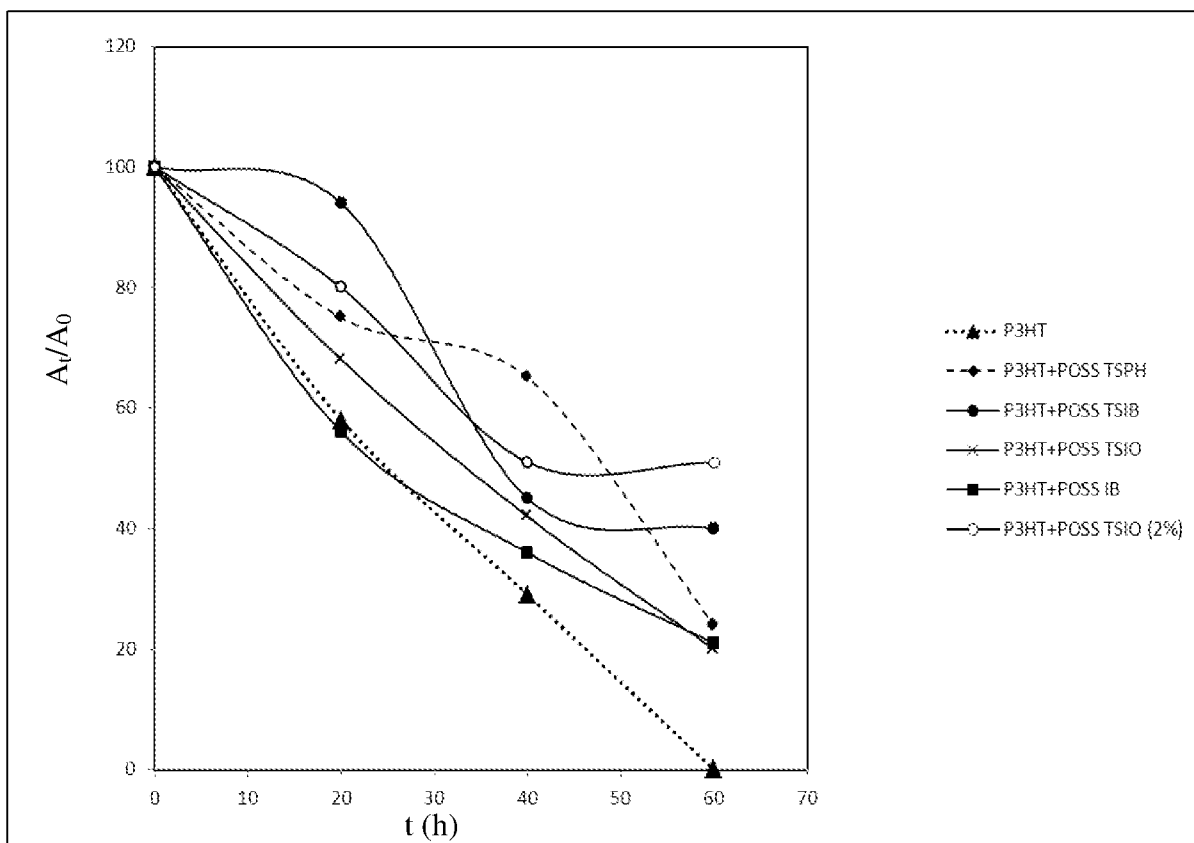
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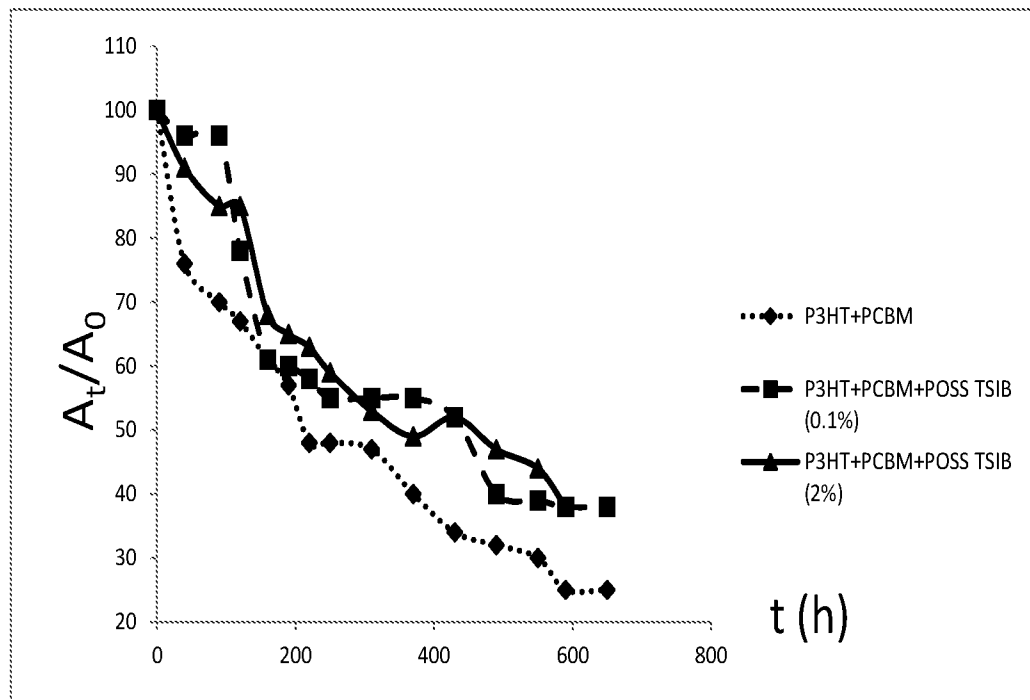
**Figure 1** - Evolution of the UV-Vis spectra of the poly(3-hexylthiophene) (P3HT) film obtained from solution A (average thickness of the film equal to 0.5  $\mu\text{m}$ ) following accelerated aging in a Solar box 3000 and for the hours indicated.

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**Figure 2** - Accelerated aging in a Solar box 3000 of the films (average thickness of the film equal to 0.5  $\mu\text{m}$ ) of: P3HT obtained from solution A; P3HT + POSS TSPH obtained from solution F; P3HT + POSS TSIB obtained from solution G; P3HT + POSS TSIO obtained from solution H; P3HT + POSS IB obtained from solution I; P3HT + POSS TSIO obtained from solution L.

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**Figure 3** - Accelerated aging in a Solar box 3000 of the film (average thickness of the film equal to 0.5  $\mu\text{m}$ ) of: P3HT + PCBM obtained from solution A1; P3HT + PCBM + POSS TSIB obtained from solution C1; P3HT + PCBM + POSS TSIB obtained from solution D1.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2014/061633

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K11/06 C08G61/12 C08G65/34 C08G77/00 H01B1/00  
H01L51/50 H05B33/14

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)

C09K C08G H01B H01L H05B

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, BEILSTEIN Data, CHEM ABS Data, PAJ, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/204038 A1 (XIAO STEVEN [CA] ET AL) 30 October 2003 (2003-10-30) paragraph [0001] - paragraph [0088]; claims 1-18; examples -----	1-20
X	JP 2003 330145 A (KONICA MINOLTA HOLDINGS INC) 19 November 2003 (2003-11-19) the whole document -----	1-20
X	US 5 721 299 A (ANGELOPOULOS MARIE [US] ET AL) 24 February 1998 (1998-02-24) column 1, line 15 - column 11, line 51; claims 1-24; examples -----	1-20
X	US 2007/138483 A1 (LEE TAE-WOO [KR] ET AL) 21 June 2007 (2007-06-21) paragraph [0001] - paragraph [0103]; claims 1-26; examples ----- -/--	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

8 August 2014

Date of mailing of the international search report

18/08/2014

Name and mailing address of the ISA/

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# INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2014/061633

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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