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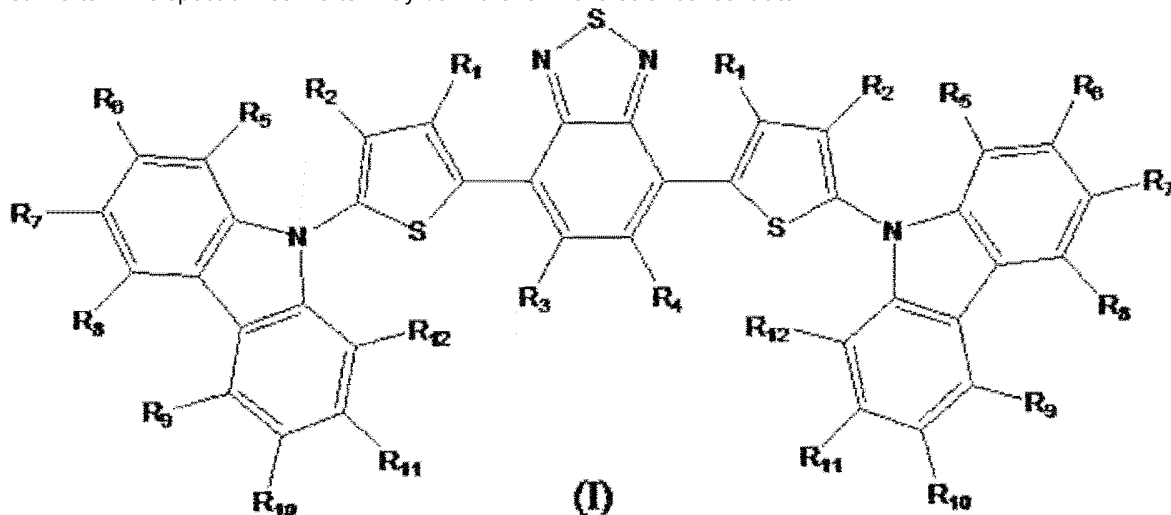
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WO 2011/060526 A1 US 20060052612 A1
Journal of Polymer Science Part A: Polymer
Chemistry, vol. 47, no. 1, 2009, Ping et al., "Synthesis
and properties of monodisperse multi-triarylamine-
substituted oligothiophenes and 4,7-bis(2'-
oligothienyl)-2,1,3-benzothiadiazoles for organic solar
cell applications", pp. 137-148.

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(54) Title of the Invention: **Luminescent compounds for spectrum converters**
Abstract Title: **Luminescent compounds for spectrum converters**

(57) Benzothiadiazole compounds according to Formula (I), where each group $R_1 - R_{12}$ is independently selected from H, linear or branched alkyl, cycloalkyl, aryl, alkyl-aryl, alkoxy, substituted alkoxy and/or at least one pair of groups chosen from $R_1 - R_{12}$ forms, together with the carbon atoms to which said groups are bound, define an aliphatic or aromatic cyclic or polycyclic system, optionally comprising one or more heteroatoms. Preferably, all groups $R_1 - R_{12}$ are H. Also claimed is a process for preparing compounds according to Formula (I) comprising the step of reacting a compound according to Formula (II) with a 4,7-dihalo-2,1,3-benzothiadiazole according to Formula (III). Preferably the reaction is performed in the presence of a palladium-containing catalyst. Also claimed are: the use of one or more compounds according to Formula (I) as fluorescent materials in spectrum converters; a spectrum converter comprising one or more compounds according to Formula (I); and a solar device comprising a spectrum converter. The spectrum converter may be in the form of a solar concentrator.



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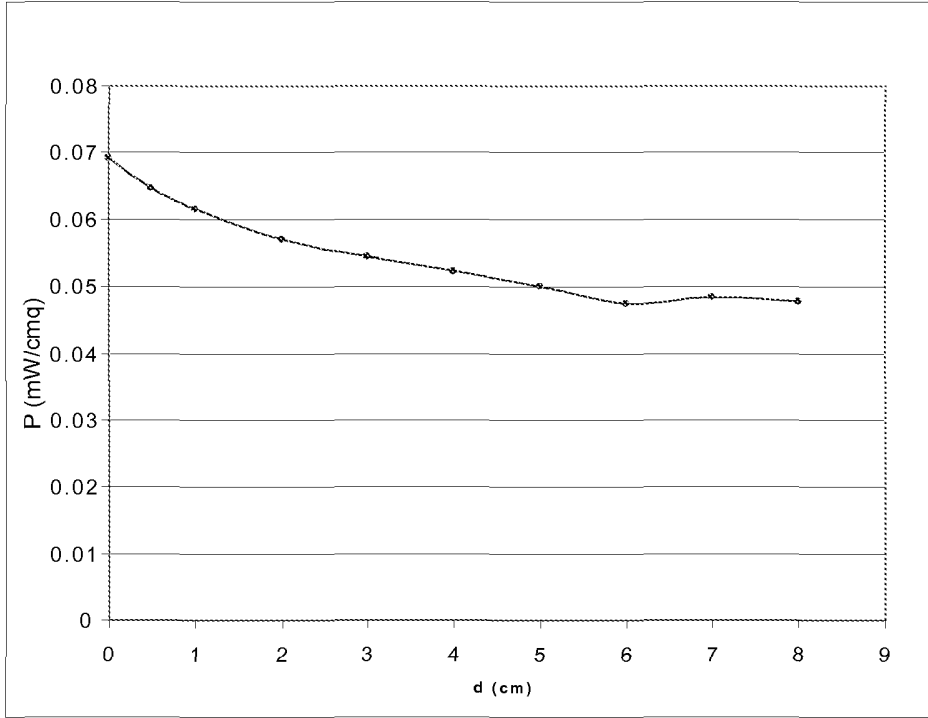


Figure 1

LUMINESCENT COMPOUNDS FOR SPECTRUM CONVERTERS

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Description

The invention refers to new benzothiadiazole compounds having general formula (I), to the preparation process thereof, as well as to the corresponding use as luminescent compounds in spectrum converters. Spectrum converters comprising said luminescent compounds and solar devices comprising such spectrum converters are also described.

It is known that photovoltaic cells, including silicon ones which are currently the most widespread ones on the market, are not capable of effectively exploiting the entire solar radiation. The maximum efficiency thereof is limited to a spectrum range which partly comprises visible radiation and partly infrared radiation. In order to improve cell efficiency, spectrum-converting materials may be used, which capture the solar radiation outside the optimal spectrum range and convert the same into effective radiation. Moreover, luminescent solar concentrators may be manufactured by using such materials, which concentrators allow to further increase the production of electric current of the cells. These concentrators consist of large sheets of a material transparent to solar radiation, within which fluorescent agents are dispersed which act as spectrum converters. Due to the optic phenomenon of total reflection, the radiation generated by the fluorescent molecules is "guided" towards the thin edges of the sheet where it is concentrated onto solar cells located there. Thereby large surfaces of low-cost materials (said photo-luminescent sheets) may be used to concentrate light onto small surfaces of high-cost materials (said solar cells).

A fluorescent agent to be employed as solar converter, and particularly for the use in luminescent solar concentrators, should be provided with different features which not always are easily mutually compatible:

- A. firstly, the frequency of the radiation emitted by fluorescence must be above the threshold below which the semiconductor, which makes up the core of the photovoltaic cell, is no longer able to operate;
- B. secondly, the absorption spectrum of the fluorescent agent should be as wide as possible, so as to absorb most of the incident solar radiation, to then emit it back at the desired frequency;
- C. moreover, it is desirable for the absorption of the solar radiation to be very high, so that the agent may perform its function at the lowest possible concentrations, avoiding the use thereof in large amounts;
- D. the process of solar radiation absorption and of its subsequent back-emission at lower frequencies must take place with the highest possible efficiency, minimising the so-called non-radiative losses, often referred to by the term "thermalisation": the efficiency of the process is measured by the quantum efficiency thereof;
- E. finally it is necessary that absorption and emission frequencies are as different as possible, because otherwise the radiation emitted by a molecule of fluorescent agent would be absorbed and, at least in part, diffused by adjacent molecules. This phenomenon, normally indicated as self-absorption, inevitably implies significant efficiency

losses. The difference between the frequencies of the lowest-frequency peak of the absorption spectrum and that of the peak of the emitted radiation is normally indicated as Stokes shift and measured in nm (i.e., not the difference between the two frequencies is measured, but between the two respective wavelengths). High Stokes shifts are definitely necessary to obtain high efficiency rates of the converters, and in particular of the concentrators, save for the previously described requirement that the emitted radiation frequency be in any case higher than the threshold below which the photovoltaic cell is unable to operate.

It is known that some benzothiadiazole materials, and in particular 4,7-di-2-thienyl-2,1,3-benzothiadiazole (DTB), are precisely fluorescent agents usable as spectrum-converting materials in luminescent solar concentrators. Materials of this type are described for example in Italian patent application n° MI2009A001796.

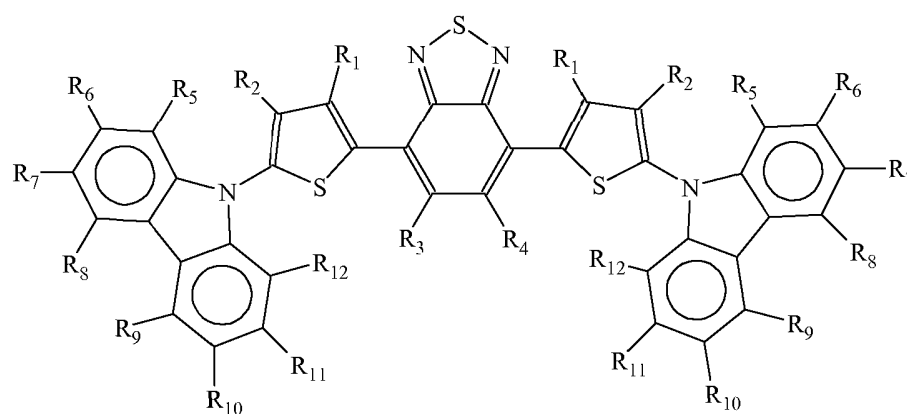
DTB is characterised by an emission centred around 579 nm, a value which corresponds to an energy rate well above the minimum operational threshold of photovoltaic cells, which threshold, for example, corresponds to a wavelength of about 1100 nm for the largest widespread silicon-based cells. Moreover, the light radiation absorption thereof is high and extended across a relatively large wavelength range, approximately comprised between 550 nm (the wavelength of green radiation) and ultraviolet. Finally, DTB displays a Stokes shift equal, in solution, to 133 nm, far higher than those of most of the commercial products proposed so far for the use in luminescent solar concentrators.

For these reasons, the use of DTB has made possible the manufacturing of excellent-quality, luminescent solar concentrators.

However, DTB, despite absorbing a significant part of the solar spectrum, displays a poor absorption level in the longest-wavelength regions, corresponding to the yellow and red radiations which, therefore, cannot be converted into other radiations, more effectively exploitable by the photovoltaic cell. For this reason it would be desirable to have fluorescent products with an absorption spectrum more extended towards red.

New benzothiadiazole compounds have now been found having excellent performances concerning the aspects described above at points (A), (C), (D) and (E), as far as regards frequency features of the emitted radiations, absorption intensity, absorption efficiency and back-emission, adequate difference between absorption and emission frequencies, where said new compounds have an absorption spectrum much more extended towards red than known benzothiadiazole compounds.

A first object of the present invention concern hence benzothiadiazole compounds having general formula **(I)**



(I)

wherein each group $R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11}$ e R_{12} is independently chosen between H, linear or branched alkyl, cycloalkyl, aryl, alkyl-aryl, alcoxy, substituted alcoxy, and/or

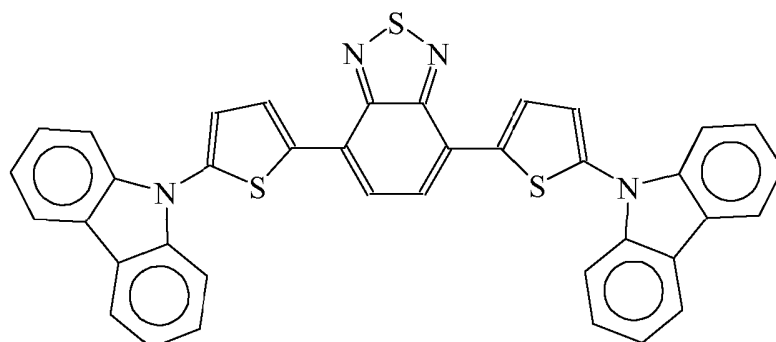
at least a pair of groups chosen between $R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11}$ and R_{12} forms, together with carbon atoms to which said groups are bound, an aliphatic or aromatic cyclic or polycyclic system, possibly containing one or more heteroatoms.

When one or more of the groups from R_1 to R_{12} is a linear or branched alkyl, cycloalkyl, aryl, alkyl-aryl, alcoxy, substituted alcoxy, preferably it contains from 1 to 10 carbon atoms, even more preferably from 1 to 6 carbon atoms.

When at least one pair of groups chosen between the groups from R_1 to R_{12} forms, together with carbon atoms to which the two groups are bound, an aliphatic or aromatic cyclic or polycyclic system, possibly containing one or more heteroatoms, said cyclic or polycyclic system preferably contains from 3 to 14 carbon atoms and, even more preferably, from 4 to 6 carbon atoms. In the case of hetero-rings, the heteroatoms thereof may be, for example, nitrogen, oxygen or sulphur. According to a particular aspect of the present invention, the two groups mutually bound to form a cyclic or a polycyclic system, as described above, are two adjacent groups, i.e. they are two groups from R_1 to R_{12} bound to carbon atoms in turn mutually bonded. For example two adjacent groups from R_1 to R_{12} may form a unit $-\text{OCH}_2\text{CH}_2\text{O}-$.

According to a preferred aspect of the invention all groups from R_1 to R_{12} are H: the 4,7-bis[5'-(9''H-carbazol-9''-yl)thien-2'-yl]-2,1,3-benzothiazole having formula (**1a**), corresponding to the compound having formula

(I) wherein all groups from R₁ to R₁₂ are hydrogen atoms, is hence a particularly preferred object of the present invention:



(Ia)

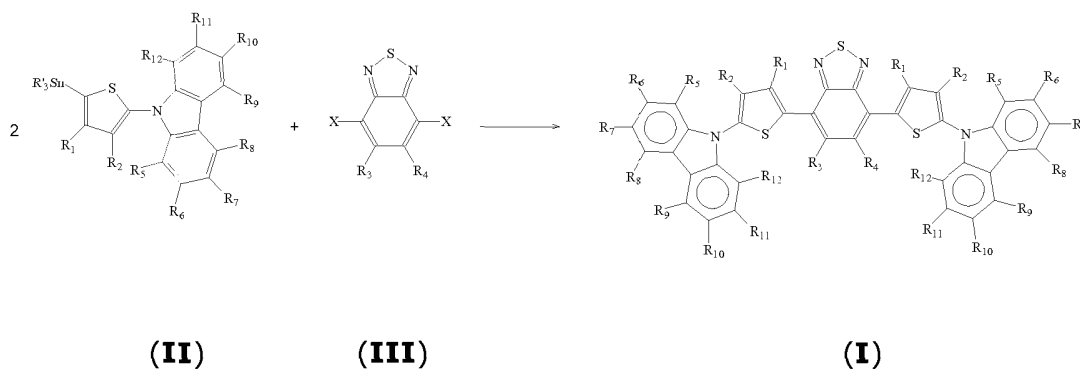
The compounds having formula (I) exhibit an absorption range which, with respect to that of DTB, is significantly more extended towards red: said absorption is high and extended across a relatively large wavelength range. For example, the absorption range for 4,7-bis[5'-(9''H-carbazol-9''-yl)thien-2'-yl]-2,1,3-benzothiadiazole (Ia), lies from 230 to 590 nm.

It is furthermore unexpected that said compounds also exhibit a particularly high Stokes shift, which, for example for 4,7-bis[5'-(9''H-carbazol-9''-yl)thien-2'-yl]-2,1,3-benzothiadiazole (Ia), is equal in solution to 190 nm and hence far higher also than the already wide one shown by DTB. As already stated, this feature is particularly desirable for fluorescent products to be employed in the manufacturing of luminescent solar concentrators.

The compounds of the present invention have a high quantum efficiency of luminescence (EQL), equal to the ratio between the number of emitted photons and the number of photons absorbed by the luminescent chromophore group. In particular the compound having formula (Ia) exhibit an EQL equal to 78%. The compounds of the present invention also have a high absorption coefficient which, for example for the compound having

formula **(Ia)**, is equal to $1.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

The compounds having formula **(I)** may be synthesised through a process which comprises causing a compound having formula **(II)** to react with a 4,7-dihalo-2,1,3-benzothiadiazole having formula **(III)**:



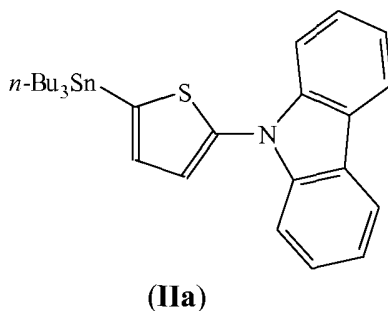
wherein

X is a halogen chosen between Cl, Br and I,

R' is an alkyl containing from 1 to 6 carbon atoms,

each group R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁ and R₁₂ is independently chosen between H, linear or branched alkyl, cycloalkyl, aryl, alkyl-aryl, alkoxy, substituted alkoxy, and/or

at least one pair of groups chosen between R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁ and R₁₂ forms, together with the carbon atoms to which said groups are bound, an aliphatic or aromatic cyclic or polycyclic system, possibly containing one or more heteroatoms. Said preparation process is a further object of the present invention. According to a preferred aspect of the invention, as compound **(II)** tri-n-butyl(2-[9'H-carbazol-9'-yl]thien-5-yl)stannane having formula **(IIa)** is used



and, in compound **(III)**, R_3 and R_4 are H, obtaining as product compound **(Ia)**.

4,7-dihalo-2,1,3-benzothiadiazoles having formula **(III)** may be prepared through halogenation of the corresponding 2,1,3-benzothiadiazoles according to the known techniques. For example, 4,7-dibromo-2,1,3-benzothiadiazole, corresponding to the compound having formula **(III)** wherein R_3 and R_4 are H and X is Br, may be prepared through bromination of 2,1,3-benzothiadiazole with bromine in a solution of concentrated hydrobromic acid as described for example in K. Pilgram et al., *J. Heterocycl. Chem.*, 1970, 7, 629. 4,7-diiodo-2,1,3-benzothiadiazole, corresponding to the compound having formula **(III)** wherein R_3 and R_4 are H and X is I, may be prepared through iodination as described in patent WO 2007/081991, example 60.

The reaction between compounds **(II)** and **(III)** is a Stille reaction and is preferably performed in the presence of a palladium-containing catalyst. Palladium complexes with oxidation state (0) or, more preferably, (II) may be positively used. In order to catalyse the reaction, by way of example, the following complexes may be used:

- bis(triphenylphosphine)palladium(II) chloride, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$;
- bis(triphenylphosphine)palladium(II) acetate, $\text{Pd}(\text{PPh}_3)_2(\text{OAc})_2$;
- tetrakis(triphenylphosphine)palladium(0), $\text{Pd}(\text{PPh}_3)_4$;

- bis(dibenzylideneacetone)palladium(0), $\text{Pd}(\text{C}_6\text{H}_5\text{CH}=\text{CHCOCH}=\text{CHC}_6\text{H}_5)_2$;
- bis(acetonitrile)palladium(II) chloride, $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$;
- benzil[bis(triphenylphosphine)]palladium(II) chloride, $\text{C}_6\text{H}_5\text{CH}_2\text{Pd}(\text{PPh}_3)_2\text{Cl}$.

One can operate by mixing dihalobenzothiadiazole having formula **(III)** and the palladium complex dissolved in a solvent, preferably dimethylsulfoxide (DMSO) or dimethylformamide (DMF). The mixture is heated to a temperature over 110°C and then, preferably in a time period ranging from 5 to 20 minutes, stannane having formula **(II)** is added, in a molar ratio with dihalobenzothiadiazole **(III)** of 2.5 to 1, in solution within the same solvent previously used to prepare the solution containing the Pd complex. One preferably operates at a temperature above 120°C, even more preferably at a temperature ranging from 120 to 150°C. The reaction is continued until completion, which preferably occurs in a time period below 2 hours, even more preferably ranging from 10 to 100 minutes.

The palladium complex may also be prepared *in situ*, according to known techniques. For example one can operate by mixing a palladium salt and a suitable binder in a solvent preferably chosen between DMF or DMSO, and then adding the solution thus obtained to dihalobenzothiadiazole having formula **(III)**. Palladium salts which may be used for this purpose are, for example, chloride, bromide, iodide, nitrate, acetate, trifluoroacetate and acetylacetonate; usable binders are, for example, trialkyl- and triarylphosphines and, in particular, triphenylphosphine, *o*-tolylphosphine, *m*-tolylphosphine and *p*-tolylphosphine. Thus, for example, the complexes bis(triphenylphosphine)palladium(II) acetate and bis(triphenylphosphine)palladium(II) chloride may be formed by reaction starting from commercial

precursors such as triphenylphosphine and palladium (II) acetate or chloride, respectively.

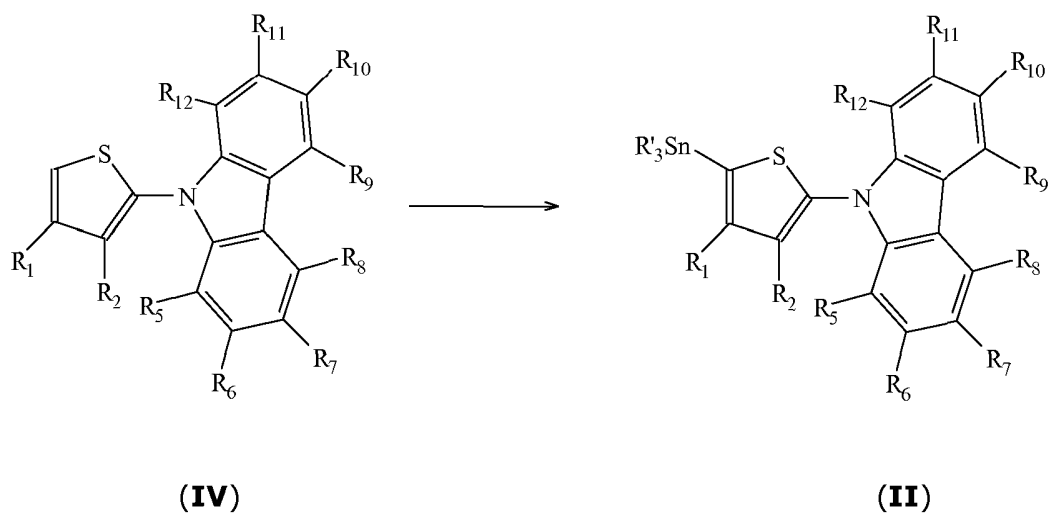
The mixture of Pd salt and binder thus obtained is added to the stannane having formula **(II)**, also in this case in a solution within the same solvent. The reaction is performed at a temperature above 110°C, preferably at a temperature above 120°C, even more preferably at a temperature ranging from 120 to 150°C. In these conditions, reaction completion may occur in a time period ranging from a few dozens of minutes to a few hours, for example from 45 minutes to 2 hours.

As far as pressure is concerned, the reaction between compounds **(II)** and **(III)** can be performed both at atmospheric pressure and at a pressure higher than the atmospheric one, and it is preferably operated at atmospheric pressure.

In both procedures, with the catalyst prepared both ex situ and in situ, at the end of the process one can proceed by drowning the reaction mixture in water and a solvent selected, for example, between ethyl acetate or toluene, preferably toluene, obtaining two phases which are then separated: from the organic phase the desired product is recovered by evaporation, which product may be purified by crystallisation.

The palladium is used in an amount ranging from 0.01 to 0.5 moles for 100 moles of dihalobenzothiadiazole and, preferably, from 0.05 to 0.2 moles for 100 moles of dihalobenzothiadiazole. These values are remarkably lower than those normally used for the Stille reaction, which are generally comprised from 0.5 to 2 moles of palladium for 100 moles of organic halide.

The compounds having formula **(II)**, used in the preparation process of the compounds having formula **(I)** of the present invention, can be prepared, according to known techniques, through lithiation and stannylation of the corresponding compounds having formula **(IV)**:



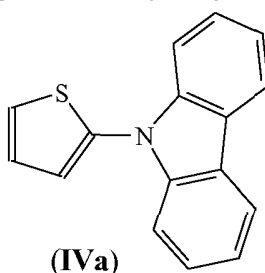
The lithiation and stannylation of the compounds **(IV)** are performed sequentially in the same reaction environment. The lithiation can be performed for example using *n*-butyl lithium or lithium di-*iso*-propylamide. The stannylation may be performed through trialkylstannanes having formula R'_3SnX' , wherein X' is a halogen chosen between Cl, Br and I and R' is an alkyl containing from 1 to 6 carbon atoms, preferably from 1 to 4, for example tri-*n*-butylchlorostannane. The lithiation is positively performed in anhydrous tetrahydrofuran (THF) at -78°C , by adding *n*-butyl lithium or lithium di-*iso*-propylamide over 2 hours and letting then to react, at the same temperature, for a time period ranging from 2 to 3 hours.

The stannylation is performed straight after the lithiation, by adding, in the same reactor, tributylchlorostannane over the course of 30-60 minutes, at the same temperature at which the lithiation has taken place, and then

letting the temperature rise again up to the room temperature and then continuing stirring for a time period ranging from 8 to 24 hours.

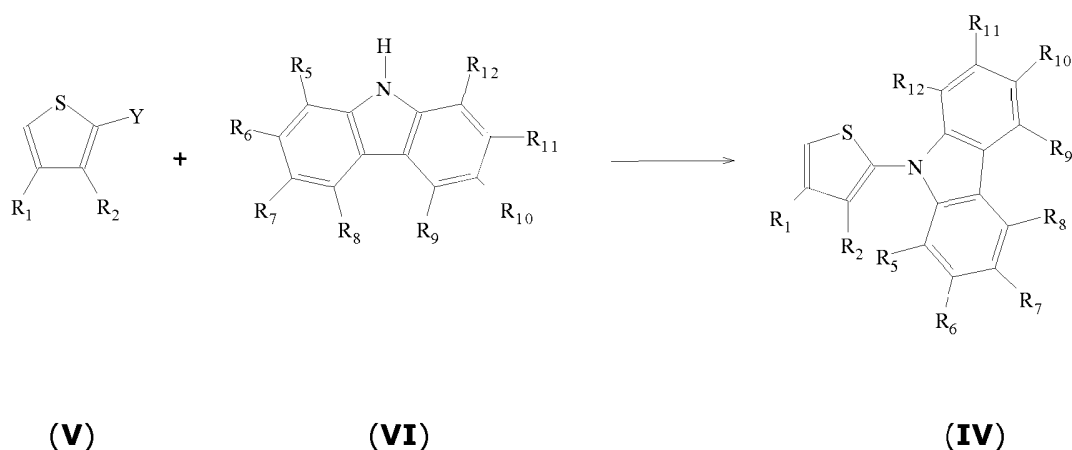
The lithiation and stannylation by successive treatments with *n*-butyl lithium and tri-*n*-butylchlorostannane are described for example in J.T. Pinhey et al., *J. Chem. Soc. Perkin Trans. 1*, 1988, 2415; the lithiation with lithium di-*iso*-propylamide (LDA) and subsequent stannylation with tri-*n*-butylchlorostannane are described for example in E. Bundgaard and F.C. Krebs in *Macromolecules* 2006, 39, 2823.

It is a preferred aspect of the invention to subject to lithiation and stannylation the compound having formula **(IVa)**



to obtain tri-*n*-butyl(2-[9'-H-carbazol-9'-yl]thien-5-yl)stannane **(IIa)**.

The compounds having formula **(IV)** may be, in turn, prepared causing a halo-thiophene having formula **(V)** wherein the halogen Y is chosen between bromine and iodine, to react, in the presence of a base, with a carbazole having formula **(VI)**:



This reaction is preferably performed using a base chosen between sodium carbonate, potassium carbonate, caesium carbonate, sodium bicarbonate, potassium bicarbonate, caesium bicarbonate, dibasic sodium phosphate (Na_2HPO_4), dibasic potassium phosphate (K_2HPO_4), tribasic sodium phosphate (Na_3PO_4), tribasic potassium phosphate (K_3PO_4), sodium acetate, potassium acetate, sodium methylate, potassium methylate, sodium ethylate, potassium ethylate, potassium *tert*-butylate (*t*-BuOK), preferably *t*-BuOK. In the compounds (**V**), Y is preferably bromine.

It is a preferred aspect of the invention that the reaction be performed in anhydrous dimethylformamide. It is operated preferably at a temperature which varies from 120 to 150°C, and for a time period ranging from 2 to 8 hours.

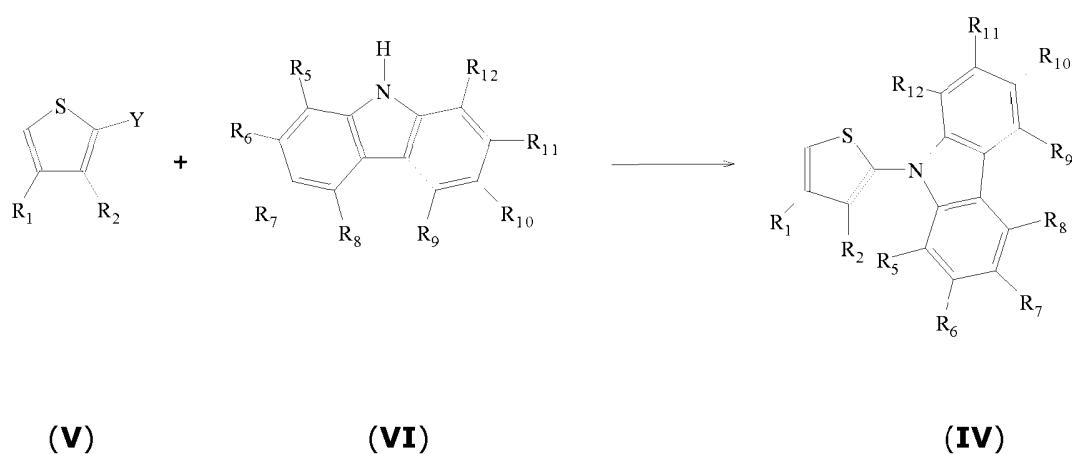
The 2-halo-thiophenes having formula (**V**) and the carbazoles having formula (**VI**) are both commercial products and compounds which may be easily prepared by a person skilled in the field according to known techniques. For example, 2-bromothiophene, i.e. the compound having formula (**V**) wherein R_1 and R_2 are H and Y is Br, in addition to being a commercial product, may be prepared as described, for example, by B. Fuchs *et al.* in *J. Chem. Soc., Chem. Commun.* 1982, 778 or by M.A. Keegstra and L. Brandsma in *Synthesis* 1988, 890.

Also carbazole, i.e. the compound having formula (**VI**) wherein all the substituents from R_5 to R_{12} are H, is a product available on the market and is typically extracted from the residues of anthracene manufacturing.

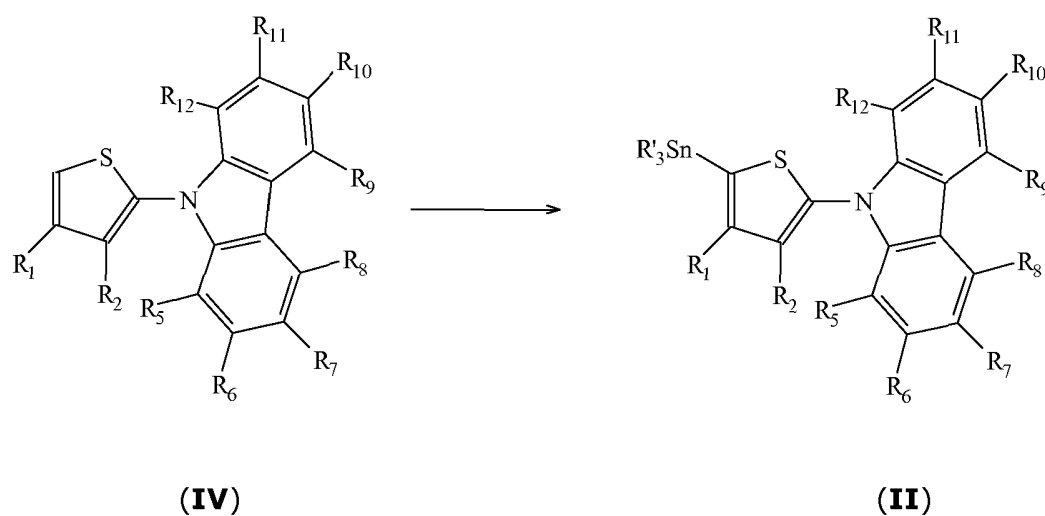
It is a preferred aspect of the invention to cause 2-bromothiophene to react with carbazole to obtain 2-(9'H-carbazol-9'-yl)-thiophene (**IVa**).

According to what has been described above, it is a further object of the present invention a preparation process of the compounds having formula **(I)** which comprises the following steps:

1) causing a halo-thiophene having formula **(V)**, wherein the halogen Y is chosen between bromine and iodine, to react, in the presence of a base, with a carbazole having formula **(VI)**, to obtain the compound having formula **(IV)**:

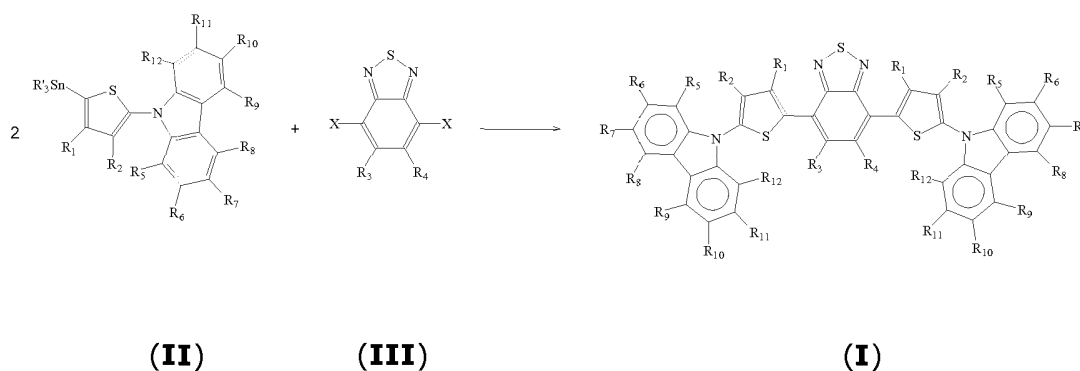


2) subjecting the compound **(IV)** to lithiation and stannylation obtaining the compound having formula **(II)** wherein R' is an alkyl containing from 1 to 6 carbon atoms



3) causing the compound **(II)** to react with 4,7-dihalo-2,1,3-

benzothiadiazole having formula **(III)**, wherein X is a halogen chosen between Cl, Br and I:



wherein each group R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} , R_{11} and R_{12} is independently chosen between H, linear or branched alkyl, cycloalkyl, aryl, alkyl-aryl, alcoxy, substituted alcoxy, and/or

at least one pair of groups chosen between R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} , R_{11} and R_{12} forms, together with the carbon atoms to which said groups are bound, an aliphatic or aromatic cyclic or polycyclic system, possibly containing one or more heteroatoms.

A further object of the present invention is the use of the above-defined compounds having formula **(I)** as fluorescent materials in spectrum converters.

The object of the present invention is also a spectrum converter comprising one or more compounds having formula **(I)**, and the solar devices comprising a spectrum converter as defined above.

The spectrum converter according to the present invention may contain one or more of said compounds having formula **(I)** and preferably contains the compound having formula **(Ia)**. The materials of the present invention having formula **(I)** may be used, in spectrum converters, in solution

or in form of gel, or said converter may additionally contain a transparent matrix, wherein under the term "transparent matrix" any transparent material must be intended, which can be used as a support, binder or material in which at least a compound having formula (I) is dispersed or embedded. The material used for the matrix is transparent, as such, to the radiations of interest, and in particular will be transparent to the radiations having a frequency comprised in the effective spectrum of the solar device. Suited materials will hence be transparent at least to the radiations having a wavelength ranging from 350 to 850 nm.

The transparent matrix which may be used in the present invention can be for example a polymeric material or a glass material. Said matrix is characterised by high transparency and high duration in respect of heat and light. Suitable polymeric materials are for example polymethacrylate, epoxy resins, silicone resins, polyalkylene terephthalates, polycarbonates, polystyrene, polypropylene. Examples of glass materials are silicas. When the matrix is of the polymeric type, one or more compounds having formula (I) may be dispersed in the matrix for example through dispersion in the molten state or solubilisation of the polymer and of the compound having formula (I) in a solvent and evaporation of the solvent to form a film comprising the polymer and at least one compound having formula (I), according to the technique known as "casting"; in the case of supports of glass material, the compounds having formula (I) may be coated as a thin film.

The solar devices comprising the wavelength converter of the present invention containing one or more compounds having formula (I) described above are also an object of the present invention.

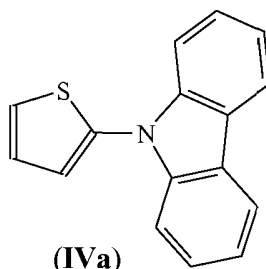
The solar devices are obtained by assembling the wavelength converter with a photovoltaic cell. It is a preferred aspect of the invention that the spectrum converters of the present invention be manufactured in the form of a luminescent solar concentrator, i.e. in the form of a plate of transparent material within which there are dispersed one or more materials having formula **(I)**, or said materials are coated on a plate as a thin film. In the solar devices the plates comprising one or more materials having formula **(I)** are hence joined with a photovoltaic cell.

The following examples have the purpose of illustrating the herewith claimed invention without, however, limiting in any way the scope thereof.

EXAMPLE 1

Synthesis of 4,7-bis[5'-(9''H-carbazol-9''-yl)thien-2'-yl]-2,1,3-benzothiadiazole (II)

Step (1) - Synthesis of 2-(9'H-carbazol-9'-yl)-thiophene (IVa)



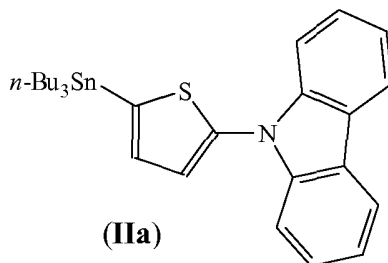
In a 1-litre, 5-necked flask, provided with a thermometer, mechanical stirrer, nitrogen entry and Marcusson apparatus, 15.4 g (92.2 mmol) of carbazole, i.e. the compound having formula **(VI)** wherein the substituents from R₅ to R₁₂ are H, have been introduced in 280 ml of anhydrous DMF. The temperature has been risen to 120°C under stirring and under nitrogen flow, then 30.0 g (0.268 mol) of potassium tert-butoxide have been added in three portions. Keeping the nitrogen flow, the formed tert-butanol has been distilled

and 1.0 g (3.78 mmol) of 18-crown-6 and 9.0 g (142 mmol) of copper powder have hence been added, bringing then the inner temperature to 145°C. At this point, through a 25-ml, pressure-equalizing dropping funnel, 50.0 ml (514 mmol) of 2-bromothiophene have been added over 30 minutes, having reduced to a minimum the nitrogen flow so that it does not drag away the 2-bromothiophene and keeping the inner temperature ranging from 140 to 145°C. At the end of the addition, the whole mixture has been left to react for further 4.5 hours, then the mixture has been cooled down to room temperature and it has been separated between ethyl acetate and water. The organic phase has been dried, under magnetic stirring, on anhydrous sodium sulphate for 30 minutes and subsequently filtered. The solvent has then been removed in a rotary evaporator and the residue has been eluted through a 6-cm silica panel using n-heptane as solvent. 22.5 g of 2-(9'H-carbazol-9'-yl)-thiophene (**IVa**) as a yellowish oil (yield 98% compared with carbazole) have thus been obtained.

The mass spectrum of the obtained product is reported in the following:

MS (EI⁺): $m/z(\%) = 249 (100) [M^+]; 204 (75) [(M-HCS)^+]$.

Step (2)- Synthesis of tri-n-butyl(2-[9'H-carbazol-9'-yl]thien-5-yl)stannane (**IIa**)



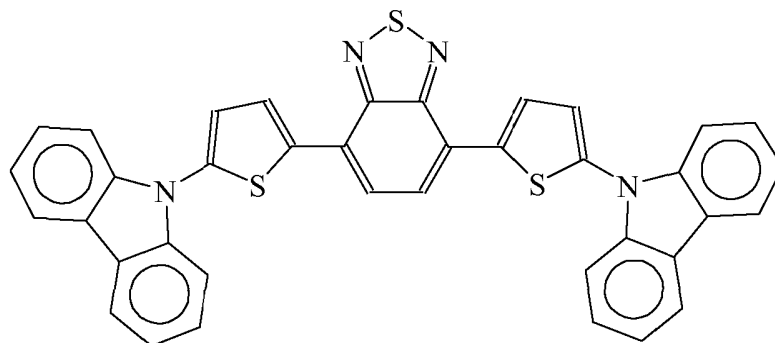
In a 500-ml, 4-necked flask provided with mechanic stirring, 100-ml pressure-equalizing dropping funnel and nitrogen entry, 250 ml of THF freshly distilled from LiAlH₄, and 9.8 g (39 mmol) of 2-(9'H-carbazol-9'-yl)-thiophene

(**IVa**) have been loaded under nitrogen flow. Through an acetone-and-dry-ice bath, the mixture has been cooled down to -78°C and, under vigorous stirring, 48 ml (77 mmol) of a 1.6 M solution of *n*-butyl lithium in heptane have been added in drops over 2 hours, causing the temperature of the cooling bath not to exceed -74°C . Once the addition has been completed, the mixture has been left to react at -74°C for further 2.5 hours, after which, still at the same temperature and under the same vigorous stirring, 26 ml (96 mmol) of *n*- Bu_3SnCl in 24 ml of anhydrous THF have been added in drops over 50 minutes. The reaction mixture has hence been kept under stirring for 15 hours, still under nitrogen, but letting the temperature rise up to room temperature and, at the end, it has been separated between ethyl ether and water. The organic phase has been dried, under magnetic stirring, on anhydrous sodium sulphate for 30 minutes and subsequently filtered. The solvent has hence been removed first in a rotary evaporator, then in a rotary pump. 20.3 g of tri-*n*-butyl(2-[9'-H-carbazol-9'-yl]thien-5-yl)stannane (**IIa**) as a highly viscous oil (yield 96%) have thus been obtained.

The mass spectrum of the obtained product is reported in the following:

MS (EI^+): $m/z(\%) = 539 (10) [\text{M}^+]; 482 (45) [(\text{M} - \text{C}_4\text{H}_9)^+]; 426 (74) [(482 - \text{C}_4\text{H}_8)^+]; 368 (45) [(\text{M} - 3 \text{C}_4\text{H}_9)^+]; 218 (100).$

Step (3) – Synthesis of 4,7-bis[5'-(9''H-carbazol-9''-yl)thien-2'-yl]-2,1,3-benzothiadiazole (**Ia**)



(**Ia**)

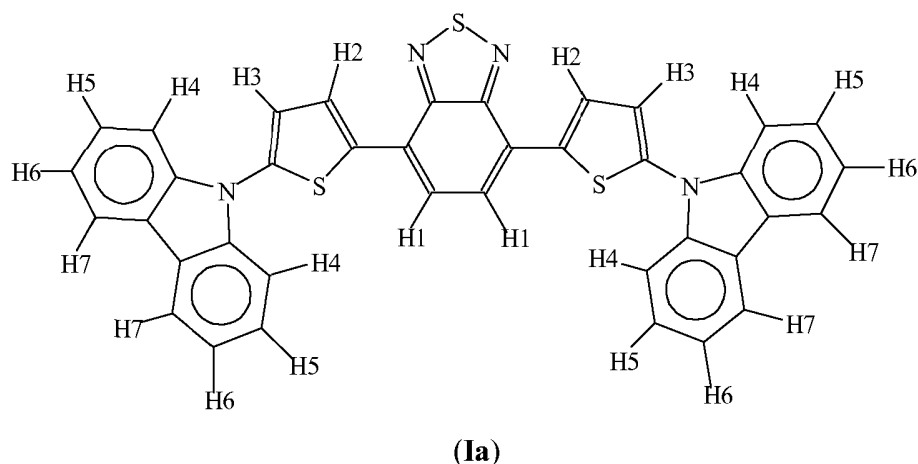
In a 250-ml, 3-necked flask, provided with bubble cooler, thermometer and nitrogen entry, 4.20 g (14.3 mmol) of 4,7-dibromo-2,1,3-benzothia-diazole, 19.2 g (35.7 mmol) of tri-*n*-butyl(2-[9'H-carbazol-9'-yl]thien-5-yl)stannane (**IIa**), 10.5 mg (0.015 mmol, 0.1 % in moles compared with 4,7-dibromo-2,1,3-benzothiadiazole) of Pd(PPh₃)₂Cl₂ and 100 ml of DMF have been loaded under a nitrogen atmosphere. Still under nitrogen, the mixture has been brought to 130°C for 1 hour and then separated between toluene and water. The organic phase has been dried, under magnetic stirring, on anhydrous sodium sulphate for 30 minutes and subsequently filtered. The solvent has then been removed in a rotary evaporator and the residue has been crystallised from acetone/methyl *tert*-butyl ether. The crystals obtained have finally been washed with methyl *tert*-butyl ether and dried in a rotary pump.

8.47 g of 4,7-bis[5'-(9''H-carbazol-9''-yl)thien-2'-yl]-2,1,3-benzothia-diazole (**II**) as a violet solid (yield 94% compared with 4,7-dibromo-2,1,3-benzothiadiazole) have thus been obtained.

For the product thus obtained the following analyses are reported:

(a) ¹H NMR (400 MHz; THF-*d*₈): δ = 7,32 (t; *J* = 8,0 Hz; 4H; H5); 7,45 (d; *J* = 4,1 Hz; 2H; H3); 7,47 (t; *J* = 8,0 Hz; 4H; H6); 7,65 (d; *J* = 8,0

Hz; 4H; H7); 8,16 (d; $J = 8,0$ Hz; 4H; H4); 8,17 (s; 2H; H1); 8,36 (d; $J = 4.1$ Hz; 2H; H2). In the following formula the attribution of the H atoms is reported:



(b) MS: (DCI, i -C₄H₉): $m/z(\%) = 629,7$ (100) [M⁺]; 382,9 (13) {[M-(9''H-carbazol-9''-yl)thien-2'-yl]}⁻.

(c) UV-vis (CH₂Cl₂, nm): 245, 291, 324, 474 (log ϵ 4,62; 4,53; 4,47; 4,23); λ_{\max} emission 664 nm. UV-vis (PMMA, nm): 292, 328, 476; λ_{\max} emission 600 nm.

EXAMPLE 2

6 g of polymethylmetacrylate Altuglas VSUVT 100 (PMMA) and 104.5 mg of 4,7-bis[5'-(9''H-carbazol-9''-yl)thien-2'-yl]-2,1,3-benzothiadiazole (**Ia**) have been dissolved in 30 ml of 1,2-dichlorobenzene. The solution obtained has been subsequently evenly coated on a PMMA plate (measures 90x90x6 mm) using a Doctor Blade Film Applicator and the solvent has been left to evaporate at room temperature in a slight air flow for 24 hours. An orange-coloured (the colour coming from the film) transparent plate has been obtained, the thickness of which ranges from 300 to 350 μm .

To one of the edges of the polymer plate a photovoltaic cell IXYS-

XOD17 having an active surface of 1 cm^2 has then been applied.

The main side of the polymer plate coated with the thin film containing compound (**Ia**) has then been lit with a light source having a power equal to the sun's one (1000 W/m^2), and the electric power generated by the lighting has been measured.

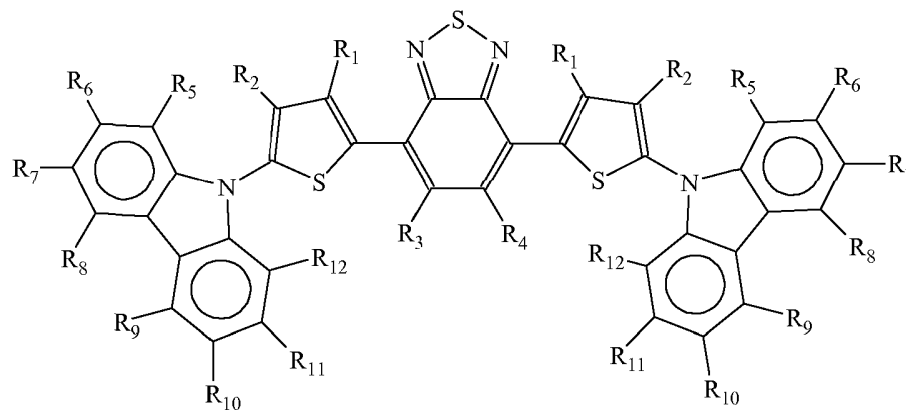
Power measurements have been accomplished by covering with an opaque coating (mask) varying-area surfaces of the polymer support, at an increasing distance from the edge whereon the photovoltaic cell was fastened. These measurements in varying masking conditions allow to quantify the contribution of any wave guide, edge or multiple diffusion effects determined by the support, and hence to subtract the same.

Figure 1 reports the curve relating to the value of generated power per unit of lit surface, in mW/cm^2 , versus the distance of the mask from the edge of the support containing the solar cell.

From fig. 1 it can be seen how, apart from the edge effects, the generated power is stably around 0.048 mW/cm^2 .

CLAIMS

1) Benzothiadiazole compounds having general formula (I)



(I)

wherein each group R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁ and R₁₂ is independently chosen between H, linear or branched alkyl, cycloalkyl, aryl, alkyl-aryl, alcoxy, substituted alcoxy, and/or

at least one pair of groups chosen between groups R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁ and R₁₂ forms, together with the carbon atoms to which said groups are bound, an aliphatic or aromatic cyclic or polycyclic system, possibly containing one or more heteroatoms.

2) Benzothiadiazole compounds as claimed in claim 1, wherein at least one group chosen between the groups from R₁ to R₁₂ is a linear or branched alkyl, cycloalkyl, aryl, alkyl-aryl, alcoxy, substituted alcoxy, and said group contains from 1 to 10 carbon atoms.

3) Benzothiadiazole compounds as claimed in claim 1, wherein at least one pair of groups chosen between groups R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁ and R₁₂ forms, together with the carbon atoms to which said groups are bound, an aliphatic or aromatic cyclic or polycyclic system, possibly containing one or more heteroatoms, and said cyclic or polycyclic system

contains from 3 to 14 carbon atoms.

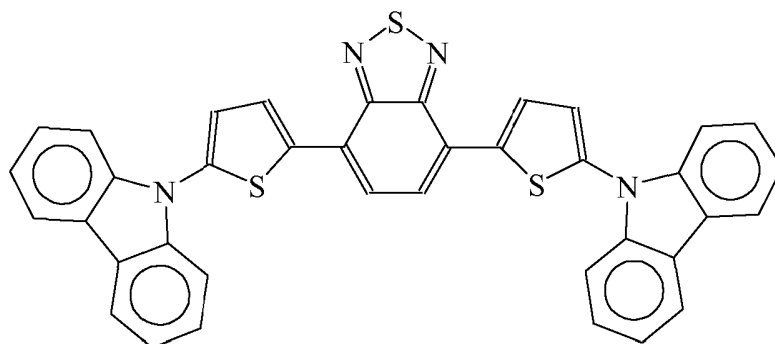
4) Benzothiadiazole compounds as claimed in claim 3, wherein said cyclic or polycyclic system contains from 4 to 6 carbon atoms.

5) Benzothiadiazole compounds as claimed in claim 1, wherein the heteroatom is chosen between nitrogen, oxygen and sulphur.

6) Benzothiadiazole compounds as claimed in claim 1, wherein the pair of groups chosen between the groups from R_1 to R_{12} consists of adjacent groups.

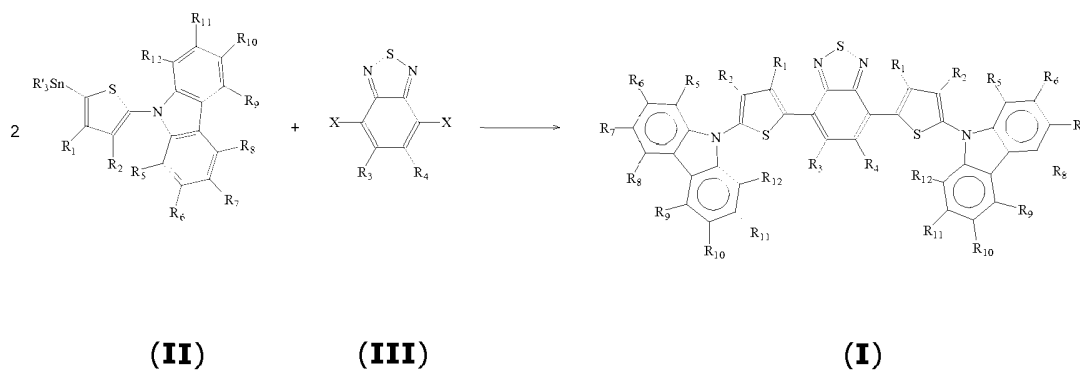
7) Benzothiadiazole compounds as claimed in claim 6, wherein the adjacent groups form a unit $-OCH_2CH_2O-$.

8) Benzothiadiazole compound as claimed in claim 1, wherein all groups from R_1 to R_{12} are hydrogen atoms, said compound having the following formula (**Ia**):



(Ia)

9) Process for preparing the compounds having formula (**I**), comprising the step of causing a compound having formula (**II**) to react with a 4,7-dihalo-2,1,3-benzothiadiazole having formula (**III**)



wherein

X is a halogen chosen between Cl, Br and I,

R' is an alkyl containing from 1 to 6 carbon atoms,

each group R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁ and R₁₂ is independently chosen between H, linear or branched alkyl, cycloalkyl, aryl, alkyl-aryl, alcoxy, substituted alcoxy, and/or

at least one pair of groups chosen between the groups R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁ and R₁₂ forms, together with the carbon atoms to which said groups are bound, an aliphatic or aromatic cyclic or polycyclic system, possibly containing one or more heteroatoms.

10) Process as claimed in claim 9, wherein the reaction is performed in the presence of a palladium-containing catalyst.

11) Process as claimed in claim 10, wherein the catalyst is a palladium complex.

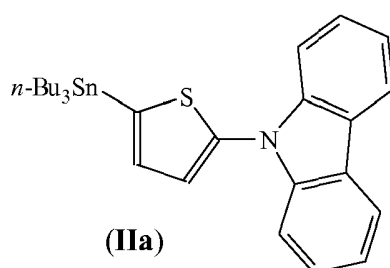
12) Process as claimed in one or more of the claims from 9 to 11, wherein the reaction is performed at a temperature higher than 110°C .

13) Process as claimed in one or more of the claims from 9 to 12, wherein the solvent is DMF or DMSO.

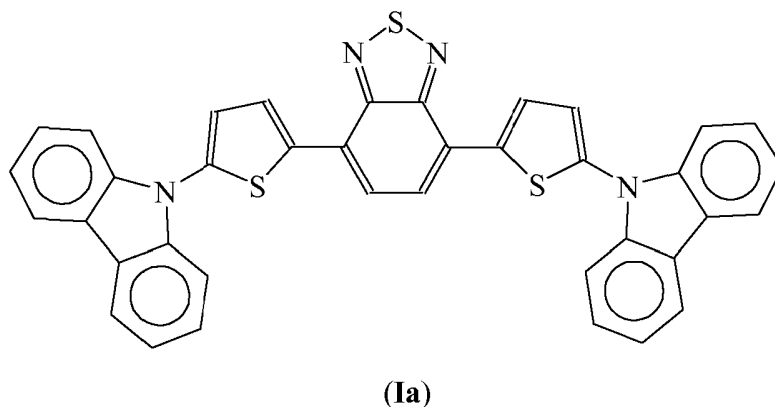
14) Process as claimed in claim 11, wherein the palladium complex is prepared *in situ*.

15) Process as claimed in claim 10, wherein palladium is used in an amount ranging from 0.01 to 0.5 moles for 100 moles of dihalobenzothiadiazole (**III**).

16) Process as claimed in claim 9, wherein the compound (**II**) is tri-*n*-butyl(2-[9'H-carbazol-9'-yl]thien-5-yl)stannane (**IIa**)

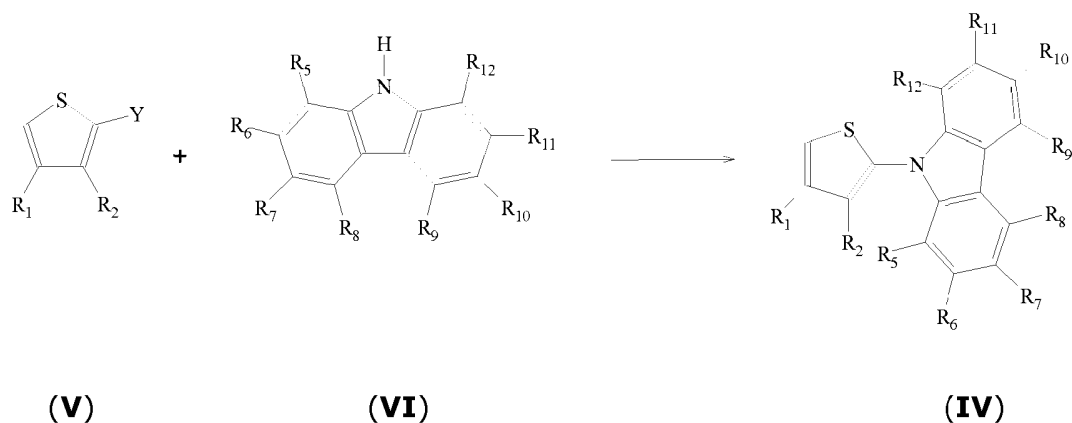


the compound (**III**) is a 4,7-dihalo-2,1,3-benzothiadiazole and the product obtained is the compound having formula (**Ia**)

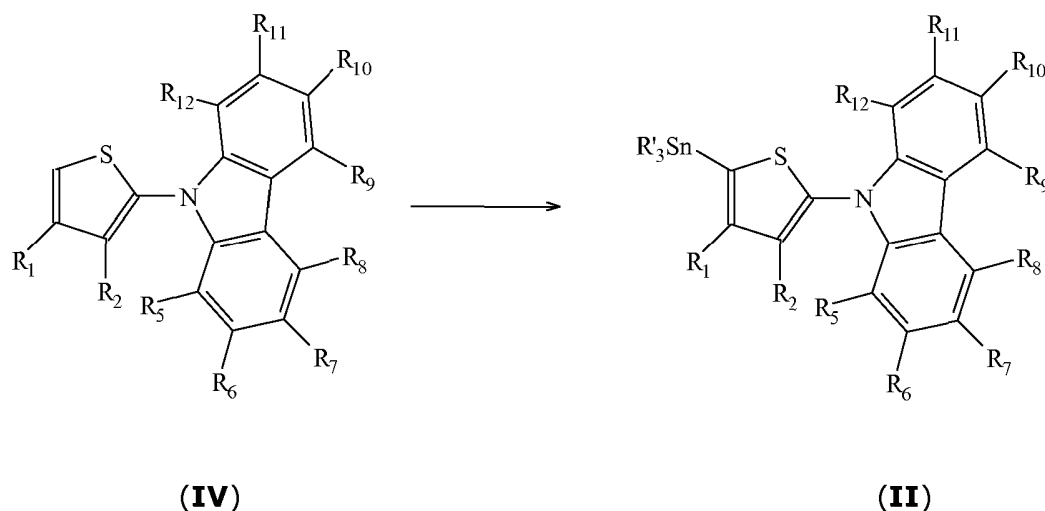


17) Process as claimed in claim 9, wherein the compound (**II**) is prepared through the following steps:

(1) causing a halo-thiophene having formula (**V**), wherein Y is chosen between bromine and iodine, to react, in the presence of a base, with a carbazole having formula (**VI**) to obtain the compound having formula (**IV**):



(2) subjecting the compound **(IV)** to lithiation and stannylation, obtaining the compound having formula **(II)**, wherein R' is an alkyl containing from 1 to 6 carbon atoms



wherein each group R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁ and R₁₂ is independently chosen between H, linear or branched alkyl, cycloalkyl, aryl, alkyl-aryl, alcoxy, substituted alcoxy, and/or

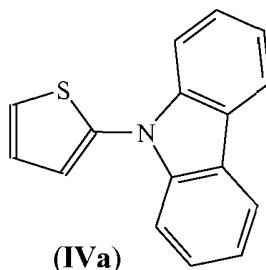
at least one pair of groups chosen between R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁ and R₁₂ forms, together with the carbon atoms to which said groups are bound, an aliphatic or aromatic cyclic or polycyclic system, possibly containing one or more heteroatoms.

18) Process as claimed in claim 17, wherein the step (1) is performed

using a base chosen between sodium carbonate, potassium carbonate, caesium carbonate, sodium bicarbonate, potassium bicarbonate, caesium bicarbonate, dibasic sodium phosphate (Na_2HPO_4), dibasic potassium phosphate (K_2HPO_4), tribasic sodium phosphate (Na_3PO_4), tribasic potassium phosphate (K_3PO_4), sodium acetate, potassium acetate, sodium methylate, potassium methylate, sodium ethylate, potassium ethylate and potassium *tert*-butylate (t-BuOK).

19) Process as claimed in claim 17, wherein the step (1) is performed in anhydrous dimethylformamide, at a temperature ranging from 120 to 150°C, and for a time period ranging from 2 to 8 hours.

20) Process as claimed in claim 17, wherein, in step (1), the compound having formula (**V**) is 2-bromothiophene and the compound having formula (**VI**) is carbazole and the compound (**IV**) is 2-(9'H-carbazol-9'-yl)-thiophene having formula (**IVa**)



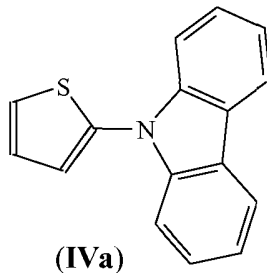
21) Process as claimed in claim 17, wherein, in step (2), the lithiation and stannylation are performed sequentially in the same reaction environment.

22) Process as claimed in claims 17 or 21, wherein, in step (2), the lithiation is performed using *n*-butyl lithium or lithium di-*iso*-propylamide.

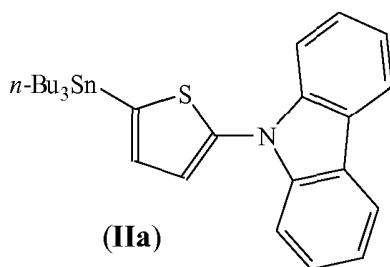
23) Process as claimed in claims 17, 21 or 22 wherein, in step (2), the stannylation is performed through trialkylstannanes having formula $\text{R}'_3\text{SnX}'$,

wherein X' is a halogen chosen between Cl, Br and I and R' is an alkyl containing from 1 to 6 carbon atoms.

24) Process as claimed in claim 17, wherein, in step (2), the compound having formula (**IVa**) is subjected to lithiation and stannylation



and the compound (**II**) obtained is tri-*n*-butyl(2-[9'H-carbazol-9'-yl]thien-5-yl)stannane having formula (**IIa**)

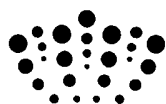


25) Use of one or more compounds as claimed in claims 1 or 8, as fluorescent materials in spectrum converters.

26) Spectrum converter comprising one or more compounds as claimed in claims 1 or 8.

27) Spectrum converter as claimed in claim 26, in the form of a solar concentrator.

28) Solar device comprising a spectrum converter as claimed in claims 26 or 27.



Application No: GB1122426.8

Examiner: Dr Richard Wood

Claims searched: 1-28

Date of search: 22 May 2012

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1,2,9-28 at least	Journal of Polymer Science Part A: Polymer Chemistry, vol. 47, no. 1, 2009, Ping et al., "Synthesis and properties of monodisperse multi-triarylamine-substituted oligothiophenes and 4,7-bis(2'-oligothienyl)-2,1,3-benzothiadiazoles for organic solar cell applications", pp. 137-148. See especially Scheme 2.
X	1,8,9-28 at least	US 2006/052612 A1 (STOSSEL et al.) - Formula (V); paras. [0055], [0062], [0073].
A	-	WO 2011/060526 A1 (NATIONAL RESEARCH COUNCIL OF CANADA)

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X :

Worldwide search of patent documents classified in the following areas of the IPC

C07D

The following online and other databases have been used in the preparation of this search report

WPI, EPODOC, CAS ONLINE

International Classification:

Subclass	Subgroup	Valid From
C07D	0417/14	01/01/2006
C07D	0409/04	01/01/2006