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(54) Title: ORGANIC PHOTOELECTRIC CONVERSION DEVICES COMPRISING FLUORINATED DYE COMPOUNDS

(57) Abstract: The present invention relates to organic photoelectric conversion devices comprising fluorinated dye compounds, in particular dye compounds based on fluoroalkyl-substituted thiophenes, method of making said dye compounds, and their use as dyes in organic photoelectric conversion devices.



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Organic photoelectric conversion devices comprising fluorinated dye compounds

This application claims priority to U.S. provisional application No. US 61/912667 filed on 06 December 2013, the whole content of this application being incorporated herein by reference for all purposes. The present invention relates to organic photoelectric conversion devices comprising fluorinated dye compounds, in particular dye compounds based on fluoroalkyl-substituted thiophenes, method(s) of making said dye compounds, and their use as dyes in organic photoelectric conversion devices.

Photovoltaic cells convert radiation, for example visible light, into direct current (DC) electricity. Organic solar cells (OSC) are organic photoelectric conversion devices which comprise conductive organic polymers or organic small molecules, for light absorption, charge generation and charge transport. Organic solar cells find use in many applications, including solar panels and photodetectors. They may also be part of larger systems comprising other organic electronic devices, such as organic light emitting diodes (OLEDs) and organic thin film transistors (OTFTs).

A common OSC structure is formed by a transparent conducting oxide (TCO) electrode, typically Indium Tin Oxide (ITO), an organic hole collecting layer (for example the doped polymer PEDOT:PSS), a photoactive layer, and the metallic contact, in some cases a thin interlayer of calcium or lithium fluoride. The photoactive layer is formed from a blend of donor and acceptor organic semiconductors. Typically, the acceptor semiconductor is a soluble fullerene derivative and the donor semiconductor is an organic polymer or a small-molecule dye compound.

Dye-sensitized solar cells (DSSCs) have also been developed. The basic element of a DSSC is generally a TiO_2 semiconductor sensitized with a dye compound used to harvest a greater portion of the solar light. The dye compound is sensitive to the visible light. The semiconductor functions as the transporter of light-induced electrons towards the external contact, a transparent conductor that lies at the basis of the semiconductor film.

Suitable organic photoelectric conversion devices have been reported in the literature.

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The invention now makes available improved organic photoelectric conversion devices comprising fluorinated dye compounds. It is an object of the present invention to provide organic photoelectric conversion devices with improved conversion efficiency. More particularly, the purpose of the present invention is to provide organic photoelectric conversion devices having a broad absorption spectrum, particularly in the visible and near-IR regions. The dye compounds comprised in the organic photoelectric conversion devices of the present invention advantageously exhibit a high molar extinction coefficient. Such dye compounds advantageously contribute to the long-term stability of such devices, for example, by showing improved resistance to water contained in trace amounts in the devices. Such dye compounds advantageously lead to an improved bandgap between the LUMO level of the acceptor semiconductor and the HOMO of the dye compound. It is another objective to provide organic photoelectric conversion devices comprising dye compounds that lead to improved open-circuit voltages (V_{OC}), short-circuit densities (J_{SC}) and/or fill factors (FF). It is yet another objective to provide organic photoelectric conversion devices comprising dye compounds with improved pi-stacking, crystallinity, solubility and/or miscibility.

Accordingly, one aspect of the present invention concerns an organic photoelectric conversion device comprising a dye compound comprising a non-fused thiophene moiety substituted with at least one fluorinated alkyl group, wherein the fluorinated alkyl group is attached to the non-fused thiophene by means of a covalent single bond or an ether linkage, preferably by means of a covalent single bond.

Fused aromatic moieties consist of aromatic rings that share at least one bond connecting two atoms within the same ring system. Thus, "non-fused thiophene" is intended to denote a thiophene ring that does not share a bond connecting two atoms within the thiophene ring with another aromatic ring system. Instead, the thiophene is connected to another aromatic ring and/or another group within the dye compound by means of covalent single bonds.

The term "ether linkage" is intended to denote a linkage of the type "-O-". Thus, the fluorinated alkyl group and the thiophene are connected by means of an oxygen atom with two covalent single bonds.

The term "alkyl" is intended to denote in particular a linear or branched substituent comprising from 1 to 20 carbon atoms, preferably 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 carbon atoms. Specific examples of such substituents are methyl, ethyl,

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n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, isopentyl, n-hexyl, 2-hexyl, n-heptyl, and n-octyl. The term “alkyl” also encompasses carbocycles containing 3 to 10 carbon atoms, preferably 5, 6 or 7 carbon atoms. Specific examples of such substituents are cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and cycloheptyl.

In a preferred embodiment, the fluorinated alkyl group is selected from the group consisting of a perfluorinated alkyl group, -CF₃, -CF₂H, and -CF₂CF₃, more preferably the fluorinated alkyl group is -CF₃.

The term “perfluorinated alkyl group” is intended to denote a branched or unbranched alkyl group comprising from 1 to 20 carbon atoms fully substituted with fluorine atoms. Suitable examples include -n-C₄F₉, -n-C₆F₁₃, and -n-C₈F₁₇.

In another preferred embodiment, the non-fused thiophene is substituted with at least one fluorinated alkyl group in position 3 and/or position 4 of the non-fused thiophene.

In a further preferred embodiment, the non-fused thiophene moiety is 3-trimethylfluorothiophene, 4-trimethylfluorothiophene, 3,4-bis(trimethylfluorothiophene), and/or 3,4-bis(trifluoromethoxy)thiophene.

In yet another preferred embodiment, the non-fused thiophene is substituted with a fluorinated alkyl group in position 2 or 5 of the non-fused thiophene, preferably the fluorinated alkyl group is -CF₃.

In still another preferred embodiment, the non-fused thiophene is connected to at least one further thiophene moiety by means of a covalent single bond, more preferably the non-fused thiophene is connected to two further thiophene moieties by means of one covalent single bond for each connection.

In still another preferred embodiment, the dye compound is a polymer.

The term “polymer” is intended to denote a molecule composed of many repeated monomers. The polymer can advantageously be composed of only one type of monomer (homopolymer). Alternatively, the polymer can be composed of regularly alternating monomers (alternating copolymer) or have two or more homopolymer subunits linked by covalent bonds (block copolymer).

In still another preferred embodiment the dye compound is a small molecule.

The term “small molecule” is intended to denote an organic compound with a molecular weight of <1000 Daltons.

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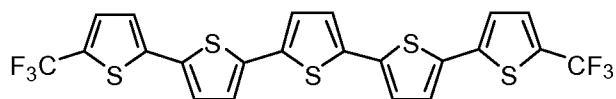
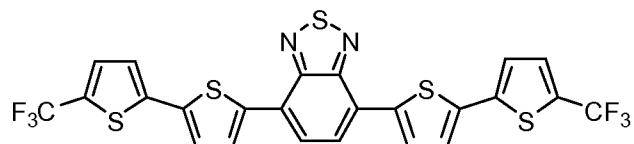
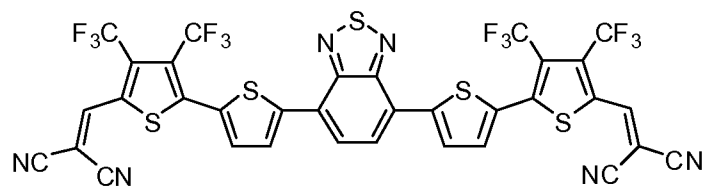
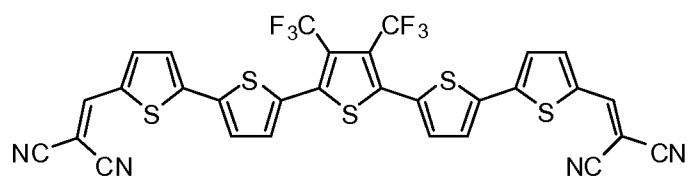
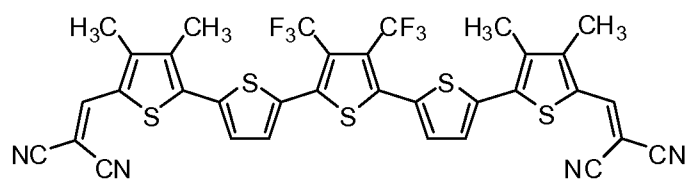
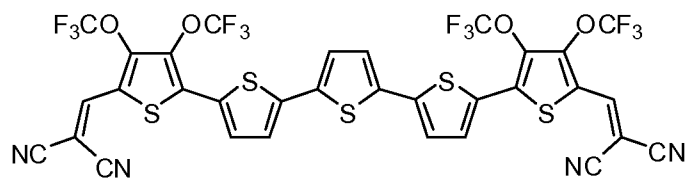
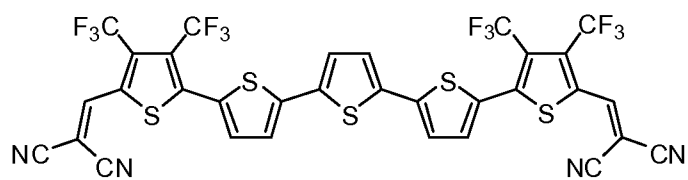
In still another preferred embodiment, the organic photoelectric conversion device is a dye-sensitized solar cell, a small-molecule organic solar cell, a polymer organic solar cell, or an organic light-emitting diode, more preferably it is a small-molecule organic solar cell.

5 An example of a small-molecule OSC is reported in Fitzner, R et al., Journal of the American Chemical Society, 2012, 134, 11064-11067, which is incorporated herein fully by reference. Dye compounds suitable for small-molecule OSC preferably have the general structure
A1-D-A2-D-A1,

10 wherein D denotes an electron-donating group, suitably an optionally alkyl-substituted thiophene, and A1 and A2 denote electron-accepting groups, suitably A1 and A2 denote thiophene moieties substituted with electron withdrawing groups such as the 2,2'-dicyanovinylene group. Surprisingly, as has now been found that the fluorinated alkyl group, preferably the -CF₃ group, may
15 advantageously be used as A1 and/or A2 group in the dye compounds. More preferably, A1 is 2-trifluoromethylthiophene or 5-trifluoromethylthiophene.

In a preferred embodiment, the small-molecule OSC according to the present invention advantageously comprises at least one dye compound selected from the following group of dye compounds:

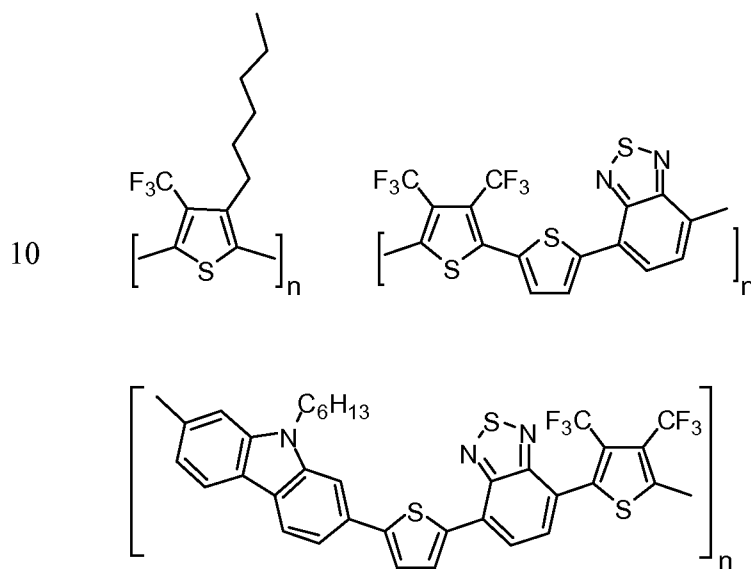
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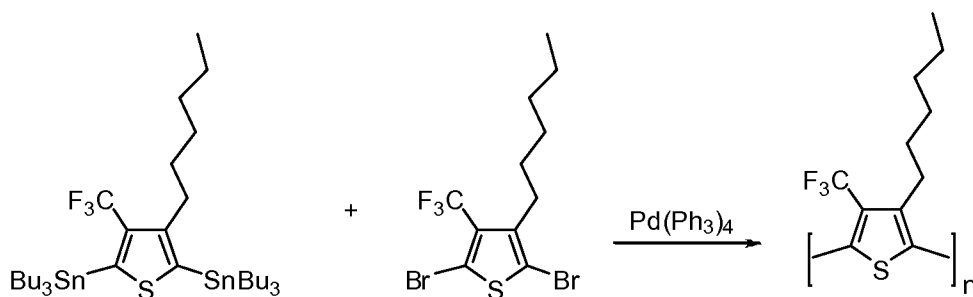
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An example of a polymer OSC is reported in Ma et al., Advanced Functional Materials, 2005, 15, 1617-1622, which is incorporated fully herein by reference.

5 In a preferred embodiment, the polymer OSC according to the present invention advantageously comprises at least one dye compound selected from the following group of compounds:



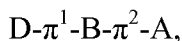
15 The polymer dye compounds can be prepared by methods known in the art, for example by using Stille-type couplings as exemplified in the following scheme:



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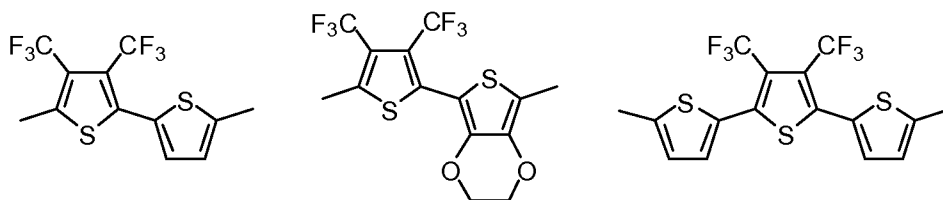
An example of a DSSC is reported in Feldt, S. M. et al, Journal of the American Chemical Society, 2010, 132, 16714-16724, which is incorporated herein fully by reference.

The DSSC according to the present invention advantageously comprise at least one dye compound of the general structure

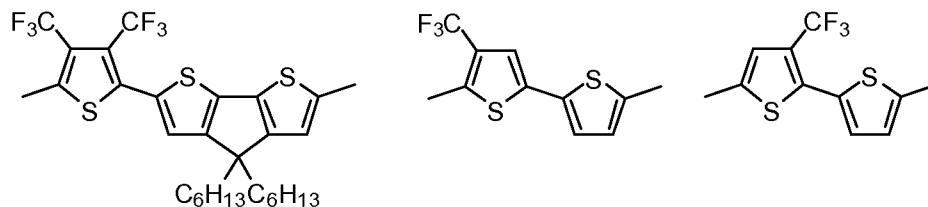


wherein D is a π -electron donor group, A is an anchor group, π^1 and π^2 are optional bridge groups, and B is a group selected from the following group of moieties:

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In a preferred embodiment, the DSSC of the present invention comprises at least one dye compound selected from the following group of compounds:

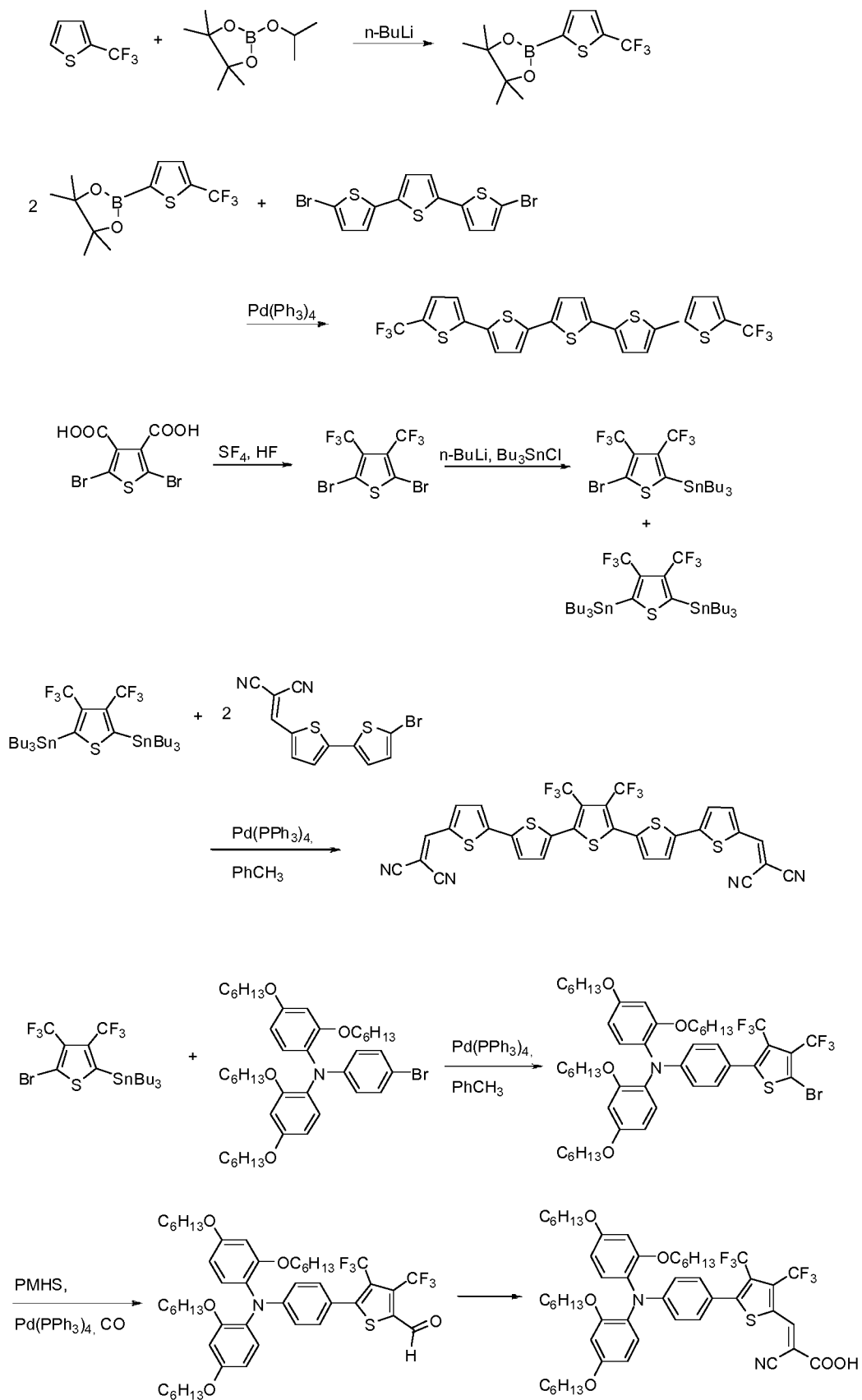
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Another aspect of the present invention is the use of a dye compound comprising a non-fused thiophene moiety substituted with at least one fluorinated alkyl group, wherein the fluorinated alkyl group is attached to the non-fused thiophene by means of a single covalent bond or an ether linkage as organic electronic material in a dye-sensitized solar cell, a small-molecule organic solar cell, a polymer organic solar cell, or an organic light-emitting diode, preferably in a small-molecule organic solar cell. Also preferably, the fluorinated alkyl group is selected from the group consisting of -CF₃, -CF₂H, and -CF₂CF₃, more preferably the fluorinated alkyl group is -CF₃. Also preferably, the non-fused thiophene moiety is 3-trimethylfluorothiophene, 4-trimethylfluorothiophene and/or 3,4-bis(trimethylfluorothiophene).

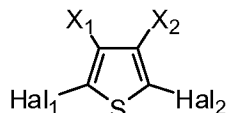
The fluorinated dye compounds comprised in the organic photoelectric conversion device according to this invention are advantageously prepared from fluorinated thiophene building blocks. The -CF₃ group is advantageously introduced by reaction of a suitably substituted thiophene carboxylic acid with a fluorinating agent. Consequently, another aspect of the present invention is a process for the manufacture of a dye compound comprising a 3-trimethylfluorothiophene, a 4-trimethylfluorothiophene and/or a 3,4-bis(trimethylfluorothiophene) moiety comprising a step wherein a suitable precursor of the 3-trimethylfluorothiophene, the 4-trimethylfluorothiophene and/or the 3,4-bis(trimethylfluorothiophene) is fluorinated in the presence of SF₄, in the presence of SF₄ and HF. Also preferably, the suitable precursor of the 3-trimethylfluorothiophene, the 4-trimethylfluorothiophene and/or the 3,4-bis(trimethylfluorothiophene) is a 3-carboxythiophene, a 4-carboxythiophene and/or 3,4-carboxythiophene.

The fluorinated thiophene building blocks can be further converted into the dye compound by conventional means as exemplified in the following scheme:

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Consequently, yet another aspect of the present invention is a compound of the general formula (I):



- 5 wherein X_1 and X_2 are independently selected from the group consisting of H, a perfluorinated alkyl group, $-CF_3$, $-OCF_3$, $-CF_2H$, and $-CF_2CF_3$, with the proviso that at least one of X_1 and X_2 is not H; and wherein Hal_1 and Hal_2 are independently a halogen atom; preferably X_1 and X_2 are $-CF_3$ and Hal_1 and Hal_2 are Br or I. Still another aspect of the present invention is the use of these
- 10 compounds for the manufacture of a dye compound for an organic photoelectric conversion device.

The compound of the present invention may be further isolated, for instance by column chromatography, preferably by high pressure liquid chromatography (HPLC).

- 15 While preferred embodiments of this invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit or teaching of this invention. The embodiments described herein are exemplary only and are not limiting. Many variations and modifications of systems and methods are possible and are within the scope of
- 20 the invention. Accordingly, the scope of protection is not limited to the embodiments described herein, but is only limited by the claims that follow, the scope of which shall include all equivalents of the subject matter of the claims.

- Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the
- 25 present application to the extent that it may render a term unclear, the present description shall take precedence.

Examples

Example 1: Synthesis of 2,5-dibromothiophene-3,4-dicarboxylic acid

- Thiophene-3,4-dicarboxylic acid (0.7 g, 4.07 mmol), glacial acetic acid (5 ml)
- 30 and bromine (2.35 ml, 26.1 mmol) were placed in a 25 ml flask with condenser. The mixture was heated to 55 °C for 18 h. The mixture was cooled in an ice-bath. Distilled water (5 ml) was added. Solid sodium metabisulfite was added

until the colour of the mixture turned to yellow-brown. The mixture was left to stand over night. The product crystallized from the mixture. It was filtered off, washed with the mother liquor and dried using a rotary evaporator (60 °C, 10 mbar) to yield 0.91 g (64%) of the product. ¹H NMR (500.50 MHz, CDCl₃ + 0.03% TMS), δ: 13.81 ppm (s, 2H); ¹³C NMR (125.85 MHz, CDCl₃ + 0.03% TMS), δ: 114,38 ppm (s, 2C), 135,16 ppm (s, 2C), 162,50 ppm (s, 2C).

Example 2: Synthesis of 2,5-dibromo-3,4-bis(trifluoromethyl)thiophene
2,5-dibromothiophene-3,4-dicarboxylic acid (0.44 g, 1.25 mmol) was provided in a Hastelloy® C4 reactor under nitrogen flush. The reactor was evacuated using a water jet pump and cooled to -70 °C in an iso-propanol/CO₂ bath. To the reactor, HF (4.4 g, 220 mmol) and SF₄ (7 g, 64 mmol) were added. The reactor was allowed to warm to room temperature and after that heated to 130 °C. After stirring for 18 h, the reactor was cooled to 0 °C in an ice-bath. The gas-phase was purged off into a scrubber. The reactor was opened and 50 ml cooled dichloromethane were added. The dichloromethane/HF mixture was carefully poured onto ice. The organic phase was separated and the aqueous phase was extracted with dichloromethane again. The combined organic phases were adjusted to pH 10-11 using 10% aqueous NH₄OH solution. The organic phase was separated, washed with water and brine and dried over MgSO₄. The solvent was removed by vacuum distillation to yield a red-brown oil (0.24g, 50%). ¹³C NMR (125.85MHz, CDCl₃ + 0.03% TMS), δ: 116.9 ppm (2C), 118.8 ppm (2C), 120.9 ppm (2C); ¹⁹F NMR (470.94 MHz, CDCl₃ + 0.03% TMS) δ: -59.67 ppm.

Example 3: 2,3,4-Tribromo-5-(2,2,2-trifluoroethoxy)thiophene

A flask with a magnetic stirring bar was flushed with nitrogen and charged with NaH (0.36 g, 15 mmol) and trifluoroethanol (8 mL, 111.2 mmol). 2,3,4,5-tetrabromothiophene (2 g, 5 mmol) and CuI (0.1 g, 0.5 mmol) were added. After refluxing for 4 days at 110 °C, the system was cooled down. The reaction solution was poured into sodium chloride solution and the mixture was stirred for 30 minutes. After extracting with pentane four times, the obtained organic layer was dried with MgSO₄, the desiccant was filtered off and solvents were removed with a rotary evaporator. Purification of the residue by column chromatography (silica gel, cyclohexanes/dichloromethane) yielded 2,3,4-

tribromo-5-(2,2,2-trifluoroethoxy)thiophene (0,5g, 24 %) as a light brown solid.

¹H NMR (400 MHz, CDCl₃): 4.4 (q, 2H). ¹³C NMR (101 MHz, CDCl₃): 147.1 (C1); 123.8 (q, CF₃); 117 (C4); 112.5 (C5); 110.3 (C3); 72.1 (q, CH₂).

Example 4: 3,4-Dibromo-5-(2,2,2-trifluoroethoxy)thiophen-2-carbaldehyd

5 A flask equipped with a magnetic stirring bar was flushed with nitrogen and charged with NaH (0.04 g, 1.6 mmol) and trifluoroethanol (0.12 mL, 1.57 mmol). 3,4,5-Tribromothiophen-2-carbaldehyd (0.5 g, 1.4 mmol, prepared according to Wong et al., Inorg. Chem. 2011, 50, 471-481) and CuI (0.03 g, 0.1 mmol) were added. After refluxing at 110 °C for 4 days, the system was cooled
10 down. The reaction solution was poured into sodium chloride solution and it was stirred for 15 more minutes. After extracting with pentane four times, the obtained organic layer was dried with MgSO₄, the desiccant was filtered and solvents were removed with a rotary evaporator. Purification of the residue by column chromatography (silica gel, cyclohexanes/dichloromethane) yielded 3,4-
15 dibromo-5-(2,2,2-trifluoroethoxy)thiophene-2-carbaldehyd as a yellow brown liquid. MS m/z = 367.7 (C₇H₃Br₂F₃O₂S).

Example 5: 5-bromo-5'-(difluoromethyl)-2,2'-bithiophene

5'-bromo-2,2'-bithiophene-5-carbaldehyde (1.02 g, 3,7 mmol) was provided in a dry Hastelloy® C4 reactor under nitrogen flush. The reactor was evacuated using
20 a water jet pump and cooled down to -70°C in an iso-propanol/CO₂ bath. 10ml CHCl₃/EtOH (97/3) mixture was sucked into the reactor. After cool-down, SF₄ (9 g, 82.9 mmol) was added. The reactor was allowed to warm-up to room temperature and after that heated to 70 °C.

After 22 h, the reactor was allowed to cool to 0 °C in an ice-bath. The gas-phase
25 was purged off into a scrubber. The reactor was opened; 50 ml of cooled dichloromethane were added. The dichloromethane/HF mixture was carefully given onto ice. The organic phase was separated and the aqueous phase was extracted with dichloromethane again. The combined organic phases were brought to pH 9 using aqueous 10%-NH₄OH. The organic phase was separated,
30 washed with water and brine and dried over MgSO₄. The solvent was removed by vacuum distillation. The obtained residue was purified by column chromatography using cyclohexane/dichloromethane to yield 420 mg of a solid.

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¹H NMR (505.5 MHz, CDCl₃ + 0.03% TMS), δ: 6.79 ppm (t, CF₂H), 6.97 ppm (q, 2H), 7.02 ppm (m, 1H), 7.17 ppm (m, 1H). ¹³C NMR (125.85MHz, CDCl₃ + 0.03% TMS), δ: 111.4 ppm (t, CF₂H), 123.4 ppm (s, 1C), 124.9 ppm (s, 1C), 128.3 ppm (t, 1C), 130.8 ppm (s, 1C).

5 *Example 6: 3-chloro-2-(trifluoromethyl)thiophene*

3-chlorothiophene-2-carboxylic acid (0.46 g, 2.83 mmol) was provided in a dry Hastelloy® C4 reactor under nitrogen flush. The reactor was evacuated using a water jet pump and cooled down to -70 °C in an iso-propanol/CO₂ bath. HF (8 g, 400 mmol) and SF₄ (4.1 g, 37.75 mmol) were added. The reactor was allowed to
10 warm-up to room temperature and after that heated to 120°C. After 16 h, the reactor was allowed to cool down to 0°C in an ice-bath. The gas-phase was purged off into a scrubber. The reactor was opened; 25 ml of cooled dichloromethane were added. The dichloromethane/HF mixture was carefully given onto ice. The organic phase was separated and the aqueous phase was
15 extracted with dichloromethane again. The combined organic phases were brought to pH 9 using aqueous 10%-NH₄OH. The organic phase was separated, washed with water and brine and dried over Na₂SO₄. The solvent was removed by vacuum distillation to yield 320 mg of the product. MS: [M-H] 185.8; [M-H-Cl] 166.8; [M-Cl] 150.8; [M-F-S] 135.8.

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C L A I M S

1. An organic photoelectric conversion device comprising a dye compound comprising a non-fused thiophene moiety substituted with at least one fluorinated alkyl group, wherein the fluorinated alkyl group is attached to the non-fused thiophene by means of a covalent single bond or an ether linkage,
5 preferably by means of a covalent single bond.
2. The organic photoelectric conversion device according to claim 1 wherein the fluorinated alkyl group is selected from the group consisting of a perfluorinated alkyl group, -CF₃, -CF₂H, and -CF₂CF₃, preferably the fluorinated
10 alkyl group is -CF₃.
3. The organic photoelectric conversion device according to claim 1 or 2 wherein the non-fused thiophene is substituted with at least one fluorinated alkyl group in position 3 and/or 4 of the non-fused thiophene.
4. The organic photoelectric conversion device according to any one of the
15 claims 1 to 3 wherein the non-fused thiophene moiety is 3-trimethylfluorothiophene, 4-trimethylfluorothiophene, 3,4-bis(trimethylfluorothiophene), and/or 3,4-bis(trifluoromethoxy)thiophene.
5. The organic photoelectric conversion device according to claim 1 or 2 wherein the non-fused thiophene is substituted with a fluorinated alkyl group in
20 position 2 or 5 of the non-fused thiophene, preferably the fluorinated alkyl group is -CF₃.
6. The organic photoelectric conversion device according to any one of claims 1 to 5 wherein the non-fused thiophene is connected to at least one further thiophene moiety by means of a covalent single bond, preferably the non-fused
25 thiophene is connected to two further thiophene moieties by means of one covalent single bond for each connection.
7. The organic photoelectric conversion device according to any one of the claims 1 to 6 wherein the dye compound is a polymer.
8. The organic photoelectric conversion device according to any one of the
30 claims 1 to 6 wherein the dye compound is a small molecule.

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9. The organic photoelectric conversion device according to any one of the claims 1 to 8 wherein the organic photoelectric conversion device is a dye-sensitized solar cell, a small-molecule organic solar cell, a polymer organic solar cell, or an organic light-emitting diode, preferably a small-molecule organic solar cell.

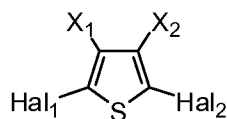
10. Use of a dye compound comprising a non-fused thiophene moiety substituted with at least one fluorinated alkyl group, wherein the fluorinated alkyl group is attached to the non-fused thiophene by means of a single covalent bond or an ether linkage as photoelectric material in a dye-sensitized solar cell, a small-molecule organic solar cell, a polymer organic solar cell, or an organic light-emitting diode, preferably in a small-molecule organic solar cell.

11. The use of claim 10 wherein the fluorinated alkyl group is selected from the group consisting of $-\text{CF}_3$, $-\text{CF}_2\text{H}$, and $-\text{CF}_2\text{CF}_3$, preferably the fluorinated alkyl group is $-\text{CF}_3$.

12. A process for the manufacture of a dye compound comprising a 3-trimethylfluorothiophene, a 4-trimethylfluorothiophene and/or a 3,4-bistrimethylfluorothiophene moiety comprising a step wherein a suitable precursor of the 3-trimethylfluorothiophene, the 4-trimethylfluorothiophene and/or the 3,4-bistrimethylfluorothiophene moiety is fluorinated in the presence of SF_4 , preferably in the presence of SF_4 and HF .

13. The process according to claim 12 wherein the suitable precursor of the 3-trimethylfluorothiophene, the 4-trimethylfluorothiophene and/or the 3,4-bistrimethylfluorothiophene is a 3-carboxythiophene, a 4-carboxythiophene and/or a 3,4-carboxythiophene.

14. A compound of the general formula (I)



wherein X₁ and X₂ are independently selected from the group consisting of H, a perfluorinated alkyl group, $-\text{CF}_3$, $-\text{OCF}_3$, $-\text{CF}_2\text{H}$, and $-\text{CF}_2\text{CF}_3$, with the proviso that at least one of X₁ and X₂ is not H; and wherein Hal₁ and Hal₂ are

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independently a halogen atom; preferably X_1 and X_2 are $-\text{CF}_3$ and Hal_1 and Hal_2 are Br or I.

15. Use of the compound according to claim 14 for the manufacture of a dye compound for an organic photoelectric conversion device.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/075032

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01G9/20 C09B57/00
ADD. H01L51/46

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)

H01G H01L C09B

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

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

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/010778 A1 (UNIV NORTHWESTERN [US]) 6 February 2003 (2003-02-06) the whole document	1-3,5,6, 8
X	JP 2008 239572 A (SAGAMI CHEM RES; TOSOH F TECH INC; TOSOH CORP) 9 October 2008 (2008-10-09) paragraph [0112] - paragraph [0113] ----- -/--	14,15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

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

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Date of the actual completion of the international search

19 February 2015

Date of mailing of the international search report

27/02/2015

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/075032

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WEIHONG ZHU ET AL: "Organic D-A-?-A Solar Cell Sensitizers with Improved Stability and Spectral Response", ADVANCED FUNCTIONAL MATERIALS, WILEY - V C H VERLAG GMBH & CO. KGAA, DE, vol. 21, no. 4, 22 February 2011 (2011-02-22), pages 756-763, XP001560462, ISSN: 1616-301X, DOI: 10.1002/ADFM.201001801 [retrieved on 2010-12-10] the whole document -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/075032

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			US 2005119440 A1 02-06-2005
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