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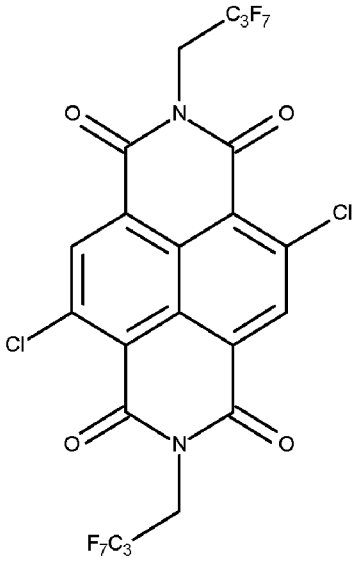
(54) Title: CRYSTALLINE FORM OF N,N'-BIS-(HEPTAFLUOROBUTYL)-2,6-DICHLORO-1,4,5,8-NAPHTHALENE TETRACARBOXYLIC DIIMIDE AND THE USE THEREOF

(57) Abstract: The present invention relates to a novel crystalline form of N,N'-Bis-(heptafluorobutyl)- 2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide of the formula (I) and the use thereof as semiconductor material, in particular as semiconductor material in organic electronics and organic photovoltaics.



(I)

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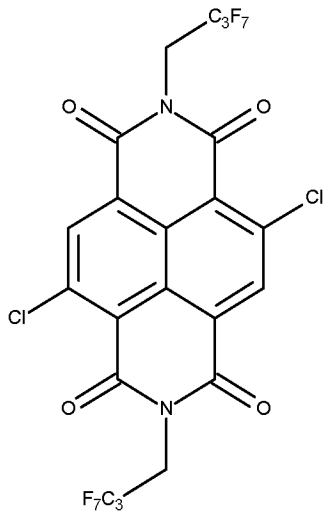
Crystalline form of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide and the use thereof

FIELD OF THE INVENTION

The present invention relates to a novel crystalline form of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide of the formula (I)



(I)

and the use thereof as semiconductor material, in particular as semiconductor material in organic electronics and organic photovoltaics.

It is expected that, in the future, not only the classical inorganic semiconductors but increasingly also organic semiconductors based on low molecular weight or polymeric materials will be used in many sectors of the electronics industry. In many cases, these organic semiconductors have advantages over the classical inorganic semiconductors, for example better substrate compatibility and better processibility of the semiconductor components based on them. They allow processing on flexible substrates and enable their orbital energies to be adjusted precisely to the particular application range by the methods of molecular modeling. The significantly reduced costs of such components have brought a renaissance to the field of research of organic electronics.

Organic electronics is concerned principally with the development of new materials and manufacturing processes for the production of electronic components based on organic semiconductor layers. These include in particular organic field-effect transistors (OFETs) and organic electroluminescent devices (hereinafter abbreviated as "EL"

devices). Great potential for development is ascribed to organic field-effect transistors, for example in storage elements, backplanes and integrated optoelectronic devices. An organic electroluminescent device is a self-emission device utilizing the principle that a fluorescent material emits light by the recombination energy of holes injected from an anode and electrons injected from a cathode when an electric field is applied. EL devices in form of organic light-emitting diodes (OLEDs) are especially of interest as an alternative to cathode ray tubes and liquid-crystal displays for producing flat visual display units. Owing to the very compact design and the intrinsically low power consumption, devices which comprise OLEDs are suitable especially for mobile applications, for example for applications in cell phones, laptops, etc.

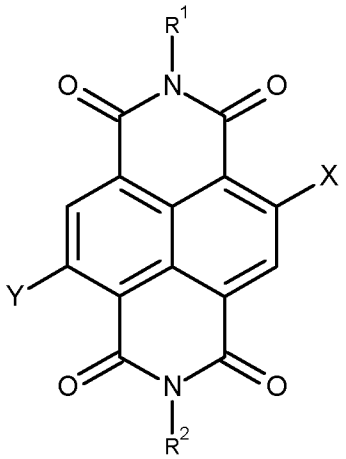
Organic photovoltaics are concerned principally with the development of new materials for organic solar cells. A great potential for development is ascribed to materials which have maximum transport widths and high mobilities for light-induced excited states (high exciton diffusion lengths) and are thus advantageously suitable for use as an active material in so-called excitonic solar cells. It is generally possible with solar cells based on such materials to achieve very good quantum yields. There is therefore a great need for organic compounds which are suitable as charge transport materials or exciton transport materials.

For the application properties of substances that are used on the industrial scale, the possible existence of crystalline modifications (also known as crystalline forms) or of solvates of the substance in question, the knowledge of the specific properties of such modifications and solvates and of methods for their preparation is in many cases of decisive importance. A substance can exist in different crystalline modifications but also in amorphous form. These cases are referred to as polymorphism. A polymorph is a solid, crystalline phase of the compound, which is characterized by a defined, uniform, packing and arrangement of the molecules in the solid substance. Different modifications of one and the same substance display different properties, for example differences in the following properties: crystal shape and size, density, solubility, filterability, dissolution rate, stability to phase conversion into another modification, stability during milling, suspension stability, optical and mechanical properties, vapour pressure, hygroscopicity, melting point, stability to decomposition, or colour.

It is known to employ core-chlorinated naphthalene tetracarboxylic diimides with various substituents bound to the imide nitrogen atoms as organic field-effect transistors.

WO 2013/164761 A2 published after the priority date of the present application describes a method for the vapor deposition of organic materials, inter alia N,N'-bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide. This document does not contain any crystallographic data.

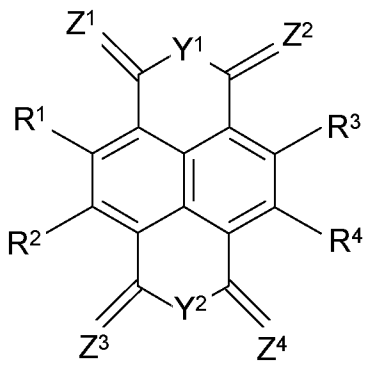
US 2003/0153005 A1 describes naphthalene-1,4,5,8-tetracarboxylic bisimides of the general formula A)



(B)

where the variables are defined as follows:
R^1 and R^2 independently of one another are hydrogen, substituted or unsubstituted alkyl or substituted or unsubstituted aryl;
X and Y independently of one another are halogen, amino or a radical with the formula -NHR^3, -OR^3, where R^3 has the formula -CH_2R^4, -CHR^4R^5, or -$CR^4R^5R^6$, where R^4, R^5, and R^6 independently of one another are hydrogen, substituted or unsubstituted alkyl, aryl, alkoxy, alkylthio, aryloxy or arylthio, and at least one of the two substituents X and Y is other than halogen,
their preparation and use as fluorescent dyes, for coloring high molecular mass organic materials and inorganic materials, as laser dyes, and also for fluorescence marking and as fluorescent labels for biomolecules.

WO 2009/147237 A1 describes compounds of the general formula (B)



(B)

where

at least two of the R^1, R^2, R^3 and R^4 radicals are Cl and the remaining radicals are hydrogen,

Y^1 is O or NR^a where R^a is hydrogen or an organyl radical,

Y^2 is O or NR^b where R^b is hydrogen or an organyl radical,

Z^1 and Z^2 are each O,

Z^3 and Z^4 are each O,

and their use as charge transport materials, exciton transport materials or emitter materials. Example 2 of this document describes the preparation of N,N´-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide (I) by reacting isomer-pure 2,6-dichloro-1,4,5,8-naphthalenetetracarboxylic dianhydride (prepared as described in J. Org. Chem. 2006, 71, 8098-8105) with 1H,1H-perfluorobutylamine in the presence of acetic acid. The purification is effected by three-zone gradient sublimation, the zones being at 180°C, 130°C and 100°C.

Adv. Funct. Mater. 2010, 20, 2148 - 2156 describes the synthesis of core-chlorinated naphthalene tetracarboxylic diimides with fluoroalkyl chains and the use thereof for n-channel organic thin-film transistors (OTFTs). Structural analysis of single crystals and thin films were performed and their charge-transport behavior was investigated in terms of structure-property relationships. According to this document, N,N'-Bis-(heptafluoro-butyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide (I) was prepared by heating a suspension of 2,6-dichloro-naphthalene tetracarboxylic dianhydride and 2,2,3,3,4,4,4-heptafluorobutylamine in acetic acid to reflux for 1 h. After cooling to room temperature, acetic acid was removed under reduced pressure. The residue was washed with methanol and purified by column chromatography with

dichloromethane/pentane 3:2. A solvent free single crystal of compound (I) was investigated using X-ray diffraction with CuKα radiation. The obtained crystal form of compound (I) crystallizes in the monoclinic space group P21/c. The crystal structure shows a slip-stacked edge-to-face herringbone arrangement with the following cell parameters: a = 11.870 Å, b = 16.633 Å, c = 5.935 Å, $\alpha = \gamma = 90°$, $\beta = 104.42°$ and Z = 2. This crystal form is denoted in the following also as "polymorph 1". Thin films of polymorph 1 have an out of plane spacing value (= d(001)-spacing value) of 19.28 Å (see Adv. Funct. Mater. 2010, 20, page 2152, table 3).

Adv. Funct. Mater. 2011, 21, 4173 - 4181 describes high mobility air-stable solution shear processed n-channel organic transistors based on core-chlorinated naphthalene diimides. The out-of-plane d(001) spacing was found to be 18.96 Å (see page 4179, left column, description regarding figure 6).

Appl. Phys. Lett. 102, 233303-1 - 233303-5 decribes contact properties of high mobility, air-stable, low-voltage organic n-channel thin-film transistors based on naphthalene tetracarboxylic diimides. This document does not contain any crystallographic data. Nevertheless, as the compounds are prepared by a method as described in Adv. Funct. Mater. 2010, 20, 2148 - 2156, the obtained products can only be polymorph 1.

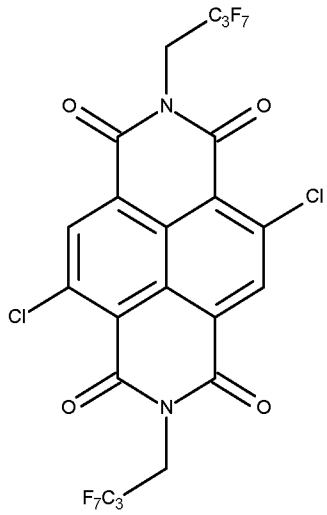
T. He, M. Stolte and F. Würthner describe in Adv. Mater. 2013, DOI: 10.1002/adma.201303392 air-stable n-channel OFET-based on microribbons of core-chlorinated naphthalene diimides. For single crystal growth and device fabrication a solution of the naphthalene diimides in $CHCl_3$ was drop-casted on an n-octadecyl triethoxysilane modified Si/SiO_2 substrate in a sealed petri dish together with a $CH_3OH/CHCl_3$ solvent mixture. The crystal form of the obtained single crystal corresponds to the afore-mentioned polymorph 1.

The electrical properties of compound I prepared according to known methods are still worthy of improvement. Further, the needle-shape of polymorph 1 of compound I is disadvantageous for the preparation of organic electronic device as needles will in many cases not span and homogeneously cover the active region of such a device. Since it is difficult to control the nucleation of the needles, it is difficult to get single needle devices.

It has now surprisingly been found that by defined processes a previously unknown crystalline, stable modification of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide which does not display the disadvantages of the known solid forms, is obtained in high purity.

SUMMARY OF THE INVENTION

A first object of the present invention relates to a crystalline form of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide of the formula (I)



(I)

which in an grazing incident X-ray diffractogram (GIXRD) using a synchrotron X-ray beam of 10.6 keV, an incident X-ray angle θ_{IN} of of 0.17°, and a temperature of 25°C displays at least 5 of the following reflections

qxy [Å^{-1}]	qz [Å^{-1}]	q [Å^{-1}]
0.01+/-0.03	0.35+/-0.03	0.35+/-0.03
0.01+/-0.03	1.40+/-0.03	1.4+/-0.03
0.01+/-0.03	1.73+/-0.03	1.73+/-0.03
1.09+/-0.03	0.13+/-0.03	1.01+/-0.03
1.09+/-0.03	0.48+/-0.03	1.19+/-0.03
1.10+/-0.03	0.61+/-0.03	1.25+/-0.03

This crystal form is denoted in the following also as polymorph 2.

A further object of the invention is a process for the preparation of the crystalline form of compound (I), as defined above and in the following, comprising:

(a) providing a source of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide of the formula (I),
(b) heating said source to a first temperature in the range of from 100 to 350°C to produce a vapor of compound (I),
(c) exposing at least one surface of a substrate having a second temperature lower than said first temperature to said vapor to deposit crystals from said vapor onto said at least one surface of said substrate,

wherein the at least one surface of the substrate is exposed also to a vapor of a solvent, selected from tetrahydrofuran and dichloromethane, prior to and/or during and/or after the deposition of the crystals of compound (I).

It has been surprisingly found that polymorph 2 can also be obtained by vapor deposition on the surface of a substrate that essentially consists of SiO_2 and/or that has been subjected to a surface modification with n-octadecyltrichlorosilane prior to the deposition of compound (I). Therefore, a further object of the invention is a process for the preparation of the crystalline form of compound I, as defined above and in the following, comprising:

(a) providing a source of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide of the formula (I),
(b) heating said source to a first temperature in the range of from 100 to 350°C to produce a vapor of compound (I),
(c) exposing at least one surface of a substrate having a second temperature lower than said first temperature to said vapor to deposit crystals from said vapor onto said at least one surface of said substrate,

wherein the surface of the substrate that is exposed to the vapor of compound (I) essentially consists of SiO_2

or wherein the surface of the substrate that is exposed to the vapor of compound (I) has been previously subjected to a surface modification with n-octadecyltrichlorosilane.

According to the last-mentioned embodiment, the surface of the substrate has preferably not been exposed to a vapor of tetrahydrofuran or dichloromethane prior to and/or during and/or after the deposition of the crystals of compound (I).

A further object of the invention is an organic field-effect transistor, comprising a substrate having at least one gate structure including a gate electrode and a gate dielectric, a source electrode and a drain electrode and as a semiconductor material the crystalline form of compound I as defined above and in the following.

A further object of the invention is a substrate comprising a plurality of organic field-effect transistors, at least some of the field-effect transistors comprising the crystalline form of compound I as defined above and in the following.

A further object of the invention is an electroluminescent arrangement comprising an upper electrode, a lower electrode, wherein at least one of said electrodes is transparent, an electroluminescent layer and optionally an auxiliary layer, wherein the electroluminescent arrangement comprises the crystalline form of compound I as defined above and in the following.

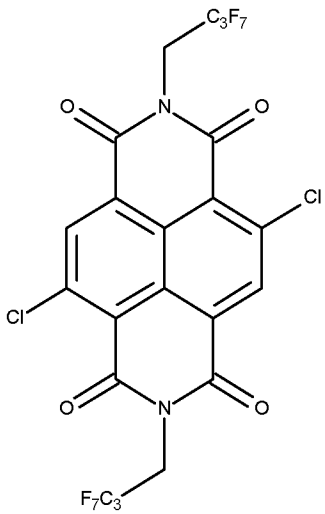
A further object of the invention is an organic solar cell comprising the crystalline form of compound I as defined above and in the following.

A further object of the invention is the use the crystalline form of compound I as defined above and in the following as a semiconductor material, preferably as a semiconductor material in organic electronics or in organic photovoltaics.

EMBODIMENTS OF THE INVENTION

The invention comprises the following embodiments:

1. A crystalline form of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide of the formula (I)



(I)

which in an grazing incident X-ray diffractogram (GIXRD) using a synchrotron X-ray beam of 10.6 keV, an incident X-ray angle θ_{IN} of 0.17°, and a temperature of 25°C displays at least 5 of the following reflections

qxy [Å^{-1}]	qz [Å^{-1}]	q [Å^{-1}]
0.01+/-0.03	0.35+/-0.03	0.35+/-0.03
0.01+/-0.03	1.40+/-0.03	1.4+/-0.03
0.01+/-0.03	1.73+/-0.03	1.73+/-0.03
1.09+/-0.03	0.13+/-0.03	1.01+/-0.03
1.09+/-0.03	0.48+/-0.03	1.19+/-0.03
1.10+/-0.03	0.61+/-0.03	1.25+/-0.03

2. The crystalline form of compound I according to embodiment 1 having the triclinic space group P-1.

3. The crystalline form of compound I according to embodiments 1 or 2, having the following cell parameters: a = 5.270 Å, b = 6.319 Å, c = 18.823 Å.

4. The crystalline form of compound I according to any of the preceding embodiments, having the following cell parameters: α = 80.43°, β = 82.15°, γ = 70.85°.

5. The crystalline form of compound I according to any of the preceding embodiments, in form of a thin film having an out of plane spacing value (= d(001)-spacing value) of 17.95 Å.

6. A composition comprising at least 10% by weight, more preferably at least 25% by weight, in particular at least 50% by weight, especially at least 75% by weight, more especially at least 90% by weight; based on the total weight of the composition, of the crystalline form of compound I as defined in any of embodiments 1 to 5.

7. A composition of compound I comprising at least two crystalline forms, selected from

- the crystalline form of compound I as defined in any of embodiments 1 to 5 (= polymorph 2),
- a crystalline form of compound I which in an grazing incident X-ray diffractogram (GIXRD) using a synchrotron X-ray beam of 10.6 keV, an incident X-ray angle θ_{IN} of 0.17°, and a temperature of 25°C displays at least 5 of the following reflections (= polymorph 1)

Miller Index	qxy [Å^{-1}]	qz [Å^{-1}]	q [Å^{-1}]
(100)	0.01+/-0.03	0.59+/-0.03	0.59+/-0.03
(200)	0.01+/-0.03	1.16+/-0.03	1.16+/-0.03
(400)	0.01+/-0.03	2.3+/-0.03	2.3+/-0.03
(020)	0.77+/-0.03	0.05+/-0.03	0.77+/-0.03
(120)	0.78+/-0.03	0.55+/-0.03	0.96+/-0.03
(011)	1.12+/-0.03	0.30+/-0.03	1.16+/-0.03

8. The composition of embodiment 7, comprising 50 to 99.99 % by weight, preferably 75% to 99.95 % by weight, in particular 90% to 99.95 % by weight of polymorph 2 based on the total weight of polymorph 1 and polymorph 2.

9. A process for the preparation of the crystalline form of compound I, as defined in any of embodiments 1 to 5, comprising:

(a) providing a source of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide of the formula (I),
(b) heating said source to a first temperature in the range of from 100 to 350°C to produce a vapor of compound (I),
(c) exposing at least one surface of a substrate having a second temperature lower than said first temperature to said vapor to deposit crystals from said vapor onto said at least one surface of said substrate,

wherein the at least one surface of the substrate is exposed also to a vapor of a solvent, selected from tetrahydrofuran and dichloromethane, prior to and/or during and/or after the deposition of the crystals of compound (I).

10. The process according to embodiment 9, wherein the pressure of the atmosphere in which compound (I) is vaporized is in a range of from 1 x 10^{-3} to 1 x 10^{-8} mbar, preferably 1 x 10^{-4} to 1 x 10^{-7} mbar, more preferably 1 x 10^{-5} to 1 x 10^{-6} mbar.

11. The process according to embodiment 9, wherein the pressure of the atmosphere in which compound (I) is vaporized is in a range of from 500 to 2000 mbar, preferably 800 to 1200 mbar, in particular ambient pressure.

12. The process according to any of embodiments 9 to 11, wherein the at least one surface of the substrate is exposed to the vapor of the solvent after the deposition of the crystals of compound (I).

13. The process according to embodiment 12, wherein the at least one surface of the substrate is exposed to the vapor of the solvent at a pressure of from 500 to 2000 mbar.

14. The process according to any of embodiments 9 to 13, wherein the surface of the substrate that is exposed to the vapor of compound (I) is coated with a dielectric, preferably SiO_2.

15. The process according to any of embodiments 9 to 13, wherein the surface of the substrate or, if present, the dielectric coating on the substrate, is subjected to a surface modification prior to the deposition of compound (I).

16. The process according to embodiment 15, wherein the compound used for the surface modification is selected from silanes, phosphonic acids, carboxylic acids, hydroxamic acids, amines, phosphines, sulfur-comprising compounds and mixtures thereof.

17. The process according to embodiment 15, wherein the compound used for the surface modification is selected from n-octadecyltrichlorosilane (OTS), n-octadecyltrimethoxysilane, n-octadecyltriethoxysilane, hexamethyldisilazane (HMDS), hexadecanethiol, mercaptoacetic acid, 3-mercaptopropionic acid, mercaptosuccinic acid and 3-mercapto-1-propanesulfonic acid, the alkali metal and ammonium salts of mercaptoacetic acid, 3-mercaptopropionic acid, mercaptosuccinic acid and 3-mercapto-1-propanesulfonic acid and mixtures thereof.

18. A process for the preparation of the crystalline form of compound I, as defined in any of embodiments 1 to 5, comprising:

(a) providing a source of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide of the formula (I),
(b) heating said source to a first temperature in the range of from 100 to 350°C to produce a vapor of compound (I),
(c) exposing at least one surface of a substrate having a second temperature lower than said first temperature to said vapor to deposit crystals from said vapor onto said at least one surface of said substrate,

wherein the surface of the substrate that is exposed to the vapor of compound (I) essentially consists of SiO_2

or wherein the surface of the substrate that is exposed to the vapor of compound (I) has been previously subjected to a surface modification with n-octadecyltrichlorosilane.

19. The process according to embodiment 18, wherein the surface of the substrate that is exposed to the vapor of compound (I) is a SiO_2 coated wafer and/or a wafer that has been subjected to a surface modification with n-octadecyltrichlorosilane.

20. The process according to embodiment 18 or 19, wherein the pressure of the atmosphere in which compound (I) is vaporized is in a range of from 1×10^{-3} to 1×10^{-8} mbar, preferably 1×10^{-4} to 1×10^{-7} mbar, more preferably 1×10^{-5} to 1×10^{-6} mbar.

21. The process according to embodiment 18 or 19, wherein the pressure of the atmosphere in which compound (I) is vaporized is in a range of from 500 to 2000 mbar, preferably 800 to 1200 mbar, in particular ambient pressure.

22. An organic field-effect transistor, comprising a substrate having at least one gate structure including a gate electrode and a gate dielectric, a source electrode and a drain electrode and as a semiconductor material the crystalline form of compound I as defined in any of embodiments 1 to 5, or a composition as defined in any of embodiments 6 to 8, or the crystalline form of compound I obtainable by the process of any of embodiments 9 to 21.

23. A substrate comprising a plurality of organic field-effect transistors, at least some of the field-effect transistors comprising the crystalline form of compound I as defined in any of embodiments 1 to , or a composition as defined in any of embodiments 2 to 4, or the crystalline form of compound I obtainable by the process of any of embodiments 5 to 17.

24. A semiconductor unit comprising at least one substrate as defined in embodiment 19.

25. An electroluminescent arrangement comprising an upper electrode, a lower electrode, wherein at least one of said electrodes is transparent, an electroluminescent layer and optionally an auxiliary layer, wherein the electroluminescent arrangement comprises the crystalline form of compound I as defined in any of embodiments 1 to 5, or a composition as defined in any of embodiments 6 to 8, or the crystalline form of compound I obtainable by the process of any of embodiments 9 to 21.

26. An electroluminescent arrangement as claimed in embodiment 25 in form of an organic light-emitting diode (OLED).

27. An organic solar cell comprising the crystalline form of compound I as defined in any of embodiments 1 to 5, or a composition as defined in any of embodiments 6 to 8, or the crystalline form of compound I obtainable by the process of any of embodiments 9 to 21.

28. The use the crystalline form of compound I as defined in any of embodiments 1 to 5, or a composition as defined in any of embodiments 6 to 8, or the crystalline form of compound I obtainable by the process of any of embodiments 9 to 21, as a semiconductor material, preferably as a semiconductor material in organic electronics or in organic photovoltaics.

29. The use according to embodiment 28 as a semiconductor in organic field-effect transistors.

30. The use according to embodiment 28 in an organic light-emitting diode (OLED).

DETAILED DESCRIPTION OF THE INVENTION

The new crystalline form of compound I according to the invention (polymorph 2) has the following advantages:

- The new polymorph 2, with its plate structure, provides a greater continuity of the obtained film within the channel region of the organic electronic device. The plates are capable of covering the entire active region. In contrast thereto only few of the needles of the known polymorph 1 will span the active region of an organic electronic device.

- The charge carrier mobility is an order of magnitude higher in the new polymorph 2 compared to known polymorph 1. If a mixture of polymorph 2 and polymorph 1 is employed an improvement of the electrical characteristics can be effected by converting at least a part of polymorph 1 into polymorph 2 by solvent vapor annealing with tetrahydrofuran or dichloromethane as described in the following.

- The crystal plates of polymorph 2 allow an easier device fabrication than the needles of polymorph 1. Since it is difficult to control nucleation of needles, it is difficult to get single needle devices.

Subject of the present invention is also a composition comprising at least 50% by weight, based on the total weight of the composition, of at least one crystalline form of compound I according to the invention. Further components of the composition may be crystalline forms of compound I different from the crystalline forms of the invention, compound I in amorphous form and components different from compound I. Preferably, the composition comprises at least 75% by weight, more preferably at least 85% by weight, in particular at least 90% by weight, especially at least 95% by weight, based on the total weight of the composition, of polymorph 2.

Preferably, the composition of compound I comprises at least two crystalline forms, selected from

- polymorph 2, and
- a crystalline form of compound I which in an grazing incident X-ray diffractogram (GIXRD) using a synchrotron X-ray beam of 10.6 keV, an incident X-ray angle θ_{IN} of 0.17°, and a temperature of 25°C displays at least 5 of the following reflections (= polymorph 1)

Miller Index	qxy [Å^{-1}]	qz [Å^{-1}]	q [Å^{-1}]
(100)	0.01+/-0.03	0.59+/-0.03	0.59+/-0.03

(200)	0.01+/-0.03	1.16+/-0.03	1.16+/-0.03
(400)	0.01+/-0.03	2.3+/-0.03	2.3+/-0.03
(020)	0.77+/-0.03	0.05+/-0.03	0.77+/-0.03
(120)	0.78+/-0.03	0.55+/-0.03	0.96+/-0.03
(011)	1.12+/-0.03	0.30+/-0.03	1.16+/-0.03

Polymorph 2

The new crystalline form of compound I (polymorph 2) can be identified by grazing incidence X-ray diffraction (GIXRD) of thin films on a suitable substrate. Thus, grazing incidence X-ray diffractograms were conducted at the G1 station (10.6 keV) of the Cornell High Energy Synchrotron Source. The beam was selected to be 0.05 mm tall and 1 mm wide. The widths of the samples were 0.5 cm. The X-ray beam was aligned at a 0.17° incident angle with the substrate. Scattered intensity was collected with a 2-D CCD detector, with a sample to detector distance of 117.6 mm. The obtained images have been background subtracted and corrected for the polarization of the beam.

Table 1 lists the most prominent peaks of polymorph 2:

Table 1

qxy [$Å^{-1}$]	qz [$Å^{-1}$]	q [$Å^{-1}$]
0.01+/-0.03	0.35+/-0.03	0.35+/-0.03
0.01+/-0.03	1.40+/-0.03	1.4+/-0.03
0.01+/-0.03	1.73+/-0.03	1.73+/-0.03
1.09+/-0.03	0.13+/-0.03	1.01+/-0.03
1.09+/-0.03	0.48+/-0.03	1.19+/-0.03
1.01+/-0.03	0.61+/-0.03	1.25+/-0.03

Polymorph 2 can be characterized by at least 5, preferably by all 6 of the reflections in table 1.

Table 2 is a more extensive list of the peaks of polymorph 2:

Table 2

qxy	qz	q
0.00	0.36	0.36
1.09	0.13	1.10
1.09	0.25	1.12
1.09	0.48	1.19
1.09	0.60	1.29
1.09	0.83	1.38
1.09	1.91	2.20
1.09	2.03	2.31
0.95	2.77	2.92
1.20	2.77	3.02
1.29	0.02	1.29
1.29	0.13	1.29
1.29	0.23	1.31
1.29	0.48	1.38
1.29	0.58	1.41
1.30	0.94	1.61
1.30	1.67	2.12
1.39	0.12	1.40
1.39	0.24	1.41
1.40	0.83	1.63
1.40	1.30	1.91
1.41	2.29	2.69
1.39	2.41	2.78
1.50	0.01	1.50
1.94	0.01	1.94
1.94	0.37	1.98
1.94	0.73	2.07
1.98	1.48	2.47
1.98	1.86	2.72
2.15	0.74	2.28
2.16	1.12	2.43
2.20	1.25	2.53

qxy	qz	q
2.67	2.41	3.60

wherein all values in table 2 are determined with an accuracy of +/- 0.03 $Å^{-1}$.

Polymorph 2 can be characterized by at least 5, preferably by at least 6, more preferably by at least 7, in particular by at least 8, especially by at least 9, more especially by at least 10 of the reflections in table 2.

The unit cell of polymorph 2 has the space group P-1.

In particular, polymorph 2 has the following cell parameters: a = 5.270 Å, b = 6.319 Å, c = 18.823 Å (a, b, c = length of the edges of the unit cell).

In particular, polymorph 2 has the following cell parameters: $\alpha = 80.43°$, $\beta = 82.15°$, $\gamma = 70.85°$ (α, β, γ = angles of the unit cell).

In particular, thin films of polymorph 2 have an out of plane spacing value (= d(001)-spacing value) of 17.95 Å. In contrast to this, known polymorph 1 is characterized by an out-of-plane spacing of 19.28 Å (see Adv. Funct. Mater. 2010, 20, page 2152, table 3). The XRD pattern of films of compound (I) obtained as decribed in Adv. Funct. Mater. 2011, 21, 4173 - 4181 have an out-of-plane d(001) spacing of 18.96 Å (see Adv. Funct. Mater. 2011, 21, page 4179, left column, description regarding figure 6).

The characteristic data of the crystal structure of polymorph 2 are summarized in the following table.

Crystallographic properties of polymorph 2

Parameter	
Crystal system	triclinic
Space group	P-1
a	5.270(1) Å
b	6.3185(16) Å
c	18.822(6) Å
α	80.43(2)°
β	82.15(2)°
γ	70.846(16)°

a, b, c = Length of the edges of the unit cell

α, β, γ = Angles of the unit cell

It has surprisingly been found that the preparation of pure polymorph 2 of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide (I) can be effected if the crystal growth is effected in the presence of a solvent vapour of tetrahydrofuran or dichloromethane or by solvent vapour annealing of polymorph 1 or mixtures of polymorph 1 and polymorph 2 with tetrahydrofuran or dichloromethane.

A further object of the invention is a process for the preparation of polymorph 2, comprising:

(a) providing a source of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide of the formula (I),
(b) heating said source to a first temperature in the range of from 100 to 350°C to produce a vapor of compound (I),
(c) exposing at least one surface of a substrate having a second temperature lower than said first temperature to said vapor to deposit crystals from said vapor onto said at least one surface of said substrate,

wherein the at least one surface of the substrate is exposed also to a vapor of a solvent, selected from tetrahydrofuran and dichloromethane, prior to and/or during and/or after the deposition of the crystals of compound (I).

In principle, the synthesis of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide (I) used as starting material for the preparation of the new crystalline form of the invention (polymorph 2), can be effected by known processes. Suitable processes for the synthesis are described e.g. in Adv. Funct. Mater. 2010, 20, 2148 - 2156 and in WO 2009/147237 A1. The teaching of those documents is incorporated herein by reference.

For the preparation of polymorph 2 of compound (I), essentially any known form of compound I can be used. Accordingly, amorphous N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide or a mixture of different crystalline modifications of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide or a mixture of amorphous N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide and crystalline N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide can be used.

Preferably, the pressure of the atmosphere in which compound (I) is vaporized is in a range of from 1 x 10^{-3} to 1 x 10^{-8} mbar, more preferably 1 x 10^{-4} to 1 x 10^{-7} mbar, in particular 1 x 10^{-5} to 1 x 10^{-6} mbar.

Thermal evaporation of compound (I) is usually effected at a very low pressure. It is in principal not necessary to perform the thermal evaporation of compound (I) in the presence of a gas or a gas mixture that is inert towards compound (I). In a preferred embodiment, the atmosphere in which compound (I) is vaporized preferably comprises or consists of air and/or of a vapor of a solvent.

In an alternative embodiment, compound (I) is vaporized in an atmosphere at a pressure comprised between 500 and 2000 mbar. More preferably said pressure is in a range of from 800 to 1200 mbar. In particular said pressure is ambient pressure (= approximately 1000 mbar)

In a further suitable embodiment, the atmosphere in which compound (I) is vaporized comprises or consists of an inert gas. Suitable gases are selected from noble gases, nitrogen, carbon dioxide and mixtures thereof. Suitable noble gases are e.g. argon, helium, neon and mixtures thereof.

According to a preferred embodiment of the invention, compound (I) is heated to a temperature at which sufficient vapor is generated in order to obtain suitable deposition rates on the substrate. Vapor of compound (I) may be generated through evaporation or sublimation. Usually, the material is heated up to a temperature above the evaporation temperature or above the sublimation temperature of compound (I). Heating of the organic material can be accomplished by a variety of methods. For instance, compound (I) can be placed on a support, for instance a metallic plate or quartz plate, which can be heated via resistive heating or inductive heating. According to another variant, compound (I) can be heated by microwave heating or via an electron gun.

Preferably, the temperature and/or the pressure are controlled in order to provide for a constant vaporization rate.

Preferably, the first temperature (temperature of the source of compound (I)) is in a range of from 120 to 300°C more preferably in a range of from 150 to 250°C.

Preferably, the second temperature (temperature of the substrate) is in a range of from 10 to 100°C.

In accordance with the method of the present invention, at least one surface of the substrate is exposed to a vapor of compound (I). This allows deposition of a layer of said vapor onto the surface of the substrate in form of a thin polycrystalline film. In order to accomplish a suitable deposition rate, the temperature of the substrate, i.e. the second temperature mentioned above, is kept below the melting temperature or the sublimation temperature of compound (I).

In a suitable embodiment of the method of the invention, the duration for which the substrate is exposed to the vapor of compound (I) is controlled. For instance, a mask provided with a shutter can be arranged in front of the surface of the substrate which allows exposing the surface of the substrate to the vapor for a predetermined time. The substrate can repeatedly be exposed to the vapor for a predetermined time. Certain thermal annealing procedures can be foreseen prior to exposure and/or during exposure and/or in between exposures, for instance by raising or lowering the temperature of the substrate.

In a special embodiment, the at least one surface of the substrate is exposed to the vapor of the solvent after the deposition of the crystals of compound (I). According to this embodiment the crystalline form of compound (I) deposited on the surface of the substrate prior to exposition to the solvent vapor consists of polymorph 1 or a mixture of polymorph 1 and polymorph 2. According to this embodiment the at least one surface of the substrate is preferably exposed to the vapor of the solvent at a pressure of from 500 to 2000 mbar. More preferably, the at least one surface of the substrate is preferably exposed to the vapor of the solvent at a pressure approximately 1000 mbar (= ambient pressure).

Preferably a source of the solvent is provided in the same container with the substrate prior to and/or during and/or after the deposition of the crystals of compound (I).

Preferably the exposition of the surface of the substrate to the vapor of the solvent is performed at a temperature of the source of the solvent that lies between room temperature and a temperature close to or slightly above the boiling point of the solvent at the employed pressure. Preferably, the temperature of the solvent is in a range of from 20 to 80°C, more preferably 25 to 70°C.

A wide variety of substrates may be used in the method of the present invention. The substrates may be made of virtually any materials which are stable under the process conditions of the method of the invention. Thus, the substrate may include organic and

inorganic materials or composite materials. Suitable substrates are in principle all materials known for this purpose. Suitable substrates comprise, for example, oxidic materials, metals, semiconductors, metal alloys, semiconductor alloys, polymers, inorganic solids, paper and combinations thereof.

Suitable substrates are preferably selected from SiO_2, inorganic glasses, quartz, ceramics, undoped or doped inorganic semiconductors, metals of groups 8, 9, 10 or 11 of the Periodic Table and metal alloys thereof, polymeric materials, filled polymeric materials and combinations thereof.

Preferred metal and metal alloy substrates comprise Au, Ag, Cu, etc. Preferred undoped or doped inorganic semiconductors are Si, doped Si, Ge and doped Ge. Preferred polymeric materials are selected from acrylics, epoxies, polyamides, polycarbonates, polyimides, polyvinyl chloride, polyolefins, polystyrene homopolymers and copolymers, polyketones, poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene (sometimes referred to as poly(ether ether ketone) or PEEK), polynorbornenes, polyphenyleneoxides, poly(ethylene naphthalenedicarboxylate) (PEN), poly(ethylene terephthalate) (PET), poly(phenylene sulfide) (PPS), fluoropolymers, polyurethanes, fiber-reinforced plastics (FRP) and combinations thereof.

Especially preferred substrates are selected from Si, SiO_2, glass, quartz, ceramics and combinations thereof. The substrate may be flexible or inflexible, and have a curved or planar geometry, depending on the desired use.

Preferably, at least the surface of the substrate comprises or consists of at least one dielectric. Suitable dielectrics are SiO_2, polystyrene, poly-α-methylstyrene, polyolefins (such as polypropylene, polyethylene, polyisobutene), polyvinylcarbazole, fluorinated polymers (e.g. Cytop, CYMM), cyanopullulans, polyvinylphenol, poly-p-xylene, polyvinyl chloride, etc. Specific dielectrics are "self-assembled nanodielectrics", i.e. polymers which are obtained from monomers comprising SiCl functionalities, for example $Cl_3SiOSiCl_3$, $Cl_3Si\text{-}(CH_2)_6\text{-}SiCl_3$, $Cl_3Si\text{-}(CH_2)_{12}\text{-}SiCl_3$, and/or which are crosslinked by atmospheric moisture or by addition of water diluted with solvents (see, for example, Facchetti Adv. Mat. 2005, 17, 1705-1725). Instead of water, it is also possible for hydroxyl-containing polymers such as polyvinylphenol or polyvinyl alcohol or copolymers of vinylphenol and styrene to serve as crosslinking components. It is also possible for at least one further polymer to be present during the crosslinking operation, for example polystyrene, which is then also crosslinked (see Facchetti, US patent application 2006/0202195).

The surface of the substrate and/or the dielectric can be subjected to a modification prior to the deposition of compound (I). This modification can have an effect on the nature of the crystalline form of compound (I) deposited on the surface of the substrate. Thus e.g. pure new polymorph 2 is formed on a surface of n-octadecyltrichlorosilane (OTS), whereas a mixture of polymorph 1 and polymorph 2 is formed on a surface of hexamethyldisilazane (HMDS). Nevertheless, if the surface of the substrate comprising pure polymorph 1 or a mixture of polymorph 1 and polymorph 2 is exposed to a vapor of a solvent, selected from tetrahydrofuran and dichloromethane, for a sufficient time, pure polymorph 2 is obtained.

In a special embodiment, the surface of the substrate and/or the dielectric is subjected to a modification prior to the deposition of compound (I) resulting in a self-assembled monolayer (SAM) of the compounds employed for the modification.

In a further modification only parts of the substrate are covered with the self-assembled monolayer (SAM). Without being bound by a theory this might be advantageous to achieve a lateral structuring of the morphology of the compound (I).

The modification of the surface of the substrate and/or the dielectric prior to the deposition of compound (I) may e.g. serve to form regions which bind the semiconductor materials and/or regions on which no semiconductor materials can be deposited. Further, the modification of the surface of the substrate and/or the dielectric may have an influence on the properties of the obtained semiconductor, e.g. its charge transport mobility, on/off ratio, etc.

Suitable compounds for the surface modification are:

- silanes, such as alkyltrichlorosilanes, e.g. n-octadecyltrichlorosilane (OTS); compounds with trialkoxysilane groups, e.g. alkyltrialkoxysilanes such as n-octadecyltrimethoxysilane, n-octadecyltriethoxysilane, n-octadecyltri(n-propyl)oxysilane, n-octadecyltri(isopropyl)oxysilane; trialkoxyaminoalkylsilanes, such as triethoxyaminopropylsilane and N[(3-triethoxysilyl)propyl]ethylenediamine; trialkoxyalkyl 3-glycidyl ether silanes, such as triethoxypropyl 3-glycidyl ether silane; trialkoxyallylsilanes, such as allyltrimethoxysilane; trialkoxy(isocyanatoalkyl)silanes; trialkoxysilyl(meth)acryloyloxyalkanes and trialkoxysilyl(meth)acrylamidoalkanes, such as 1-triethoxysilyl-3-acryl-oyl-oxypropane,
- phosphonic acids,
- carboxylic acids,
- hydroxamic acids,

- amines,
- phosphines,
- sulfur-comprising compounds, especially thiols, and
- mixtures thereof.

The compounds for the surface modification are preferably selected from alkyltrichlorosilanes, alkyltrialkoxysilanes, hexaalkyldisilazanes, C_8-C_{30}-alkylthiols, mercaptocarboxylic acids, mercaptosulfonic acids and mixtures thereof-

In a special embodiment, the compounds for the surface modification are selected from n-octadecyltrichlorosilane (OTS), n-octadecyltrimethoxysilane, n-octadecyltriethoxysilane, hexamethyldisilazane (HMDS), hexadecanethiol, mercaptoacetic acid, 3-mercaptopropionic acid, mercaptosuccinic acid and 3-mercapto-1-propanesulfonic acid, the alkali metal and ammonium salts of mercaptoacetic acid, 3-mercaptopropionic acid, mercaptosuccinic acid and 3-mercapto-1-propanesulfonic acid and mixtures thereof.

It has surprisingly been found that the preparation of pure polymorph 2 of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide (I) can also be effected if the crystal growth is effected on the surface of a substrate that essentially consists of SiO_2. According to this embodiment it is not necessary that the surface of the substrate is exposed to a vapor of tetrahydrofuran or dichloromethane prior to and/or during and/or after the deposition of the crystals of compound (I).

A further object of the invention is a process for the preparation of polymorph 2, comprising:

(a) providing a source of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide of the formula (I),
(b) heating said source to a first temperature in the range of from 100 to 350°C to produce a vapor of compound (I),
(c) exposing at least one surface of a substrate having a second temperature lower than said first temperature to said vapor to deposit crystals from said vapor onto said at least one surface of said substrate,

wherein the surface of the substrate that is exposed to the vapor of compound (I) essentially consists of SiO_2

or wherein the surface of the substrate that is exposed to the vapor of compound (I) has been previously subjected to a surface modification with n-octadecyltrichlorosilane.

In a special embodiment of this variant, the surface of the substrate that is exposed to the vapor of compound (I) is a SiO_2 coated silicon wafer or a wafer that is optionally pretreated with OTS.

Preferably, the first temperature (temperature of the source of compound (I)) is in a range of from 120 to 300°C more preferably in a range of from 150 to 250°C.

Preferably, the second temperature (temperature of the substrate) is in a range of from 10 to 100°C.

Preferably, the pressure of the atmosphere in which compound (I) is vaporized is in a range of from 1×10^{-3} to 1×10^{-8} mbar, more preferably 1×10^{-4} to 1×10^{-7} mbar, in particular 1×10^{-5} to 1×10^{-6} mbar.

In an alternative embodiment, the pressure of the atmosphere in which compound (I) is vaporized is in a range of from 500 to 2000 mbar. More preferably said pressure is in a range of from 800 to 1200 mbar. In particular said pressure is ambient pressure.

Polymorph 1

It has been found that the preparation of crystalline forms of N,N'-Bis-(heptafluoro-butyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide (I) with a high amount of polymorph 1 can be effected if the crystal growth is effected in the presence of a solvent vapour of chloroform or by solvent vapour annealing of polymorph 2 or mixtures of polymorph 1 and polymorph 2 with chloroform.

The crystallographic properties of polymorph 1 are shown in table 3.

Table 3

Parameter	
Crystal system	monoclinic
Space group	P21/c
a	11.870 Å
b	16.633 Å
c	5.935 Å
α	90°

Parameter	
β	104.42°
γ	90°
Z	2

a,b,c = Length of the edges of the unit cell
α,β,γ = Angles of the unit cell
Z = Number of molecules, in the unit cell

The new crystalline form of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide of the formula (I) denoted as polymorph 2 is in particular suitable as a semiconductor material in organic electronics or in organic photovoltaics.

Polymorph 2 has at least one of the following advantages over polymorph 1 and further known organic semiconductor materials:

- high charge transport mobility,
- high on/off ratio.

Polymorph 2 is advantageously suitable as semiconductor material in organic field-effect transistors, organic solar cells and in organic light-emitting diodes. It is also particularly advantageous as an exciton transport material in excitonic solar cells.

Polymorph 2 is advantageously suitable for the fabrication of organic field-effect transistors. They may be used, for example, for the production of integrated circuits (ICs), for which customary n-channel MOSFETs (metal oxide semiconductor field-effect transistors) have been used to date. These are then CMOS-like semiconductor units, for example for microprocessors, microcontrollers, static RAM and other digital logic circuits. OFET on the basis of polymorph 1 are especially suitable for use in displays (specifically large-surface area and/or flexible displays), RFID tags, smart labels and sensors.

The invention further provides organic field-effect transistors comprising a substrate having at least one gate structure including a gate electrode and a gate dielectric, a source electrode and a drain electrode and as a semiconductor material the crystalline form of compound (I) denoted as polymorph 2.

The invention also provides semiconductor units which comprise at least one such substrate.

A specific embodiment is a substrate with a pattern (topography) of organic field-effect transistors, each transistor comprising

- an organic semiconductor disposed on the substrate;
- a gate structure for controlling the conductivity of the conductive channel; and
- conductive source and drain electrodes at the two ends of the channel,

the organic semiconductor comprising or consisting of the crystalline form of compound (I) denoted as polymorph 2. In addition, the organic field-effect transistor generally comprises a dielectric.

As a buffer layer, any dielectric material is suitable, for example anorganic materials such LIF, AlO_x, SiO_2 or silicium nitride or organic materials such as polyimides or polyacrylates, e.g. polymethylmethacrylate (PMMA).

A further specific embodiment is a substrate having a pattern of organic field-effect transistors, each transistor forming an integrated circuit or being part of an integrated circuit and at least some of the transistors comprising the crystalline form of compound (I) denoted as polymorph 2.

Suitable substrates are those mentioned above. A typical substrate for semiconductor units comprises a matrix (for example a silicon, quartz or polymer matrix) and, optionally, a dielectric top layer. Suitable dielectrics are those mentioned above, wherein SiO_2 is especially preferred.

The substrate may additionally have electrodes, such as gate, drain and source electrodes of OFETs, which are normally localized on the substrate (for example deposited onto or embedded into a nonconductive layer on the dielectric). The substrate may additionally comprise conductive gate electrodes of the OFETs, which are typically arranged below the dielectric top layer (i.e. the gate dielectric).

In a specific embodiment, an insulator layer (gate insulating layer) is present on at least part of the substrate surface. The insulator layer comprises at least one insulator which is preferably selected from inorganic insulators, such as SiO_2, silicon nitride (Si_3N_4), etc., ferroelectric insulators, such as Al_2O_3, Ta_2O_5, La_2O_5, TiO_2, Y_2O_3, etc., organic insulators such as polyimides, benzocyclobutene (BCB), polyvinyl alcohols, polyacrylates, etc., and combinations thereof.

Suitable materials for source and drain electrodes are in principle electrically conductive materials. These include metals, preferably metals of groups 6, 7, 8, 9, 10 or 11 of the Periodic Table, such as Pd, Au, Ag, Cu, Al, Ni, Cr, etc. Also suitable are conductive polymers, such as PEDOT (= poly(3,4-ethylenedioxythiophene)):PSS (= poly(styrenesulfonate)), polyaniline, surface-modified gold, etc. Preferred electrically

conductive materials have a specific resistance of less than 10^{-3} ohm x meter, preferably less than 10^{-4} ohm x meter, especially less than 10^{-6} or 10^{-7} ohm x meter.

In a specific embodiment, drain and source electrodes are present at least partly on the organic semiconductor material. It will be appreciated that the substrate may comprise further components as used customarily in semiconductor materials or ICs, such as insulators, resistors, capacitors, conductor tracks, etc.

The electrodes may be applied by customary processes, such as evaporation or sputtering, lithographic processes or another structuring process, such as printing techniques.

The resulting semiconductor layers based on polymorph 2 generally have a thickness which is sufficient for forming a semiconductor channel which is in contact with the source/drain electrodes.

The compound of the formula (I) is preferably deposited on the substrate in a thickness of from 10 to 1000 nm, more preferably from 15 to 250 nm.

In a preferred embodiment, the inventive field-effect transistor is a thin-film transistor (TFT). In a customary construction, a thin-film transistor has a gate electrode disposed on the substrate or buffer layer (the buffer layer being part of the substrate), a gate insulation layer disposed thereon and on the substrate, a semiconductor layer disposed on the gate insulator layer, an ohmic contact layer on the semiconductor layer, and a source electrode and a drain electrode on the ohmic contact layer.

In a preferred embodiment, the surface of the substrate, before the deposition of at least one compound of the general formula (I) (and if appropriate of at least one further semiconductor material), is subjected to a modification as mentioned above.

Various semiconductor architectures comprising the inventive semiconductors are also conceivable, for example top contact, top gate, bottom contact, bottom gate, or else a vertical construction, for example a VOFET (vertical organic field-effect transistor), as described, for example, in US 2004/0046182.

Preferred semiconductor architectures are the following:

1. substrate, dielectric, organic semiconductor, preferably gate, dielectric, organic semiconductor, source and drain, known as "Bottom Gate Top Contact";
2. substrate, dielectric, organic semiconductor, preferably substrate, gate, dielectric, source and drain, organic semiconductor, known as "Bottom Gate Bottom Contact";

3. substrate, organic semiconductor, dielectric, preferably substrate, source and drain, organic semiconductor, dielectric, gate, known as "Top Gate Bottom Contact";
4. substrate, organic semiconductor, dielectric, preferably substrate, organic semiconductor, source and drain, dielectric, gate, known as "Top Gate Top Contact";

The layer thicknesses are, for example, from 10 nm to 5 μm in semiconductors, from 50 nm to 10 μm in the dielectric; the electrodes may, for example, be from 20 nm to 10 μm. The OFETs may also be combined to form other components, such as ring oscillators or inverters.

A further aspect of the invention is the provision of electronic components which comprise a plurality of semiconductor components, which may be n- and/or p-semiconductors. Examples of such components are field-effect transistors (FETs), bipolar junction transistors (BJTs), tunnel diodes, converters, light-emitting components, biological and chemical detectors or sensors, temperature-dependent detectors, photodetectors, such as polarization-sensitive photodetectors, gates, AND, NAND, NOT, OR, TOR and NOR gates, registers, switches, timer units, static or dynamic stores and other dynamic or sequential, logical or other digital components including programmable switches.

A specific semiconductor element is an inverter. In digital logic, the inverter is a gate which inverts an input signal. The inverter is also referred to as a NOT gate. Real inverter switches have an output current which constitutes the opposite of the input current. Typical values are, for example, (0, +5V) for TTL switches. The performance of a digital inverter reproduces the voltage transfer curve (VTC), i.e. the plot of input current against output current. Ideally, it is a staged function and, the closer the real measured curve approximates to such a stage, the better the inverter is.

The crystalline form of compound (I) denoted as polymorph 2 is also particularly advantageously suitable for use in organic photovoltaics (OPVs). Preference is given to their use in solar cells which are characterized by diffusion of excited states (exciton diffusion). In this case, one or both of the semiconductor materials utilized is notable for a diffusion of excited states (exciton mobility). Organic solar cells generally have a layer structure and generally comprise at least the following layers: anode, photoactive layer and cathode. These layers are generally applied to a substrate suitable for this purpose. The structure of organic solar cells is described, for example, in US 2005/0098726 and US 2005/0224905.

The invention provides an organic solar cell which comprises a substrate with at least one cathode and at least one anode, and the crystalline form of compound (I) denoted

as polymorph 2 as a photoactive material. The inventive organic solar cell comprises at least one photoactive region. A photoactive region may comprise two layers, each of which has a homogeneous composition and forms a flat donor-acceptor heterojunction. A photoactive region may also comprise a mixed layer and form a donor-acceptor heterojunction in the form of a donor-acceptor bulk heterojunction.

Suitable substrates for organic solar cells are those mentioned above, for example, oxidic materials, polymers and combinations thereof. Preferred oxidic materials are selected from glass, ceramic, SiO_2, quartz, etc. Preferred polymers are selected from polyethylene terephthalates, polyolefins (such as polyethylene and polypropylene), polyesters, fluoropolymers, polyamides, polyurethanes, polyalkyl (meth)acrylates, polystyrenes, polyvinyl chlorides and mixtures and composites.

Suitable electrodes (cathode, anode) are in principle metals, semiconductors, metal alloys, semiconductor alloys, nanowire thereof and combinations thereof. Preferred metals are those of groups 2, 8, 9, 10, 11 or 13 of the periodic table, e.g. Pt, Au, Ag, Cu, Al, In, Mg or Ca. Preferred semiconductors are, for example, doped Si, doped Ge, indium tin oxide (ITO), fluorinated tin oxide (FTO), gallium indium tin oxide (GITO), zinc indium tin oxide (ZITO), poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS), etc. Preferred metal alloys are, for example, alloys based on Pt, Au, Ag, Cu, etc. A specific embodiment is Mg/Ag alloys.

The material used for the electrode facing the light (the anode in a normal structure, the cathode in an inverse structure) is preferably a material at least partly transparent to the incident light. This preferably includes electrodes which have glass and/or a transparent polymer as a carrier material. Transparent polymers suitable as carriers are those mentioned above, such as polyethylene terephthalate. The electrical contact connection is generally effected by means of metal layers and/or transparent conductive oxides (TCOs). These preferably include ITO, doped ITO, FTO (fluorine doped tin oxide), AZO (aluminum doped tin oxide), ZnO, TiO_2, Ag, Au, Pt or graphene or multi layer graphene or carbon nanotubes. Particular preference is given to ITO for contact connection. For electrical contact connection, it is also possible to use a conductive polymer, for example a poly-3,4-alkylenedioxythiophene, e.g. poly-3,4-ethyleneoxythiophene poly(styrenesulfonate) (PEDOT).

The electrode facing the light is configured such that it is sufficiently thin to bring about only minimal light absorption but thick enough to enable good charge transport of the extracted charge carriers. The thickness of the electrode layer (without carrier material) is preferably within a range from 20 to 200 nm.

In a specific embodiment, the material used for the electrode facing away from the light (the cathode in a normal structure, the anode in an inverse structure) is a material

which at least partly reflects the incident light. This includes metal films, preferably of Ag, Au, Al, Ca, Mg, In, and mixtures thereof. Preferred mixtures are Mg/Al. The thickness of the electrode layer is preferably within a range from 20 to 300 nm.

The photoactive region comprises or consists of at least one layer which comprises polymorph 2. In addition to the photoactive layer there may be one or more further layer(s). These are, for example, selected from

- layers with electron-conducting properties (electron transport layer, ETL),
- layers which comprise a hole-conducting material (hole transport layer, HTL), which need not absorb any radiation,
- exciton- and hole-blocking layers (e.g. EBLs), which must not absorb, and
- multiplication layers.

Suitable materials for these layers are described in detail hereinafter.
Suitable exciton- and hole-blocking layers are described, for example, in US 6,451,415.
Suitable materials for exciton-blocking layers are, for example, bathocuproin (BCP), 4,4',4''-tris[3-methylphenyl-N-phenylamino]triphenylamine (m-MTDATA).

The inventive solar cells comprise at least one photoactive donor-acceptor heterojunction. Optical excitation of an organic material generates excitons. In order that a photocurrent occurs, the electron-hole pair has to be separated, typically at a donor-acceptor interface between two unlike contact materials. At such an interface, the donor material forms a heterojunction with an acceptor material. When the charges are not separated, they can recombine in a process also known as "quenching", either radiatively by the emission of light of a lower energy than the incident light or nonradiatively by generation of heat. Both processes are undesired.

If at least one compound of the general formula (I) is used as a n-semiconductor (electron conductor, acceptor) it is employed as the ETM (electron transport material) of the solar cell. It can then be combined with an appropriate p-semiconductor (electron donor material) that is employed as the HTM (hole transport material) of the solar cell. Hole-conducting materials preferably comprise at least one material with high ionization energy. The materials may be organic or inorganic materials.

Suitable HTMs for combination with polymorph 1 are, for example,
N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-9,9-dimethylfluoren,
N,N'-Bis(3-methylphenyl)-N,N'-bis(phenyl)-9,9-diphenylfluoren,
N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-9,9-diphenylfluoren,
N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-2,2-dimethylbenzidin,
N,N'-Bis(3-methylphenyl)-N,N'-bis(phenyl)-9,9-spirobifluoren,
2,2',7,7'-Tetrakis(N,N-diphenylamino)-9,9'-spirobifluoren,

N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidin,
N,N'-Bis(naphthalen-2-yl)-N,N'-bis(phenyl)-benzidin,
N,N'-Bis(3-methylphenyl)-N,N'-bis(phenyl)-benzidin,
N,N'-Bis(3-methylphenyl)-N,N'-bis(phenyl)-9,9-dimethylfluoren,
N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-9,9-spirobifluoren,
Di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexan,
2,2',7,7'-tetra(N,N-di-tolyl)amino-spiro-bifluoren,
9,9-Bis[4-(N,N-bis-biphenyl-4-yl-amino)phenyl]-9H-fluoren,
2,2',7,7'-Tetrakis[N-naphthalenyl(phenyl)-amino]-9,9-spirobifluoren,
2,7-Bis[N,N-bis(9,9-spiro-bifluorene-2-yl)-amino]-9,9-spirobifluoren,
2,2'-Bis[N,N-bis(biphenyl-4-yl)amino]-9,9-spirobifluoren,
N,N'-bis(phenanthren-9-yl)-N,N'-bis(phenyl)-benzidin,
N,N,N',N'-tetra-naphthalen-2-yl-benzidin,
2,2'-Bis(N,N-di-phenyl-amino)-9,9-spirobifluoren,
9,9-Bis[4-(N,N-bis-naphthalen-2-yl-amino)phenyl]-9H-fluoren,
9,9-Bis[4-(N,N'-bis-naphthalen-2-yl-N,N'-bis-phenyl-amino)phenyl]-9H-fluoren,
Titanium oxide phthalocyanin, Copper phthalocyanin,
2,3,5,6-Tetrafluoro-7,7,8,8,-tetracyano-quinodimethan,
4,4',4''-Tris(N-3-methylphenyl-N-phenyl-amino)triphenylamin,
4,4',4''-Tris(N-(2-naphthyl)-N-phenyl-amino)triphenylamin,
4,4',4''-Tris(N-(1-naphthyl)-N-phenyl-amino)triphenylamin,
4,4',4''-Tris(N,N-diphenyl-amino)triphenylamin,,
Pyrazino[2,3-f][1,10]phenanthroline-2,3-dicarbonitril
N,N,N',N'-Tetrakis(4-methoxyphenyl)benzidin,
2,7-Bis[N,N-bis(4-methoxy-phenyl)amino]-9,9-spirobifluoren,
2,2'-Bis[N,N-bis(4-methoxy-phenyl)amino]-9,9-spirobifluoren,
N,N'-di(naphthalen-2-yl)-N,N'-diphenylbenzene-1,4-diamin,
N,N'-di-phenyl-N,N'-di-[4-(N,N-di-tolyl-amino)phenyl]benzidin,
N,N'-di-phenyl-N,N'-di-[4-(N,N-di-phenyl-amino)phenyl]benzidin.

Examples of polymeric hole transport materials, are PEDOT (poly (3, 4-ethylene-dioxythiophene), polyvinylcarbazole (PVK), poly(N,N'-bis (4-butylphenyl)-N,N'-bis(phenyl) benzidine (PTPD), polyaniline (PANI) and poly (3-hexylthiophene (P3HT).

In a first embodiment, the heterojunction has a flat configuration (see: Two layer organic photovoltaic cell, C. W. Tang, Appl. Phys. Lett., 48 (2), 183-185 (1986) or N. Karl, A. Bauer, J. Holzäpfel, J. Marktanner, M. Möbus, F. Stölzle, Mol. Cryst. Liq. Cryst., 252, 243-258 (1994).).

In a second preferred embodiment, the heterojunction is configured as a bulk (mixed) heterojunction, also referred to as an interpenetrating donor-acceptor network. Organic photovoltaic cells with a bulk heterojunction are described, for example, by C. J.

Brabec, N. S. Sariciftci, J. C. Hummelen in Adv. Funct. Mater., 11 (1), 15 (2001) or by J. Xue, B. P. Rand, S. Uchida and S. R. Forrest in J. Appl. Phys. 98, 124903 (2005). Bulk heterojunctions are discussed in detail hereinafter.

Polymorph 2 can be used as a photoactive material in cells with MiM, pin, pn, Mip or Min structure (M = metal, p = p-doped organic or inorganic semiconductor, n = n-doped organic or inorganic semiconductor, i = intrinsically conductive system of organic layers; see, for example, J. Drechsel et al., Org. Electron., 5 (4), 175 (2004) or Maennig et al., Appl. Phys. A 79, 1-14 (2004)).

Polymorph 2 can also be used as a photoactive material in tandem cells. Suitable tandem cells are described, for example, by P. Peumans, A. Yakimov, S. R. Forrest in J. Appl. Phys., 93 (7), 3693-3723 (2003) (see also US 4,461,922, US 6,198,091 and US 6,198,092) and are described in detail hereinafter.

Polymorph 2 can also be used as a photoactive material in tandem cells which are constructed from two or more than two stacked MiM, pin, Mip or Min structures (see DE 103 13 232.5 and J. Drechsel et al., Thin Solid Films, 451452, 515-517 (2004)).

The layer thickness of the M, n, i and p layers is typically within a range from 10 to 1000 nm, more preferably from 10 to 400 nm. The other layers which form the solar cell can be produced by customary processes known to those skilled in the art. These include vapor deposition under reduced pressure or in an inert gas atmosphere, laser - ablation or solution or dispersion processing methods such as spincoating, knifecoating, casting methods, spray application, dipcoating or printing (e.g. inkjet, flexographic, offset, gravure; intaglio, nanoimprinting). In a specific embodiment, the entire solar cell is produced by a gas phase deposition process.

In a suitable embodiment, the inventive solar cells are present as an individual cell with flat heterojunction and normal structure. In a specific embodiment, the cell has the following structure:

- an at least partly transparent conductive layer (top electrode, anode) (11)
- a hole-conducting layer (12)
- a layer which comprises a donor material (13)
- a layer which comprises an acceptor material (14)
- an exciton-blocking and/or electron-conducting layer (15)
- a second conductive layer (back electrode, cathode) (16)

The acceptor material preferably comprises polymorph 2.

The essentially transparent conductive layer (11) (anode) comprises a carrier, such as glass or a polymer (e.g. polyethylene terephthalate) and a conductive material, as described above. Examples include ITO, doped ITO, FTO, ZnO, AZO, etc. The anode material can be subjected to a surface treatment, for example with UV light, ozone, oxygen plasma, Br_2, etc. The layer (11) should be sufficiently thin to enable maximum light absorption, but also sufficiently thick to ensure good charge transport. The layer thickness of the transparent conductive layer (11) is preferably within a range from 20 to 200 nm.

Solar cells with normal structure optionally have a hole-conducting layer (= layer 12). This layer comprises at least one hole-conducting material (hole transport material, HTM). Hole-conducting materials (HTM) suitable for forming layers with hole-conducting properties (HTL) preferably comprise at least one material with high ionization energy. The ionization energy is preferably at least 5.0 eV, more preferably at least 5.5 eV. The materials may be organic or inorganic materials. Organic materials suitable for use in a layer with hole-conducting properties are preferably selected from poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS), Ir-DPBIC (tris-N,N'-diphenylbenzimidazol-2-ylideneiridium(III)), N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-diphenyl-4,4'-diamine (α-NPD), 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD), etc. and mixtures thereof. The organic materials may, if desired, be doped with a p-dopant which has a LUMO within the same range as or lower than the HOMO of the hole-conducting material. Suitable dopants are, for example, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquino-dimethane (F_4TCNQ), WO_3, MoO_3, etc. Inorganic materials suitable for use in a layer with hole-conducting properties are preferably selected from WO_3, MoO_3, etc.

If present, the thickness of the layers with hole-conducting properties is preferably within a range from 5 to 200 nm, more preferably 10 to 100 nm.

Layer (13) comprises at least one donor material. The thickness of the layer should be sufficient to absorb a maximum amount of light, but thin enough to enable effective dissipation of the charge. The thickness of the layer (13) is preferably within a range from 5 nm to 1 µm, more preferably from 5 to 100 nm.

Layer (14) comprises polymorph 2 as acceptor material. Additionally suitable acceptor materials are specified hereinafter. The thickness of the layer should be sufficient to absorb a maximum amount of light, but thin enough to enable effective dissipation of the charge. The thickness of the layer (14) is preferably within a range from 5 nm to 1 µm, more preferably from 5 to 80 nm.

Solar cells with normal structure optionally comprise an exciton-blocking and/or electron-conducting layer (15) (EBL/ETL). Suitable materials for exciton-blocking layers

generally have a greater band gap than the materials of layer (13) and/or (14). They are firstly capable of reflecting excitons and secondly enable good electron transport through the layer. The materials for the layer (15) may comprise organic or inorganic materials. Suitable organic materials are preferably selected from 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), 4,7-diphenyl-1,10-phenanthroline (Bphen), 1,3-bis[2-(2,2´-bipyridin-6-yl)-1,3,4-oxadiazo-5-yl]benzene (BPY-OXD), etc. The organic materials may, if desired, be doped with an n-dopant which has a HOMO within the same range as or lower than the LUMO of the electron-conducting material. Suitable dopants are, for example, Cs_2CO_3, Pyronin B (PyB), Rhodamine B, cobaltocenes, etc. Inorganic materials suitable for use in a layer with electron-conducting properties are preferably selected from ZnO, etc. If present, the thickness of the layer (15) is preferably within a range from 5 to 500 nm, more preferably 10 to 100 nm.

Layer 16 is the cathode and preferably comprises at least one compound with low work function, more preferably a metal such as Ag, Al, Mg, Ca, etc. The thickness of the layer (16) is preferably within a range from about 10 nm to 10 µm, e.g. 10 nm to 60 nm.

In a further suitable embodiment, the inventive solar cells are present as an individual cell with a flat heterojunction and inverse structure.

In a specific embodiment, the cell has the following structure:

- an at least partly transparent conductive layer (cathode) (11)
- an exciton-blocking and/or electron-conducting layer (12)
- a layer which comprises an acceptor material (13)
- a layer which comprises a donor material (14)
- a hole-conducting layer (15)
- a second conductive layer (back electrode, anode) (16)

With regard to suitable and preferred materials for the layers (11) to (16), reference is made to the above remarks regarding the corresponding layers in solar cells with normal structure.

In a suitable embodiment, the inventive solar cell is a tandem cell.

A tandem cell consists of two or more than two (e.g. 3, 4, 5, etc.) subcells. A single subcell, some of the subcells or all subcells may have photoactive donor-acceptor heterojunctions. Each donor-acceptor heterojunction may be in the form of a flat heterojunction or in the form of a bulk heterojunction. According to the invention, the photoactive layer of at least one subcell comprises polymorph 2. The subcells which form the tandem cell may be connected in parallel or in series. The subcells which form the tandem cell are preferably connected in series. There is preferably an additional

recombination layer in each case between the individual subcells. The individual subcells have the same polarity, i.e. generally either only cells with normal structure or only cells with inverse structure are combined with one another.

"Subcell" refers here to a cell as defined above without cathode and anode. The subcells may, for example, either all have polymorph 2 in the photoactive layer or have other combinations of semiconductor materials, for example C60 with zinc phthalocyanine, C60 with oligothiophene (such as DCV5T). In addition, individual subcells may also be configured as dye-sensitized solar cells or polymer cells.

In addition to the compounds of the general formula (I) in form of polymorph 2, the following semiconductor materials are suitable for use in organic photovoltaics:

Acenes such as anthracene, tetracene, pentacene and substituted acenes. Substituted acenes comprise at least one substituent selected from electron-donating substituents (e.g. alkyl, alkoxy, ester, carboxylate or thioalkoxy), electron-withdrawing substituents (e.g. halogen, nitro or cyano) and combinations thereof. These include 2,9-dialkyl-pentacenes and 2,10-dialkylpentacenes, 2,10-dialkoxypentacenes, 1,4,8,11-tetra-alkoxypentacenes and rubrene (5,6,11,12-tetraphenylnaphthacene). Suitable substituted pentacenes are described in US 2003/0100779 and US 6,864,396. A preferred acene is rubrene (5,6,11,12-tetraphenylnaphthacene).

Phthalocyanines, such as hexadecachlorophthalocyanines and hexadecafluorophthalocyanines, metal-free phthalocyanine and phthalocyanine comprising divalent metals, especially those of titanyloxy, vanadyloxy, iron, copper, zinc, especially copper phthalocyanine, zinc phthalocyanine and metal-free phthalocyanine, copper hexadecachlorophthalocyanine, zinc hexadecachlorophthalocyanine, metal-free hexadecachlorophthalocyanine, copper hexadecafluorophthalocyanine, hexadecafluorophthalocyanine or metal-free hexadecafluorophthalocyanine.

Porphyrins, for example 5,10,15,20-tetra(3-pyridyl)porphyrin (TpyP).

Liquid-crystalline (LC) materials, for example hexabenzocoronene (HBC-PhC12) or other coronenes, coronenediimides, or triphenylenes such as 2,3,6,7,10,11-hexahexylthiotriphenylene (HTT6) or 2,3,6,7,10,11-hexakis(4-n-nonylphenyl)triphenylene (PTP9), 2,3,6,7,10,11-hexakis(undecyloxy)triphenylene (HAT11). Particular preference is given to LCs which are discotic.

Thiophenes, oligothiophenes and substituted derivatives thereof. Suitable oligothiophenes are quaterthiophenes, quinquethiophenes, sexithiophenes, α,ω-di(C_1-C_8)alkyloligothiophenes such as α,ω-dihexylquaterthiophenes,

α,ω-dihexylquinquethiophenes and α,ω-dihexylsexithiophenes, poly(alkylthiophenes) such as poly(3-hexylthiophene), bis(dithienothiophenes), anthradithiophenes and dialkylanthradithiophenes such as dihexylanthradithiophene, phenylene-thiophene (P-T) oligomers and derivatives thereof, especiallyα,ω-alkyl-substituted phenylene-thiophene oligomers.

Preferred thiophenes, oligothiophenes and substituted derivatives thereof, are poly-3-hexylthiophene (P3HT) or compounds of the α α'-bis(2,2-dicyanovinyl)quinquethiophene (DCV5T) type, poly(3-(4-octylphenyl)-2,2'-bithiophene) (PTOPT), poly(3-(4'-(1",4",7"-trioxaoctyl)phenyl)thiophene) (PEOPT), poly(3-(2'-methoxy-5'-octylphenyl)thiophenes) (POMeOPTs), poly(3-octylthiophene) (P3OT), pyridine-containing polymers such as poly(pyridopyrazine vinylene), poly(pyridopyrazine vinylene) modified with alkyl groups e.g. EHH-PpyPz, PTPTB copolymers, polybenzimidazobenzophenanthroline (BBL), poly(9,9-dioctylfluorene-co-bis-N,N'-(4-methoxyphenyl)-bis-N,N'-phenyl-1,4-phenylenediamine) (PFMO); see Brabec C., Adv. Mater., 2996, 18, 2884. (PCPDTBT) poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-4,7-(2,1,3-benzothiadiazoles)].

Paraphenylenevinylene and paraphenylenevinylene-comprising oligomers and polymers, for example polyparaphenylenevinylene (PPV), MEH-PPV (poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene)), MDMO-PPV (poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene)), cyano-paraphenylenevinylene (CN-PPV), CN-PPV modified with alkoxy groups.

PPE-PPV hybrid polymers (phenylene-ethynylene/phenylene-vinylene hybrid polymers).

Polyfluorenes and alternating polyfluorene copolymers, for example with 4,7-dithien-2'-yl-2,1,3-benzothiadiazoles, and also poly(9,9'-dioctylfluorene-*co*-benzothiadiazole) (F_8BT), poly(9,9'-dioctylfluorene-*co*-bis-*N,N*'-(4-butylphenyl)-bis-*N,N*'-phenyl-1,4-phenylenediamine) (PFB).

Polycarbazoles, i.e. carbazole-comprising oligomers and polymers, such as (2,7) and (3,6).

Polyanilines, i.e. aniline-comprising oligomers and polymers.

Triarylamines, polytriarylamines, polycyclopentadienes, polypyrroles, polyfuran, polysilols, polyphospholes, N,N'-Bis-(3-methylphenyl)-N,N'-bis-(phenyl)-benzidine (TPD), 4,4'-bis(carbazol-9-yl) biphenyl (CBP), 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-MeOTAD).

Fullerenes, especially C60 and derivatives thereof such as PCBM (= [6,6]-phenyl-C_{61}-butyric acid methyl ester). In such cases, the fullerene derivative would be a hole conductor.

Copper(I) iodide, copper(I) thiocyanate.

p-n-Mixed materials, i.e. donor and acceptor in one material, polymer, block copolymers, polymers with C60s, C60 azo dyes, trimeric mixed material which comprises compounds of the carotenoid type, porphyrin type and quinoid liquid-crystalline compounds as donor/acceptor systems, as described by Kelly in S. Adv. Mater. 2006, 18, 1754.

The invention further provides an electroluminescent (EL) arrangement comprising an upper electrode, a lower electrode, wherein at least one of said electrodes is transparent, an electroluminescent layer and optionally an auxiliary layer, wherein the electroluminescent arrangement comprises polymorph 2. An EL arrangement is characterized by the fact that it emits light when an electrical voltage is applied with flow of current. Such arrangements have been known for a long time in industry and technology as light-emitting diodes (LEDs). Light is emitted on account of the fact that positive charges (holes) and negative charges (electrons) combine with the emission of light. In the sense of this application the terms electroluminescing arrangement and organic light-emitting diode (OLEDs) are used synonymously. As a rule, EL arrangements are constructed from several layers. At least on of those layers contains one or more organic charge transport compounds. The layer structure is in principle as follows:

1. Carrier, substrate
2. Base electrode (anode)
3. Hole-injecting layer
4. Hole-transporting layer
5. Light-emitting layer
6. Electron-transporting layer
7. Electron-injecting layer
8. Top electrode (cathode)
9. Contacts
10. Covering, encapsulation.

This structure represents the most general case and can be simplified by omitting individual layers, so that one layer performs several tasks. In the simplest case an EL arrangement consists of two electrodes between which an organic layer is arranged, which fulfills all functions, including emission of light. The structure of organic light-emitting diodes and processes for their production are known in principle to those

skilled in the art, for example from WO 2005/019373. Suitable materials for the individual layers of OLEDs are disclosed, for example, in WO 00/70655. Reference is made here to the disclosure of these documents. In principle OLEDs according to the invention can be produced by methods known to those skilled in the art. In a first embodiment, an OLED is produced by successive vapor deposition of the individual layers onto a suitable substrate. In an alternative embodiment, the organic layers different from polymorph 2 may be coated from solutions or dispersions in suitable solvents, for which coating techniques known to those skilled in the art are employed.

Suitable as substrate 1 are transparent carriers, such as glass or plastics films (for example polyesters, such as polyethylene terephthalate or polyethylene naphthalate, polycarbonate, polyacrylate, polysulphone, polyimide foil). Suitable as transparent and conducting materials are a) metal oxide, for example indium-tin oxide (ITO), tin oxide (NESA), etc. and b) semi-transparent metal films, for example Au, Pt, Ag, Cu, etc.

Polymorph 2 preferably serves as a charge transport material (electron conductor). Thus, polymorph 2 is preferably used in an electron-injecting layer, electron transporting layer or as part of a transparent electrode.

In the EL applications according to the invention low molecular weight or oligomeric as well as polymeric materials may be used as light-emitting layer 5. The substances are characterized by the fact that they are photoluminescing. Accordingly, suitable substances are for example fluorescent dyes and fluorescent products that are forming oligomers or are incorporated into polymers. Examples of such materials are coumarins, perylenes, anthracenes, phenanthrenes, stilbenes, distyryls, methines or metal complexes such as Alq_3 (tris(8-hydroxyquinolinato)aluminium), etc. Suitable polymers include optionally substituted phenylenes, phenylene vinylenes or polymers with fluorescing segments in the polymer side chain or in the polymer backbone. A detailed list is given in EP-A-532 798. Preferably, in order to increase the luminance, electron-injecting or hole-injecting layers (3 and/or 7) can be incorporated into the EL arrangements. A large number of organic compounds that transport charges (holes and/or electrons) are described in the literature. Mainly low molecular weight substances are used, which are for example vacuum evaporated in a high vacuum. A comprehensive survey of the classes of substances and their use is given for example in the following publications: EP-A 387 715, US 4,539,507, US 4,720,432 and US 4,769,292. A preferred material is PEDOT (poly-(3,4-ethylenedioxythiophene)) which can also be employed in the transparent electrode of the OLEDs.

As a result of the inventive use of polymorph 2, it is possible to obtain OLEDs with high efficiency. The inventive OLEDs can be used in all devices in which electroluminescence is useful. Suitable devices are preferably selected from stationary and mobile visual display units. Stationary visual display units are, for example, visual

display units of computers, televisions, visual display units in printers, kitchen appliances and advertising panels, illuminations and information panels. Mobile visual display units are, for example, visual display units in cell phones, laptops, digital cameras, vehicles and destination displays on buses and trains. Moreover, polymorph 2 may be used in OLEDs with inverse structure. The structure of inverse OLEDs and the materials typically used therein are known to those skilled in the art.

The following figures and examples serve to illustrate the invention and should not be interpreted as limiting.

EXAMPLES

N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide (I):

Compound (I) was prepared as described in Adv. Funct. Mater. 2010, 20, 2148– 2156. A suspension of 84.0 mg (0.249 mmol) of 2,6-dichloro-naphthalene tetracarboxylic dianhydride and 198 mg (0.995 mmol) of 2,2,3,3,4,4,4-heptafluorobutylamine in 4 mL acetic acid was heated to reflux for 1 h. After cooling to room temperature, acetic acid was removed under reduced pressure. The residue was washed with methanol and purified by column chromatography (dichloromethane/pentane 3:2) to afford 82.4 mg (47%) of a yellowish solid.

General procedure of sample preparation:

Si/SiO_2 wafers with a 300 nm thermally grown oxide layer are used as a substrate. The substrates were cleaned by first rinsing with water, followed by sonication in acetone and isopropanol for 10 minutes each. The substrates were then exposed to UV-ozone treatment for 10 minutes.

Substrates with surfaces modified with n-octadecyltrichlorosilane (OTS) were prepared by spin-coating from a 3 mM solution of OTS in trichloroethylene. The solution is allowed to sit on the substrate surface for 10 seconds and then spun at 3000 rpm for 10 seconds. The substrates are then exposed to an ammonia vapor for 15 hours, followed by rinsing and sonication in toluene.

For hexamethyldisilazane (HMDS) treatment, substrates are placed under vacuum (1 torr) and exposed to an HMDS vapor at a temperature between 120 and 170 °C and a pressure of 1 to 10 mbar.

Compound (I) is deposited onto the substrates using thermal evaporation at a source temperature of 200 to 300°C, a substrate temperature of 20 to 30°C, a pressure of 2 x 10^{-6} mbar and a rate of 0.1 to 1 Angstroms/second. The thickness of the obtained films is about 40 nm.

To anneal the thin films, a small petri dish is filled with the appropriate solvent. Next, the wafer is placed directly next to the small petri dish, with the film facing upwards. A larger petri dish is used to enclose both the wafer and the small, solvent petri dish, creating a closed environment. Films are analyzed periodically using optical microscopy to determine the extent of annealing and crystal growth.

Top-contact, bottom-gate transistors were fabricated by depositing 50 nm gold contacts through stencil masks by thermal evaporation. The width (W) of the transistor channel was 2000 µm, the length (L) 100 µm.

The OTFT transfer and output characteristics were recorded under vacuum at room temperature in a Lakeshore cryoprobestation by using an Agilent semiconductor parametric analyzer.

Description of synchrotron grazing-incidence x-ray diffraction (GIXRD) measurements:

GIXRD experiments were conducted at the G1 station (10.6 keV) of the Cornell High Energy Synchrotron Source. The beam was selected to be 0.05 mm tall and 1 mm wide. The width of the samples was 0.5 cm. The X-ray beam was aligned at a 0.17° incident angle with the substrate. Scattered intensity was collected with a 2-D CCD detector, with a sample to detector distance of 117.6 mm. The obtained images have been background subtracted and corrected for the polarization of the beam. Measurements were performed at 25°C, the accuracy was +/- 0.03 [$Å^{-1}$].

Example 1: preparation of known polymorph 1

A sample was fabricated by vacuum deposition of compound (I) according to the general procedure onto the SiO_2 surface of a Si/SiO_2 wafer pretreated with OTS. The deposition was followed by solvent vapor annealing with chloroform. Figure 1 shows the corresponding GIXRD image. The peaks indicate that predominantly polymorph 1 was obtained. Also the optical image (figure 2) shows the typical needles of polymorph 1.

Example 2: preparation of new polymorph 2 (pristine Si/SiO_2 wafer)

A sample was fabricated by vacuum deposition of compound (I) according to the general procedure onto the untreated SiO_2 surface of a Si/SiO_2 wafer without solvent vapor annealing. The peaks of the corresponding GIXRD image indicate that pure polymorph 2 was obtained.

Example 3: preparation of new polymorph 2 (Si/SiO_2 wafer, pretreatment with OTS)

A sample was fabricated by vacuum deposition of compound (I) according to the general procedure onto the SiO_2 surface of a Si/SiO_2 wafer pretreated with OTS without solvent vapor annealing. The peaks of the corresponding GIXRD image indicate that pure polymorph 2 was obtained.

Example 4: preparation of new polymorph 2
(Si/SiO_2 wafer, OTS, solvent vapor annealing with THF)

A sample was fabricated by vacuum deposition of compound (I) according to the general procedure onto the SiO_2 surface of a Si/SiO_2 wafer pretreated with OTS. Afterwards the substrate was subjected to a solvent vapor annealing with tetrahydrofurane (THF). Again, pure polymorph 2 was obtained. Figure 3 shows the corresponding GIXRD image. The optical image (figure 4) shows the typical platelets of polymorph 2.

Example 5: preparation of new polymorph 2
(Si/SiO_2 wafer, HMDS, solvent vapor annealing with THF)

A sample was fabricated by vacuum deposition of compound (I) according to the general procedure onto the SiO_2 surface of a Si/SiO_2 wafer pretreated with hexamethyldisilazane (HMDS). Afterwards the substrate was subjected to a solvent vapor annealing with tetrahydrofurane (THF). Figure 5 shows the corresponding GIXRD image (x-axis: q_z-values in $Å^{-1}$, y-axis: normalized intensity). The lower curve depicts the GIXRD image of the surface of the wafer before solvent vapor annealing with THF. As can be seen, a mixture of polymorph 1 and polymorph 2 was obtained. The lower curve depicts the GIXRD image of the surface of the wafer after solvent vapor annealing with THF. As can be seen, pure polymorph 2 was obtained.

Example 6: preparation of new polymorph 2
(Si/SiO_2 wafer, HMDS, solvent vapor annealing with DCM)

A sample was fabricated by vacuum deposition of compound (I) according to the general procedure onto the SiO_2 surface of a Si/SiO_2 wafer pretreated with hexamethyldisilazane (HMDS). Afterwards the substrate was subjected to a solvent vapor annealing with dichloromethane (DCM). Figure 5 shows the corresponding GIXRD image (x-axis: q_z-values in $Å^{-1}$, y-axis: normalized intensity). The lower curve depicts the GIXRD image of the surface of the wafer before solvent vapor annealing with DCM. As can be seen, a mixture of polymorph 1 and polymorph 2 was obtained. The lower curve depicts the GIXRD image of the surface of the wafer after solvent vapor annealing with DCM. As can be seen, pure polymorph 2 was obtained.

Example 7: preparation of a mixture of polymorph 1 and polymorph 2 (Si/SiO_2 wafer, HMDS)

A sample was fabricated by vacuum deposition of compound (I) according to the general procedure onto the SiO_2 surface of a Si/SiO_2 wafer pretreated with hexamethyldisilazane (HMDS). The vacuum evaporation yields a mixture of the two polymorphs. The charge carrier mobility in the mixture of the two polymorphs μ is 9 x 10^{-5} cm^2/Vs. This is remarkably lower than the charge carrier mobilities of OFET on the basis of new polymorph 2.

Electrical properties

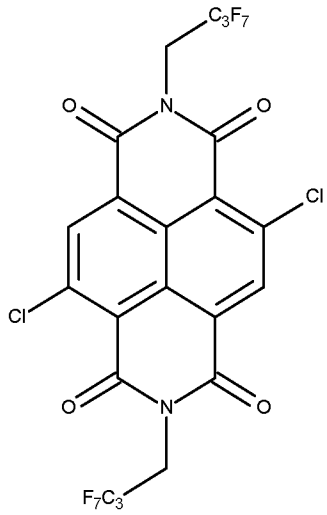
Figure 7 shows the current-voltage characteristics of OFET obtained by vacuum deposition of compound (I) onto an Si/SiO_2 wafer pretreated with OTS without solvent vapor annealing (upper curve, polymorph 2), the untreated SiO_2 surface of a Si/SiO_2 wafer (curve in the middle, polymorph 2) and an Si/SiO_2 wafer pretreated with OTS without solvent vapor annealing (lower curve, mixture of polymorph 1 and polymorph 2). This shows that polymorph 2 is a semiconductor with remarkably better application properties than a mixture of polymorph 1 and polymorph 2.

The upper curve of figure 8 shows the current-voltage characteristics of an OFET obtained by vacuum deposition of compound (I) onto an Si/SiO_2 wafer pretreated with OTS and subjected to a solvent vapor annealing with THF to obtain polymorph 2. The lower curve of figure 8 shows the current-voltage characteristics of an OFET obtained by vacuum deposition of compound (I) onto an Si/SiO_2 wafer pretreated with OTS and subjected to a solvent vapor annealing with $CHCl_3$ to obtain polymorph 1. As can be seen, the semiconductor properties of polymorph 2 are superior over polymorph 1.

The charge carrier mobility of the OFET on the basis of polymorph 2 obtained by solvent vapor annealing with THF μ is 3 x 10^{-2} +/- 9.6 x 10^{-3} cm^2/Vs. In contrast, the charge carrier mobility of the OFET on the basis of polymorph 2 obtained by solvent vapor annealing with $CHCl_3$ μ is only 1.4 x 10^{-3} +/- 6.4 x 10^{-4} cm^2/Vs.

Claims

1. A crystalline form of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide of the formula (I)



(I)

which in an grazing incident X-ray diffractogram (GIXRD) using a synchrotron X-ray beam of 10.6 keV, an incident X-ray angle θ_{IN} of 0.17°, and a temperature of 25°C displays at least 5 of the following reflections

qxy [Å^{-1}]	qz [Å^{-1}]	q [Å^{-1}]
0.01+/-0.03	0.35+/-0.03	0.35+/-0.03
0.01+/-0.03	1.40+/-0.03	1.4+/-0.03
0.01+/-0.03	1.73+/-0.03	1.73+/-0.03
1.09+/-0.03	0.13+/-0.03	1.01+/-0.03
1.09+/-0.03	0.48+/-0.03	1.19+/-0.03
1.10+/-0.03	0.61+/-0.03	1.25+/-0.03

2. The crystalline form of compound I according to claim 1 having the triclinic space group P-1.

3. The crystalline form of compound I according to claim 1 or 2, having the following cell parameters: a = 5.270 Å, b = 6.319 Å, c = 18.823 Å.

4. The crystalline form of compound I according to any of the preceding claims, having the following cell parameters: $\alpha = 80.43°$, $\beta = 82.15°$, $\gamma = 70.85°$.

5. The crystalline form of compound I according to any of the preceding claims, in form of a thin film having an out of plane spacing value (= d(001)-spacing value) of 17.95 Å.

6. A composition comprising at least 10% by weight, more preferably at least 25% by weight, in particular at least 50% by weight, especially at least 75% by weight, more especially at least 90% by weight; based on the total weight of the composition, of the crystalline form of compound I as defined in any of claims 1 to 5.

7. A composition of compound I comprising at least two crystalline forms, selected from
   - the crystalline form of compound I as defined in any of claims 1 to 5 (= polymorph 2),
   - a crystalline form of compound I which in an grazing incident X-ray diffractogram (GIXRD) using a synchrotron X-ray beam of 10.6 keV, an incident X-ray angle θ_{IN} of 0.17°, and a temperature of 25°C displays at least 5 of the following reflections (= polymorph 1)

Miller Index	qxy [Å^{-1}]	qz [Å^{-1}]	q [Å^{-1}]
(100)	0.01+/-0.03	0.59+/-0.03	0.59+/-0.03
(200)	0.01+/-0.03	1.16+/-0.03	1.16+/-0.03
(400)	0.01+/-0.03	2.3+/-0.03	2.3+/-0.03
(020)	0.77+/-0.03	0.05+/-0.03	0.77+/-0.03
(120)	0.78+/-0.03	0.55+/-0.03	0.96+/-0.03
(011)	1.12+/-0.03	0.30+/-0.03	1.16+/-0.03

8. The composition of claim 7, comprising 50 to 99.99 % by weight, preferably 75% to 99.95 % by weight, in particular 90% to 99.95 % by weight of polymorph 2 based on the total weight of polymorph 1 and polymorph 2.

9. A process for the preparation of the crystalline form of compound I, as defined in any of claims 1 to 5, comprising:

(a) providing a source of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide of the formula (I),
(b) heating said source to a first temperature in the range of from 100 to 350°C to produce a vapor of compound (I),
(c) exposing at least one surface of a substrate having a second temperature lower than said first temperature to said vapor to deposit crystals from said vapor onto said at least one surface of said substrate,

wherein the at least one surface of the substrate is exposed also to a vapor of a solvent, selected from tetrahydrofuran and dichloromethane, prior to and/or during and/or after the deposition of the crystals of compound (I).

10. The process according to claim 9, wherein the pressure of the atmosphere in which compound (I) is vaporized is in a range of from 1 x 10^{-3} to 1 x 10^{-8} mbar, preferably 1 x 10^{-4} to 1 x 10^{-7} mbar, more preferably 1 x 10^{-5} to 1 x 10^{-6} mbar.

11. The process according to claim 9, wherein the pressure of the atmosphere in which compound (I) is vaporized is in a range of from 500 to 2000 mbar, preferably 800 to 1200 mbar, in particular ambient pressure.

12. The process according to any of claims 9 to 11, wherein the at least one surface of the substrate is exposed to the vapor of the solvent after the deposition of the crystals of compound (I).

13. The process according to claim 12, wherein the at least one surface of the substrate is exposed to the vapor of the solvent at a pressure of from 500 to 2000 mbar.

14. The process according to any of claims 9 to 13, wherein the surface of the substrate that is exposed to the vapor of compound (I) is coated with a dielectric, preferably SiO_2.

15. The process according to any of claims 9 to 13, wherein the surface of the substrate or, if present, the dielectric coating on the substrate, is subjected to a surface modification prior to the deposition of compound (I).

16. The process according to claim 15, wherein the compound used for the surface modification is selected from silanes, phosphonic acids, carboxylic acids, hydroxamic acids, amines, phosphines, sulfur-comprising compounds and mixtures thereof.

17. The process according to claim 15, wherein the compound used for the surface modification is selected from n-octadecyltrichlorosilane (OTS), n-octadecyltrimethoxysilane, n-octadecyltriethoxysilane, hexamethyldisilazane (HMDS), hexadecanethiol, mercaptoacetic acid, 3-mercaptopropionic acid, mercaptosuccinic acid and 3-mercapto-1-propanesulfonic acid, the alkali metal and ammonium salts of mercaptoacetic acid, 3-mercaptopropionic acid, mercaptosuccinic acid and 3-mercapto-1-propanesulfonic acid and mixtures thereof.

18. A process for the preparation of the crystalline form of compound I, as defined in any of claims 1 to 5, comprising:

(a) providing a source of N,N'-Bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide of the formula (I),
(b) heating said source to a first temperature in the range of from 100 to 350°C to produce a vapor of compound (I),
(c) exposing at least one surface of a substrate having a second temperature lower than said first temperature to said vapor to deposit crystals from said vapor onto said at least one surface of said substrate,

wherein the surface of the substrate that is exposed to the vapor of compound (I) essentially consists of SiO_2

or wherein the surface of the substrate that is exposed to the vapor of compound (I) has been previously subjected to a surface modification with n-octadecyltrichlorosilane.

19. The process according to claim 18, wherein the surface of the substrate that is exposed to the vapor of compound (I) is a SiO_2 coated wafer and/or a wafer that has been subjected to a surface modification with n-octadecyltrichlorosilane.

20. The process according to claim 18 or 19, wherein the pressure of the atmosphere in which compound (I) is vaporized is in a range of from 1 x 10^{-3} to 1 x 10^{-8} mbar, preferably 1 x 10^{-4} to 1 x 10^{-7} mbar, more preferably 1 x 10^{-5} to 1 x 10^{-6} mbar.

21. The process according to claim 18 or 19, wherein the pressure of the atmosphere in which compound (I) is vaporized is in a range of from 500 to 2000 mbar, preferably 800 to 1200 mbar, in particular ambient pressure.

22. An organic field-effect transistor, comprising a substrate having at least one gate structure including a gate electrode and a gate dielectric, a source electrode and a drain electrode and as a semiconductor material the crystalline form of compound I as defined in any of claims 1 to 5, or a composition as defined in any of claims 6 to 8, or the crystalline form of compound I obtainable by the process of any of claims 9 to 21.

23. A substrate comprising a plurality of organic field-effect transistors, at least some of the field-effect transistors comprising the crystalline form of compound I as defined in any of claims 1 to 5, or a composition as defined in any of claims 6 to 8, or the crystalline form of compound I obtainable by the process of any of claims 9 to 21.

24. A semiconductor unit comprising at least one substrate as defined in claim 23.

25. An electroluminescent arrangement comprising an upper electrode, a lower electrode, wherein at least one of said electrodes is transparent, an electroluminescent layer and optionally an auxiliary layer, wherein the electroluminescent arrangement comprises the crystalline form of compound I as defined in any of claims 1 to 5, or a composition as defined in any of claims 6 to 8, or the crystalline form of compound I obtainable by the process of any of claims 9 to 21.

26. An electroluminescent arrangement as claimed in claim 25 in form of an organic light-emitting diode (OLED).

27. An organic solar cell comprising the crystalline form of compound I as defined in any of claims 1 to 5, or a composition as defined in any of claims 6 to 8, or the crystalline form of compound I obtainable by the process of any of claims 9 to 21.

28. The use the crystalline form of compound I as defined in any of claims 1 to 5, or a composition as defined in any of claims 6 to 8, or the crystalline form of compound I obtainable by the process of any of claims 9 to 21, as a semiconductor material, preferably as a semiconductor material in organic electronics or in organic photovoltaics.

29. The use according to claim 28 as a semiconductor in organic field-effect transistors.

30. The use according to claim 28 in an organic light-emitting diode (OLED).

figure 1

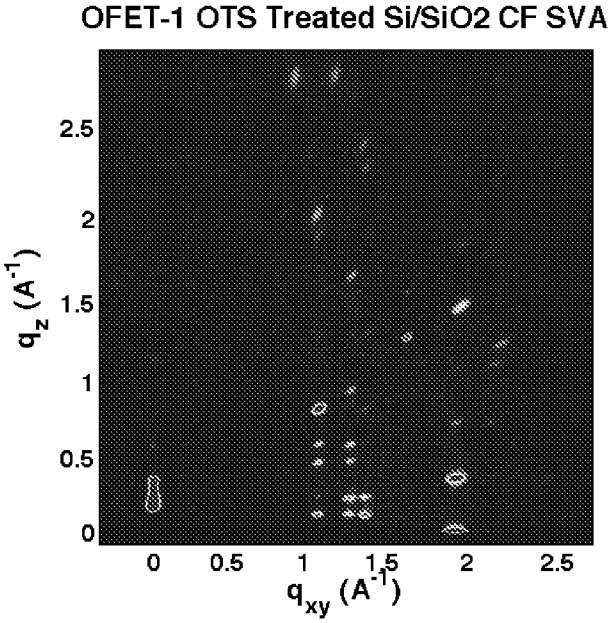


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figure 2

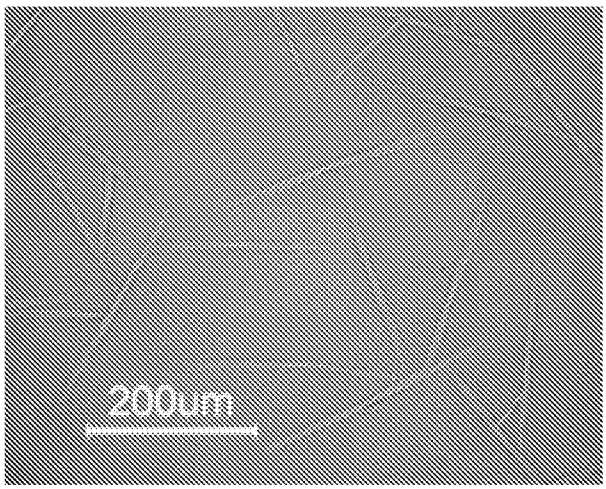


figure 3

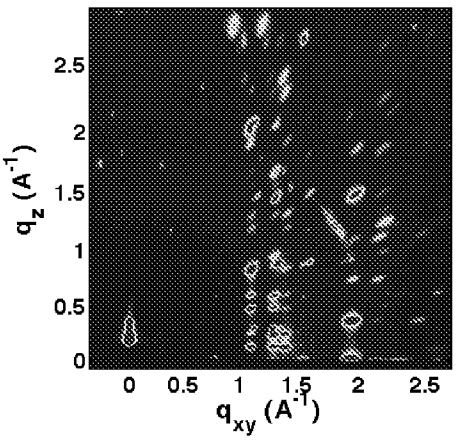


figure 4

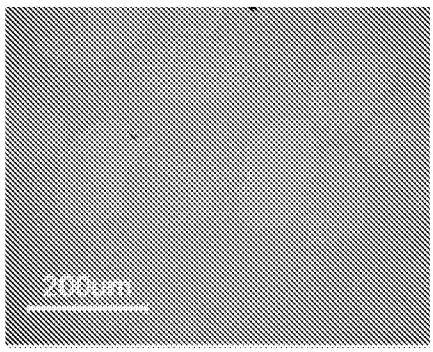


figure 5

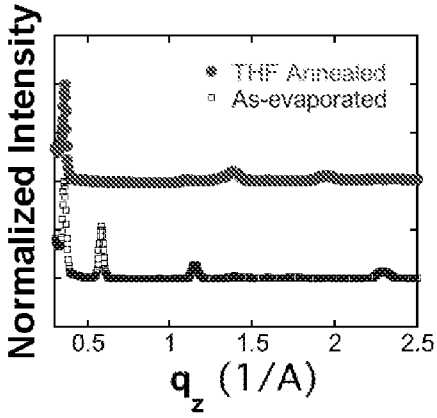


figure 6

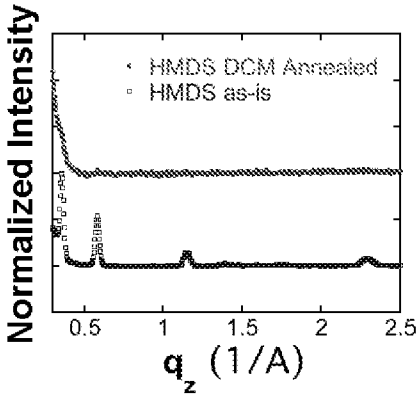


figure 7

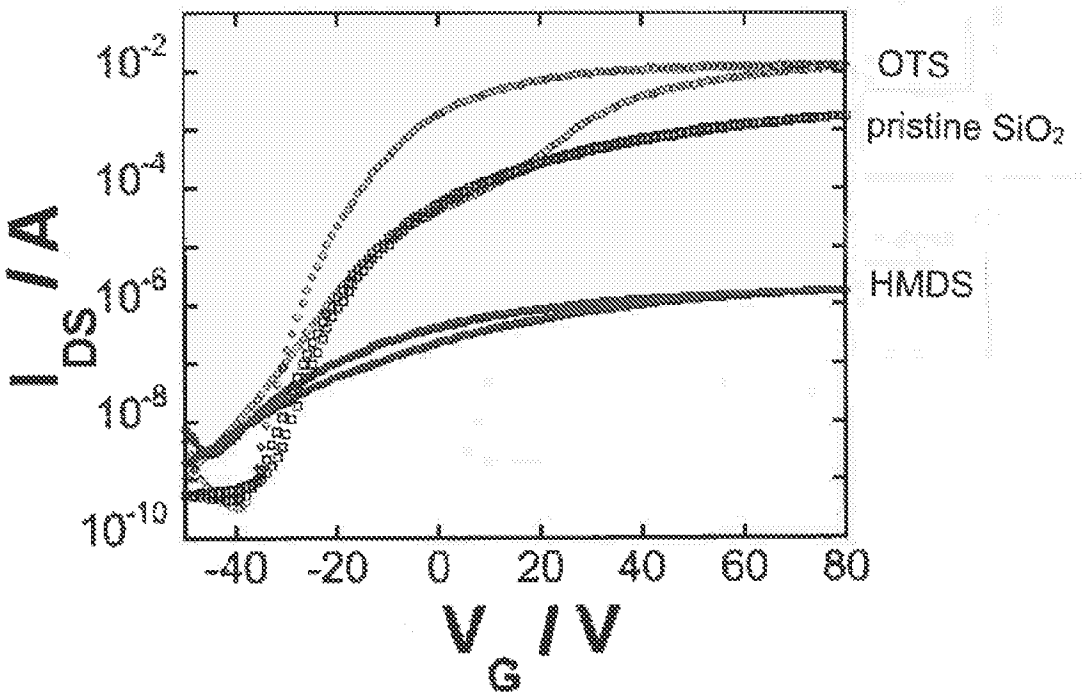
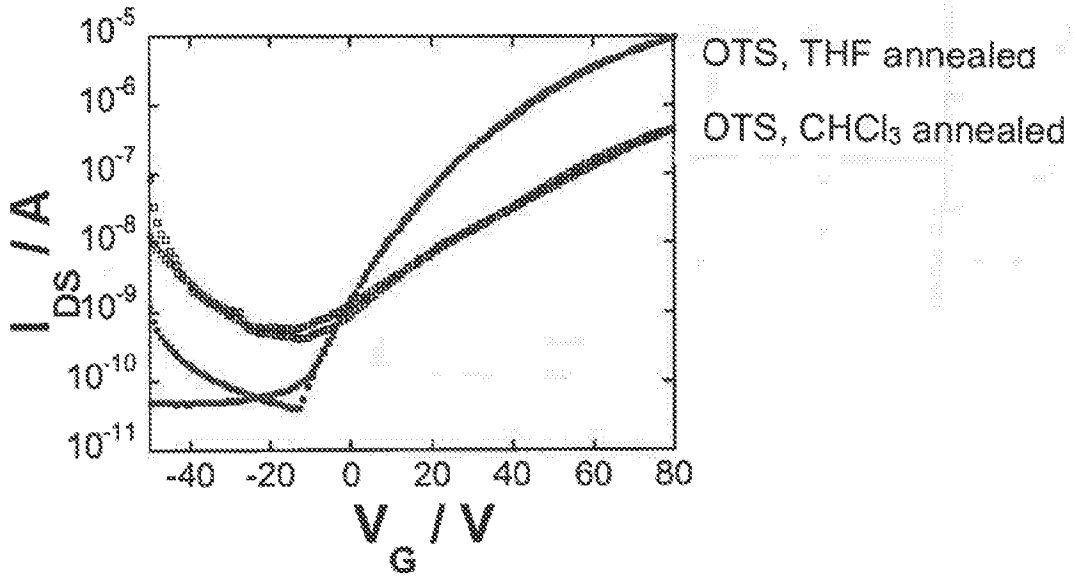


figure 8



INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2014/065535

A. CLASSIFICATION OF SUBJECT MATTER

C07D 471/06(2006.01)i; C09K 11/06(2006.01)i; H01L 51/50(2006.01)i; H01L 51/42(2006.01)i

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)

C07D471/06, C09K11/06, H01L51/-

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)

CNABS;CNKI;WPI; EPODOC;REG;CAPLUS: Naphthalene Tetracarboxylic Diimide, 1199269-54-9/rn

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	WO 2013164761 A1 (BASF SE) 07 November 2013 (2013-11-07) example 1	1-30
X	OH, Joon Hak, et al. "High-performance air-stable n-type organic transistors based on core-chlorinated naphthalene tetracarboxylic diimides" *Advanced Functional Materials*, Vol. Vol. 20, No. No.13, 09 July 2010 (2010-07-09), ISSN: ISSN: 1616-301X, pages 1-13, figur 6; & OH, Joon Hak, et al., "Supporting Information for High-Performance Air-Stable n-Type Organic Transistors Based on Core-Chlorinated Naphthalene Tetracarboxylic Diimides", Advanced Functional Materials, 09 July 2010, Vol. 20, pages 1-13, tables S1 and S3	1-30
X	LEE, Wen-Ya, et al. "High-Mobility Air-Stable Solution-Shear-Processed n-Channel Organic Transistors Based on Core-Chlorinated Naphthalene Diimides" *Advanced Functional Materials*, Vol. Vol. 21, No. No. 21, 08 November 2011 (2011-11-08), ISSN: ISSN: 1616-301X, pages 4173-4181, table 1	1-30
X	WO 2009147237 A1 (BASF SE) 10 December 2009 (2009-12-10) examples	1-30

☑ 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)

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 February 2015	**10 March 2015**
Name and mailing address of the ISA/CN **STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA(ISA/CN)** **6,Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088, China** Facsimile No. **(86-10)62019451**	Authorized officer **XU,Chi** Telephone No. **(86-10)62086349**

Form PCT/ISA/210 (second sheet) (July 2009)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ROEDEL, R., et al. "Contact properties of high-mobility, air-stable, low-voltage organic n-channel thin-film transistors based on a naphthalene tetracarboxylic diimide" *Applied Physics Letters,* Vol. Vol. 102, No. No. 23, 12 June 2013 (2013-06-12), ISSN: ISSN: 0003-6951, pages 233303/1-233303/5	1-30

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IB2014/065535

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2013164761 A1	07 November 2013	TW 201411898 A	16 March 2014
		CN 104284996 A	14 January 2015
WO 2009147237 A1	10 December 2009	JP 2011522097 A	28 July 2011
		JP 5496189 B2	21 May 2014
		KR 20110015454 A	15 February 2011
		US 2009301552 A1	10 December 2009
		WO 2009147237 A9	28 January 2010
		TW 201002709 A	16 January 2010
		EP 2297274 A1	23 March 2011
		CN 102057015 A	11 May 2011
		EP 2297274 B1	19 November 2014