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(71) Applicant *(for all designated States except US)*: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(72) Inventors: **GERLACH, Christopher P.**; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **ENDER, David A.**; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **VOGEL, Dennis E.**; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(74) Agents: **KOKKO, Kent S.** et al.; 3M Center, Office Of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

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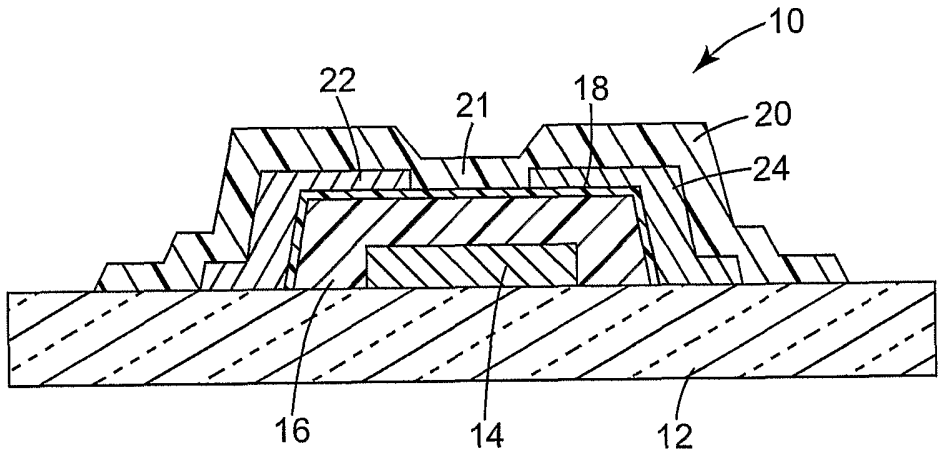
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(54) Title: SEMICONDUCTORS CONTAINING PERFLUOROETHER ACYL OLIGOTHIOPHENE COMPOUNDS



(57) Abstract: Semiconductor devices are described that include a semiconductor layer that comprises a perfluoroether acyl oligothiophene compound, preferably an α,ω-bis-perfluoroether acyl oligothiophene compound. Additionally, methods of making semiconductor devices are described that include depositing a semiconductor layer that contains a perfluoroether acyl oligothiophene compound, preferably an α,ω-bis(2- perfluoroether acyl oligothiophene compound.

WO 2006/098859 A1

Semiconductors Containing Perfluoroether Acyl Oligothiophene Compounds

Technical Field

The present invention provides semiconductor devices and methods of making semiconductor devices that include a semiconductor layer that contains a perfluoroether acyl oligothiophene compound.

Background

Traditionally, inorganic materials have dominated the semiconductor industry. For example, silicon arsenide and gallium arsenide have been used as semiconductor materials, silicon dioxide has been used as an insulator material, and metals such as aluminum and copper have been used as electrode materials. In recent years, however, there has been an increasing research effort aimed at using organic materials rather than the traditional inorganic materials in semiconductor devices. Among other benefits, the use of organic materials may enable lower cost manufacturing of electronic devices, may enable large area applications, and may enable the use of flexible circuit supports for display backplanes or integrated circuits.

A variety of organic semiconductor materials have been considered, the most common being fused aromatic ring compounds as exemplified by tetracene and pentacene, bis(acenyl)acetylene, and acene-thiophenes; oligomeric materials containing thiophene or fluorene units; and polymeric materials such as regioregular poly(3-alkylthiophene). At least some of these organic semiconductor materials have performance characteristics such as charge-carrier mobility, on/off current ratios, and sub-threshold voltages that are comparable or superior to those of amorphous silicon-based devices.

Thiophene chemistry and the chemical stability of the thiophene ring hold potential for use of thiophene materials in molecular-based electronics and photonics. In particular, α,α'-conjugated thiophene oligomers (nTs) and polymers (polythiophenes-PTs) have attracted great interest as semiconducting elements in organic thin-film transistors (TFTs). To be useful in such devices and related structures, the organic material must support a channel of holes or electrons (p- or n-type semiconductor, respectively) created by the gate electrode bias, which switches the device "on". Furthermore, the charge mobility of the

material must be sufficiently large to increase the source-drain on-conduction by many orders of magnitude over the "off" state. The density of the charge carrier in the channel is modulated by voltage applied at the gate electrode

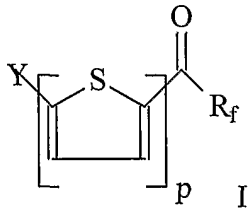
U.S. 6,585,914 (Marks et al.) describe α,ω-diperfluoroalkylsexithiophene-evaporated films of which behave as n-type semiconductors, and can be used to fabricate thin film transistors with FET mobilities about 0.01 cm^2/Vs.

Summary

Novel perfluoroether acyl (oligo)thiophene compounds, including α,ω-bis-perfluoroether acyl oligothiophene compounds are provided. Additionally, a novel method of preparing the compounds is provided. The compounds are useful, for example, as n-channel semiconductor layers in electronic devices, such as thin film transistors. There are a considerable number of problems and deficiencies associated with the prior art relating to useful organic n-type semiconductor compounds, compositions and/or materials. There is a demonstrated need for such materials, compositions, layers and/or composites for thin film deposition and related applications useful in conjunction with the fabrication of thin film transistors and related devices as can be incorporated into an integrated circuit. Accordingly, it is an object of the present invention to provide new and useful n-type organic materials, together with one or more methods of preparation.

Semiconductor devices and methods of making the semiconductor devices are provided. More specifically, the semiconductor devices include a semiconductor layer that contains at least one perfluoroether acyl oligothiophene compound, preferably at least one α,ω-bis-perfluoroether acyl oligothiophene compound.

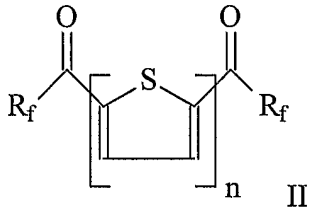
The novel compounds may be represented by the formula



I

wherein Y is a hydrogen atom, a halogen atom, an alkyl group, an aryl group or a perfluoroether acyl group, p is at least one, preferably at least two, and R_f is a perfluoroether group.

Preferred compounds are those α,ω-bis-perfluoroether acyl oligothiophene compounds of Formula II:



II

wherein each R_f is a perfluoroether group, and n is at least 1, preferably at least 2, more preferably 3 to 6. Using the conventional nomenclature, the successive thiophene rings are connected by a covalent bond, as indicated in Formulas I and II. In one aspect, semiconductor devices are provided that include a semiconductor layer that contains a α,ω-bis-perfluoroether acyl oligothiophene compound of Formulas I or II.

In another aspect, a method of preparing a semiconductor device is provided. The method involves preparing a semiconductor layer that contains a compound of Formula II. The semiconductor layer is often formed using a vapor deposition technique.

Some of the methods of preparing semiconductor devices are methods of preparing organic thin film transistors. One such method involves providing a gate electrode; depositing a gate dielectric layer on a surface of the gate electrode; preparing a semiconductor layer adjacent to a surface of the gate dielectric layer opposite the gate electrode; and positioning a source electrode and a drain electrode on a surface of the semiconductor layer that is opposite the gate dielectric layer. The source electrode and the drain electrode are separated from each other in an area on the surface of the semiconductor layer. The semiconductor layer contains a compound of Formulas I or II.

An additional method of preparing an organic thin film transistor involves providing a gate electrode; depositing a gate dielectric layer on a surface of the gate electrode; positioning a source electrode and a drain electrode adjacent to the gate dielectric layer opposite the gate electrode, wherein the source electrode and the drain electrode are separated by an area over the gate dielectric layer; and preparing a semiconductor layer on the source electrode, the drain electrode, and in the area between the source electrode and the drain electrode. The semiconductor layer includes a compound of Formulas I or II.

The above summary of the present invention is not intended to describe each disclosed embodiment or every implementation of the present invention. The Figures, Detailed Description, and Examples that follow more particularly exemplify these embodiments. While the invention is amenable to various modifications and alternative forms, specifics thereof have been shown by way of example in the drawings and will be described in detail. It should be understood, however, that the intention is not to limit the invention to the particular embodiments described. On the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention.

Brief Description of the Drawings

The invention may be more completely understood in consideration of the following detailed description of various embodiments of the invention in connection with the accompanying drawings, in which:

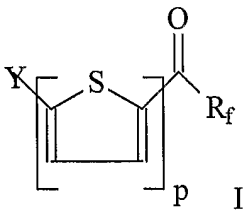
Figures 1a and b show cross-sectional representations of exemplary organic thin film transistors.

Figure 2 is a graph of the performance of a semiconductor device of using the oligothiophene semiconductor of Example 10.

Figure 3 is a graph of the performance of a semiconductor device using the oligothiophene semiconductor of Example 11.

Detailed Description

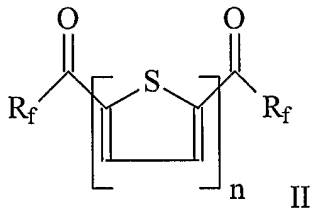
Novel perfluoroether acyl (oligo)thiophene compounds are provided. The novel compounds are of the general formula:



I

wherein Y is a hydrogen atom, a halogen atom, an alkyl group, and aryl group or a perfluoroether acyl group, p is at least one, preferably at least two, and R_f is a perfluoroether group.

Preferred α,ω-bis-perfluoroether acyl oligothiophene compounds are provided. The novel compounds are of the general formula:



II

wherein each R_f is a perfluoroether group, and n is at least 2.

The present invention provides semiconductor devices and methods of preparing semiconductor devices that include a semiconductor layer that contains a perfluoroether acyl (oligo)thiophene compound. Suitable thiophene groups include those having two to six successively linked thiophene rings.

Definition

As used herein, the terms "a", "an", and "the" are used interchangeably with "at least one" to mean one or more of the elements being described.

"Alkyl" means a saturated monovalent hydrocarbon radical having from one to about twelve carbon atoms or a branched saturated monovalent hydrocarbon radical having from three to about twelve carbon atoms, for example, methyl, ethyl, 1-propyl, 2-propyl, pentyl, and the like.

"Alkylene" means a saturated divalent hydrocarbon radical having from one to about twelve carbon atoms or a branched saturated divalent hydrocarbon radical having from three to about twelve carbon atoms, for example, methylene, ethylene, propylene, 2-methylpropylene, pentylene, hexylene, and the like.

"Alkyleneoxy" has essentially the meaning given above for alkylene except the alkylene group is terminated by an oxygen atom, for example, $-CH_2CH_2O-$, $-CH_2CH_2CH_2O-$, $-CH_2CH_2CH_2CH_2O-$, $-CH_2CH(CH_3)CH_2O-$, and the like.

The term "aryl" refers to monovalent unsaturated aromatic carbocyclic radicals having a single ring, such as phenyl, or multiple condensed rings, such as naphthyl or anthryl.

As used herein, the term "oligothiophene" refers to oligomers having at least two thiophene repeat units, linked by a covalent bond at the successive 2 positions. "(Oligo)thiophene" shall be inclusive of thiophene compounds having one thiophene ring and oligomeric thiophene compounds (oligothiophenes) having two or more thiophene rings.

"Perfluoroalkyl" has essentially the meaning given above for "alkyl" except that all or essentially all of the hydrogen atoms of the alkyl radical are replaced by fluorine atoms and the number of carbon atoms is from 1 to about 12, for example, perfluoropropyl, perfluorobutyl, perfluorooctyl, and the like.

"Perfluoroalkylene" has essentially the meaning given above for "alkylene" except that all or essentially all of the hydrogen atoms of the alkylene radical are replaced by fluorine atoms, for example, perfluoropropylene, perfluorobutylene, perfluorooctylene, and the like.

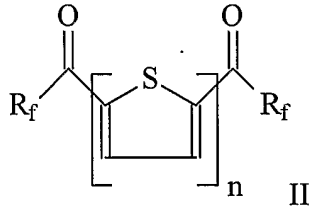
"Perfluoroalkyloxy" has essentially the meaning given above for "alkyloxy" except that all or essentially all of the hydrogen atoms of the alkyoxy radical are replaced by fluorine atoms and the number of carbon atoms is from 3 to about 12, for example, CF_3CF_2O-, $CF_3CF_2CF_2CF_2O$-, $C_3F_7CF(CF_3)O$-, and the like.

"Perfluoroalkyleneoxy" has essentially the meaning given above for "alkyleneoxy" except that all or essentially all of the hydrogen atoms of the alkyleneoxy radical are replaced by fluorine atoms, for example, -CF_2O-, -CF_2CF_2O-, -$CF_2CF(CF_3)O$-, and the like.

"Perfluoroether" is a saturated, perfluoroinated monovalent alkyl radical having from 2 to about 50 carbon atoms and at least one ether oxygen atom, for example, $CF_3CF_2OCF_2$-, $CF_3CF_2CF_2CF_2OCF_2CF_2$-, $CF_3CF(CF_3)O$ $CF_2CF_2OCF_2CF_2$-, $CF_3CF(CF_3)O$-[$CF(CF_3)$-CF_2O]$_n$-$CF(CF_3)$-, and the like. "Perfluoroether" is inclusive of perfluoro monoethers and perfluoro polyethers.

Semiconductor Devices

Semiconductor devices are provided that have a semiconductor layer that contains compound of the formula



II

wherein each R_f is a perfluoroether group, and n is at least 2, preferably 3 to 6.

R_f may be a monoether or a polyether, that is, a monovalent perfluoroalkoxyalkylene group or a monovalent perfluoropolyether group.

The perfluoroheteroalkyl group, R_f, of the fluorinated ether of Formulas I and II preferably corresponds to the formula:

$$R_f^1\text{-}O\text{-}(R_f^2)_x\text{-}(R_f^3)\text{-} \qquad \text{(III)}$$

wherein R_f^1 represents a perfluoroalkyl group having 1 to 10 carbon atoms, preferably 1 to 6 carbon atoms, $(R_f^2)_x$ represents a perfluoropolyalkyleneoxy group consisting of perfluoroalkyleneoxy groups, R_f^2, having 1 to 10 perfluorinated carbon atoms, preferably 1 to 6 carbon atoms, R_f^3 represents a perfluoroalkylene group having 1 to 10 perfluorinated carbon atoms, preferably 1 to 6 carbon atoms, and x is 0 to 25, preferably at least one, more preferably 1 to 4. The perfluoroalkyl and perfluoroalkylene groups in formula (III) may be linear or branched. A typical perfluoroalkyl group is $CF_3\text{-}CF_2\text{-}CF_2\text{-}$. For example, R_f^3 is $-CF_2-$ or $-CF(CF_3)-$.

Examples of perfluoroalkyl groups R_f^1 include $CF_3\text{-}CF_2\text{-}$, $CF_3\text{-}CF(CF_3)\text{-}$, $CF_3\text{-}CF_2\text{-}CF_2\text{-}$, $CF_3\text{-}$, $CF_3\text{-}CF_2CF_2\text{-}CF(CF_3)\text{-}$, $CF_3\text{-}CF_2CF(C_3F_7)\text{-}$, $CF_3\text{-}CF(C_3F_7)CF_2\text{-}$, and $CF_3\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}$.

Examples of perfluoroalkyleneoxy groups of perfluorinated polyalkyleneoxy group R_f^2 include: $-CF_2\text{-}CF_2\text{-}O-$, $-CF(CF_3)\text{-}CF_2\text{-}O-$, $-CF_2\text{-}CF(CF_3)\text{-}O-$, $-CF_2\text{-}CF_2\text{-}CF_2\text{-}O-$, $-CF_2\text{-}O-$, $-CF(CF_3)\text{-}O-$, and $-CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}O-$.

Examples of perfluoroalkylene groups, R_f^3 include: $-CF_2\text{-}CF_2-$, $-CF(CF_3)\text{-}CF_2-$, $-CF_2\text{-}CF(CF_3)-$, $-CF_2\text{-}CF_2\text{-}CF_2-$, $-CF_2-$, $-CF(CF_3)-$, and $-CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2-$.

The perfluoroalkyleneoxy group, R_f^2, may be comprised of the same perfluoroalkyleneoxy units or of a mixture of different perfluoroalkylene oxy units. When the perfluoroalkyleneoxy group is composed of different perfluoroalkylene oxy units, they can be present in a random configuration, alternating configuration or they can be present

as blocks. Typical examples of perfluoropolyalkyleneoxy groups include $-[CF_2-CF_2-O]_n-$; $-[CF(CF_3)-CF_2-O]_n-$; $-[CF_2CF_2-O]_i-[CF_2O]_j-$ and $-[CF_2-CF_2-O]_l-[CF(CF_3)-CF_2-O]_m-$; wherein n is an integer of 1 to 25, and i, l, m and j each are integers of 1 to 25.

In a particular embodiment, the fluorinated polyether, R_f, corresponds to the following formula (IV):

$$R_f^1\text{-}O\text{-}[CF(CF_3)\text{-}CF_2O]_x\text{-}CF(CF_3)\text{-} \qquad (IV)$$

wherein R_f^1 represents a perfluorinated alkyl group, for example, a linear or branched perfluorinated alkyl group having 1 to 6 carbon atoms, x is an integer of 0 to 25, preferably at least one, more preferably 1 to 4. A preferred perfluorinated polyether group that corresponds to formula (IV) is $CF_3\text{-}CF(CF_3)\text{-}O\text{-}[CF(CF_3)\text{-}CF_2O]_x\text{-}CF(CF_3)\text{-}$ wherein x is an integer of 1 to 4. This perfluoropolyether can be derived from an oligomerization of hexafluoropropylene oxide.

Preferred perfluoroether groups, R_f, are dimers, trimers and tetramers derived from the hexafluoropropylene oxide (HFPO) and correspond to the structures:

$$F(\underset{\displaystyle CF_3}{\underset{|}{CF}}CF_2O)_{1\text{-}4}\underset{\displaystyle CF_3}{\underset{|}{CF}}-$$

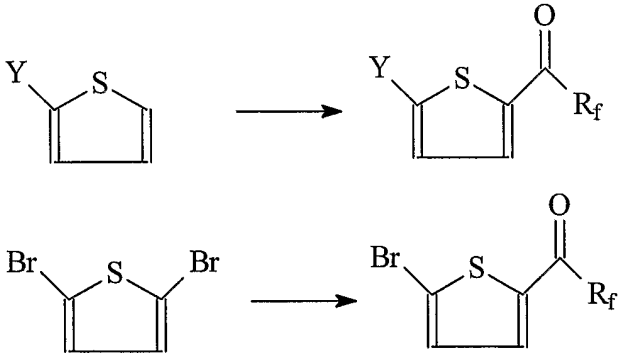
The corresponding acids, acid halides and esters may be prepared from the oligomerization of hexafluoropropylene oxide, or the oxidative oligomerization of hexafluoropropylene, such as is known in the art. Many of these compounds are commercially available from Matrix Scientific, Columbia, SC.

Compounds according to formula (IV) can for example be obtained by oligomerization of hexafluoropropylene oxide, which results in a perfluoropolyether carbonyl fluoride. This carbonyl fluoride may be converted into an acid, or ester by reactions well known to those skilled in the art. The carbonyl fluoride or acyl fluoride, acid, or ester derived therefrom may then be reacted further to introduce the desired perfluoroether groups into the oligothiophene compounds according to known acylation procedures. For example, U.S. 6,127,498 or U.S. 3,536,710 describe suitable methods to produce compounds according to formula (IV) having desired acyl moieties.

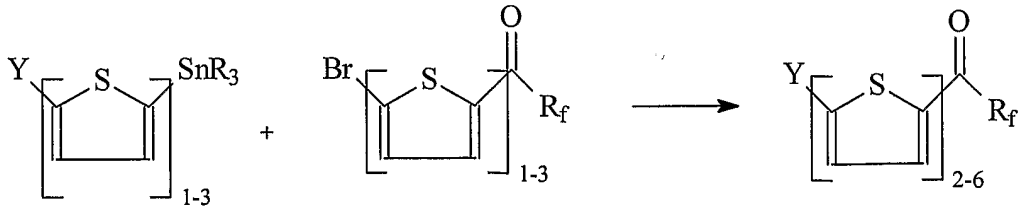
Further details concerning the materials and procedures for the preparation of perfluorinated polyethers can be found in, for example, U.S. Pat. Nos. 3,242,218 (Miller); 3,322,826 (Moore); 3,250,808 (Moore et al.); 3,274,239 (Selman); 3,293,306 (Le Bleu et al.); 3,810,874 (Mitsch et al.); 3,544,537 (Brace); 3,553,179 (Bartlett); 3,864,318

(Caporiccio et al.); 4,321,404 (Williams et al.), 4,647,413 (Savu); 4,818,801 (Rice et al.); 4,472,480 (Olson); 4,567,073 (Larson et al.); U.S. Pat. No. 4,830,910 (Larson); US 5362919 (Costello) US 5578278 (Fall) and 5,306,758 (Pellerite). See also Patricia M. Savu, Fluorinated Higher Carboxylic Acids, 11 Kirk-Othmer Encyclopedia of Chemical Technology 551-58 (4th ed. 1994).

Perfluoroether acyl (oligo)thiophene compounds of Formula I, where Y is not a perfluoroether acyl group, may be prepared as follows. Thiophene (Y=H) may be treated with an alkyl lithium reagent, followed by acylation with a perfluoroether ester (in presence of a Lewis acid catalyst such as BF_3-Et_2O) to produce the mono perfluoroether acyl compound. The corresponding 5-alkyl or 5-aryl compounds (Y= alkyl or aryl) may be prepared by an analogous route starting from 2-alkyl or 2-aryl thiophene (such as are known in the art), followed by acylation and optional bromination. The corresponding 2-bromo-5-perfluoroether acyl compound may be prepared by monoacylation of 2,5-dibromothiophene to directly produce the 2-bromo-5-perfluoroether acyl compound.



Higher thiophene compounds, where Y is H, halogen, alkyl or aryl may be prepared by Stille coupling of a thienyl stannane with an α-bromo-ω-perfluoroether acyl thiophene according to the following general scheme:

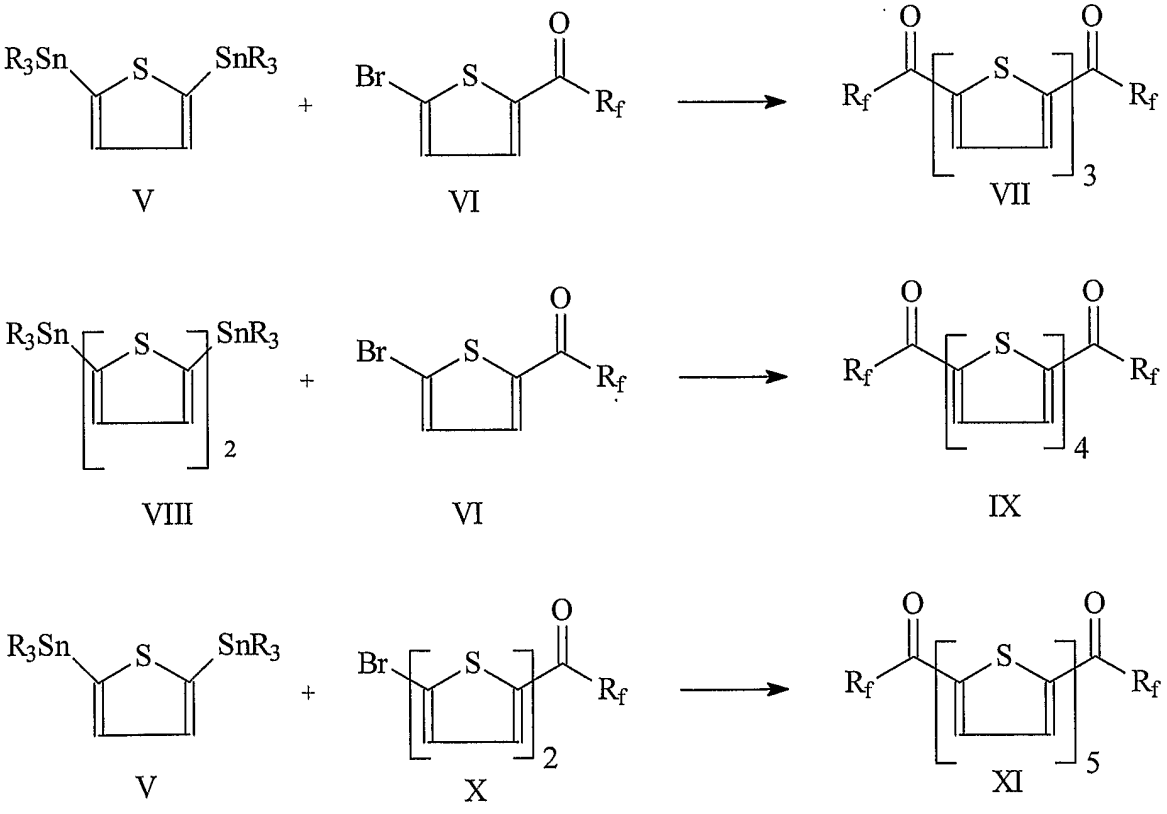


Preferred α,ω-bis-perfluoroether acyl oligothiophene compounds of Formula II may be prepared according to Reaction Scheme A by a Stille coupling reaction. Generally, the oligothiophenes may be prepared by reacting a

bis(trialkylstannyl)thiophene (such as a 2,5-bis(trialkylstannyl)thiophene or a 5,5'-bis(trialkylstannyl)bithiophene) with a 2-perfluoroether acyl 5-halothiophene (or a 5-perfluoroether acyl 5'-halobithiophene) in the presence of a palladium catalyst.

A 2-halo-5-perfluoroetheracyl thiophene (such compounds of formulas VI) or a 5-halo-5'-perfluoroetheracylbithiophene (such compounds of formulas X) can be reacted with a bis(trialkylstannyl) compound (that is, Formula V or VIII, where R is an alkyl group) to form a α,ω-bis(2-perfluoroetheracyl oligothiophene (that is, Formula VII, IX, XI or XII). The Stille coupling reaction may be performed as outlined in Farina V. and Krishnamurthy, V. in Organic Reactions; L.A. Paquette, Ed., John Wiley and Sons., 1997; vol. 50, pp. 1-652. The reaction products may be purified to a semiconductor grade material by any known process such as by vacuum sublimation.

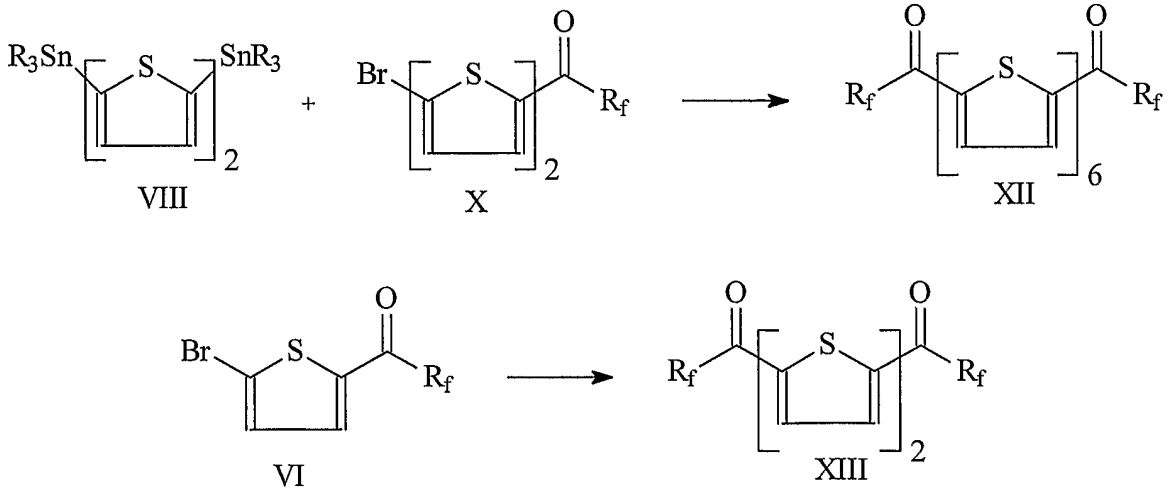
Reaction Scheme A



V + VI → VII

VIII + VI → IX

V + X → XI

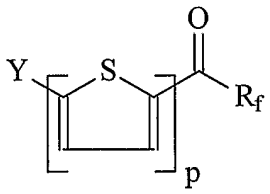


The bis-trialkylstannyl thiophene compounds of formulas V and VIII are known. Reference may be made to Y. Wei et al. Chem. Mater. Vol. 8, 1996, pp.2659-2666.

The monoacyl compound of formula VI may be made by treatment of 2,5-dihalothiophene with an alkyl lithium compound, to produce the 2-bromo-5-lithio thiophene, followed by reaction with a perfluorinated ether ester (or equivalent) in the presence of boron trifluoride etherate. This method yields the desired product V in high yields, and has proven superior to other known methods, such as formation of the cuprate, followed by reaction with a perfluorinated acyl compound.

The monoacyl bithiophene compound X may be prepared by a two-step synthesis comprising first reacting 5-lithio-2,2'-bithiophene (generated *in situ*) with a perfluorinated ether ester (or equivalent) in the presence of boron trifluoride etherate), followed by bromination, such as by N-bromosuccinimide.

With reference to compounds VI and X, 5-halo-5'-perfluoroether acyl thiophene compounds are useful in the preparation of the bis-perfluoroether thiophene compounds of the present invention. Such novel compounds are of the general formula:



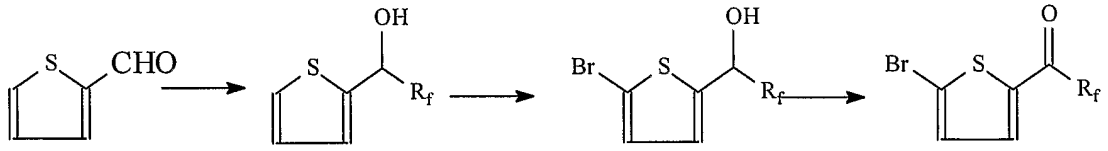
where Y is H, a halogen, an aryl or an alkyl group, R_f is a perfluoroether group and p is 1 to 6 Compounds where p is 2 or greater may be prepared by a Stille coupling reaction of a compound of formula VI or X with a mono-trialkylstannyl thiophene or a mono-

trialkylstannyl bithiophene, followed by halogenation of the ω-5 position of the terminal thiophene ring.

The bithiophene compound of formula XIII may be prepared by coupling of the 5-bromo-2-thienyl magnesium bromide and a perfluoroether acid halide according to the procedure described in Portnoy, J. Org. Chem, vol. 32, 1967, pp 233-4. The Ullman coupling reactions may also prove useful.

Asymmetric α,ω-bis-perfluoroether acyl oligothiophenes (that is, a oligothiophenes with different perfluoroether acyl groups can be prepared, for example, through using a mixture of compounds of Formulas VI or X having different R_f groups, although a mixture of products will result. With respect to each of the reaction schemes, the preferred bromo-substituted thiophenes are illustrated, but other halides may also be used.

Other synthetic approaches can be used to prepare α,ω-bis-perfluoroether acyl oligothiophene compounds. For example, the thiophene-2-aldehyde may be reacted with a perfluoroether organometallic compounds (such as R_f-Li, generated *in situ*) to produce the alcohol shown. This may be brominated at the 5-position, followed by oxidation of the hydroxyl group to the ketone. Reference may be made to the general methods described in U.S. 6,608,323 and 6,585,914 (Marks et al.).



VI

The compounds of the invention may be used as a n-channel semiconductor. The semiconductor layer that contains a α,ω-bis-perfluoroether acyl oligothiophene compound can be included in any type of semiconductor device. Semiconductor devices have been described, for example, by S. M. Sze in Physics of Semiconductor Devices, 2nd edition, John Wiley and Sons, New York (1981). Such devices may include rectifiers, transistors (of which there are many types, including p-n-p, n-p-n, and thin-film transistors), photoconductors, current limiters, thermistors, p-n junctions, field-effect diodes, Schottky diodes, and the like.

Semiconductor devices can include components such as transistors, arrays of transistors, diodes, capacitors, embedded capacitors, and resistors that are used to form circuits. Semiconductor devices also can include arrays of circuits that perform an electronic function. Examples of these arrays, or integrated circuits, are inverters, oscillators, shift registers, and logic. Applications of these semiconductor devices and arrays include radio frequency identification devices (RFIDs), smart cards, displays backplanes, sensors, memory devices, and the like.

Each semiconductor device contains a semiconductor layer with a compound according to Formulas I or II. The semiconductor layer can be combined with a conductive layer, a dielectric layer, or a combination thereof to form the semiconductor device. Semiconductor devices can be prepared or manufactured by known methods such as, for example, those described by Peter Van Zant in Microchip Fabrication, Fourth Edition, McGraw-Hill, New York (2000).

Some of the semiconductor devices are organic thin-film transistors. One embodiment of an organic thin-film transistor 10 is shown in Figure 1a. The organic thin-film transistor (OTFT) 10 includes an optional substrate 12, a gate electrode 14 disposed on the optional substrate 12, a gate dielectric material 16 disposed on the gate electrode 14, an optional surface treatment layer 18 disposed on the gate dielectric layer 16, a source electrode 22, a drain electrode 24, and a semiconductor layer 20 that is in contact with both the source electrode 22 and the drain electrode 24. The source electrode 22 and the drain electrode 24 are separated from each other in an area on the surface of the semiconductor layer 20 (that is, the source electrode 22 does not contact the drain electrode 24). The portion of the semiconductor layer that is positioned between the source electrode and the drain electrode is referred to as the channel 21. The channel is positioned over the gate electrode 14, the gate dielectric layer 16, and the optional surface treatment layer 18. The semiconductor layer 20 contacts the gate dielectric layer 16 or the surface treatment layer 18.

A second embodiment of an organic thin-film transistor is shown in Figure 1b. This OTFT 100 includes a gate electrode 14 disposed on an optional substrate 12, a gate dielectric layer 16 disposed on the gate electrode 14, an optional surface treatment layer 18 disposed on the gate dielectric layer 16, a semiconductor layer 20, and a source electrode 22 and a drain electrode 24 disposed on the semiconductor layer 20. In this embodiment,

the semiconductor layer 20 is between the gate dielectric layer 16 and both the source electrode 22 and the drain electrode 24. The semiconductor layer 20 can contact the gate dielectric layer 16 or the optional surface treatment layer 18. The source electrode 22 and the drain electrode 24 are separated from each other (that is, the source electrode 22 does not contact the drain electrode 24) in an area on the surface of the semiconductor layer 20. The channel 21 is the portion of the semiconductor layer that is positioned between the source electrode 22 and the drain electrode 24. The channel 21 is positioned over the gate electrode 14, the gate dielectric layer 16, and the optional surface treatment layer 18.

In operation of the semiconductor device configurations shown in Figures 1a and 1b, voltage can be applied to the drain electrode 24. However, no charge (that is, current) is passed to the source electrode 22 unless positive voltage is also applied to the gate electrode 14, relative to the source electrode 22. That is, unless voltage is applied to the gate electrode 14, the channel 21 in the semiconductor layer 20 remains in a non-conductive state. Upon application of voltage to the gate electrode 14, the channel 21 becomes conductive and charge flows through the channel 21 from the source electrode 22 to the drain electrode 24.

A substrate 12 often supports the OTFT during manufacturing, testing, and/or use. Optionally, the substrate can provide an electrical function for the OTFT. For example, the backside of the substrate can provide electrical contact. Useful substrate materials include, but are not limited to, inorganic glasses, ceramic materials, polymeric materials, filled polymeric materials (for example, fiber-reinforced polymeric materials), metals, paper, woven or non-woven cloth, coated or uncoated metallic foils, or a combination thereof. Suitable polymeric substrates include acrylics, epoxies, polyamides, polycarbonates, polyimides, polyketones, polynorbornenes, polyphenyleneoxides, poly(ethylene naphthalate), poly(ethylene terephthalate), poly(phenylene sulfide), poly(ether ether ketones) such as poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene), and the like.

The gate electrode 14 can include one or more layers of a conductive material. For example, the gate electrode can include a doped silicon material, a metal, an alloy, a conductive polymer, or a combination thereof. Suitable metals and alloys include, but are not limited to, aluminum, chromium, gold, silver, nickel, palladium, platinum, tantalum, titanium, indium tin oxide (ITO) or a combination thereof. Exemplary conductive

polymers include, but are not limited to, polyaniline or poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate). In some organic thin film transistors, the same material can provide both the gate electrode function and the support function of the substrate. For example, doped silicon can function as both the gate electrode and as a substrate.

The gate dielectric layer 16 is disposed on the gate electrode 14. This gate dielectric layer 16 electrically insulates the gate electrode 14 from the balance of the OTFT device. Useful materials for the gate dielectric include, for example, an inorganic dielectric material, a polymeric dielectric material, or a combination thereof. The gate dielectric can be a single layer or multiple layers of suitable materials. Each layer in a single or multilayer dielectric can include one or more dielectric materials.

Exemplary inorganic dielectric materials include strontiates, tantalates, titanates, zirconates, aluminum oxides, silicon oxides, tantalum oxides, titanium oxides, silicon nitrides, barium titanate, barium strontium titanate, barium zirconate titanate, zinc selenide, zinc sulfide, hafnium oxides, and the like. In addition, alloys, combinations, and multiple layers of these materials can be used for the gate dielectric layer 16.

Exemplary polymeric dielectric materials include polyimides, parylene C, crosslinked benzocyclobutene, cyanoethylpullulan, polyvinyl alcohol, and the like. See, for example, C.D. Sheraw et al., "Spin-on polymer gate dielectric for high performance organic thin film transistors", Materials Research Society Symposium Proceedings, vol. 558, pages 403-408 (2000), Materials Research Society, Warrendale, PA, USA; and U.S. Patent No. 5,347,144 (Garnier).

Other exemplary organic polymeric dielectrics include cyano-functional polymers such as cyano-functional styrenic copolymers as disclosed in U.S. Patent Application Serial No. 10/434,377, filed May 8, 2003. Some of these polymeric materials can be coated from solution, can be crosslinked, can be photo-patterned, can have high thermal stability (for example, stable up to a temperature of about 250 °C), can have a low processing temperature (for example, less than about 150 °C or less than about 100 °C), can be compatible with flexible substrates, or combinations thereof.

Exemplary cyano-functional polymers that can be used as organic dielectric materials include, but are not limited to, styrene maleic anhydride copolymers modified by adding a methacrylate functional group for crosslinking purposes and by attaching cyano-

functional groups; the reaction product of bis(2-cyanoethyl)acrylamide with an acrylated polystyrene macromer; polymers formed from 4-vinylbenzylcyanide; polymers formed from 4-(2,2'-dicyanopropyl)styrene; polymers formed from 4-(1,1',2-tricyanoethyl)styrene; and polymers formed from 4-(bis-(cyanoethyl)aminoethyl)styrene; and a copolymer formed from 4-vinylbenzylcyanide and 4-vinylbenzylacrylate.

The organic thin film transistors can include an optional surface treatment layer 18 disposed between the gate dielectric layer 16 and at least a portion of the organic semiconductor layer 20. In some embodiments, the optional surface treatment layer 18 serves as an interface between the gate dielectric layer and the semiconductor layer. The surface treatment layer can be a self-assembled monolayer or a polymeric material.

Suitable self-assembled monolayer surface treatment layers are disclosed, for example, in U.S. Patent No. 6,433,359 B1 (Kelley et al.). Exemplary self-assembled monolayers can be formed from 1-phosphono-2-ethylhexane, 1-phosphono-2,4,4-trimethylpentane, 1-phosphono-3,5,5-trimethylhexane, 1-phosphonoctane, 1-phosphonohexane, 1-phosphonohexadecane, 1-phosphono-3,7,11,5-tetramethylhexadecane, and the like.

Useful polymers and copolymers for a surface treatment layer are usually non-polar, glassy solids at room temperature. The polymeric materials in this layer typically have glass transition temperature (T_g) measured in the bulk of at least 25 °C, of at least 50 °C, or of at least 100 °C. Suitable polymeric surface treatment layers are described, for example, in U.S. Patent Application Publication 2003/0102471 A1 (Kelley et al.) and U.S. Patent No. 6,617,609 (Kelley et al.)

Exemplary polymeric surface treatment layers can contain polystyrene, polyfluorene, polynorbornene, poly(1-hexene), poly(methyl methacrylate), poly(acenaphthylene), poly(vinylnaphthalene), poly(butadiene), and poly(vinyl acetate). Other exemplary polymeric surface treatment layers can contain polymers or copolymers derived from α-methylstyrene, 4-tert-butylstyrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, 4-(phosphonomethyl)styrene, divinyl benzene, and combinations thereof. Examples of still other useful polymeric materials for the surface treatment layer include poly(dimethylsiloxane), poly(dimethylsiloxane-co-diphenylsiloxane), poly(methylphenylsiloxane-co-diphenylsiloxane), poly(dimethylsiloxane-co-methylphenylsiloxane), and the like.

The surface treatment layer often has a maximum thickness less than 400 Angstroms (Å). For example, the surface treatment layer can be less than 200 Å, less than 100 Å, or less than 50 Å. The surface treatment layer generally has a thickness of at least about 5 Å, at least about 10 Å, or at least 20 Å. The thickness can be determined through known methods such as ellipsometry.

The source electrode 22 and drain electrode 24 can be metals, alloys, metallic compounds, conductive metal oxides, conductive ceramics, conductive dispersions, and conductive polymers, including, for example, gold, silver, nickel, chromium, barium, platinum, palladium, aluminum, calcium, titanium, indium tin oxide (ITO), fluorine tin oxide (FTO), antimony tin oxide (ATO), indium zinc oxide (IZO), poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate), polyaniline, other conducting polymers, alloys thereof, combinations thereof, and multiple layers thereof. Some of these materials are appropriate for use with n-type semiconductor materials and others are appropriate for use with p-type semiconductor materials, as is known in the art.

The thin film electrodes (for example, the gate electrode, the source electrode, and the drain electrode) can be provided by any means known in the art such as physical vapor deposition (for example, thermal evaporation or sputtering), ink jet printing, or the like. The patterning of these electrodes can be accomplished by known methods such as shadow masking, additive photolithography, subtractive photolithography, printing, microcontact printing, and pattern coating.

The semiconductor devices that contain the perfluoroether acyl oligothiophene compounds tend to have performance characteristics such as charge-carrier mobility and current on/of ratio that are comparable to known organic semiconductor devices such as those that contain pentacene. For example, semiconductor devices can be prepared that have an n-channel mobility of about 1 cm^2/volt-sec and on-off ratio greater than about 10^5.

In another aspect, a method of preparing a semiconductor device is provided. The method involves preparing a semiconductor layer that contains a perfluoroether acyl oligothiophene compound of Formulas I or II, where n is preferably 3 to 6. The semiconductor layer is usually formed using a vapor deposition process.

In some exemplary methods of preparing a semiconductor device, the method involves preparing a semiconductor layer that contains a perfluoroether acyl oligothiophene compound of Formulas I or II; and depositing a dielectric layer, a

conductive layer, or a combination thereof adjacent to the semiconductor layer. As used herein, the term "adjacent" refers to a first layer that is positioned near a second layer. The first layer often contacts the second layer but another layer could be positioned between the first and second layer. No specific order of preparing or depositing is necessary; however, the semiconductor layer is often prepared on the surface of another layer such as the dielectric layer, conductive layer, or a combination thereof.

One exemplary method of preparing a semiconductor device provides an organic thin film transistor. The method includes preparing a semiconductor layer that contains a perfluoroether acyl oligothiophene compound of Formulas I or II; positioning a source electrode and a drain electrode on a surface of the semiconductor layer such that the source electrode and the drain electrode are separated in an area on the surface of the semiconductor layer (that is, the source electrode does not contact the drain electrode). The method can further include providing a gate dielectric layer, a gate electrode, and an optional surface treatment layer.

More specifically, an organic thin film transistor can be prepared by providing a gate electrode; depositing a gate dielectric layer on a surface of the gate electrode; preparing a semiconductor layer adjacent to the gate dielectric layer (that is, the gate dielectric is positioned between the gate electrode and the semiconducting layer); and positioning a source electrode and a drain electrode on a surface of the semiconductor layer that is opposite the gate dielectric layer. The source electrode and the drain electrode are separated from each other in an area on the surface of the semiconductor layer.

In one embodiment of this method, the various layers of the semiconductor device are arranged in the following order: gate electrode; gate dielectric layer; semiconductor layer; and a layer containing a source electrode and a drain electrode. In another embodiment, the various layers of the semiconductor device are arranged in the following order: gate electrode, gate dielectric layer, surface treatment layer, semiconductor layer, and a layer containing a source electrode and a drain electrode. The source electrode does not contact the drain electrode in these embodiments. That is, the source electrode and the drain electrode are separated from each other in an area on the surface of the semiconductor device. One surface of the semiconductor layer contacts both the source electrode and the drain electrode while the opposite surface of the semiconductor layer contacts the gate dielectric layer or the surface treatment layer.

The organic thin film transistor exemplified in Figure 1b can be prepared by providing a substrate, depositing a gate electrode on the substrate, depositing a gate dielectric layer on a surface of the gate electrode such that the gate electrode is positioned between the substrate and the gate dielectric layer; applying a surface treatment layer to a surface of the gate dielectric layer opposite the gate electrode; preparing a semiconductor layer on a surface of the surface treatment layer opposite the gate dielectric layer; and positioning a source electrode and a drain electrode on a surface of the semiconductor layer that is opposite the polymeric treatment layer. The source electrode and the drain electrode are separated from each other in an area on the surface of the semiconductor layer. The area of separation between the source electrode and the drain electrode can define a channel in the semiconductor layer.

Another organic thin film transistor can be prepared by providing a gate electrode; depositing a gate dielectric layer on a surface of the gate electrode; positioning a source electrode and a drain electrode adjacent to the gate dielectric material such that the source electrode and the drain electrode are separated from each other in an area over the gate dielectric layer; preparing a semiconductor layer that is deposited on the source electrode, drain electrode, and in the area between the source electrode and the drain electrode. The semiconductor layer contacts both the source electrode and the drain electrode. The portion of the semiconductor layer that is positioned in the area between the source electrode and the drain electrode defines the channel.

In one embodiment of this method, the various layers of the semiconductor device are arranged in the following order: gate electrode; gate dielectric layer; a layer containing a source electrode and a drain electrode; and a semiconductor layer. In another embodiment, the various layers of the semiconductor device are arranged in the following order: gate electrode; gate dielectric layer; surface treatment layer; a layer containing a source electrode and a drain electrode; and semiconductor layer. The source electrode does not contact the drain electrode in these embodiments. A portion of the semiconductor layer can extend between the source electrode and the drain electrode.

The organic thin film transistor exemplified in Figure 1a can be prepared by providing a substrate, depositing a gate electrode on the substrate, depositing a gate dielectric layer on a surface of the gate electrode such that the gate electrode is positioned between the substrate and the gate dielectric layer; applying a surface treatment layer to a

surface of the gate dielectric layer opposite the gate electrode; positioning a source electrode and a drain electrode on a surface of the polymeric treatment layer such that the two electrodes are separated from each other in an area; preparing a semiconductor layer on the source electrode, drain electrode, and in the area between the source electrode and the drain electrode. The semiconductor layer contacts both the source electrode and the drain electrode. The portion of the semiconductor layer that is positioned in the area between the source electrode and the drain electrode defines a channel in the semiconductor layer.

The organic thin film transistors or other semiconductor devices such as integrated circuits can be prepared using flexible, repositionable polymeric aperture masks. The technique involve sequentially depositing material through a number of polymeric aperture masks formed with patterns that define layers, or portions of layers, of the semiconductor device. The use of such polymeric aperture masks are further described in U.S. Patent Publication Nos. 2003/0094959-A1, 2003/0150384-A1, 2003/0152691-A1, and 2003/0151118-A1.

Repositionable polymeric aperture masks often have a thickness of 5 to 50 micrometers or 15 to 35 micrometers. The various deposition apertures in the aperture masks usually have widths less than 1000 micrometers, less than 50 micrometers, less than 20 micrometers, less than 10 micrometers, or even less than 5 micrometers. Apertures of these sizes are particularly useful in creating small circuit elements for integrated circuits. Moreover, one or more gaps between deposition apertures are typically less than 1000 micrometers, less than 50 micrometers, less than 20 micrometers, or less than 10 micrometers, which is also useful in creating small circuit elements. The aperture masks can have a pattern with a width greater than 1 centimeter, 25 centimeters, 100 centimeters, or even 500 centimeters. Patterns having these widths can be useful in creating various circuits over a larger surface area.

Various laser ablation techniques may be used to facilitate the creation of polymeric aperture masks having patterns of deposition apertures. In addition, stretching techniques and other techniques may be used to facilitate alignment of flexible polymeric aperture masks. Furthermore, methods of controlling sag in aperture masks may be used which can be particularly useful in using masks that include a pattern that extends over a large width.

Other methods known in the art can be used to prepare the semiconductor devices. These methods include, for example, metal shadow masks; photolithography and/or etching; and printing methods such as inkjet, screen-printing, gravure printing, and the like.

In some methods that involve the use of aperture masks, semiconductor devices (for example, integrated circuits) can be created solely using aperture mask deposition techniques, without requiring any of the etching or photolithography steps typically used to form such devices. The techniques can be particularly useful in creating circuit elements for electronic displays such as liquid crystal displays and low-cost integrated circuits such as radio frequency identification (RFID) circuits. In addition, such techniques can be advantageous in the fabrication of integrated circuits incorporating organic semiconductors, which typically are not compatible with photolithography or other wet chemical processes.

EXAMPLES

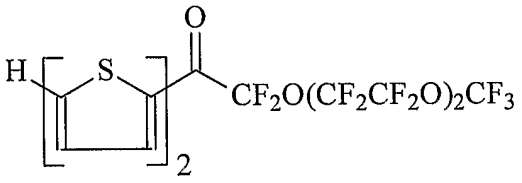
Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

All reactions were carried out under nitrogen. Melting points were determined by DSC analyses under N_2 at a ramp rate of 20 °C/min and are reported as the range between the onset temperature and the peak maximum. Combustion analyses were run using a LECO 932 CHNS elemental analyzer (LECO Corporation, St. Joseph, MI). Infrared spectra were recorded using pellets pressed with KBr. Positive ion mass spectrometry was done using an Applied Biosystems Inc. DE/STR MALDI/TOF mass spectrometer (Applied Biosystems, Inc., Foster City, CA). Dilute $CHCl_3$ solutions of the samples were deposited directly on the probe tip without a matrix. ^1H and ^{19}F NMR spectra were collected in d_6-acetone at 200 MHz and 188 MHz, respectively, unless otherwise indicated. Internal tetramethylsilane and fluorotrichloromethane were referenced to 0.0 ppm. Silica gel for column chromatography was purchased from Aldrich (Milwaukee, WI; Merck, grade 9385, 230-400 mesh, 60Å). Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium/benzophenone ketyl. N,N-dimethylformamide (DMF) was vacuum distilled under nitrogen from $MgSO_4$ or purchases as anhydrous grade from

Aldrich. All other solvents were used as obtained. Bithiophene, 2,5-dibromothiophene, 3-bromothiophene, boron trifluoride diethyl etherate, aluminum trichloride, *n*-butyl lithium (1.6 M or 2.5 M in hexanes), *N*-bromosuccimide (NBS), and dimethylamine borane were purchased from Aldrich. NBS was recrystallized from hot water and dried under vacuum prior to use. Perfluoro(2,5-dimethyl-3,6-dioxanonanoic) acid methyl ester (HFPO trimer carbomethoxylate), methyl 3,6-dioxadecanoate, and methyl 3,6,9-trioxadecanoate were purchased from Matrix Scientific (Columbia, SC) and used as received. Tetrakis(triphenylphosphine)palladium (0) was purchased from Strem Chemicals, Newburyport, MA. 5,5′-bis(tri-*n*-butylstannyl)-2,2′-bithiophene and 5,5′-bis(tri-*n*-butylstannyl)thiophene were synthesized using the procedure published by Y. Wei, Y. Yand, and J.-M Yeh, Chem. Mater. , 8, 2659-2666 (1996).

Example 1

5-Perfluoro(3,6,9-trioxadecanoyl)-2,2′-bithiophene



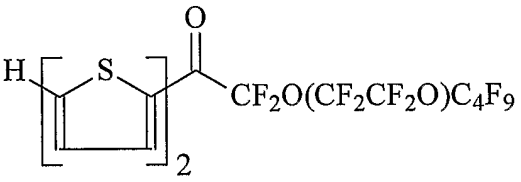
A hexanes solution of BuLi (10.18 mL, 16.3 mmol) was added drop wise to a cold (–70 °C) THF solution (250 mL) of bithiophene (2.71 g, 16.3 mmol). After 30 min, $CF_3(OC_2F_4)_2OCF_2CO_2Me$ (7.66 g , 16.4 mmol) and $BF_3{\bullet}OEt_2$ (2.5 mL, 19.6 mmol, 1.2 eq) were added sequentially and the mixture stirred at –70 °C for 90 min. A few mL of saturated NH_4Cl (aq) were charged, the mixture was warmed to room temperature, and the volatile materials removed under reduced pressure. Et_2O (400 mL) and brine (250 mL) were charged and the reaction was stirred vigorously.

The mixture was filtered through a Celite pad and the amber organic washed with 2 × 100 mL brine, dried with $MgSO_4$, and filtered. The solvent was stripped and the material adsorbed onto silica gel. The crude product was purified by column chromatography (hexanes/EtOAc, 0%–3%) to aford 6.38 g (70%) of yellow product. Mp (ΔH): 50–53 °C (51 J/g). IR: 1684 (ν_{CO}), 1505 w, 1450 m, 1423w, 1229 s, 1193 s, 1139 s, 1103 s, 1077 s, 906 m, 869 m, 842 m, 803 m, 741 m, 706 s, 682 m, 619 w, 546 w, 522 w, 508 w, 453 w cm^{-1}. ^1H NMR: δ 7.22 (dd, J = 5.1 Hz, 3.8 Hz, 5′-H), 7.56 (d, J = 4.3 Hz, 3-

H), 7.67 (dd, J = 3.7 Hz, 1.1 Hz, 4′-H), 7.73 (dd, J = 5.1 Hz, 1.1 Hz, 3′-H), 8.01 (dt, J = 4.3 Hz, 1.7 Hz, 4-H). ^{19}F NMR: δ –55.03 (t, J = 9.0 Hz, CF_3), –74.43 (m, 8-lines, COCF_2), –87.50 (m, 5 lines, CF_2), –88.16 (br, 2 CF_2 groups), –90.19 (q, J = 9.4 Hz, CF_2OCF_3). Anal. Calcd for $C_{15}H_5F_{13}O_4S_2$: C, 32.15; H, 0.90; S, 11.45. Found: C, 32.2; H, 0.9; S, 11.6.

Example 2

5-Perfluoro(3,6-dioxadecanoyl)-2,2′-bithiophene

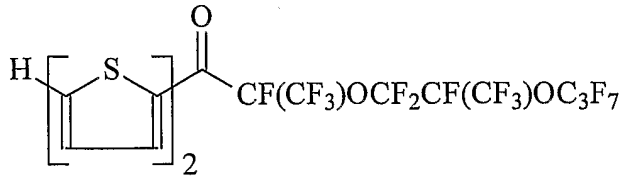


This compound was prepared analogously to Example 1. A reaction between BuLi (36.75 mL, 58.8 mmol) and bithiophene (9.75 g, 58.6 mmol) in cold THF (250 mL, –70 °C) was stirred for 30 min, followed by a sequential addition of $C_4F_9OC_2F_4OCF_2CO_2Me$ (30.2 g , 65.7 mmol) and BF_3OEt_2 (9.0 mL, 71 mmol).

The material was purified by chromatography to afford 18.7 g (54%) of yellow product. Mp (ΔH):50–53 °C (45 J/g). IR: 1666 m (ν_{CO}), 1504 w, 1448 m, 1309 m, 1233 s, 1202 s, 1153 s, 1081 m, 1027 m, 993 m, 851 w, 837 w, 802 m, 763 w, 752 w, 802 m, 763 w, 752 w, 721 m, 710 m, 654 w, 616 w, 532 w, 460 w cm^{-1}. ^{1}H NMR: δ 7.20 (dd, J= 5.17 Hz, 3.8 Hz, 5′-H), 7.53 (d, J = 4 Hz, 3-H), 7.64 (dd, J = 4 Hz, 1 Hz, 4′-H), 7.69 (dd, J = 5.1 Hz, 1.1 Hz, 3′-H), 7.98 (dt, J = 4.2 Hz, 1.6 Hz, 4-H). ^{19}F NMR: δ –74.46 (t, J = 12.2 Hz, CF_3), –80.88 (br, COCF_2O), –83.08 (br, OCF_2CF_2O), –87.60 ('t', J =12.0 Hz, -OCF_2CF_2O), –88.05 ('t', J = 12.7 Hz, OCF_2C$_3$F$_7$), –126.14 (m, CF_2CF_2CF_2CF_3). Anal. Calcd for $C_{16}H_5F_{15}O_3S_2$: C, 32.33; H, 0.85; S, 10.79. Found: C, 32.1; H, 0.8; S, 10.9.

Example 3

5-Perfluoro(2,5-dimethyl-3,6-dioxanonanoyl)-2,2′-bithiophene

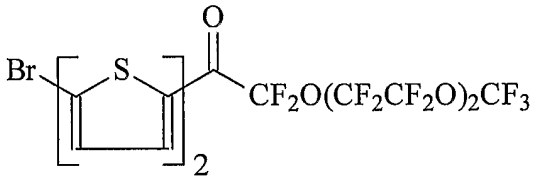


This compound was prepared analogously to Example 1. Reaction between bithiophene (7.90 g, 47.5 mmol), BuLi (47.6 mmol), HFPO trimer carbomethoxylate (26.7

g, 52.2 mmol), and BF_3OEt_2 (7.0 mL, 55 mmol) in 250 mL of cold THF yielded 24.8 g (81%) of product. Mp (ΔH):37–40°C 37 (J/g). IR: 1666 s (ν_{CO}), 1504 w, 1449 s, 1310 s, 1233 s, 1202 vs, 1153 s, 1081 m,1027 m, 993 s, 897 w, 850 m, 837 m, 802 s, 763 m, 752 m, 721 m, 710 s, 654 m, 616 m,532 m, 456 w cm^{-1}. ^1H NMR: δ 7.23 (dd, J = 4.0 Hz, 5.0 Hz, 5′-H), 7.59 (d, J = 4.4 Hz,3-H), 7.70 (dd, J = 3.8 Hz, 1.2 Hz, 4′-H), 7.74 (dd, J = 5.2 Hz, 1.2 Hz, 3′-H), 8.16 ('t', J =4.0 Hz, 4-H). ^{19}F NMR: δ –76.8 to -82.1 (m, 4 F $OCF_2CF(CF_3)OCF_2$-), –79.8 (s, 3 F, CF_2CFCF_3), –81.1 (s, 6 F, $COCFCF_3$ and CF_2CF_3), –129.2 (br m, 1 F, $COCFCF_3$), –129.2 (s, 2 F, $OCF_2CF_2CF_3$), –144.6 (br m, 1 F, OCF_2CFCF_3O). A number of the resonances in the ^{19}F NMR data are observed as pairs due to the asymmetric centers of the fluorinated group. Anal. calcd for $C_{17}H_5F_{17}O_3S_2$: C, 31.69; H, 0.78; S, 9.95. Found: C, 31.3; H, 0.8; S, 9.9.

Example 4

5-Bromo-5′-perfluoro(3,6,9-trioxadecanoyl)-2,2′-bithiophene.

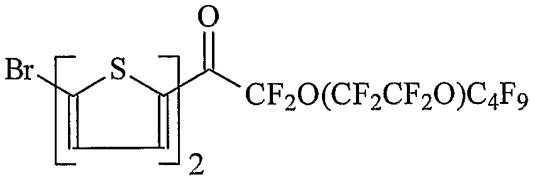


NBS (2.50 g, 13.32 mmol) was added to a stirred mixture of DMF (250 mL) and 5-perfluoro(3,6,9-trioxadecanoyl)-2,2′-bithiophene (6.22 g, 11.1 mmol) that was covered with aluminum foil. The solution was stirred overnight, poured into 500 mL of brine, and extracted with Et_2O (500 mL) and hexanes (250 mL). The yellow extract was separated, washed with 100 mL brine, 100 mL water, dried with $MgSO_4$, and filtered.

Concentration of the filtrate followed by cooling at –15 °C overnight afforded 5.32 g (75%) of bright yellow product. Mp (ΔH): 78–81 °C (47 J/g). IR: 1677 s (ν_{CO}), 1509 w, 1452 m, 1421 m, 1231 s, 1191 s, 1153 s, 1104 s, 1076 s, 906 m, 891 m, 861 m, 837 w, 791 m, 740 m, 714 m, 683 m, 648 w, 545 w, 523 w, 510 w, 457 w cm^{-1}. ^1H NMR: δ 7.30 (d, J = 4.0 Hz, 3′-H), 7.51 (d, J = 4.0 Hz, 4-H), 7.56 (d, J = 4.3 Hz, 3-H), 8.02 (dt, J = 4.3 Hz, 1.4 Hz, 4′-H). ^{19}F NMR: δ –55.03 (t, J = 9.2 Hz, CF_3), –74.49 (m, $COCF_2$), –87.49 (m, CF_2), –88.15 (br 2 CF_2 groups), –90.19 (q, J = 8.1Hz, CF_2OCF_3). Anal. Calcd for $C_{15}H_4BrF_{13}O_4S_2$: C, 28.19; H, 0.63; S, 10.03. Found:C, 28.2; H, 0.4; S, 10.1.

Example 5

5-Bromo-5′-perfluoro(3,6-dioxadecanoyl)-2,2′-bithiophene

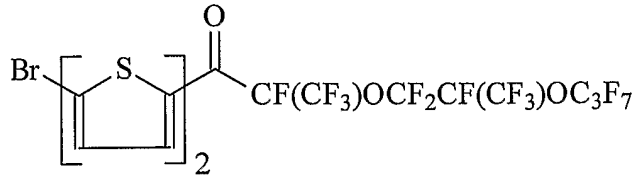


A DMF solution (200 mL) of 5-perfluoro(3,6-dioxadecanoyl)-2,2′-bithiophene (17.20 g, 28.94 mmol) was charged with NBS (6.70 g, 37.6 mmol) and stirred overnight covered with foil. Orange crystals of the product precipitated from the solution. Et_2O (200 mL) and brine (200 mL) were added to the reaction and the solution washed in a separatory funnel. The organic layer was separated and washed with 3 × 200 mL of brine.

The organic was dried with $MgSO_4$, filtered, and the volatile materials removed under reduced pressure to afford 18.63 g (96%) of yellow product. The crude product was clean by NMR spectroscopy and used directly in further reactions. Mp (ΔH): 86–89 °C (49 J/g); an endothermic transition at 82 °C was present in the first scan only. IR: 1671 s, 1508 w, 1446 s, 1420 w, 1337 w, 1312 m, 1290 w, 1219 s, 1192 s, 1144 s, 1114 m, 1082 m, 975 w, 954 w, 901 w, 891 w, 860 w, 821 w, 788 m, 736 w, 714 w, 693 w, 684 w, 649 w, 597 w, 543 w, 509 w, 457 w, 409 w cm^{-1}. ^1H NMR: δ 7.30 (d, J = 4.0 Hz, 3′- H), 7.51 (d, J = 4.0 Hz, 4-H), 7.56 (d, J = 4.3 Hz, 3-H), 8.02 (dt, J = 4.3 Hz, 1.6 Hz, 4′H). ^{19}F NMR: δ –74.20 (t, J = 12 Hz, CF_3), –80.76 (m, $COCF_2O$), –82.99 (m, OCF_2CF_2O), –87.52 (m, OCF_2CF_2O), –87.97, (m, $OCF_2C_3F_7$), –126.09 (br m, $OCF_2C_2F_4CF_3$).

Example 6

5-Bromo-5′-perfluoro(2,5-dimethyl-3,6-dioxanonanoyl)-2,2′-bithiophene

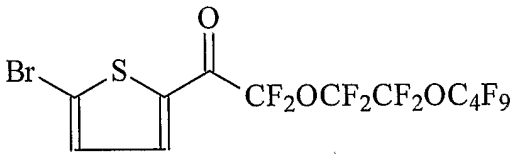


This compound was prepared using an identical procedure to that used in Example 5 to afford 16.1 g (94%) of yellow product. Mp (ΔH):51–55 °C (34 J/g). IR: 1661 s (ν_{CO}), 1505 w, 1448 s, 1421 m, 1299 s, 1237 vs, 1203 s, 1149 s, 1081 s, 1029 s, 994 s, 884 m, 835 m, 814 m, 790 s, 752 w, 743w, 723 m, 705 m, 651 m, 615 m, 532 m, 458 m cm^{-1}. $_1H$ NMR: δ 7.30 (d, J = 3.8 Hz, 3′- H), 7.53 (d, J = 4.0 Hz, 4-H), 7.57 (d, J = 4,4 Hz, 3-H),

8.15 ('t', J = 4.0 Hz, 4'-H). ^{19}F NMR: δ –76.7 to –82.1 (m, 4 F, OC*F*2), –79.4 (s, 3 F, CF_3), –81.1 (s, 6 F, CF_3), –129.0 (m, 1 F, C*F*), –129.2 (m, 2 F, $CF_2CF_2CF_3$), –144.7 (m, 1 F, C*F*). A number of the resonances in the ^{19}F data are observed as pairs due to the two asymmetric centers of the fluorinated end group. Anal. Calcd for $C_{17}H_4BrF_{17}O_3S_2$: C, 28.23; H, 0.56; S, 8.87. Found: 28.6; H, 1.1; 9.1.

Example 7

2-Bromo-5-perfluoro(3,6-dioxadecanoyl)-thiophene

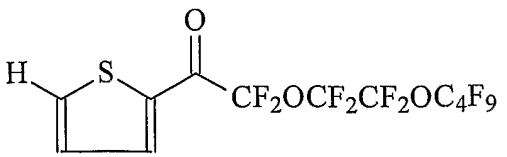


BuLi (3.7 mL, 9.3 mmol) was charged drop wise to a cold (–70 °C) mixture of THF (40 mL) and 2,5- dibromothiophene (1.0 mL, 8.9 mmol). After 40 min at –70 °C, $C_4F_9OC_2F_4OCF_2CO_2Me$ (4.1 g, 8.9 mmol) and BF_3OEt_2 (1.3 mL, 10.3 mmol) were added successively turning the clear, colorless mixture light yellow. After stirring overnight, the volatile materials were removed under reduced pressure.

The remaining liquid was extracted with 100 mL ether, washed with 2 × 100 mL brine, dried with $MgSO_4$, and stripped to a clear orange liquid. Purification by column chromatography on silica gel afforded a yellow liquid that was dried under vacuum to afford 3.80 g (73%). A larger scale preparation (71 g theoretical yield) afforded 37.8 g (53%) of clean product after it was purified by distillation (bp 55-56 °C, 0.1 mm Torr); a precut of 7.7 g collected from 50–55 °C that was approximately 63% product/37% $C_4H_3SCOR_f$; a 1.1 g post cut was 91% product and 9% $C_4HBr_2SCOR_f$. IR (neat, KBr plates): 1701 cm–1 (s, ν_{CO}). ^{1}H NMR: δ 7.52 (d, J = 4.4 Hz, 3-H), 7.91 (dt, J = 4.4 , 1.4 Hz, 4-H). ^{19}F NMR: δ –74.79 (m, CF_3), –80.87 (m, $COCF_2O$), –83.07 (m, OCF_2CF_2O), –87.61 (m, OCF_2CF_2O), –88.05 (m, $OCF_2C_3F_7$), –126.1 (m, $CF_2CF_2CF_2CF_3$).

Example 8

2-Perfluoro(3,6-dioxadecanoyl)-thiophene

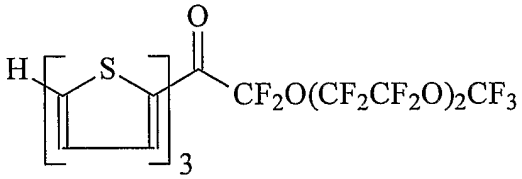


BuLi (7.8 mL, 12.5 mmol) was added to a cold (–65 °C) mixture of THF (50 mL) and thiophene (1.0 mL, 12.5 mmol. The clear, colorless solution was warmed to room temperature, cooled to –65 °C, and $C_4F_9OC_2F_4OCF_2CO_2Me$ (5.84 g, 12.7 mmol) and $BF_3(OEt_2)$ (1.9 mL, 15 mmol) added successively. The yellow solution was stirred cold for 2 hr and then mixed with 2 mL of saturated NH_4Cl (aq). The volatile material was removed under reduced pressure, and the residue extracted with 50 mL hexanes.

The solution was filtered, dried with $MgSO_4$, filtered again, and stripped to afford 5.53 g (86%) of clear orange liquid that was clean by NMR spectroscopy. IR: 1700 cm^{-1} (s, ν_{CO}). ^1H NMR: δ 7.41 (dd, J = 6.0 Hz, 4.0 Hz, 5-H), 8.08 (m, 3-H), 8.33 (dd, J = 4.9 Hz, 1.1 Hz, 4-H). ^{19}F NMR: δ –74.93 (m, CF_3), –80.91 (m, $COCF_2O$), –83.12 (m, OCF_2CF_2O), –87.67 (m, OCF_2CF_2O), –88.11 (m, $OCF_2C_3F_7$), –126.18 (m, $CF_2CF_2CF_2CF_3$).

Example 9

5-Perfluoro(3,6,9-trioxadecanoyl)-2,2′:5′,2′′-terthiophene



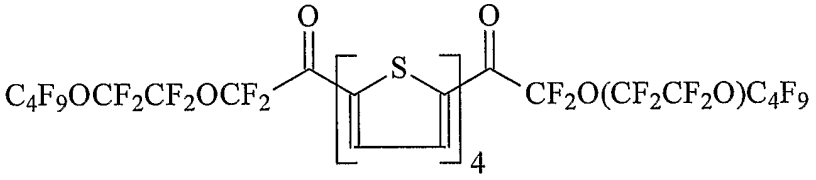
Under nitrogen, a vessel was loaded with 2,2′:5′,2′′-terthiophene (878 mg, 3.53 mmol) and anhydrous THF (75 mL). The solution was cooled at –78 °C and ^nBuLi (2.2 mL, 3.5 mmol) was added gradually by syringe. The mixture was stirred cold for 30 min, and then methyl 3,6,9-trioxadecanoate (1.0 mL, 3.8 mmol, 1.1 eq) and BF_3OEt_2 (0.54 mL, 4.3 mmol, 1.2 eq) were successively added. After another 90 min at –78 °C, sat NH_4Cl (aq) (20 mL) was added and the mixture was warmed to ambient temperature and further diluted with ether (100 mL) and water (50 mL). The aq phase was separated, and the yellow-green organic phase was washed with 2 × 100 mL of brine, dried with $MgSO_4$, and filtered.

Analysis by TLC (SiO_2 on glass) with 5% EtOAc/balance hexanes showed the main reaction product with R_f = 0.45. The organic solution was concentrated, adsorbed onto silica gel, and purified by column chromatography (silica gel/hexanes, 1.25 in × 10 in) using hexanes eluent to afford 1.03 g (45%) of bright orange product. ^1H NMR: δ

7.15 (dd, J = 5.2 Hz, 3.6 Hz), 7.37 (d, J = 4.0 Hz), 7.44 (dd, J = 3.6 Hz, 1.2 Hz), 7.55 (dd, J = 5.2 Hz, 1.2 Hz), 7.59 (d, J = 4.0 Hz), 7.65 (d, J = 4.0 Hz), 8.02 (dt, $^3J_{HH}$ = 4.0 Hz, $^5J_{HF}$ = 1.6 Hz). ^{19}F NMR: δ –54.9 (t, J = 9.4 Hz, CF_3), –74.3 (m, $COCF_2$), –87.4 (m, CF_2), –88.1 (br, 2 CF_2- groups), –90.1 (q, J = 9.4 Hz, CF_2OCF_3).

Example 10

Synthesis of 5,5′′′-bis[perfluoro(3,6-dioxadecanoyl)]-2,2′:5′,2′′:5′′,2′′′-quaterthiophene.

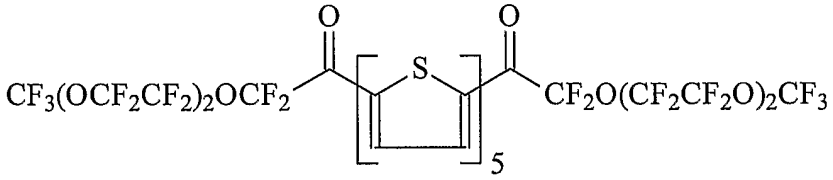


Under a nitrogen atmosphere, a vessel was successively charged with 2-bromo-5-perfluoro(3,6-dioxadecanoyl)thiophene (3.24 g, 5.48 mmol), dry DMF (30 mL), 5,5′-bis(tri-*n*-butylstannyl)-2,2′-bithiophene (2.04 g, 2.74 mmol), and $Pd(PPh_3)_4$ (63 mg, 0.055 mmol). The mixture was bubbled through with nitrogen for 20 min, and then stirred at 85 °C overnight. The reaction mixture was transferred into a mixture of EtOAc (100 mL) and CH_2Cl_2 (100 mL), stirred, and then poured through a 10- 20 μm glass filter frit to isolate the product. The red solid was washed on the frit with methanol (100 mL) and air-dried overnight to afford 2.28 g (70%).

Material used in OTFTs was sublimed at least 2 times. In a typical experiment, 1.01 g was loaded into a train sublimation system. With P = 3 x 10^{-6} Torr, the source zone was ramped to 240 °C, with the product zone at 180 °C. The product was melted in the source at this point, but not mobile. The source and product zones were ramped to 280 °C and 220 °C, respectively, and the sublimation was done in 30 min. Only a negligible film remained at the source. From the product zone was isolated 884 mg (87% of input). TGA: 1% wt loss at 271 °C; 5% wt loss at 285 °C; no residue at 988°C. DSC (20 °C/min): 185 °C (–71 J/g), reversible melting point. MALDI-TOF mass spectrometry showed a molecular ion isotopic cluster that contained an abundant peak at m/z1186 1200 (M^+), and peaks at M+1 (76%), M+2 (55%), M+3 (22%), and M+4 (8%).

Example 11

Synthesis of 5,5′′′′-bis[perfluoro(3,6,9-trioxadecanoyl)]- 2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethiophene.

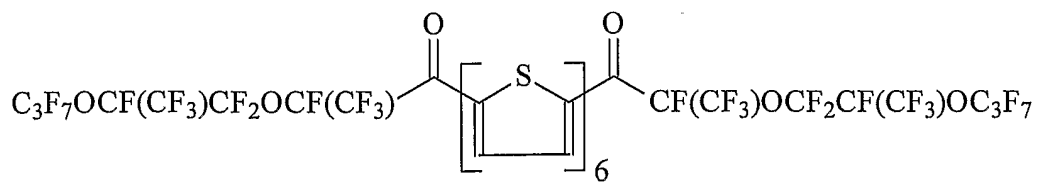


Under nitrogen, a vessel was charged with $Pd(PPh_3)_4$ (65 mg, 0.056 mmol, 0.5 mol% per coupling site), 5-Bromo-5′-perfluoro(3,6,9-trioxadecanoyl)-2,2′-bithiophene (3.54 g, 5.54 mmol), DMF (40 mL), and 5,5′-bis(tri-*n*-butylstannyl)thiophene (1.83 g, 2.76 mmol). The mixture was bubbled through with nitrogen for 20 min, and then stirred at 90 °C for 20 h. The red mixture was cooled to room temperature and the solid was collected on a 10-20 μm filter frit, washed with 2 × 60 mL isopropanol, and air-dried overnight to afford 2.34 g (71%) of crude, burgundy product.

The material was train sublimed at $P = 4 \times 10^{-6}$ Torr with a source temperature of 315 °C (material is melted) and the product collection zone at 180 °C to afford 2.23 g (67%) of red-purple product. The product was sublimed an additional time before device preparation. ^1H NMR (600 MHz, d_4-*o*-dichlorobenzene, 100 °C): Due to the high temperature used during the data collection (the material has very low solubility), broad, singlets were observed for each of the 5 chemically inequivalent protons; δ 7.79, 7.16, 7.10, 7.06, 7.04. ^{19}F NMR (564 MHz, d_4-*o*-dichlorobenzene, 100 °C): Data was identical to that reported in preparative examples 1 and 4. MALDI-TOF mass spectrometry showed a molecular ion isotopic cluster that contained an abundant peak at m/z 1200 (M^+), and peaks at M+1 (65%), M+2 (45%), M+3 (20%), and M+4 (10%).

Example 12

Synthesis of 5,5′′′′′-bis[perfluoro(2,5-dimethyl-3,6-dioxanonanoyl)]-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′-sexithiophene.



Under a nitrogen atmosphere, a vessel was successively charged with 5-bromo-5′-perfluoro(2,5- dimethyl-3,6-dioxanonanoyl)-2,2′-bithiophene (3.49 g, 4.83 mmol), dry DMF (75 mL), 5,5′-bis(tri-*n*-butylstannyl)-2,2′-bithiophene (1.80 g, 2.42 mmol), and $Pd(PPh_3)_4$ (30 mg, 0.026 mmol). The mixture was bubbled through with nitrogen for 30 min, and then stirred at 100 °C for 5 h. A red ppt formed in the mixture. The solution was cooled to room temperature, and then further with an ice water bath. The solution was poured through a 10-20 μm glass filter frit, and the red solid was washed with methanol (100 mL), hexanes (100 mL), and then air-dried overnight. Yield: 2.79 g, 80%. Material used in OTFTs was sublimed at least 2 times.

In one experiment, 994 mg of material was loaded into a train sublimation system and sublimed with $P = 2 \times 10^{-6}$ Torr, source temperature 320 °C, and product zone at 240 °C. The material melted at the source before volatilizing and moving to the product zone. Isolated 918 mg (92% of input).

IR spectroscopy (KBr pellet, $\nu_{CO} = 1663$ cm–1), combustion analysis, and high resolution mass spectroscopy were consistent with the proposed structure. ^{1}H NMR (400 MHz, *d*6-acetone, internal TMS ref to 0 pm): δ 8.18 (m, 1 H), 7.71 (d, $J = 4$ Hz, 1 H), 7.62 (d, $J = 4$ Hz, 1 H), 7.44 ('d', $J = 4$ Hz, 2 H), 7.38 (d, J = 4 Hz, 1 H). TGA: 1% wt loss at 365°C; 5% wt loss at 381 °C; no residue at 988 °C. DSC (20 °C/min): 150 °C (–17 J/g), 218°C (–2 J/g), reversible melting point. ^{19}F NMR data was virtually identical to that in preparative examples 3 and 6. A number of the resonances in the ^{19}F data are observed as pairs due to the two asymmetric centers of the fluorinated end group. IR (KBr): 1663 s (ν_{CO}), 1436 s, 1236 vs, 1202 s, 1151 s, 1079 m, 1029 m, 994 s, 981 m, 790 m cm^{-1}.

High performance liquid chromatography (HPLC) with a THF solution of the product was carried out using an Agilent Model LC/MSD quadrupole mass spectrometer equipped with an atmospheric pressure chemical ionization (APCI) source. The sample solution was injected into a mobile phase of THF/water (1:1) and data were collected over the mass range of 1,000–2,000 Daltons at a scan rate of approximately 2 scans/second. The only significant ions in the spectrum were seen a m/z 1451, m/z 1452, and m/z 1453, corresponding to a compound having a molecular eight of 1,450, consistent with the proposed product.

Example 13

Fabrication and Testing of OTFTs.

OTFTs were fabricated on doped silicon <100> wafers obtained from Silicon Valley Microelectronics (San Jose, CA) with 5 kÅ aluminum on the backside and 1.5 kÅ of sputtered Al_2O_3 on the front. A 0.1 wt % solution of poly(α-methylstyrene) (average M_w ca 100,300 by GPC) was applied to the surface from toluene by spin coating (500 rpm for 20 s, followed by 2000 rpm for 40 s). Samples were placed in a 110 °C oven and baked for 30 min after spin coating. The resultant polymer layer was about 100 Å, as measured by single beam ellipsometry. Thin films (~ 600 Å) of the perfluoroacyl thiophenes described above were deposited by physical vapor deposition at a pressure ≤ 5×10^{-6} Torr. Samples were then moved to another vacuum chamber where gold source-drain contacts (600 Å) were evaporated on to the organic film through a polymeric shadow mask.

Figure 2 shows characterization data ($I_D^{1/2}$ vs V_G curves calculated from I_D-V_G transfer curves) for thin film transistors made using 5,5‴-bis[perfluoro(3,6-dioxadecanoyl)]-2,2′:5′,2″:5″,2‴-quaterthiophene (Example 10) in the semiconductor layer. The data is in the saturated regime, with drain voltages (V_D) equal to the maximum gate voltage (V_G) in each case. The devices were measured under 10^{-6} torr vacuum. Data is plotted for both negative-to-positive (–/+) and positive-to-negative (+/–) scans of the gate voltage. The saturation electron mobility (μ_e) was calculated from the slope of the $I_D^{1/2}$ vs V_G trace at the points indicated using standard metal-oxide-semiconductor field-effect transistor (MOSFET) equations (See Sze, S. M. *Physics of Semiconductor Devices*; 2nd ed.; John Wiley & Sons: New York, 1981). For the device shown in Figure 2, the mobility was 1.8 cm^2/Vs for a negative-to-positive V_G scan, and 2.6 cm^2/Vs for a positive-to-negative scan. Additional data for other devices on the same wafer are tabulated in Table 1.

Figure 3 shows $I_D^{1/2}$ vs V_G curves for a thin film transistor made using 5,5⁗-bis[perfluoro(3,6,9-trioxadecanoyl)]- 2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (Example 11) in the semiconductor layer. Devices were fabricated and tested as described above. Table 2 lists additional data for other devices on the same wafer.

With regard to the thin film transistors using the n-channel semiconductor oligothiophene of the invention, the resulting mobility values are the highest values

reported to date for n-channel organic semiconductor materials, and are comparable in performance to p-channel semiconductors such as pentacene.

Table 1.

Additional data for devices made with 5,5‴-bis[perfluoro(3,6-dioxadecanoyl)]-2,2′:5′,2″:5″,2‴-quaterthiophene (Example 10)

Test # and scan direction	n-channel mobility (cm^2/Vs)
1 -/+	1.3
+/-	not measured
2 -/+	not measured
+/-	1.7
3 -/+	not measured
+/-	1.6
4 -/+	1.6
+/-	not measured
5 -/+	1.7
+/-	not measured
6 -/+	1.7
+/-	not measured
7 -/+	1.7
+/-	1.8
8 -/+	1.6
+/-	not measured

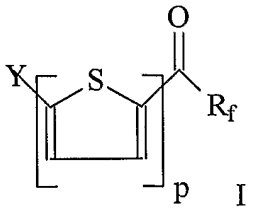
Table 2

Additional data for devices made using 5,5⁗-bis[perfluoro(3,6,9-trioxadecanoyl)]-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (Example 11)

Test # and scan direction	n-channel mobility (cm^2/Vs)
1 -/+	0.47
+/-	0.89
2 -/+	0.34
+/-	1.1
3 -/+	0.40
+/-	1.7
4 -/+	0.40
+/-	1.1
5 -/+	0.46
+/-	1.1

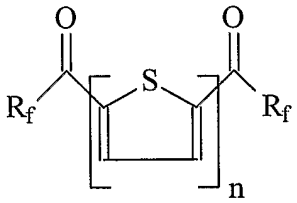
WE CLAIM:

1. A compound of the formula:



wherein Y is a hydrogen atom, a halogen atom, an alkyl group, and aryl group or a perfluoroether acyl group, p is at least one, and R_f is a perfluoroether group.

2. The compounds of claim 1 of the formula:



wherein each R_f is independently a perfluoroether group, and n is at least 1.

3. The compounds of claim 2 wherein each R_f is a perfluoroalkoxyalkylene group or a perfluoropolyether group.

4. The compounds of claim 2 wherein each R_f corresponds to the formula:

R_f^1-O-$(R_f^2)_x$-(R_f^3)-

wherein R^1_f represents a perfluoroalkyl group, R_f^2 represents a perfluorinated polyalkyleneoxy group consisting of perfluoroalkyleneoxy groups having 1 to 4 perfluorinated carbon atoms or a mixture of such perfluoroalkyleneoxy groups, R_f^3 represents a perfluoroalkylene group, x is 0 to 25.

5. The compounds of claim 4 wherein each R_f^2 is independently selected from -CF_2-CF_2-O-, -$CF(CF_3)$-CF_2-O-, -CF_2-$CF(CF_3)$-O-, -CF_2-CF_2-CF_2-O-, -CF_2-O-, -$CF(CF_3)$-O-, and -CF_2-CF_2-CF_2-CF_2-O-.

6. The compounds of claim 4 wherein each R_f^3 is independently selected from $-CF_2-CF_2-$, $-CF(CF_3)-CF_2-$, $-CF_2-CF(CF_3)-$, $-CF_2-CF_2-CF_2-$, $-CF_2-O-$, $-CF(CF_3)-$, and $-CF_2-CF_2-CF_2-CF_2-$.

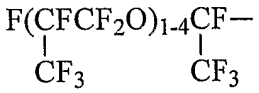
7. The compounds of claim 4 wherein x is 1 to 4.

8. The compounds of claim 2 wherein each R_f is $R_f^1-O-[CF(CF_3)-CF_2O]_x-CF(CF_3)-$ wherein R_f^1 is a perfluoroalkyl group and x is at least one.

9. The compounds of claim 4 wherein R_f^1 represents a perfluorinated alkyl group having 1 to 6 carbon atoms.

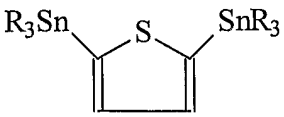
10. The compounds of claim 2 wherein n is 3 to 6.

11. The compounds of claim 2 wherein R_f is

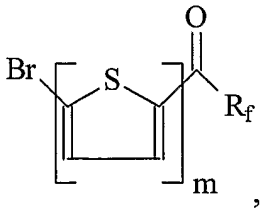


12. A method of preparing a compound of claim 2 comprising
    a. reacting a bis-trialkylstannyl (oligo)thiophene with a
    b. 2-halo-5-perfluoroetheracyl thiophene or a 5-halo-5'-perfluoroetheracyl oligothiophene
    c. in the presence of a palladium catalyst.

13. The method of claim 12 comprising the steps of
reacting a bis-trialkylstannyl thiophene of the formula



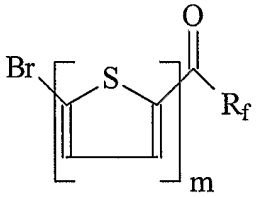
wherein each R is selected from a lower alkyl group,
with a 2-halo-5-perfluoroetheracylthiophene of the formula:



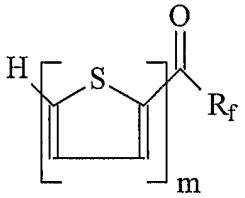
where m is 1 to 3, and R_f is a perfluoroether group,

c) in the presence of a palladium catalyst.

14. The method of claim 13 wherein the compound of the formula

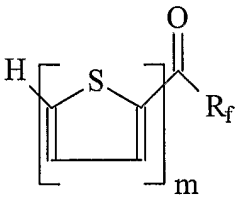


is prepared by brominating a compound of the formula:

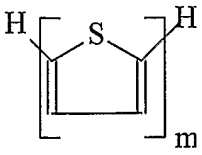


each m is 2 to 3, and R_f is a perfluoroether group.

15. The method of claim 14 where the compound of the formula



is prepared by treating of the oligothiophene compound of the formula:

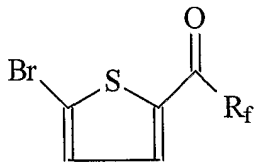


with an alkyl lithium compound, followed by quenching the thienyl anion with a perfluorinated ether ester of the formula

R_f-CO-OR, where R_f is a perfluorinated ether group and R is an alkyl group, in the presence of a Lewis acid catalyst, where m is 1 to 3.

16. The method of claim 15, where the Lewis acid catalyst is a boron trifluoride etherate.

17. The method of claim 14 where the compound of the formula



is prepared by treating of the 2,5-dihalothiophene with an alkyl lithium compound, followed by quenching the thienyl anion with a perfluorinated ether ester of the formula R_f-CO-OR, where R_f is a perfluorinated ether group and R is an alkyl group, in the presence of a Lewis acid catalyst, where m is 1 to 3.

18. A n-channel semiconductor device wherein the semiconductor layer comprises a compound of the formula comprising any of claims 1-11.

19. The semiconductor device of claim 18, further comprising a conducting layer, a dielectric layer, or a combination thereof adjacent to the semiconductor layer.

20. The semiconductor device of claim 18, wherein said semiconductor device comprises an organic thin film transistor.

21. The semiconductor device of claim 18, further comprising a source electrode and a drain electrode in contact with the semiconductor layer, wherein the source electrode and the drain electrode are separated by an area on the surface of the semiconductor layer.

22. The semiconductor device of claim 18, further comprising a conducting layer adjacent to one surface of the semiconducting layer and a dielectric layer adjacent to an opposite surface of the semiconducting layer.

23. A method of preparing an organic thin film transistor, said method comprising:
providing a gate electrode;
depositing a gate dielectric layer on a surface of the gate electrode;
preparing a semiconductor layer adjacent to the gate dielectric layer opposite the gate electrode, said semiconductor layer comprising a compound of the formula of any of claims 1-11.

24. The method of claim 23 further comprising the step of positioning a source electrode and a drain electrode on a surface of the semiconductor layer that is opposite the gate dielectric layer, wherein the source electrode and the drain electrode are separated from each other in an area on the surface of the semiconductor layer.

25. The method of claim 23, further comprising depositing a surface treatment layer between the gate dielectric layer and the semiconductor layer.

26. A method of preparing an organic thin film transistor, said method comprising:
providing a gate electrode;
depositing a gate dielectric layer on a surface of the gate electrode;
positioning a source electrode and a drain electrode adjacent to the gate dielectric layer opposite the gate electrode, wherein the source electrode and the drain electrode are separated by an area over the gate dielectric layer;
preparing a semiconductor layer on a surface of the source electrode, on the surface of the drain electrode, and in the area between the source electrode and the drain electrode, said semiconductor layer comprising a compound of any of claims 1-11.

27. A Schottky diode comprising the device of claim 18, wherein a first metal is in contact with a first surface of said semiconductor, and a second metal in contact with a second surface of said semiconductor layer.

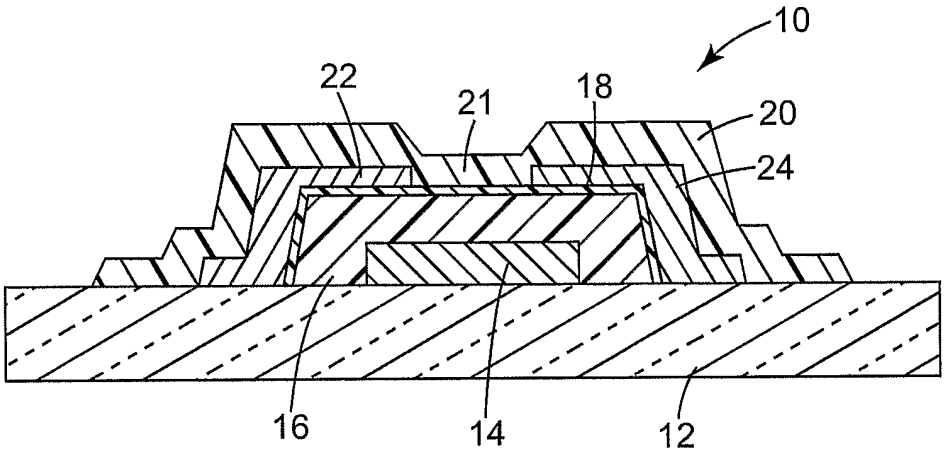


FIG. 1A

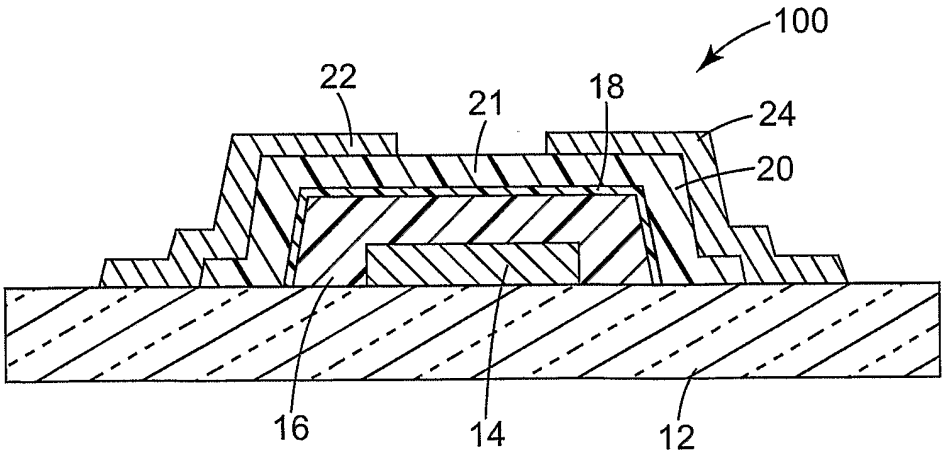


FIG. 1B

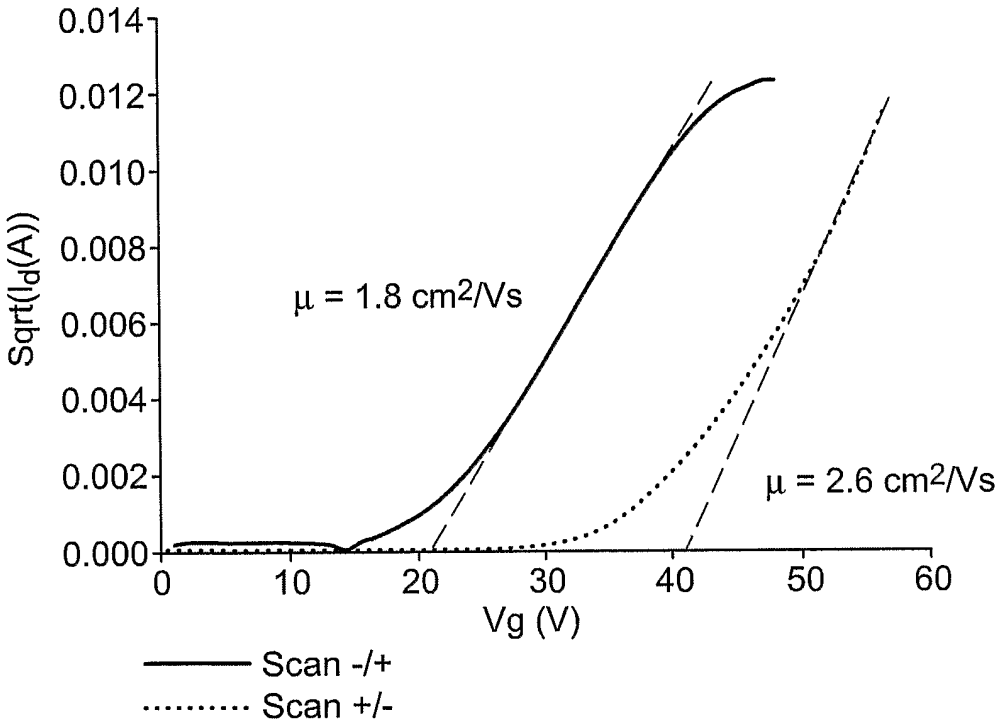

0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
Sqrt(Id(A))
μ = 1.8 cm2/Vs
μ = 2.6 cm2/Vs
0
10
20
30
40
50
60
Vg (V)
Scan -/+
Scan +/-

FIG. 2

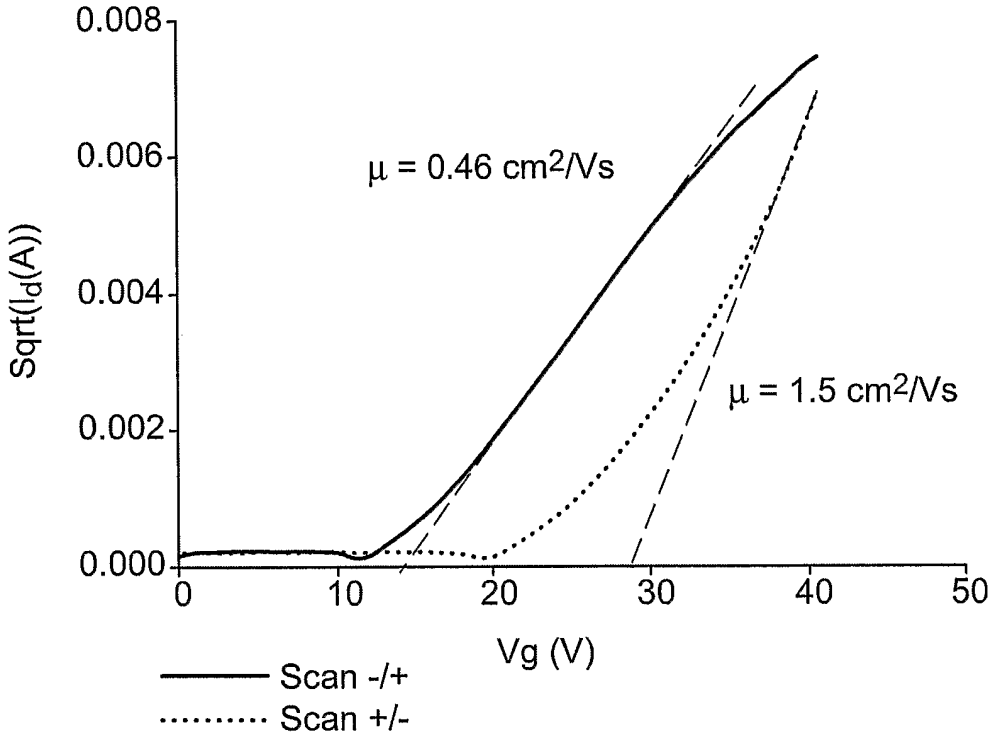

0.008
0.006
0.004
0.002
0.000
Sqrt(Id(A))
μ = 0.46 cm2/Vs
μ = 1.5 cm2/Vs
0
10
20
30
40
50
Vg (V)
Scan -/+
Scan +/-

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/006545

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G61/12 C07D333/22 C07D333/28 H01L51/00

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)
C08G C07D H01L

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 practical, search terms used)
EPO-Internal, BEILSTEIN Data, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MYUNG-HAN YOON, SARA A. DIBENEDETTO, ANTONIO FACCHETTI, TOBIN J. MARKS: "Organic Thin-Film Transistors Based on Carbonyl-Functionalized Qaterthiophenes: High Mobility N-Channel Semiconductors and Ambipolar Transport" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 127, 15 January 2005 (2005-01-15), pages 1348-1349, XP002385661 the whole document	1-27
A	US 5 306 758 A (PELLERITE ET AL) 26 April 1994 (1994-04-26) cited in the application claims 6-9	1-27

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

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

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

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 June 2006	29/06/2006

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Meier, S

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/006545

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 393 263 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 24 October 1990 (1990-10-24) cited in the application claims 1-7	1-27

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2006/006545

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