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(54) Title: PRODUCTION METHOD OF ORGANIC PHOTOVOLTAIC ELEMENT

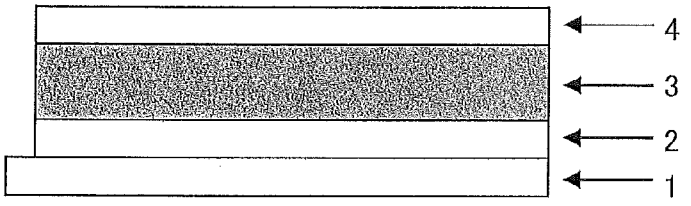
[Fig. 1]

1 Substrate

2 Anode

3 Organic photo-active layer

4 Cathode



(57) Abstract: A method for producing an organic photovoltaic element with an organic photo-active layer comprising a conjugated block copolymer comprising a polymer A block containing a thiophene group and a polymer B block containing a thiophene group, or a polymer composition comprising a conjugated polymer A containing a thiophene group and a conjugated polymer B containing a thiophene group, wherein the difference between the melting points of the polymers being 10 degrees Centigrade or more, and a fullerene derivative, and wherein the method includes a process of exposing an organic photo-active layer to a vapor of solvent having a surface tension between a surface tension of the conjugated polymer (A or B) containing a thiophene group and a surface tension of the fullerene derivative.

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DESCRIPTION

PRODUCTION METHOD OF ORGANIC PHOTOVOLTAIC ELEMENT

TECHNICAL FIELD

The present invention relates to a production method of an organic photovoltaic element.

BACKGROUND ART

A solar cell attracts attention as an environmentally-friendly and important energy source. Currently, as a semiconductor material for an organic photovoltaic element in a solar cell, inorganic matters such as monocrystal silicon, polycrystal silicon, amorphous silicon, and a compound semiconductor are used. The main factor of high cost lies in the process of producing a semiconductor thin film at a high temperature in vacuum. Consequently, an organic solar cell using a conjugated polymer, an organic semiconductor such as organic crystal, or organic dye as a semiconductor material the production process of which is expected to be simplified has been studied. The organic solar cell draws attention as a solar cell of a low cost because it can be mass-produced by roll to roll coating.

An organic solar cell is structured in the manner of interposing an organic photo-active layer between two dissimilar electrodes. An organic photo-active layer generally comprises a mixture of a conjugated polymer and

a fullerene derivative. As a representative example, a composition containing poly(3-hexylthiophene) as a conjugated polymer and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as a fullerene derivative is named (Mayer, A.C.; Scully, S.R.; Hardin, B.E.; Rowell, M.W.; McGehee, M.D. Mater. Today 2007, 10, 28-33: and Gunes, S.; Neugebauer, H.; Sariciftci, N.S. Chem. Rev. 2007, 107, 1324-1338).

A challenge of an organic solar cell is to improve power conversion efficiency and in particular it is reported that the improvement of power conversion efficiency is achieved by changing the morphology of an organic photo-active layer. For example, a method of processing by heat or solvent vapor, a method of devising a solvent for dissolving a conjugated polymer and a fullerene derivative, a method of adding a high boiling point compound, and a method of decreasing the vaporizing rate of a solvent of a solution for a photo-active layer are named (WO 2004/025746: JP 2009-260324 A: Nature Materials 4, 864-868 2005: Journal of Applied Polymer Science, Vol. 111, 1799-1804 (2009): and J. Phys. Chem. C 2009, 113, 17579-17584).

Further, as another approach for improving a power conversion efficiency, it is reported that the improvement of a power conversion efficiency is attempted by controlling morphology with a conjugated block copolymer (WO 2009/056496: JP 2007-211237 A and JP 2008-223015 A: JP

No. 4126019: Macromolecules, 2009, 42(18), pp 7008-7015: Macromolecules, 2010, 43, 3306-3313: Organic Electronics 10 (2009) 1541-1548: Soft Matter, 2009, 5, 4219-4230: and Adv. Mater. 2010, 22, 763-768).

In the case of using a conjugated block copolymer, however, since it is generally difficult to control not only the morphology of a fullerene derivative and a conjugated copolymer but also the morphology of the conjugated block copolymer itself. Therefore there is no obvious guideline and only the measure has been to apply ordinary thermal annealing. By the thermal annealing, nanometer-size morphology that is intrinsically formed by a block copolymer is not expected to be formed and hence the power conversion efficiency has not necessarily been high.

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

An object of the present invention is to provide a method for producing an organic photovoltaic element that has a high power conversion efficiency, can be processed for a short period of time, and is economical by controlling the morphology of an organic photo-active layer including a conjugated block copolymer or conjugated polymer blends, and a fullerene derivative. Another object of the present invention is to provide an organic photovoltaic element comprising an organic photo-active

layer that is processed as stated above and has a high power conversion efficiency.

EFFECTS OF THE INVENTION

The present invention makes it possible to provide an organic photovoltaic element comprising an organic photo-active layer having a high power conversion efficiency through an economically advantageous and short production process.

MODE FOR CARRYING OUT THE INVENTION

An organic photovoltaic element according to the present invention has at least an anode and a cathode and includes an organic photo-active layer between the electrodes. Fig. 1 is a schematic view showing an example of an organic photovoltaic element according to the present invention. In Fig. 1, the symbol 1 represents a substrate, the symbol 2 represents an anode, the symbol 3 represents an organic photo-active layer, and the symbol 4 represents a cathode. The symbol 2 may represent a cathode and the symbol 4 may represent an anode in some types of electrodes.

An organic photo-active layer includes at least a conjugated polymer A containing a thiophene group, a conjugated polymer B containing a thiophene group, and a fullerene derivative.

[I] Conjugated polymer A containing a thiophene group and

conjugated polymer B containing a thiophene group

A conjugated polymer containing a thiophene group used in the present invention is a conjugated polymer comprising an unsubstituted or substituted thiophene group. The substitution group: includes an alkyl group having a carbon number of 1 to 18, an alkoxy group having a carbon number of 1 to 18, an aryl group, halogen, a hydroxyl group, a thiol group, a carbonyl group, an amino group, an ether bond, and the like; and also may be a combination of them.

It is also possible to copolymerize another monomer unit to the extent not lowering the performance of an organic photovoltaic element. As another monomer unit, any monomer unit is acceptable as long as the monomer unit forms, when it copolymerizes with a thiophene group, (1) a polymer substantially structured so that a double bond and a single bond may be aligned alternately, (2) a polymer substantially structured so that a double bond and a single bond may be aligned in the manner of interposing a nitrogen atom, or (3) a polymer substantially structured so that a double bond and a single bond may be aligned alternately and a double bond and a single bond may be aligned in the manner of interposing a nitrogen atom. More specifically, another monomer unit is selected from the group consisting of an unsubstituted or substituted fluorenediyl group, an unsubstituted or substituted benzofluorenediyl group, an unsubstituted or substituted

dibenzofurandiyl group, an unsubstituted or substituted dibenzothiophenediyl group, an unsubstituted or substituted carbazolediyl group, an unsubstituted or substituted thiophenediyl group, an unsubstituted or substituted furandiyl group, an unsubstituted or substituted pyrrolediyl group, an unsubstituted or substituted benzothiadiazolediyl group, an unsubstituted or substituted phenylenevinylenediyl group, an unsubstituted or substituted thiophenevinylenediyl group, and an unsubstituted or substituted triphenylaminediyl group. The content of monomers other than the polymerizing thiophene group is not particularly limited unless the performance of an organic photovoltaic element is deteriorated but generally the content is preferably in the range of 1 to 30 mass % and yet preferably in the range of 1 to 10 mass %.

A conjugated polymer A containing a thiophene group and a conjugated polymer B containing a thiophene group must have structures different from each other from the viewpoints of inducing phase separation and controlling morphology. It is known that generally a mixture of two kinds of polymers or a block copolymer causes phase separation because of difference in structure. The term "difference in structure" cited here includes not only difference in structure of main chains but also difference in structure of side chains and existence or non-existence of a functional group.

It is preferable that a conjugated polymer A containing a thiophene group and a conjugated polymer B containing a thiophene group are semicrystalline polymers from the viewpoint of hole mobility. When a conjugated polymer A containing a thiophene group and a conjugated polymer B containing a thiophene group are semicrystalline polymers, the semicrystalline polymers have melting points but it is preferable that the melting point of the conjugated polymer A containing a thiophene group and the melting point of the conjugated polymer B containing a thiophene group are different from each other by 10°C or more from the viewpoint of inducing phase separation. By differentiating the melting points by 10°C or more, it is possible to: only crystallize either the conjugated polymer A containing a thiophene group or the conjugated polymer B containing a thiophene group; thereby cause phase separation; and thereafter crystallize the other conjugated polymer. The melting points of a conjugated polymer A containing a thiophene group and a conjugated polymer B containing a thiophene group are not particularly limited but preferable melting points are room temperature or higher from the viewpoint of the structural stability of an obtained organic thin film.

Concrete examples of a conjugated polymer A containing a thiophene group and a conjugated polymer B containing a thiophene group are: a conjugated polymer containing unsubstituted thiophene as the main chain; a

conjugated polymer containing 3-alkylthiophene having a carbon number of 4 to 18 as the main chain; a conjugated polymer containing 3-alkoxythiophene having a carbon number of 4 to 18 as the main chain; a conjugated polymer containing 3-haloalkylthiophene having a carbon number of 4 to 18 as the main chain; a conjugated polymer containing 3-haloalkoxythiophene having a carbon number of 4 to 18 as the main chain; a conjugated polymer containing 3-(6-hydroxyhexyl)thiophene as the main chain; a conjugated polymer containing 3-(6-bromohexyl)thiophene as the main chain; a conjugated polymer containing 3-hexylthiol thiophene as the main chain; a conjugated polymer containing 3-(2'-(2"-methoxyethoxy)ethoxy)thiophene as the main chain; a conjugated polymer containing 3-phenoxymethylthiophene as the main chain; a conjugated polymer containing 3-(hexylthio)thiophene as the main chain; and a conjugated random copolymer and a conjugated block copolymer of those conjugated polymers.

The number-average molecular weight of each of a conjugated polymer A containing a thiophene group and a conjugated polymer B containing a thiophene group is not particularly limited but is preferably in the range of 600 to 1,000,000 g/mol, yet preferably in the range of 5,000 to 500,000 g/mol, and still yet preferably in the range of 10,000 to 200,000 g/mol from the viewpoints of hole mobility and mechanical properties. Here, a number-average molecular weight means a molecular weight of

polystyrene equivalent by gel permeation chromatography.

Since the purpose of a conjugated polymer A containing a thiophene group and a conjugated polymer B containing a thiophene group is to induce phase separation in a mixed state and control morphology, it is possible to use: a polymer blend of a conjugated polymer A containing a thiophene group and a conjugated polymer B containing a thiophene group; and a conjugated block copolymer comprising a polymer A block containing a thiophene group and a polymer B block containing a thiophene group. It is preferable to use a conjugated block copolymer comprising a polymer A block containing a thiophene group and a polymer B block containing a thiophene group. Here, the block copolymer includes a diblock copolymer, a triblock copolymer, and a multiblock copolymer.

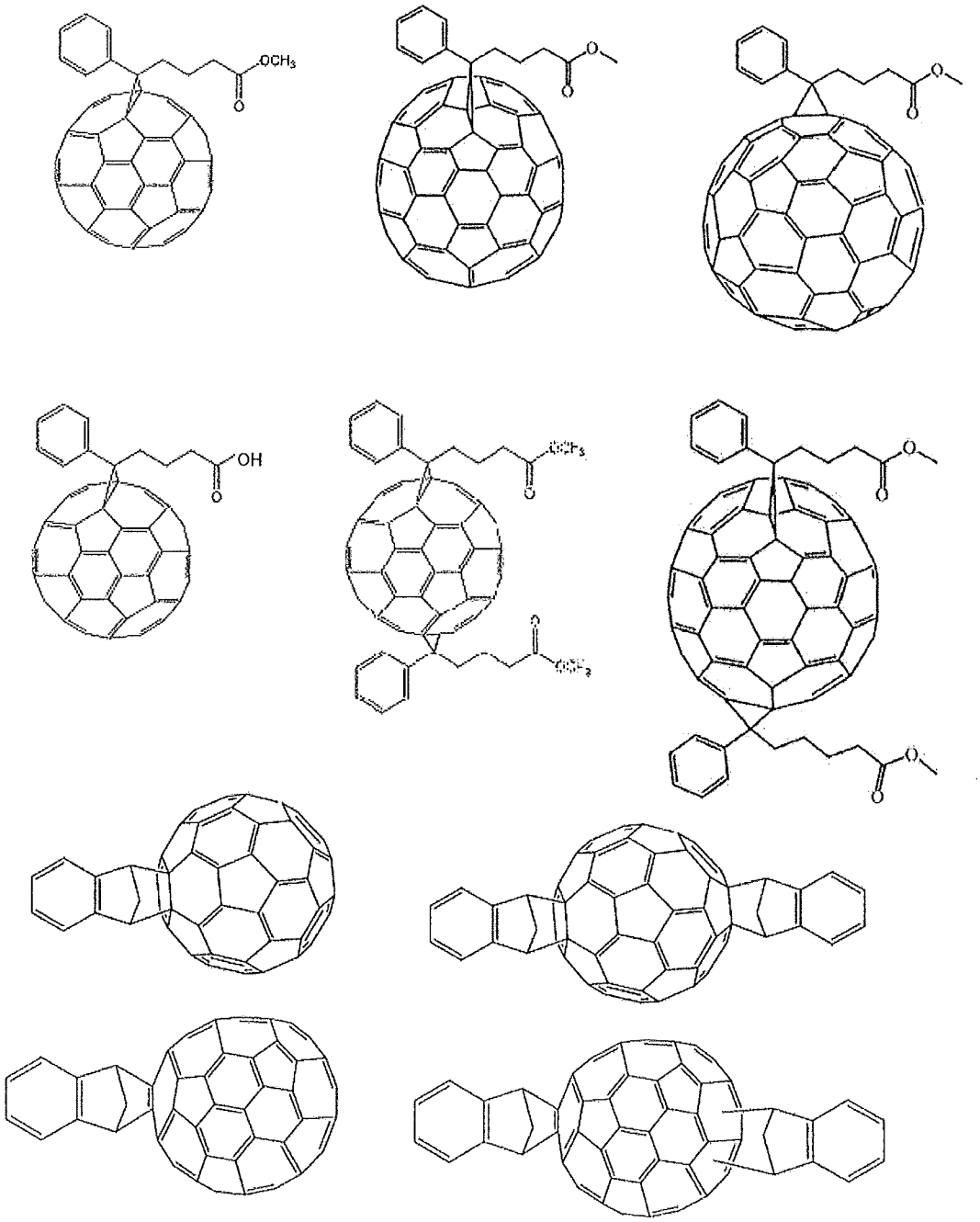
In the present invention, the total weight of a conjugated polymer A containing a thiophene group and a conjugated polymer B containing a thiophene group is preferably in the range of 5 to 90 mass % and yet preferably in the range of 10 to 70 mass % in an organic photo-active layer. If the total weight is excessively small or excessively large, there is a possibility that a high conversion efficiency is not obtained.

In the present invention, the mass ratio of a conjugated polymer A containing a thiophene group and a conjugated polymer B containing a thiophene group contained in an organic photo-active layer is not

particularly limited but is preferably in the range of 95:5 to 5:95 and yet preferably in the range of 90:10 to 10:90. It is preferable that either a conjugated polymer A containing a thiophene group or a conjugated polymer B containing a thiophene group, whichever gives higher power conversion efficiency than the other, is contained more.

[II] Fullerene derivative

As a fullerene derivative, C60, C70, C84, and a derivative thereof are named. As the concrete structure of a fullerene derivative, the following structures are named.



The part of a fullerene derivative in an organic photo-active layer is preferably in the range of 10 to 1,000 parts by weight and yet preferably in the range of 50 to 500 parts by weight when a conjugated polymer A containing a thiophene group and a conjugated polymer B

containing a thiophene group are 100 parts by weight in total.

A method for mixing a conjugated polymer A containing a thiophene group, a conjugated polymer B containing a thiophene group, and a fullerene derivative is not particularly limited but a method of dissolving those in a solvent by means of one or a combination of two or more kinds of heating, stirring, and ultrasonic irradiation after they are added to the solvent at a desired proportion is named.

A solvent used when a conjugated polymer A containing a thiophene group, a conjugated polymer B containing a thiophene group, and a fullerene derivative are mixed is not particularly limited as long as most of them are dissolved in the solvent. Concrete examples are: ether such as tetrahydrofuran; halogen solvents such as dichloromethane and chloroform; aromatic solvents such as benzene, toluene, o-xylene, chlorobenzene, o-dichlorobenzene, and pyridine.

The film thickness of an organic photo-active layer is generally in the range of 1 nm to 1 μm, preferably in the range of 2 nm to 1,000 nm, yet preferably in the range of 5 nm to 500 nm, and still yet preferably in the range of 20 nm to 300 nm. If the photo-active layer thickness is too thin, light is absorbed insufficiently and, if it is too thick inversely, a carrier hardly reaches an electrode.

[III] Electrode

In an organic photovoltaic element according to the present invention, it is preferable that either an anode 2 or a cathode 4 has light permeability. The light permeability of an electrode is not particularly limited as long as the extent is that incident light reaches an organic photo-active layer 3 and electromotive force is developed. The thickness of an electrode may be any thickness as long as the thickness is in the range of securing light permeability and electrical conductivity but is preferably in the range of 20 nm to 300 nm although it varies in accordance with an electrode material. Here, with regard to the other electrode, light permeability is not always necessary as long as the electrode has electrical conductivity, and the thickness is not particularly limited.

With regard to an electrode material, it is preferable that a conductive material having a large work function is used for an electrode and a conductive material having a small work function is used for the other electrode. The electrode using a conductive material having a large work function is an anode. As a conductive material having a large work function, in addition to metal such as gold, platinum, chromium, and nickel, metal oxide of indium or tin having transparency or combined metal oxide such as indium tin oxide (ITO), indium zinc oxide (IZO), and fluorine-doped tin oxide

(FTO) is preferably used. Here, it is preferable that a conductive material used for an anode 2 is in ohmic contact with an organic photo-active layer 3. Further, in the case of using a hole transport layer that will be described later, it is preferable that a conductive material used for an anode 2 is in ohmic contact with a hole transport layer.

The electrode using a conductive material having a small work function is a cathode, and an alkali metal or an alkali earth metal, more specifically lithium, magnesium, calcium or Barium is used as the conductive material having a small work function. Further, tin, silver, or aluminum is also preferably used. Furthermore, an electrode comprising an alloy containing above metals or comprising a laminated body of above metals is also preferably used. In addition, it is also possible to increase the current by introducing metal fluoride such as lithium fluoride or cesium fluoride to an interface between a cathode 4 and an electron transport layer. Here, it is preferable that a conductive material used for a cathode 4 is in ohmic contact with an organic photo-active layer 3. Moreover, when an electron transport layer is used, it is preferable that a conductive material used for a cathode 4 is in ohmic contact with the electron transport layer.

[IV] Substrate

A substrate 1 may be any material as long as it can

form an electrode and does not change when an organic photo-active layer is formed. For example, a film or a plate produced from an inorganic material such as alkali-free glass or quartz glass, a film of metal such as aluminum, or an organic material such as polyester, polycarbonate, polyolefin, polyamide, polyimide, polyphenylene sulfide, poly-p-xylene, epoxy resin, or fluorine contained resin by an arbitrary method can be used. When an opaque substrate is used, an opposite electrode (namely, an electrode remoter from the substrate) has to be transparent or translucent. The film thickness of a substrate 1 is not particularly limited but generally in the range of 1 μm to 10 mm.

Further, it is preferable that the surface is cleaned and reformed by a physical means such as UV ozone treatment, corona discharge treatment, or plasma treatment in order to improve the wettability of the substrate and the adhesiveness at an interface between an organic layer and the substrate. Furthermore, a method of applying chemical modification with a silane coupling agent, a titanate type coupling agent, or a self-assembled monolayer to the surface of a solid substrate is effective likewise.

In the present invention, a hole transport layer may be formed between an anode 2 and an organic photo-active layer 3. As a material for forming a hole transport layer, an electroconductive polymer such as a polythiophene

derivative, a poly-p-phenylenevinylene derivative, or a polyfluorene derivative, or a low-molecular organic compound showing P-type semiconductor characteristics such as a phthalocyanine derivative (H2Pc, CuPc, ZnPc, or the like) or a porphyrin derivative is preferably used. In particular, polyethylenedioxythiophene (PEDOT) or a substance produced by adding polystylene sulfonate (PSS) to PEDOT is preferably used. The thickness of a hole transport layer is preferably in the range of 5 nm to 600 nm and yet preferably in the range of 20 nm to 300 nm.

[V] Method for forming film

As a method for forming an organic photo-active layer, a known method such as a spin coating method, a casting method, a micro gravure coating method, a gravure coating method, a slot-die coating method, a bar-coating method, a roll coating method, a dip coating method, a spray coating method, a screen printing method, a flexo printing method, an offset printing method, an ink jet printing method, a nozzle coating method, or a capillary coating method can be used.

[VI] Solvent treatment

A feature of the present invention is that, after an organic photo-active layer is formed, the thin film of the organic photo-active layer is exposed to a vapor of solvent having a surface tension between a surface tension of a conjugated polymer (A or B) containing a thiophene group and a surface tension of a fullerene derivative at

25°C. A surface tension of a conjugated polymer (A or B) containing a thiophene group is a surface tension of a conjugated polymer containing a thiophene group larger difference from a surface tension of a fullerene derivative than a surface tension of another polymer. A surface tension of a fullerene derivative is larger than a surface tension of a conjugated polymer (A or B) containing a thiophene group in most cases. In this case, a surface tension of a conjugated polymer (A or B) containing a thiophene group is the smaller surface tension of conjugated polymers (A and B) containing a thiophene group. By applying solvent treatment, it is possible to induce phase separation between a conjugated polymer containing a thiophene group and a fullerene derivative at a small scale of a nanometer level. By reducing a phase separation size, it is possible to increase the area of the interface between the conjugated polymer containing a thiophene group and the fullerene derivative and thereby dramatically heighten a power conversion efficiency. Further, by applying solvent treatment, respective phase separation domains of the conjugated polymer containing a thiophene group and the fullerene derivative are oriented perpendicularly to a substrate and hence there is a possibility that morphology close to a structure most suitable for the transportation of holes and electrons is formed.

Further, a solvent used for the solvent treatment

can be selected arbitrarily. As exemplified in JP 2009-260324 A, in the method of devising a solvent so as to dissolve a polymer and a fullerene derivative, it is impossible to use a solvent having a poor solubility of a polymer and a fullerene derivative and a most suitable morphology is not always formed. On the other hand, by using a method of solvent treatment according to the present invention, it is possible to use an arbitrary solvent most suitable for controlling the morphology of an organic photo-active layer and there is no restriction in the selection of a solvent for solvent treatment.

Further, in the method disclosed in JP 2009-260324 A, a solvent to control morphology not always has a good film-formability and there is a possibility that both the formation of an organic photo-active layer having a good film surface and the control of morphology are not obtained simultaneously. By the present method, film forming and morphology control can be attained independently and hence such problems as stated above do not occur.

A solvent used for solvent treatment in the present invention must be a solvent having a surface tension between a surface tension of a conjugated polymer A or B containing a thiophene group and a surface tension of a fullerene derivative. If a solvent having a surface tension other than an above surface tension is used, either a long solvent treatment time is required and the

solvent treatment is uneconomical or the effect of improving a power conversion efficiency is not obtained. Further, since a surface tension varies in accordance with temperature, it is necessary to take a surface tension at a temperature in the environment of solvent treatment into consideration.

Such a solvent is not particularly limited as long as it satisfies the above conditions and can be selected from the group consisting of, for example: aliphatic hydrocarbon solvents such as n-pentane, n-hexane, and cyclohexane; halogenated hydrocarbon solvents such as methylene chloride, 1,2-dichloroethane, and chloroform; aromatic hydrocarbon solvents such as benzene, toluene, and xylene; halogenated aromatic solvents such as chlorobenzene, ortho-dichlorobenzene, and bromobenzene; oxygenated solvents such as acetone, tetrahydrofuran, dioxane, ethyl acetate, anisole, and methyl benzoate; and nitrogen-containing solvents such as acetonitrile, triethylamine, and pyridine. Those solvents can be used singularly or in combination of two or more kinds. In the case of the combination of two or more kinds, it is possible to compute the surface tension of a composition from the surface tensions of the components. Further, when the surface tension of a solvent is unknown, it is possible to measure the surface tension by a known method such as a sessile drop method or a Wilhelmy method.

Usually, the surface tension of a conjugated polymer

containing a thiophene group is in the range of 20 to 27 mN/m^2 in most cases and the surface tension of a fullerene derivative is in the range of 34 to 37 mN/m^2 in most cases (Synthetic Metals 157 (2007) 726-732: Langmuir 2006, 22, 9287-9294: Macromolecules 2007, 40, 8291-8301: and Organic Electronics 11 (2010) 899-904), and hence it is preferable that a solvent having a surface tension in the range of 27 to 37 mN/m^2, which is intermediate between them, at 25°C is used in the present invention. As such solvents, methylene chloride (27.2 mN/m^2), 1,2-dichloroethane (31.9 mN/m^2), benzene (28.2 mN/m^2), toluene (27.9 mN/m^2), ortho-xylene (29.8 mN/m^2), chlorobenzene (33.0 mN/m^2), bromobenzene (35.2 mN/m^2), ortho-dichlorobenzene (35.6 mN/m^2), and anisole (35.1 mN/m^2) are named. The values of the surface tensions are described on the basis of the values described in J. Phys. Chem. Ref. Data, 1, 841, 1972 or "Lange's Handbook of Chemistry 15th edition", written and edited by John A. Dean, McGraw-Hill Professional, published in 1998.

The boiling point of a solvent used in the present invention is not particularly limited but, from the necessity of exposure in solvent vapor, if a boiling point is too high, vapor pressure lowers and effects are hardly obtained. In such a case, it is also possible to raise the temperature of an atmosphere at solvent treatment.

The temperature of an atmosphere at exposure in solvent vapor is not particularly limited but is

preferably not lower than room temperature and not higher than the boiling point of a solvent from the viewpoint of easiness in handling. Generally a temperature close to room temperature is adopted.

A method of solvent treatment applied in the present invention is not particularly limited as long as an organic thin film can be exposed in the vapor of a solvent. For example, a method of introducing an organic thin film into a container containing a solvent in the manner of not touching the solvent or a method of conveying solvent vapor generated by bubbling a solvent together with a gas such as air or nitrogen and exposing an organic thin film can be used.

In the present invention, it is preferable that the time of exposure in solvent vapor is short because it is economical. By using a solvent having a surface tension in the above range, it is possible to shorten the time of solvent treatment and realize an economical process. A treatment time is preferably in the range of 1 sec. to 30 min., yet preferably in the range of 5 sec. to 20 min., and still yet preferably in the range of 10 sec. to 10 min.

If the surface tensions of a conjugated polymer containing a thiophene group and a fullerene derivative are unknown, they can be computed by measuring contact angles. That is, a known measurement method can be used, such as: a method of obtaining critical surface tensions by using several kinds of liquids having different surface

tensions, measuring the contact angles with the films of a conjugated polymer containing a thiophene group and a fullerene derivative to be measured, and applying Zismann plotting; or an Owens-Wendt method of computing surface tensions by measuring the contact angles of two kinds of liquids wherein nonpolar dispersion force components γ^d and polar hydrogen-bonding components γ^h are known.

An organic photovoltaic element according to the present invention may further have an inorganic layer. As materials contained in an inorganic layer, named are for example: metallic oxide such as titanium oxide, tin oxide, zinc oxide, iron oxide, tungsten oxide, zirconium oxide, hafnium oxide, strontium oxide, indium oxide, cerium oxide, yttrium oxide, lanthanum oxide, vanadium oxide, niobium oxide, tantalum oxide, gallium oxide, nickel oxide, strontium titanate, barium titanate, potassium niobate, and sodium tantalite; metallic halide such as silver iodide, silver bromide, copper iodide, copper bromide, and lithium fluoride; metallic sulfide such as zinc sulfide, titanium sulfide, indium sulfide, bismuth sulfide, cadmium sulfide, zirconium sulfide, tantalum sulfide, molybdenum sulfide, silver sulfide, copper sulfide, tin sulfide, tungsten sulfide, and antimony sulfide; metallic selenide such as cadmium selenide, zirconium selenide, zinc selenide, titanium selenide, indium selenide, tungsten selenide, molybdenum selenide, bismuth selenide, and lead selenide; metallic telluride such as cadmium telluride,

tungsten telluride, molybdenum telluride, zinc telluride, and bismuth telluride; metallic phosphide such as zinc phosphide, gallium phosphide, indium phosphide, and cadmium phosphide; gallium arsenide; copper-indium-selenide; copper-indium-sulfide; silicon; and germanium. Further a mixture of two or more kinds of those substances is also acceptable. As the mixtures, a mixture of zinc oxide and tin oxide and a mixture of tin oxide and titanium oxide are named for example.

An organic photovoltaic element according to the present invention can be applied to various photoelectric conversion devices that make use of a photoelectric conversion function, an optical rectification function (photo diode), and other functions. For example, the organic photovoltaic element is useful for a photovoltaic cell, an electron device (an optical sensor, an optical switch, a phototransistor, or the like), an optical memory material (an optical memory or the like), and the like.

EXAMPLES

The present invention is hereunder explained further in detail in reference to examples but is not limited to these examples.

[Synthesis of conjugated block copolymer containing a thiophene group (P1)]

After a sufficiently-dried glass recovery flask A was argon-substituted sufficiently, 45 parts by mass of

THF and 0.054 parts by mass of $NiCl_2$(dppp) which was a polymerization catalyst were added. Meanwhile, 29 parts by mass of THF, 2.8 parts by mass of 2-bromo-3-hexyl-5-iodothiophene, and 3.5 parts by mass of 2.0 M solution of isopropylmagnesium bromide were added and stirred for 30 minutes at 0°C in another dried recovery flask B. Then the reacted solution was added into the recovery flask A and polymerized for 90 minutes at 35°C. Successively, a solution produced by adding 16 parts by mass of THF, 1.4 parts by mass of 2-bromo-3-(2-ethyl)hexyl-5-iodothiophene, and 1.7 parts by mass of 2.0 M solution of isopropylmagnesium bromide and reacting them for 30 minutes at 0°C in another dried recovery flask C was added into the recovery flask A and reacted for 7 hours. After the reaction, 4 parts by mass of 1.0 M THF solution of tert-butylmagnesium chloride was added and stirred for 1 hour, further 100 parts by mass of 5 M hydrochloric acid was added and stirred for 1 hour, and then polymerization was stopped. Thereafter, extraction with 900 parts by mass of chloroform, washing with 200 parts by mass of sodium bicarbonate water and 200 parts by mass of distilled water, concentration, drying, and solidification were applied. The obtained black and purple solid substance was dissolved in 56 parts by mass of chloroform, re-precipitated in 600 parts by mass of acetone, and dried sufficiently and thus a conjugated block copolymer (polymer name: poly[(3-hexylthiophene)-*block*-(3-(2-

ethylhexyl)thiophene)]) (P1) was obtained. The weight-average molecular weight of the obtained conjugated block copolymer containing a thiophene group (P1) was 21,600 g/mol and the number-average molecular weight thereof was 17,900 g/mol. The content of poly(3-hexylthiophene) block was 79 mol %.

Here, with regard to materials obtained in each of the processes stated above and materials produced through the following processes, physical properties of the polymers were measured as follows.

o Weight-average molecular weight and number-average molecular weight

Each of a number-average molecular weight and a weight-average molecular weight was obtained in terms of a polystyrene equivalent on the basis of measurement by gel permeation chromatography (GPC). Here, an HLC-8320GPC made by Tosoh Corporation was used as the GPC device and two tandemly-connected TSKgel SuperMultipore HZ-Ms made by Tosoh Corporation were used as a column.

[Synthesis of conjugated block copolymer containing a thiophene group (P2)]

After a sufficiently-dried glass recovery flask A was argon-substituted sufficiently, 45 parts by mass of THF and 0.054 parts by mass of $NiCl_2$(dppp) which was a polymerization catalyst were added. Meanwhile, 27 parts by mass of THF, 2.2 parts by mass of 2-bromo-3-hexyl-5-iodothiophene, and 3.2 parts by mass of 2.0 M solution of

isopropylmagnesium bromide were added and stirred for 30 minutes at 0°C in another dried recovery flask B. Then the reacted solution was added into the recovery flask A and polymerized for 90 minutes at 35°C. Successively, a solution produced by adding 18 parts by mass of THF, 1.6 parts by mass of 2-bromo-3-(2-ethyl)hexyl-5-iodothiophene, and 2.2 parts by mass of 2.0 M solution of isopropylmagnesium bromide and reacting them for 30 minutes at 0°C in another dried recovery flask C was added into the recovery flask A and reacted for 7 hours. After the reaction, 4 parts by mass of 1.0 M THF solution of tert-butylmagnesium chloride was added and stirred for 1 hour, further 100 parts by mass of 5 M hydrochloric acid was added and stirred for 1 hour, and then polymerization was stopped. Thereafter, extraction with 900 parts by mass of chloroform, washing with 200 parts by mass of sodium bicarbonate water and 200 parts by mass of distilled water, concentration, drying, and solidification were applied. The obtained black and purple solid substance was dissolved in 56 parts by mass of chloroform, re-precipitated in 600 parts by mass of acetone, and dried sufficiently, and thus a conjugated block copolymer containing a thiophene group (polymer name: poly[(3-hexylthiophene)-*block*-(3-(2-ethylhexyl)thiophene)]) (P2) was obtained. The weight-average molecular weight of the obtained conjugated block copolymer containing a thiophene group (P2) was 24,500 g/mol and the number-average

molecular weight thereof was 21,300 g/mol. The content of the poly(3-hexylthiophene) block was 68 mol %.

[Synthesis of conjugated polymer containing a thiophene group (P3)]

After a sufficiently-dried glass recovery flask was argon-substituted sufficiently, 33 parts by mass of THF and 0.04 parts by mass of $NiCl_2$(dppp) which was a polymerization catalyst were added therein. Meanwhile, 33 parts by mass of THF, 2.8 parts by mass of 2-bromo-3-hexyl-5-iodothiophene, and 4.0 parts by mass of 2.0 M THF solution of isopropylmagnesium bromide were added and stirred for 30 minutes at 0°C in another dried three-necked flask. Then the reacted solution was added into the former flask and polymerized for 90 minutes at 35°C. Successively, 3 parts by mass of 1.0 M THF solution of tert-butylmagnesium chloride was added and stirred for 3 hours, further 50 parts by mass of 5 M hydrochloric acid was added and stirred for 1 hour, and then polymerization was stopped. Thereafter, extraction with 680 parts by mass of chloroform, washing with 150 parts by mass of sodium bicarbonate water and 150 parts by mass of distilled water, concentration, drying, and solidification were applied. The obtained black and purple solid substance was dissolved in 42 parts by mass of chloroform, re-precipitated in 450 parts by mass of acetone, and dried sufficiently and thus a conjugated polymer containing a thiophene group (polymer name: poly(3-hexylthiophene) (P3)

was obtained. The weight-average molecular weight of the obtained conjugated polymer containing a thiophene group (P3) was 28,400 g/mol and the number-average molecular weight thereof was 24,100 g/mol.

[Synthesis of conjugated random copolymer containing a thiophene group (P4)]

After a sufficiently-dried glass recovery flask A was argon-substituted sufficiently, 22 parts by mass of THF and 0.03 parts by mass of $NiCl_2$(dppp) which was a polymerization catalyst were added. Meanwhile, 16 parts by mass of THF, 1.3 parts by mass of 2-bromo-3-hexyl-5-iodothiophene, and 1.3 parts by mass of 2.0 M solution of isopropylmagnesium bromide were added and stirred for 30 minutes at 0°C in another dried recovery flask B. Further, 7 parts by mass of THF, 0.6 parts by mass of 2,5-dibromo-3-(6-(2-tetrahydropyranyloxy)hexyl)thiophene, and 1.6 parts by mass of 1.0 M THF solution of tert-butylmagnesium bromide were added and stirred for 2 hours at 65°C in another dried recovery flask C. After the reaction, the solutions in the recovery flasks B and C were added into the recovery flask A and polymerization was applied for 2 hours. After the reaction, 2 parts by mass of 1.0 M THF solution of tert-butylmagnesium chloride was added and stirred for 1 hour, further 50 parts by mass of 5 M hydrochloric acid was added and stirred for 1 hour, and then polymerization was stopped. Thereafter, extraction with 450 parts by mass of chloroform, washing with 100

parts by mass of sodium bicarbonate water and 100 parts by mass of distilled water, concentration, drying, and solidification were applied. The obtained black and purple solid substance was dissolved in 28 parts by mass of chloroform, re-precipitated in 300 parts by mass of methanol, and dried sufficiently and thus a conjugated random copolymer containing a thiophene group (polymer name: poly[(3-hexylthiophene)-*co*-(3-(6-hydroxy)thiophene)]) (P4) was obtained. The weight-average molecular weight of the obtained conjugated random copolymer containing a thiophene group (P4) was 23,100 g/mol and the number-average molecular weight thereof was 20,200 g/mol. The content of the 3-(6-hydroxy)thiophene unit was 17 mol %.

[Synthesis of conjugated random copolymer containing a thiophene group (P5)]

After a sufficiently-dried glass recovery flask was argon-substituted sufficiently, 33 parts by mass of THF and 0.04 parts by mass of $NiCl_2$(dppp) which was a polymerization catalyst were added therein. Meanwhile, 33 parts by mass of THF, 2.5 parts by mass of 2-bromo-3-hexyl-5-iodothiophene, 0.3 parts by mass of 2-bromo-3-(2-ethyl)hexyl-5-iodothiophene, and 4.0 parts by mass of 2.0 M THF solution of isopropylmagnesium bromide were added and stirred for 30 minutes at 0°C in another dried three-necked flask. Then the reacted solution was added into the former flask and polymerized for 7 hours at 35°C.

Successively, 3 parts by mass of 1.0 M THF solution of tert-butylmagnesium chloride was added and stirred for 3 hours, further 50 parts by mass of 5 M hydrochloric acid was added and stirred for 1 hour, and then polymerization was stopped. Thereafter, extraction with 680 parts by mass of chloroform, washing with 150 parts by mass of sodium bicarbonate water and 150 parts by mass of distilled water, concentration, drying, and solidification were applied. The obtained black and purple solid substance was dissolved in 42 parts by mass of chloroform, re-precipitated in 450 parts by mass of acetone, and dried sufficiently and thus a conjugated polymer containing a thiophene group (polymer name: poly[(3-hexylthiophene)-*co*-(3-(2-ethylhexyl)thiophene)] (P5) was obtained. The weight-average molecular weight of the obtained conjugated polymer containing a thiophene group (P5) was 26,500 g/mol and the number-average molecular weight thereof was 22,300 g/mol. The content of the(3-(2-ethylhexyl)thiophene) unit was 8 mol %.

Here, a purifying method in the above processes was as follows.

o Purification of polymer

A high performance liquid chromatograph LC-10A made by Shimadzu Corporation was used in purification using a GPC column. Here, a Shodex GPC K-LG and a Shodex GPC K-2006M tandemly-connected were used as the column. Further, an RID-10A was used as a detector.

The surface tensions of the conjugated polymers containing a thiophene group and the fullerene derivatives used in the present examples were shown in Table 1. A surface tension was calculated from contact angles of water and ethanol by an Owens-Wendt method. Contact angles were measured at 10 sites and the average was used.

The melting points of the conjugated polymers containing a thiophene group used in the present examples were shown in Table 1. A melting point was measured by differential scanning calorimetry (DSC). After heat history was once reset by raising temperature from 50°C to 270°C, a polymer was cooled down to -50°C and then heated again to 270°C. The temperature was raised and lowered at a rate of 10°C/min. in all the cases.

Example 1

(Production of Composition 1)

16.0 parts by mass of a conjugated block copolymer containing a thiophene group (P1) as a conjugated polymer containing a thiophene group, 12.8 parts by mass of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) (E100H made by Frontier Carbon Corporation) as a fullerene derivative, and 1,100 parts by mass of chlorobenzene as a solvent were mixed for 12 hours at 40°C. Successively, the mixture was cooled to a room temperature of 20°C and filtered with a PTFE filter having a pore size of 45 μm, and thus Composition 1 was produced.

(Production and evaluation of organic solar cell)

A glass substrate to which an ITO film (resistance value 10 Ω/□) 150 nm in thickness was attached by a sputtering method was subjected to surface treatment for 15 minutes by UV ozone treatment. A film acting as a hole transport layer was formed into a thickness of 40 nm on the substrate by applying a PEDOT:PSS aqueous solution (CLEVIOS PH500 made by H. C. Starck GmbH) by a spin coat method. The substrate was heated and dried for 20 minutes at 140°C with a hot plate and successively coated with Composition 1 by spin coating, and thus an organic photo-active layer (about 100 nm in film thickness) A1 of an organic solar cell was obtained.

(Solvent treatment)

200 μl of chlorobenzene (surface tension: 33.0 mN/m^2) was put to the bottom of a lid-attached glass container 300 ml in capacity, a glass table about 4 cm in height is placed in the lid-attached glass container, and the container was closed with the lid. The organic photo-active layer A1 was placed on the glass table in the glass container, the container was immediately closed with the lid, and then the organic photo-active layer A1 was exposed in chlorobenzene vapor for 5 minutes at a room temperature of 25°C. After the lapse of 5 minutes, the organic photo-active layer A1 was taken out from the container and dried under vacuum at room temperature.

Thereafter, lithium fluoride was vapor-deposited on the organic photo-active layer to a film thickness of 1 nm

and successively aluminum was vapor-deposited on the lithium fluoride layer to a film thickness of 100 nm with a vacuum vapor deposition apparatus. The degree of vacuum at the vapor deposition was always 1×10^{-4} to 3×10^{-4} Pa. Further, the shape of the obtained organic solar cell was a true circle of 5.64 mm in diameter and the effective area thereof was 0.25 cm^2. The organic solar cell was taken out from the vacuum vapor deposition apparatus under nitrogen atmosphere and irradiated with a 300 W solar simulator (Model 91160 made by Newport Corporation: AM1.5G filter, light intensity of 100 mW/cm^2) and electric current values when the applied voltage was varied from -1 V to +1 V were measured. The light intensity was adjusted with a standard cell (BS-520 made by BUNKOUKEIKI Co., Ltd.). A short-circuit current density Jsc (a value of current density when applied voltage is 0 V) on this occasion was compared with the current density on an occasion where solvent treatment was not applied.

Jsc improvement rate = (Jsc when solvent treatment is applied)/(Jsc when solvent treatment is not applied) × 100 (%)

Example 2

An organic solar cell was produced in the same way as Example 1 except that 200 μl of toluene (27.9 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Example 3

An organic solar cell was produced in the same way as Example 1 except that 200 μl of ortho-xylene (29.8 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Example 4

An organic solar cell was produced in the same way as Example 1 except that 200 μl of 1,2-dichloroethane (31.9 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Example 5

An organic solar cell was produced in the same way as Example 1 except that 200 μl of anisole (35.1 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 1

An organic solar cell was produced in the same way as Example 1 except that 200 μl of acetone (23.5 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 2

An organic solar cell was produced in the same way as Comparative Example 1 except that solvent treatment was applied for 60 minutes at a room temperature of 25°C. The results were shown in Table 2.

Example 6 (Composition 2)

Composition 2 was obtained in the same way as

Composition 1 of Example 1 except that 16.0 parts by mass of a conjugated block copolymer containing a thiophene group (P2) was used instead of a conjugated block copolymer containing a thiophene group (P1) as a conjugated polymer.

An organic photo-active layer (about 100 nm in film thickness) A2 of an organic solar cell was obtained in the same way as Example 1 except that Composition 2 was used instead of Composition 1. An organic solar cell was produced by using A2 and applying solvent treatment with chlorobenzene in the same way as Example 1. The results were shown in Table 2.

Example 7

An organic solar cell was produced in the same way as Example 6 except that 200 μl of toluene (27.9 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Example 8

An organic solar cell was produced in the same way as Example 6 except that 200 μl of ortho-xylene (29.8 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Example 9

An organic solar cell was produced in the same way as Example 6 except that 200 μl of ortho-dichlorobenzene (35.6 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in

Table 2.

Example 10

An organic solar cell was produced in the same way as Example 6 except that 200 μl of 1,2-dichloroethane (31.9 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Example 11

An organic solar cell was produced in the same way as Example 6 except that 200 μl of anisole (35.1 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 3

An organic solar cell was produced in the same way as Example 6 except that 200 μl of acetone (23.5 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 4

An organic solar cell was produced in the same way as Example 6 except that 200 μl of ethyl acetate (23.4 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 5

An organic solar cell was produced in the same way as Example 6 except that 200 μl of cyclohexane (24.7 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 6

An organic solar cell was produced in the same way as Example 6 except that 200 μl of ethylene glycol (48.0 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 7

An organic solar cell was produced in the same way as Example 6 except that 200 μl of water (72.0 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 8

An organic solar cell was produced in the same way as Example 6 except that heat treatment was applied for 5 minutes at 150°C instead of applying solvent treatment. The heat treatment was applied while an organic photo-active layer A2 was placed on a hot plate under nitrogen atmosphere. The results were shown in Table 2.

Comparative Example 9

An organic solar cell was produced in the same way as Example 6 except that heat treatment was applied for 30 minutes at 150°C instead of applying solvent treatment. The results were shown in Table 2.

Comparative Example 10 (Composition 3)

Composition 3 was obtained in the same way as Composition 1 of Example 1 except that 16.0 parts by mass of a conjugated polymer containing a thiophene group (P3) was used instead of a conjugated block copolymer

containing a thiophene group (P1) as a conjugated polymer containing a thiophene group.

An organic photo-active layer (about 100 nm in film thickness) A3 of an organic solar cell was obtained in the same way as Example 1 except that Composition 3 was used instead of Composition 1. An organic solar cell was produced by using A3 and applying solvent treatment with chlorobenzene in the same way as Example 1. The results were shown in Table 2.

Comparative Example 11

An organic solar cell was produced in the same way as Comparative Example 10 except that 200 μl of toluene (27.9 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 12

An organic solar cell was produced in the same way as Comparative Example 10 except that 200 μl of ortho-xylene (29.8 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 13

An organic solar cell was produced in the same way as Comparative Example 10 except that 200 μl of ortho-dichlorobenzene (35.6 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 14

An organic solar cell was produced in the same way as Comparative Example 10 except that 200 μl of 1,2-dichloroethane (31.9 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 15

An organic solar cell was produced in the same way as Comparative Example 10 except that 200 μl of anisole (35.1 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 16

An organic solar cell was produced in the same way as Comparative Example 10 except that 200 μl of acetone (23.5 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 17

An organic solar cell was produced in the same way as Comparative Example 10 except that 200 μl of ethyl acetate (23.4 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 18

An organic solar cell was produced in the same way as Comparative Example 10 except that 200 μl of

cyclohexane (24.7 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 19

An organic solar cell was produced in the same way as Comparative Example 10 except that 200 μl of ethylene glycol (48.0 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 20

An organic solar cell was produced in the same way as Comparative Example 10 except that 200 μl of water (72.0 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Example 12 (Composition 4)

Composition 4 was obtained in the same way as Composition 1 of Example 1 except that 11.2 parts by mass of a conjugated polymer containing a thiophene group (P3) and 4.8 parts by mass of a conjugated random copolymer containing a thiophene group (P4) were used instead of a conjugated block copolymer containing a thiophene group (P1) as a conjugated polymer containing a thiophene group.

An organic photo-active layer (about 100 nm in film thickness) A4 of an organic solar cell was obtained in the same way as Example 1 except that Composition 4 was used instead of Composition 1. An organic solar cell was

produced by using A4 and applying solvent treatment with chlorobenzene in the same way as Example 1. The results were shown in Table 2.

Example 13

An organic solar cell was produced in the same way as Example 12 except that 200 μl of toluene (27.9 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Example 14

An organic solar cell was produced in the same way as Example 12 except that 200 μl of ortho-xylene (29.8 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Example 15

An organic solar cell was produced in the same way as Example 12 except that 200 μl of ortho-dichlorobenzene (35.6 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Example 16

An organic solar cell was produced in the same way as Example 12 except that 200 μl of anisole (35.1 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 21

An organic solar cell was produced in the same way as Example 12 except that 200 μl of acetone (23.5 mN/m^2)

was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 22

An organic solar cell was produced in the same way as Example 12 except that 200 μl of cyclohexane (24.7 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Comparative Example 23 (Composition 5)

Composition 5 was obtained in the same way as Composition 1 of Example 1 except that 11.2 parts by mass of a conjugated polymer containing a thiophene group (P3) and 4.8 parts by mass of a conjugated random copolymer containing a thiophene group (P5) were used instead of a conjugated block copolymer containing a thiophene group (P1) as a conjugated polymer containing a thiophene group.

An organic photo-active layer (about 100 nm in film thickness) A5 of an organic solar cell was obtained in the same way as Example 1 except that Composition 5 was used instead of Composition 1. An organic solar cell was produced by using A5 and applying solvent treatment with chlorobenzene in the same way as Example 1. The results were shown in Table 2.

Comparative Example 24

An organic solar cell was produced in the same way as Comparative Example 23 except that 200 μl of toluene (27.9 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in

Table 2.

Comparative Example 25

An organic solar cell was produced in the same way as Comparative Example 23 except that 200 μl of ortho-xylene (29.8 mN/m^2) was used instead of chlorobenzene as a solvent for solvent treatment. The results were shown in Table 2.

Examples 1 to 11 and Comparative Examples 1 to 7 show that it is verified that Jsc of an organic photovoltaic element improves remarkably when the surface tension of a solvent used for solvent treatment is in the range of 27 to 37. Meanwhile, Comparative Examples 1 and 2 show that Jsc of an organic photovoltaic element improves by prolonging solvent treatment time even when a surface tension is outside the preferred range. It is uneconomical, however, since it takes a long time of 60 minutes for solvent treatment. Comparative Examples 8 and 9 show that Jsc of an organic photovoltaic element improves also by heat treatment but the effect is limited with a short treatment time. Comparative Examples 10 to 20 show that the effect of solvent treatment is low when only one kind of conjugated polymer containing a thiophene group is used but a high Jsc improvement rate can be attained by using two kinds of conjugated polymers containing a thiophene group having melting points different from each other by 10°C. Examples 12 to 16 and Comparative Examples 21 and 22 show that an organic

photovoltaic element having a remarkably improved Jsc can be obtained also when two kinds of conjugated polymers containing a thiophene group having melting points different from each other by 10°C are blended instead of a conjugated block copolymer containing a thiophene group. Comparative Examples 23, 24 and 25 show that a Jsc improvement rate was low by using two kinds of conjugated polymers containing a thiophene group having melting points different from each other less than 10°C.

Table 1

Conjugated polymer	Surface tension mN/m	Melting point 1 °C	Melting point 2 °C
Conjugated block copolymer (P1)	25.7	236	220
Conjugated block copolymer (P2)	26.5	238	216
Conjugated polymer (P3)	27.0	236	
Conjugated random copolymer (P4)	27.7	222	
PCBM	37.0	-	-
Conjugated random copolymer (P5)	27.2	230	

Table 2

	Film	Solvent	Surface tension of solvent (mN/m^2)	Treatment time (min)	Jsc improvement rate (%)
Example 1	A1	Chlorobenzene	33.0	5	407
Example 2	A1	Toluene	27.9	5	398
Example 3	A1	Ortho-xylene	29.8	5	404
Example 4	A1	1,2-dichloroethane	31.9	5	395
Example 5	A1	Anisole	35.1	5	412
Comparative example 1	A1	Acetone	23.5	5	110
Comparative example 2	A1	Acetone 60 min.	23.5	60	400
Example 6	A2	Chlorobenzene	33.0	5	358
Example 7	A2	Toluene	27.9	5	325
Example 8	A2	Ortho-xylene	29.8	5	331
Example 9	A2	Ortho-dichlorobenzene	35.6	5	319
Example 10	A2	1,2-dichloroethane	31.9	5	324
Example 11	A2	Anisole	35.1	5	387
Comparative example 3	A2	Acetone	23.5	5	75
Comparative example 4	A2	Ethyl acetate	23.4	5	134
Comparative example 5	A2	Cyclohexane	24.7	5	165
Comparative example 6	A2	Ethylene glycol	48.0	5	80
Comparative example 7	A2	Water	72.0	5	87
Comparative example 8	A2	Thermal annealing 150 °C		5	191
Comparative example 9	A2	Thermal annealing 150 °C		30	276
Comparative example 10	A3	Chlorobenzene	33.0	5	133
Comparative example 11	A3	Toluene	27.9	5	124
Comparative example 12	A3	Ortho-xylene	29.8	5	122
Comparative example 13	A3	Ortho-dichlorobenzene	35.6	5	120
Comparative example 14	A3	1,2-dichloroethane	31.9	5	115
Comparative example 15	A3	Anisole	35.1	5	118
Comparative example 16	A3	Acetone	23.5	5	62
Comparative example 17	A3	Ethyl acetate	23.4	5	82
Comparative example 18	A3	Cyclohexane	24.7	5	78
Comparative example 19	A3	Ethylene glycol	48.0	5	59
Comparative example 20	A3	Water	72.0	5	62
Example 12	A4	Chlorobenzene	33.0	5	229
Example 13	A4	Toluene	27.9	5	223
Example 14	A4	Ortho-xylene	29.8	5	223
Example 15	A4	Ortho-dichlorobenzene	35.6	5	230
Example 16	A4	Anisole	35.1	5	226
Comparative example 21	A4	Acetone	23.5	5	174
Comparative example 22	A4	Cyclohexane	24.7	5	188
Comparative example 23	A5	Chlorobenzene	33.0	5	148
Comparative example 24	A5	Toluene	27.9	5	140
Comparative example 25	A5	Ortho-xylene	29.8	5	138

CLAIMS

1. A method for producing an organic photovoltaic element with an organic photo-active layer comprising;

a conjugated block copolymer comprising a polymer A block containing a thiophene group and a polymer B block containing a thiophene group, or

a polymer composition comprising a conjugated polymer A containing a thiophene group and a conjugated polymer B containing a thiophene group,

wherein the difference between the melting points of the polymers being 10°C or more, and a fullerene derivative, and

wherein the method includes a process of exposing an organic photo-active layer to a vapor of solvent having a surface tension between a surface tension of the conjugated polymer (A or B) containing a thiophene group and a surface tension of the fullerene derivative.

2. The method for producing an organic photovoltaic element according to claim 1, wherein the organic photo-active layer is exposed to vapor of solvent the surface tension of which is in the range of 27 to 37 mN/m^2 at 25°C.

3. A method for producing an organic photovoltaic element, wherein the organic photo-active layer according to claim 1 is exposed to the vapor of solvent in the range

of 1 sec. to 30 min.

4. An organic photovoltaic element produced by the production method according to claim 1.

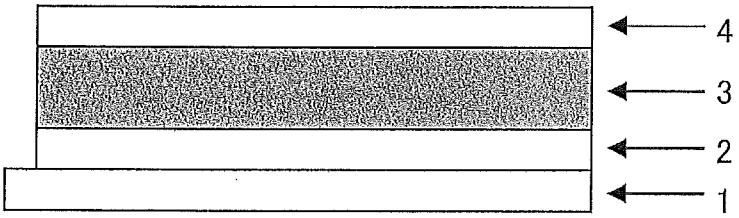
[Fig. 1]

1 Substrate

2 Anode

3 Organic photo-active layer

4 Cathode



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/34857

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - H01L 31/02, 31/18 (2012.01)
USPC - 136/255; 136/263
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)
IPC(8)- H01L 31/02, 31/18 (2012.01)
USPC- 136/255; 136/263

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC- 257/E31.124, 438/98, 977/773;
Patents and NPL (classification, keyword; search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWest (US Pat, PgPub, EPO, JPO), GoogleScholar (PL, NPL), FreePatentsOnline (US Pat, PgPub, EPO, JPO, WIPO, NPL); search terms: conjugate, block, diblock, AB, thiophene, fullerene, n anotube, photovoltaic, solar, surface, tension, melt, melting, point, temp, temperature, degree

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2009/0256117 A1 (SESHADRI et al.) 15 October 2009 (15.10.2009), para [0004]-[0006], [0012], [0020], [0023], [0024], [0027], [0029], [0044], [0130], [0160]	1-4
Y	US 2007/0037012 A1 (KIM et al.) 15 February 2007 (15.02.2007), para [0020], [0021], [0093], [0098], [0113], [0118]	1-4
Y	US 2010/0193777 A1 (TAKAHASHI et al.) 05 August 2010 (05.08.2010), para [0017]-[0232]	1-4
Y	US 2009/0085012 A1 (CHOCHOS et al.) 02 April 2009 (02.04.2009), para [0005]-[0050]	1-4
Y	US 2005/0267264 A1 (TAKEI et al.) 01 December 2005 (01.12.2005), para [0012]-[0170]	1-4

☐ Further documents are listed in the continuation of Box C. ☐

* 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
04 July 2012 (04.07.2012)	16 JUL 2012
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

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