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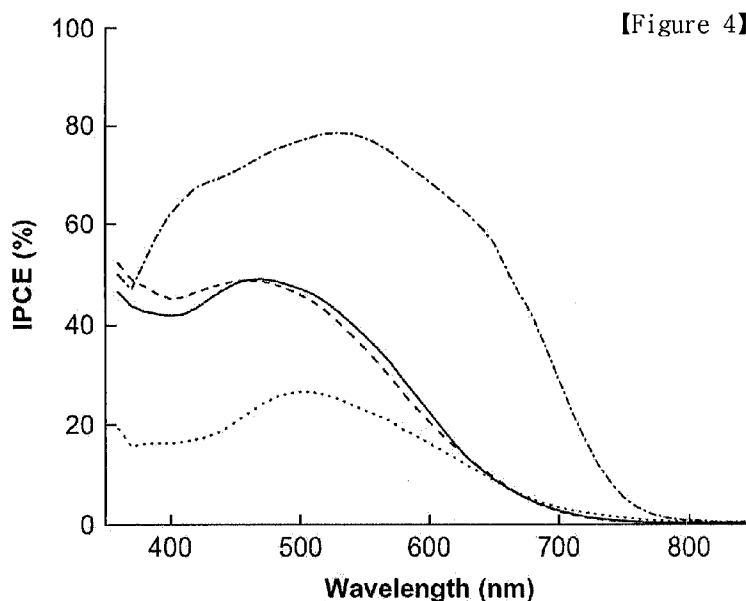
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(54) Title: NOVEL JULOLIDINE-BASED DYE AND PREPARATION THEREOF



(57) Abstract: The present invention relates to novel julolidine-based dye and preparation thereof. The dye compound of the present invention which comprises julolidine as an electron donor, a bithiophene unit as a middle linking part, and cyanoacrylic acid as an electron acceptor can be used for a dye-sensitized solar cell (DSSC). The dye of the present invention shows improved molar absorptivity, J_{sc} (short circuit photocurrent density) and photoelectric conversion efficiency, compared to dyes of the prior art, and thus it can greatly improve solar cell efficiency. And, it can dramatically decrease dye synthesis cost because the dye of the present invention can be purified without using expensive columns.



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NOVEL JULOLIDINE-BASED DYE AND PREPARATION THEREOF

【Technical Field】

The present invention relates to novel julolidine-based dye
5 comprising a bithiophene derivative, used for a dye-sensitized solar
cell (DSSC), and a process for preparing the same.

【Background Art】

Many studies regarding a dye-sensitized nanoparticle titanium
oxide solar cell have been progressed since it was developed by Swiss
10 Federal Institute of Technology Lausanne (EPFL), Michael Gratzel et
al. on the year 1991. Because a dye-sensitized solar cell has higher
efficiency and lower manufacture cost than the existing silicone-
based solar cell, it can replace the existing amorphous silicone-
based solar cell. And, differently from the silicone-based solar
15 cell, the dye-sensitized solar cell is a photoelectrochemical solar
cell essentially consisting of a dye molecule capable of absorbing a
visible ray and generating electron-hole pair and a transition metal
oxide for transmitting the generated electrons.

As the dye for a dye-sensitized solar cell, ruthenium complex having high photoelectric conversion efficiency has been widely used. However, the ruthenium complex had a defect of high cost.

Recently, it has been discovered that metal-free organic dye,
5 which has excellent properties in terms of an absorption efficiency, oxidation-reduction stability and charge-transfer(CT) absorption in a molecule, can be used as the dye for a solar cell instead of the expensive ruthenium complex. Thus, studies focus on the metal-free organic dye.

10 In general, the organic dye has a structure consisting of an electron donor - electron acceptor moieties which are linked by π -bond. For most organic dyes, an amine derivative functions as an electron donor, 2-cyanoacrylic acid or rhodanine moiety functions as an electron acceptor, and the two parts are linked by a π -bond
15 system such as methaine unit or thiophene chain.

In general, the structural change of electron donor amine causes a change in electron's properties, for example, a blue-shifted absorption spectrum, and causes a change in the π -bond length thus controlling absorption spectrum and redox potential.

However, most organic dyes so far known show lower conversion efficiencies and lower operation stability, compared to ruthenium complex dyes. Thus, there are continued efforts for developing novel dyes showing improved molar absorptivity and high photoelectric
5 conversion efficiency compared to the existing organic dye compounds by changing the kinds of electron donor and acceptor or π -bond length.

【Disclosure】

【Technical Problem】

10 Accordingly, it is an object of the present invention to provide organic dyes showing improved molar absorptivity and photoelectric conversion efficiency compared to metal complex dyes of the prior art, thus capable of largely improving the efficiency of solar cells, and a process for preparing the same.

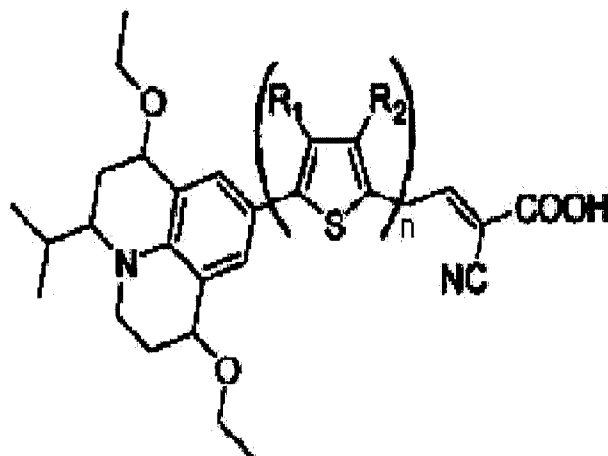
15 It is another object of the present invention to provide a dye-sensitized photoelectric conversion element comprising the dye of the present invention thus showing remarkably improved photoelectric conversion efficiency and having excellent J_{sc} (short circuit

photocurrent density) and molar absorptivity, and a solar cell having remarkably improved efficiency.

【Technical Solution】

In order to achieve said objects, the present invention provides
 5 julolidine-based dye of the following Formula 1:

[Formula 1]



wherein, each R_1 and R_2 is independently hydrogen, C_{1-12} alkyl or C_{1-12} alkoxy, and when R_1 or R_2 is C_{1-12} alkoxy, they may be bonded to
 10 each other to form an oxygen-containing heterocycle; n is an integer of 2 to 5, and two or more thiophene units can be optionally linked by a vinyl group.

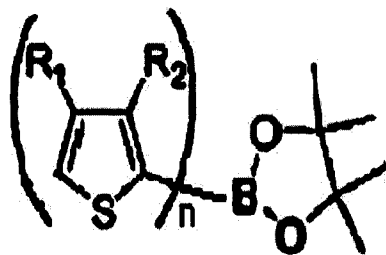
Also, the present invention provides a process for preparing the julolidine-based dye having the Formula 1, comprising the steps of:

(1) subjecting bromojulolidine to a Suzuki coupling reaction with a compound of the following Formula 2 to form a compound of the following Formula 3;

(2) lithiating the compound of the Formula 3 with n-butyllithium, and then continuously cooling it with dimethylformamide to form a compound of the following Formula 4:

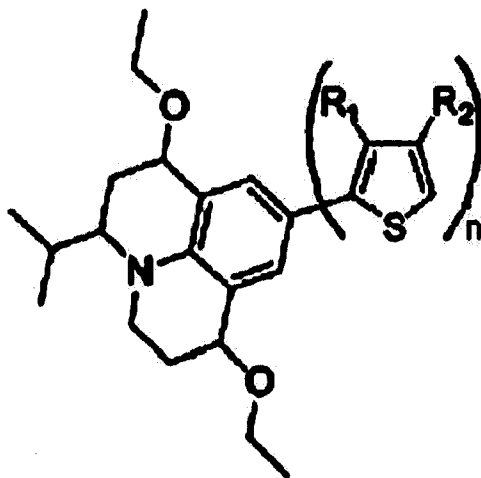
(3) reacting the compound of the Formula 4 with cyanoacetic acid in CH_3CN in the presence of piperidine:

[Formula 2]

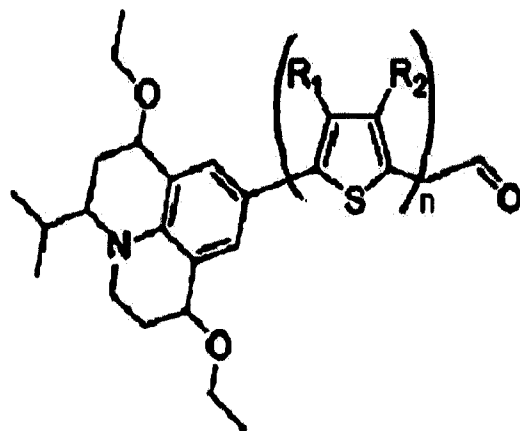


10

[Formula 3]



[Formula 4]



wherein, each R_1 , R_2 and n has the same meaning as defined above.

Also, the present invention provides a dye-sensitized
 5 photoelectric conversion element comprising oxide semiconductor
 particles where the julolidine-based dye of the above Formula 1 is
 supported.

Also, the present invention provides a dye-sensitized solar cell
 comprising said dye-sensitized photoelectric conversion element.

10 **【Advantageous Effects】**

The novel julolidine-based dye of the present invention shows
 improved molar absorptivity, J_{sc} (short circuit photocurrent density)
 and photoelectric conversion efficiency compared to dyes of the prior
 art, and thus it can greatly improve solar cell efficiency. And, it

can dramatically decrease dye synthesis cost because the dye of the present invention can be purified without using expensive columns.

【Description of Drawings】

Fig. 1 shows absorption and emission spectrums of each of the dye compounds 1a to 1c of the present invention in ethanol, and emission spectrums of the dye compounds supported on TiO₂ layer.

Fig. 2 (a), (b) and (c) are diagrams respectively showing the optimized structure of each of the dye compounds 1a to 1c of the present invention (TD-DFT (time-dependent density functional theory) computation at B3LYP/3-21G).

Fig. 3 (a) and (b) are diagrams respectively showing the geometrical structure of each of the dye compounds 1a to 1c of the present invention (HOMO and LUMO molecular orbitals, TD-DFT computation at B3LYP/3-21G).

Fig. 4 shows IPCE(incident photon-to-current conversion efficiency) spectrums of the solar cells respectively prepared using each of the dye compounds 1a to 1c of the present invention.

Fig. 5 shows photocurrent voltage curves of the solar cell respectively prepared using each of the dye compounds 1a to 1c of the present invention (under AM 1.5 radiation).

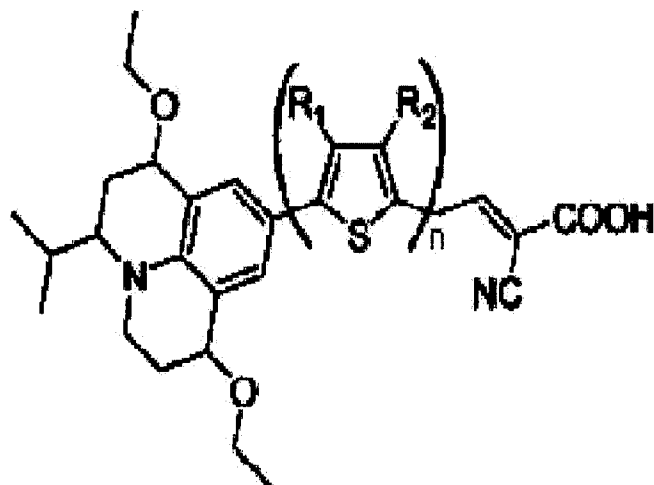
【Mode for Invention】

5 The present invention will now be explained in detail.

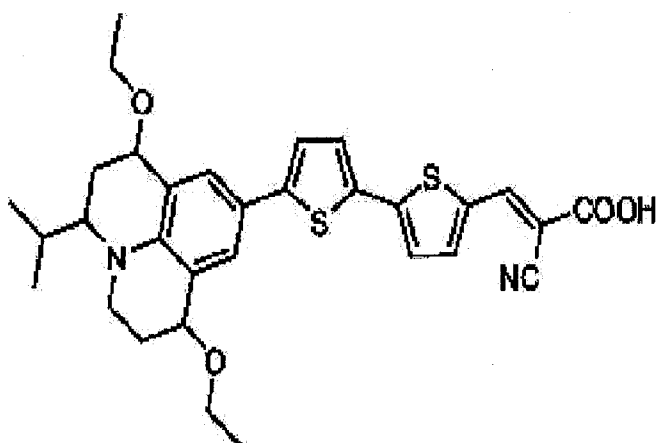
The present inventors have discovered that a dye-sensitized solar cell prepared by supporting, on oxide semiconductor particles, a compounds of the Formula 1, which has a novel organic dye structure of using julolidine as an electron donor, introducing bithiophene
10 unit in the middle linking part for increasing molar absorptivity and stability of the element, and using cyanoacrylic acid which is closely connected with TiO_2 reforming and has the best electron transport capacity as an electron acceptor, has high photoelectric conversion efficiency, J_{sc} (short circuit photocurrent density) and
15 molar absorptivity, and thus has superior efficiency to the existing dye-sensitized solar cells, and completed the present invention.

The julolidine-based organic dye of the present invention has the following Formula 1, and preferably one of the following Formulas 1a to 1c.

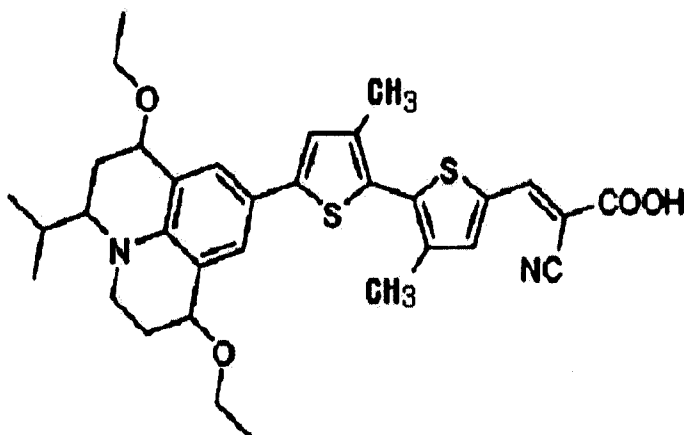
[Formula 1]



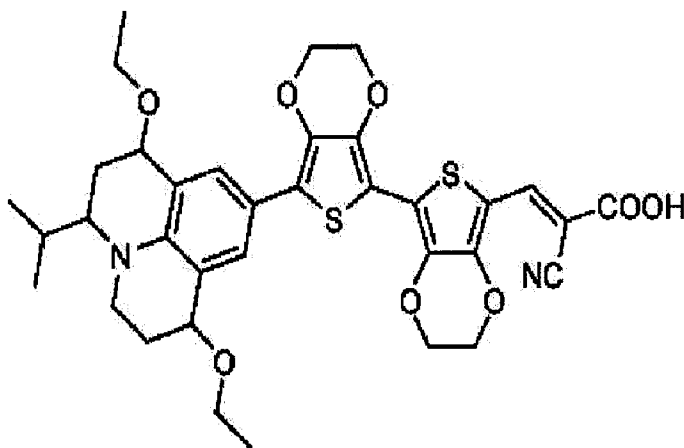
[Formula 1a]



[Formula 1b]



[Formula 1c]



wherein, each R_1 , R_2 and n has the same meanings as defined above.

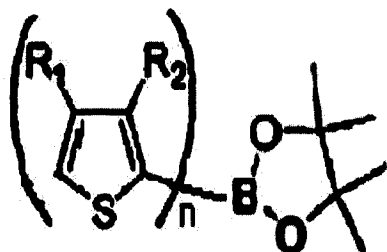
5 The dye of the above Formula 1 can be prepared by the process comprising the steps of:

(1) subjecting bromojulolidine to a Suzuki coupling reaction with a compound of the following Formula 2 (1.2 equivalent) to form a compound of the following Formula 3;

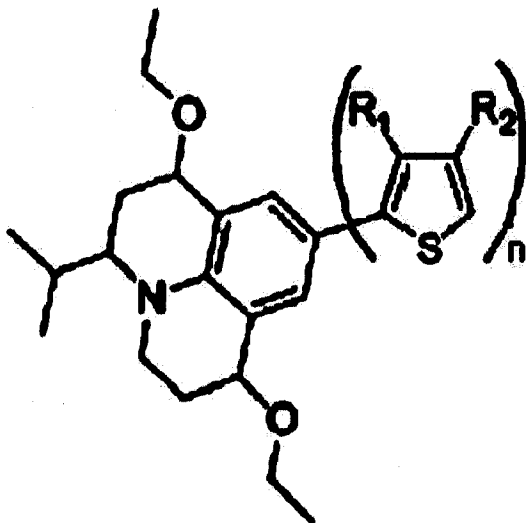
(2) lithiating the compound of the Formula 3 with n-butyllithium(1.2 equivalent), and then continuously cooling it with dimethylformamide to form a compound of the following Formula 4; and

(3) reacting the compound of the Formula 4 with cyanoacetic acid
5 in CH₃CN in the presence of piperidine (see the reaction Formula 1).

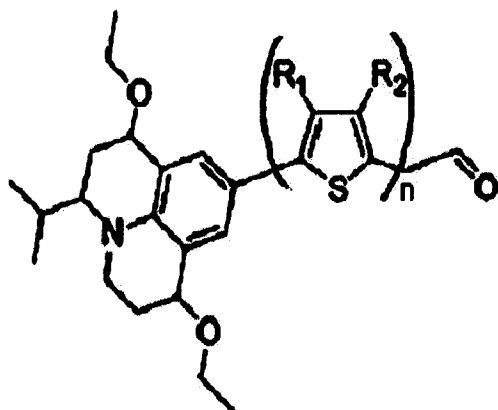
[Formula 2]



[Formula 3]

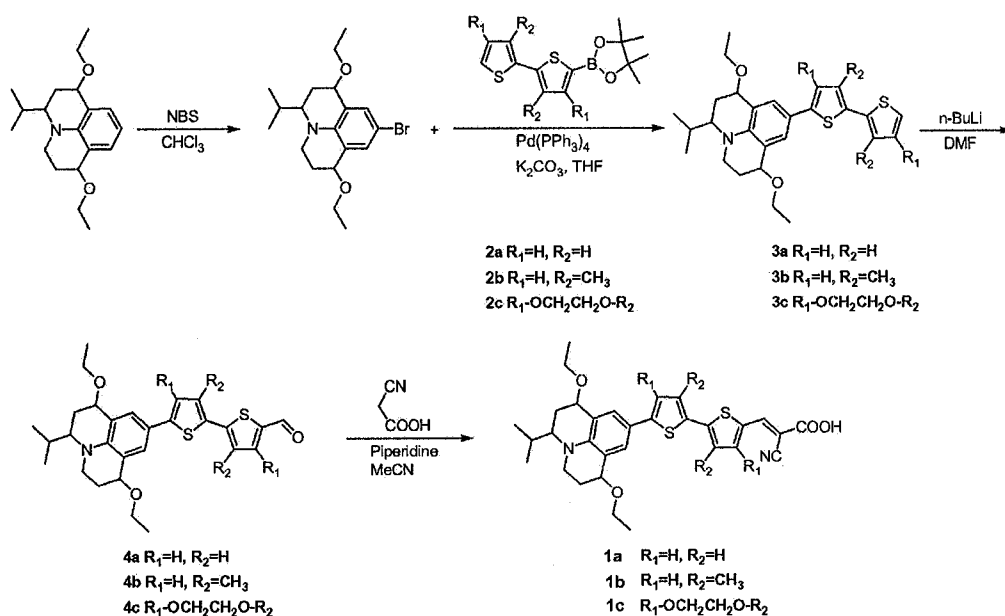


[Formula 4]



wherein, each R_1 , R_2 and n has the same meaning as defined above.

[Reaction Formula 1]



wherein, each R_1 , R_2 and n has the same meaning as defined above.

In the Reaction Formula 1, the bromojulolidine used as starting material for the preparation of the dye of the Formula 1 can be obtained by bromination of julolidine with NBS in $CHCl_3$.

And, the present invention provides a dye-sensitized photoelectric conversion element, wherein the dye of the Formula 1 is supported on oxide semiconductor particles. For the preparation of the dye-sensitized photoelectric conversion element of the present invention, any processes for preparing a dye-sensitized photoelectric conversion element for solar cells of the prior art can be applied, except using the dye of the above Formula 1. Preferably, the dye-sensitized photoelectric conversion element of the present invention is prepared by forming an oxide semiconductor thin film on a substrate, using oxide semiconductor particles, and then supporting the dye of the present invention on the thin film.

As the substrate on which the oxide semiconductor thin film is formed, a substrate having conductive surface is preferably used, but any commercially available substrates can be used. For examples, a substrate wherein a thin film of metal such as copper, silver, gold, etc. or conductive metal oxide such as tin oxide coated with indium, fluorine, or antimony, etc. is formed on the surface of glass or transparent polymer such as polyethyleneterephthalate or

polyethersulfone, etc. The conductivity is preferably 1000Ω or less, and more preferably 100Ω or less.

As the oxide semiconductor particles, a metal oxide is preferably used. For examples, oxides of titanium, tin, zinc, tungsten, 5 zirconium, gallium, indium, itrium, niobium, tantalum, vanadium, etc. can be used. Specifically, an oxide of titanium, tin, zinc, niobium, or indium is preferable, titanium oxide, zinc oxide and tin oxide are more preferable, and titanium oxide is most preferable. The oxide semiconductor can be used alone or in combination, and can be coated 10 on the surface of the semiconductor.

And, the oxide semiconductor particles preferably have an average particle size of 1 ~ 500 nm, and more preferably 1 ~ 100 nm. And, oxide semiconductor particles having large particle size and those having small particle size can be mixed, or they can be used in 15 multi-layers.

The oxide semiconductor thin film can be prepared by directly forming a thin film of oxide semiconductor particles by spraying, etc.; by electrically depositing semiconductor thin film using a substrate as an electrode; or by coating on a substrate a paste

containing semiconductor particles which is obtained by hydrolyzing a precursor of semiconductor particles such as a slurry of semiconductor particles or semiconductor alkoxide, etc., and then drying, curing or calcining. Preferably, a process of coating a
5 paste on a substrate is used, wherein a slurry can be obtained by dispersing secondary condensed oxide semiconductor particles in a dispersion medium by a common method so that a first average particle size is 1 ~ 200 nm.

As the dispersion medium for dispersing the slurry, any
10 dispersion medium capable of dispersing semiconductor particles can be used without limitation. For examples, water, alcohol such as ethanol, etc., ketone such as acetone, acetylacetone, etc., or hydrocarbon such a hexane, etc. can be used. They can be used in combination, and water is preferable because it reduces viscosity
15 change of the slurry. And, a dispersion stabilizer can be used for stabilizing the dispersion state of the oxide semiconductor particles. Examples of the dispersion stabilizer include acid such as acetic acid, hydrochloric acid, nitric acid, etc. acetylacetone, acrylic acid, polyethyleneglycol, polyvinylalcohol, etc.

The substrate coated with the slurry can be subjected to calcination. The calcination temperature is 100 °C or more, preferably 200 °C or more, and the upper limit of the calcination temperature is melting point(softening point) of the substrate or
5 less, commonly 900 °C, preferably 600 °C or less. In the present invention, the calcination time is not specifically limited, but preferably within 4 hours.

In the present invention, the thickness of the thin film on the substrate is suitably 1 ~ 200 μm , and preferably 1 ~ 50 μm . When
10 subjected to calcination, a thin layer of the oxide semiconductor particles is partly welded, which does not specifically cause any troubles in the present invention.

And, a secondary treatment can be conducted on the oxide semiconductor thin film. For example, the thin film can be immersed
15 in a solution of alkoxide, chloride, nitride or sulfide of the same metal as the semiconductor, and dried or re-calcined, thereby improving the performance of the semiconductor thin film. The metal alkoxide includes titanium ethoxide, titanium isopropoxide, titanium t-butoxide, n-dibutyl-diacetyl tin, etc., and the alcohol solution

thereof can be used. The chloride includes titanium chloride, tin chloride, zinc chloride, etc., and the aqueous solution thereof can be used. Thus obtained oxide semiconductor thin film consists of oxide semiconductor particles.

5 And, the method for supporting dye on the oxide semiconductor thin film is not specifically limited in the present invention. For example, a substrate on which the oxide semiconductor thin film is formed can be immersed in a solution obtained by dissolving the dye of the Formula 1 in a solvent capable of dissolving it, or in a
10 dispersion obtained by dispersing the dye. The concentration of the dye in the solution or dispersion can be appropriately determined according to the dye. The immersion temperature is generally from a room temperature to a boiling point of the solvent, and the immersion time is from about 1 minute to 48 hours. The solvent for dissolving
15 the dye includes methanol, ethanol, acetonitrile, dimethylsulfoxide, dimethylformamide, acetone, t-butanol, etc. The concentration of the dye in the solution is suitably 1×10^{-6} M ~ 1 M, and preferably 1×10^{-5} M ~ 1×10^{-1} M. Thus, the dye-sensitized photoelectric

conversion element of the present invention comprising oxide semiconductor particles in the form of a thin film can be obtained.

One kind of the dye of the Formula 1 can be supported, or some kinds of the dyes can be mixed and supported. And, the dye of the present invention can be mixed with other dyes or metal complex dyes. The examples of the metal complex dyes which can be mixed with the dye of the present invention are not specifically limited, but ruthenium complex or the quaternary salt thereof, phthalocyanine, or porphyrin is preferable. And, the examples of the organic dyes which can be mixed with the dye of the present invention include metal-free phthalocyanine, porphyrin or cyanine, merocyanine, oxonol, triphenylmethane-based dyes, methyne-based dyes such as acrylic acid based dyes described in WO2002/011213, xanthene-based, azo-based, anthraquinone-based, or perylene-based dyes (see the literature [M.K.Nazeeruddin, A.Kay, I.Rodicio, R.Humphry-Baker, E.Muller, P.Liska, N.Vlachopoulos, M.Gratzel, *J. Am. Chem. Soc.*, vol 115, p 6382(1993)]). In case two or more kinds of dyes are used, the dyes can be sequentially absorbed to the semiconductor thin film, or they can be mixed, dissolved and absorbed.

And, when the dye is supported on the thin film of the oxide semiconductor particles, it is preferable to support the dye in the presence of an inclusion compound in order to prevent bonding between the dyes. As the inclusion compound, cholic acid such as deoxycholic acid, dehydrodeoxycholic acid, kenodeoxycholic acid, cholic acid methyl ester, sodium cholic acid, etc., steroid-based compound, crown ether, cyclodextrin, calix arene, polyethylene oxide, etc. can be used.

After the dye is supported, the electrode surface of the semiconductor can be treated with amine compound such as pyridine, etc., or compounds having acid group such as acetic acid, propionic acid, etc. For example, a substrate on which a dye-supported semiconductor thin film is formed can be immersed in an ethanol solution of amine.

The present invention also provides a dye-sensitized solar cell comprising the dye-sensitized photoelectric conversion element of the present invention. For the manufacture of the dye-sensitized solar cell, commonly used methods for preparing a solar cell using a photoelectric conversion element of the prior art can be applied,

except using the dye-sensitized photoelectric conversion element comprising oxide semiconductor particles on which the dye of the Formula 1 is supported. For example, the dye-sensitized solar cell may consist of a photoelectric conversion element electrode(anode), a
5 counter electrode(cathode), redox electrolyte, hole transport material or p-type semiconductor, etc.

Preferably, the dye-sensitized solar cell of the present invention can be prepared by a process comprising the steps of coating a titanium oxide on a transparent conductive substrate;
10 subjecting the coated substrate to calcination so as to form a titanium oxide thin film; impregnating the titanium oxide thin film with a mixed solution in which the dye of the Formula 1 is dissolved, so as to form a dye-absorbed titanium oxide film electrode; providing a second glass substrate on which a counter electrode is formed;
15 forming a hole through the second glass substrate and the counter electrode; placing a thermoplastic polymer film between the counter electrode and the dye-absorbed titanium oxide film electrode, and conducting heat pressing, so as to join the counter electrode and the titanium oxide film electrode; injecting an electrolyte in the

thermoplastic polymer film placed between the counter electrode and the titanium oxide film electrode through the hole; and, sealing the thermoplastic polymer.

The redox electrolyte, hole transport material, p-type
5 semiconductor, etc. can be a liquid, condensed(gel and gel-type), or solid type. The liquid type includes those prepared by dissolving redox electrolyte, dissolved salt, hole transport material, or p-type semiconductor in a solvent, or a room temperature dissolved salt. The condensed type (gel and gel-type) includes those containing redox
10 electrolyte, dissolved salt, hole transport material, or p-type semiconductor in a polymer matrix or low molecule gelling agent. The solid type includes redox electrolyte, dissolved salt, hole transport material, or p-type semiconductor.

As the hole transport material, those using discotic liquid
15 crystal phase such as amine derivatives, conductive polymer such as polyacetylene, polyaniline, polythiophene, etc., or triphenylene-based compounds can be used. As the p-type semiconductor, CuI, CuSCN, etc. can be used. The counter electrode preferably has conductivity, and functions as a catalyst for the reduction of oxidation-reduction

electrolyte. For example, those prepared by depositing platinum, carbon, rhodium, ruthenium, etc. on a glass or polymer film, or by coating conductive particles on a glass or polymer film can be used.

As the redox electrolyte used for the solar cell of the present
5 invention, halogen redox electrolyte consisting of a halogen compound with halogen ions as a counter ion and a halogen molecule, metal redox electrolyte such as ferrocyanide-ferricyanide, ferrocene-ferricinium ion, metal complex such as cobalt complex, etc., organic redox electrolyte such as alkylthiol-alkyldisulfide, vologen dye,
10 hydroquinone-quinone, etc. can be used. Specifically, halogen redox electrolyte is preferable. As the halogen molecule for the halogen redox electrolyte, iodine molecule is preferably used. And, as the halogen compound, halogenated metal salt such as LiI, NaI, KI, CaI₂, MgI₂, CuI, etc., or organic ammonium salt of halogen such as
15 tetraalkyl ammonium iodide, imidazolium iodide, pyridium iodide, etc., or I₂ can be used.

In case the redox electrolyte is a solution comprising the same, an electrochemically inert solvent can be used. For examples, acetonitrile, propylene carbonate, ethylene carbonate, 3-

methoxypropionitrile, methoxyacetonitrile, ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, butyrolactone, dimethoxyethane, dimethylcarbonate, 1,3-dioxolane, methylformate, 2-methyl tetrahydrofuran, 3-methoxy-oxazolidin-2-on, sulfolane, 5 tetrahydrofuran, water, etc. can be used. Specifically, acetonitrile, propylene carbonate, ethylene carbonate, 3-methoxypropionitrile, ethylene glycol, 3-methoxy-oxazolidin-2-on, or butyrolactone is preferable. One kind of solvent can be used or some kinds of solvents can be mixed and used. As a gel-type positive 10 electrolyte, those containing electrolyte or electrolyte solution in a matrix of oligomer or polymer, or those containing an electrolyte or an electrolyte solution in a starch gelling agent can be used. The concentration of the redox electrolyte is preferably 0.01 - 99 wt%, and more preferably 0.1 - 30 wt%.

15 The solar cell of the present invention can be obtained by placing on a substrate, a photoelectric conversion element (anode) where the dye of the Formula 1 is supported on the oxide semiconductor particles and a counter electrode (cathode), and filling a solution comprising a redox electrolyte therebetween.

The present invention will be explained with reference to the following examples. However, these examples are only intended to illustrate the present invention and the scope of the present invention is not limited thereto.

5 [Example]

[Example 1] Synthesis of dye

All the reactions were conducted under argon atmosphere, and a solvent was distilled with suitable agent purchased from Sigma-Aldrich Company. ^1H and ^{13}C NMR spectrums were measured by Varian
10 Mercury 300 spectrometer, elementary analysis was measured by Carlo Elba Instruments CHNS-O EA 1108 spectrometer, and mass spectrum was measured by JEOL JMS-SX102A apparatus. Absorption and emission spectrums were respectively measured by Perkin-Elmer Lambda 2S UV-visible spectrometer and Perkin LS fluorescence spectrometer.

15 < Cyclic voltammetry > BAS 100B(Bioanalytical Systems, Inc.) was used as a cyclic voltammeter. A 3-electrode system consisting of a gold disc, a working electrode and a platinum wire electrode was used. The redox potential of dye on TiO_2 was measured at a scan ratio of 50 mV s^{-1} (vs. Fc/Fc^+) using 0.1M (*n*- C_4H_9) $_4\text{N-PF}_6$ in CH_3CN .

I) 9-bromo-*cys, cys*-1,7-diethoxy-3-isopropyljulolidine

cys, cys-1,7-diethoxy-3-isopropyljulolidine (5g, 16.47mmol) and *N*-bromosuccinimide(2.91g, 16.47mmol) were mixed in chloroform(100ml) for 2 hours. Water (30ml) and brine were added to the mixed solution.
5 Then, an organic layer was separated and dried with magnesium sulfate. After the solvent was removed under vacuum, the obtained solid was subjected to chromatography (eluant MC:Hx=1:1, *Rf*=0.5) to obtain a colorless oily title compound (yield 70%).

¹H NMR (CDCl₃): δ 7.27 (s, 1H), 7.17 (s, 1H), 4.34 (t, J=6.0 Hz, 1H),
10 4.19 (t, J=3.9 Hz, 1H), 3.72 (m, 2H), 3.57 (m, 2H), 3.22 (m, 2H), 3.00 (m, 1H), 2.36 (oct, J=6.6 Hz, 1H), 1.97 (m, 4H), 1.26 (q, J=6.6 Hz, 6H), 0.97 (d, J=6.6 Hz, 3H), 0.85 (d, J=6.9 Hz, 3H). ¹³C¹H NMR (CDCl₃): δ 141.0, 131.3, 130.3, 125.0, 124.1, 107.2, 73.8, 64.2, 63.7, 61.9, 42.9, 28.8, 27.4, 27.1, 20.5, 17.0, 15.7, 15.6. MS: *m/z* 381 [M⁺]. Anal. Calcd for
15 C₁₉H₂₈BrNO₂: C, 59.69; H, 7.38. Found: C, 59.42; H, 7.24.

II) 9-(2,2'-bithiophen-5-yl)-*cys, cys*-1,7-diethoxy-3-isopropyljulolidine (compound 3a)

The compound obtained in the above step I)(1g, 2.61mmol), 2-(2,2'-biothiophen-5-yl)-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane (0.915g, 3.132mmol), Pd(PPh₃)₄(0.150g, 0.13mmol) and 2M K₂CO₃ aqueous solution(2ml) were refluxed in THF(100ml) for 12 hours. The reaction
5 solution was cooled, and water(30ml) and brine were added thereto. Then, an organic layer was separated and dried with magnesium sulfate. After the solvent was removed under vacuum, the obtained solid was subjected to chromatography(eluant MC:Hx=1:1, Rf=0.3) to obtain an yellow solid title compound (yield 70%).

10 Mp: 189°C. ¹H NMR (CDCl₃): δ 7.42 (s, 1H), 7.32 (s, 1H), 7.15 (t, J=6.3 Hz, 1H), 7.08 (d, J=3.9 Hz, 1H), 7.03 (d, J=3.9 Hz, 1H), 7.00 (d, J=3.3 Hz, 1H), 6.99 (d, J=3.3 Hz, 1H), 4.42 (t, J=5.1 Hz, 1H), 4.30 (t, J=3.9 Hz, 1H), 3.75 (m, 2H), 3.67 (m, 2H), 3.27 (m, 2H), 3.05 (m, 1H), 2.42 (oct, J=6.9 Hz, 1H), 2.06 (m, 4H), 1.29 (q, J=7.1 Hz, 6H), 0.99 (d,
15 J=6.6 Hz, 3H), 0.88 (d, J=6.9 Hz, 3H). ¹³C¹H NMR (CDCl₃): δ 139.8, 138.7, 136.4, 135.5, 133.9, 133.3, 132.2, 131.5, 130.3, 128.2, 127.4, 124.8, 122.1, 109.8, 72.7, 70.8, 65.8, 63.8, 62.7, 42.8, 28.8, 27.4, 27.2, 20.4, 19.3, 15.4, 15.2. MS: m/z 467 [M⁺]. Anal. Calcd for C₂₇H₃₃NO₂S₂: C, 69.34; H, 7.11. Found: C, 69.12; H, 6.95.

III) 9-(3,3'-dimethyl-2,2'-bithiophen-5-yl)-*cys, cys*-1,7-diethoxy-3-isopropyljulolidine (compound 3b)

The same process as the above step II) was conducted, except that
5 2-(3,3'-dimethyl-2,2'-bithiophen-5-yl)-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane was used instead of 2-(2,2'-bithiophen-5-yl)-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane, to obtain a title compound (yield 65%).

Mp: 187°C. ¹H NMR (CDCl₃): δ 7.40 (s, 1H), 7.29 (s, 1H), 7.24 (d, J=5.1 Hz, 1H), 6.95 (s, 1H), 6.91 (d, J=5.1 Hz, 1H), 4.42 (t, J=5.1 Hz, 1H), 4.29 (t, J=3.9 Hz, 1H), 3.77 (m, 2H), 3.63 (m, 2H), 3.26 (m, 2H), 3.05 (m, 1H), 2.40 (oct, J=6.9 Hz, 1H), 2.22 (s, 3H), 2.17 (s, 3H), 2.01 (m, 4H), 1.27 (q, J=6.9 Hz, 6H), 0.99 (d, J=6.6 Hz, 3H), 0.89 (d, J=6.1 Hz, 3H). ¹³C{¹H} NMR (CDCl₃): δ 139.0, 138.5, 137.3, 135.8, 134.1, 133.3, 130.5, 130.3, 129.4, 125.9, 125.3, 122.1, 121.0, 109.8, 72.1, 70.7, 65.8, 64.5, 63.8, 48.0, 31.9, 31.5, 29.2, 27.2, 27.1, 20.4, 19.4, 15.5, 15.1. MS: m/z 467 [M⁺]. Anal. Calcd for C₂₉H₃₇NO₂S₂: C, 70.26; H, 7.52. Found: C, 69.89; H, 7.13.

IV) 9-(2,2'-bis(3,4-ethylenedioxythiophene)-5-yl)-*cys, cys*-1,7-diethoxy-3-isopropyljulolidine (compound 3c)

The same process as the above step II) was conducted, except that 4,4,5,5,-tetramethyl-2-(2,2',3,3'-tetrahydro-5,7'-bithieno[3,4-
5 *b*][1,4]dioxin-7-yl)-1,3,2-dioxaborolane(1.278g, 3.132mmol) was used instead of 2-(2,2'-bithiophen-5-yl)-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane, to obtain a title compound (yield 77%).

Mp: 198°C. ¹H NMR (CDCl₃): δ 7.55 (s, 1H), 7.42 H. Choi et al. / Tetrahedron 63 (2007) 1553.1559 (s, 1H), 6.23 (s, 1H), 4.43 (t, J=5.1
10 Hz, 1H), 4.34.4.25 (m, 8H), 4.24 (t, J=3.7 Hz, 1H), 3.74 (m, 2H), 3.66 (m, 2H), 3.26 (m, 2H), 3.03 (m, 1H), 2.41 (oct, J=6.9 Hz, 1H), 2.06 (m, 4H), 1.26 (q, J=7.2 Hz, 6H), 0.98 (d, J=6.9 Hz, 3H), 0.88 (d, J=6.3 Hz, 3H).
¹³C¹H NMR (CDCl₃): δ 141.4, 137.8, 136.5, 136.0, 127.9, 126.8, 122.5, 121.5, 119.8, 116.9, 110.6, 105.4, 97.0, 92.9, 73.9, 73.1, 65.9, 65.1,
15 65.0, 64.7, 63.7, 63.3, 62.3, 42.9, 29.2, 27.5, 25.7, 20.6, 17.6, 15.8, 15.7.
MS: m/z 583 [M⁺]. Anal. Calcd for C₃₁H₃₇NO₆S₂: C, 63.78; H, 6.39.
Found: C, 63.55; H, 6.18.

V) 9-(5'-formyl-2,2'-bithiophen-5-yl)-*cys, cts*-1,7-diethoxy-3-isopropyljulolidine (compound 4a)

To an anhydrous ethanol solution of the compound 3a obtained in the above step II) (0.22g, 0.47mmol), *n*-BuLi (0.35ml, 1.6M solution in
5 hexane) was added under argon. After 3 hours, DMF (0.05g, 0.7mmol) was added thereto at 0°C under argon and washed with 5% KOH. The reaction solution was dried with magnesium sulfate. After the solvent was removed, the obtained solid was subjected to silica gel chromatography (eluant MC:Hx=1:1, *R*_f=0.2) to obtain a title compound
10 (yield 75%).

Mp: 186°C. ¹H NMR (CDCl₃): δ 9.82 (s, 1H), 7.64 (d, *J*=3.9 Hz, 1H), 7.43 (s, 1H), 7.33 (s, 1H), 7.28 (d, *J*=3.9 Hz, 1H), 7.28 (d, *J*=3.9 Hz, 1H), 7.20 (d, *J*=3.9 Hz, 1H), 7.08 (d, *J*=3.9 Hz, 1H), 4.41 (t, *J*=5.4 Hz, 1H), 4.30 (t, *J*=3.7 Hz, 1H), 3.77 (m, 2H), 3.65 (m, 2H), 3.28 (m, 2H), 3.08 (m,
15 1H), 2.41 (oct, *J*=6.3 Hz, 1H), 2.02 (m, 4H), 1.29 (q, *J*=6.9 Hz, 6H), 0.99 (d, *J*=6.6 Hz, 3H), 0.88 (d, *J*=6.3 Hz, 3H). ¹³C¹H NMR (CDCl₃): δ 182.6, 145.8, 143.2, 136.2, 134.5, 133.9, 133.3, 132.2, 131.5, 130.8, 128.2, 127.4, 124.8, 122.1, 111.8, 72.5, 70.1, 65.8, 63.8, 62.7, 42.8, 28.8, 27.4,

27.2, 20.4, 19.3, 15.4, 15.2. MS: m/z 495 $[M^+]$. Anal. Calcd for $C_{28}H_{33}NO_3S_2$: C, 67.84; H, 6.71. Found: C, 67.36; H, 6.24.

VI) 9-(5'-formyl-3,3'-dimethyl-2,2'-bithiophen-5-yl-*cys, cys*-1,7-
5 diethoxy-3-isopropyljulolidine (compound 4b)

The same process as the above step V) was conducted, except that a compound 3b was used instead of the compound 3a, to obtain a title compound (yield 72%).

Mp: 179°C. ^1H NMR ($CDCl_3$): δ 9.82 (s, 1H), 7.58 (s, 1H), 7.40 (s,
10 1H), 7.29 (d, $J=5.1$ Hz, 1H), 6.98 (s, 1H), 4.41 (t, $J=5.1$ Hz, 1H), 4.29 (t,
 $J=3.9$ Hz, 1H), 3.74 (m, 2H), 3.63 (m, 2H), 3.27 (m, 2H), 3.07 (m, 1H),
2.41 (oct, $J=6.9$ Hz, 1H), 2.31 (s, 3H), 2.25 (s, 3H), 2.00 (m, 4H), 1.28 (d,
 $J=7.2$ Hz, 6H), 0.99 (d, $J=6.9$ Hz, 3H), 0.88 (d, $J=6.3$ Hz, 3H). ^{13}C ^1H
NMR ($CDCl_3$): δ 182.8, 143.0, 141.2, 140.4, 139.2, 138.4, 137.0, 130.5,
15 127.1, 126.0, 125.0, 122.9, 122.0, 120.6, 112.1, 73.7, 73.1, 64.0, 63.5,
62.3, 42.9, 31.9, 31.5, 29.1, 27.2, 27.1, 22.6, 17.4, 15.8, 15.7. MS: m/z
523 $[M^+]$. Anal. Calcd. for $C_{30}H_{37}NO_3S_2$: C, 68.80; H, 7.12. Found: C,
68.55; H, 6.89.

VII) 9-(5'-formyl-2,2'-bis(3,4-ethylenedioxythiophen)-5-yl)-
cys,cys-1,7-diethoxy-3-isopropyljulolidine (compound 4c)

The same process as the above step V) was conducted, except that
a compound 3c was used instead of the compound 3a, to obtain a title
5 compound (yield 75%).

Mp: 186°C. ¹H NMR (CDCl₃): δ 9.86 (s, 1H), 7.58 (s, 1H), 7.45 (s,
1H), 4.42 (m, 9H), 4.31 (t, J=3.7 Hz, 1H), 3.73 (m, 2H), 3.64 (m, 2H),
3.27 (m, 2H), 3.04 (m, 1H), 2.41 (oct, J=6.3 Hz, 1H), 2.08 (m, 4H), 1.27
(q, J=7.5 Hz, 6H), 0.99 (d, J=6.6 Hz, 3H), 0.88 (d, J=6.0 Hz, 3H). ¹³C¹H
10 NMR (CDCl₃): δ 179.6, 159.0, 156.0, 138.9, 137.7, 136.5, 133.4, 132.1,
130.5, 129.8, 128.7, 125.9, 124.9, 121.0, 106.9, 73.7, 73.3, 65.8, 65.4,
65.1, 64.7, 63.7, 63.3, 62.3, 42.3, 29.1, 27.2, 25.5, 20.7, 17.6, 15.8, 15.7.
MS: m/z 611 [M⁺]. Anal. Calcd for C₃₂H₃₇NO₇S₂: C, 62.82; H, 6.10.
Found: C, 62.55; H, 5.95.

15

VIII) 2-cyano-3-(5'-(*cys,cys*-1,7-diethoxy-3-isopropyljulolidinyl)-
2,2'-bithiophen-5-yl)acrylic acid (compound 1a)

After a mixture of the compound 4a(0.38g, 0.76mmol) and
cyanoacetic acid(0.13g, 1.53mmol) was vacuum dried, it was added to

MeCN(60ml) and piperidine(0.07ml, 0.76mmol), and the mixed solution was refluxed for 6 hours. The reaction solution was cooled and an organic layer was removed under vacuum. Then, the obtained solid was subjected to silica gel chromatography (eluant: MC:MeOH=2:1, R_f =0.6) to obtain a title compound (yield 51%).

Mp: 225°C. ^1H NMR ($\text{DMSO}-d_6$): δ 8.12 (s, 1H), 7.65 (d, J =3.3 Hz, 1H), 7.39 (d, J =3.6 Hz, 1H), 7.37 (d, J =3.6 Hz, 1H), 7.35 (s, 1H), 7.32 (s, 1H), 7.22 (d, J =3.3 Hz, 1H), 4.37 (t, J =5.8 Hz, 1H), 4.28 (t, J =3.9 Hz, 1H), 3.70 (m, 2H), 3.61 (m, 2H), 3.20 (m, 2H), 3.06 (m, 1H), 2.25 (oct, J =6.3 Hz, 1H), 1.90 (m, 4H), 1.19 (q, J =6.9 Hz, 6H), 0.94 (d, J =6.9 Hz, 3H), 0.82 (d, J =6.9 Hz, 3H). ^{13}C NMR ($\text{DMSO}-d_6$): δ 164.3, 150.6, 145.8, 142.3, 142.0, 141.7, 140.6, 136.6, 135.3, 134.8, 131.7, 126.9, 123.6, 122.5, 122.0, 119.1, 118.7, 73.7, 72.8, 64.2, 63.0, 62.5, 41.4, 29.7, 28.6, 28.2, 22.5, 17.0, 15.4, 15.3. MS: m/z 562 $[\text{M}^+]$. Anal. Calcd for $\text{C}_{31}\text{H}_{34}\text{N}_2\text{O}_4\text{S}_2$: C, 66.16; H, 6.09. Found: C, 65.78; H, 5.87.

IX) 2-cyano-3-(5'-(*cys, cys*-1,7-diethoxy-3-isopropyljulolidinyl)-3,3'-dimethyl-2,2'-bithiophen-5-yl)acrylic acid (compound 1b)

The same process as the above step VIII) was conducted, except that a compound 4b was used instead of the compound 4a, to obtain a title compound (yield 56%).

Mp: 212°C. ¹H NMR (DMSO-*d*₆): δ 8.03 (s, 1H), 7.55 (s, 1H), 7.32 (s, 1H), 7.28 (s, 1H), 7.15 (s, 1H), 4.37 (t, J=5.3 Hz, 1H), 4.28 (t, J=3.9 Hz, 1H), 3.69 (m, 2H), 3.57 (m, 2H), 3.27 (m, 2H), 3.08 (m, 1H), 2.35 (oct, J=6.8 Hz, 1H), 2.20 (s, 3H), 2.17 (s, 3H), 1.90 (m, 4H), 1.18 (q, J=7.2 Hz, 6H), 0.94 (d, J=6.9 Hz, 3H), 0.83 (d, J=6.9 Hz, 3H). ¹³C{¹H} NMR (DMSO-*d*₆): δ 163.3, 149.0, 145.4, 144.8, 141.5, 137.8, 136.1, 135.6, 135.3, 134.8, 132.2, 128.9, 127.3, 125.5, 124.6, 124.1, 119.0, 73.8, 72.8, 64.3, 63.1, 61.5, 41.4, 40.4, 38.6, 29.7, 28.6, 28.4, 23.0, 17.2, 15.4, 15.1. MS: m/z 523 [M⁺]. Anal. Calcd. for C₃₃H₃₈N₂O₄S₂: C, 67.09; H, 6.48. Found: C, 66.79; H, 6.33.

15 X) 2-cyano-3-(5'-(*cys*, *cys*-1,7-diethoxy-3-isopropyljulolidinyl)-2,2'-bis(3,4-ethylene-dioxythiophene)-5-yl)acrylic acid (compound 1c)

The same process as the above step VIII) was conducted, except that a compound 4c was used instead of the compound 4a, to obtain a title compound (yield 60%).

Mp: 232°C. ¹H NMR (DMSO-*d*₆): δ 8.03 (s, 1H), 7.44 (s, 1H), 7.35 (s, 1H), 4.42 (m, 8H), 4.35 (t, J=5.9 Hz, 1H), 4.27 (t, J=3.8 Hz, 1H), 3.70 (m, 2H), 3.57 (m, 2H), 3.16 (m, 2H), 3.10 (m, 1H), 2.35 (oct, J=6.8 Hz, 1H), 1.93 (m, 4H), 1.17 (q, J=7.3 Hz, 6H), 0.95 (d, J=6.3 Hz, 3H), 0.83 (d, J=6.9 Hz, 3H). ¹³C¹H NMR (DMSO-*d*₆): δ 161.8, 155.9, 144.6, 140.9, 140.4, 135.9, 126.1, 125.4, 122.4, 120.1, 118.4, 118.1, 115.3, 109.1, 108.1, 104.7, 103.8, 72.5, 72.1, 67.2, 65.2, 64.4, 63.0, 61.2, 59.6, 47.3, 28.6, 23.0, 22.5, 20.1, 17.2, 15.5, 15.4. MS: m/z 678 [M⁺]. Anal. Calcd for C₃₅H₃₈N₂O₈S₂: C, 61.93; H, 5.64. Found: C, 61.56; H, 5.34.

10

[Example 2] Preparation of a dye-sensitized solar cell

In order to evaluate the current-voltage properties of the dye compound, a solar cell was prepared using a 12+8 μm TiO₂ transparent layer. A TiO₂ paste(Solaronix, 13nm paste) was screen printed to prepare a first TiO₂ layer having a thickness of 12 μm, and a second TiO₂ layer having a thickness of 8 μm was prepared using another paste(CCIC, HWP-400) for light diffusion. The TiO₂ bi-layered film was treated with a 40mM TiCl₄ solution and dried at 500 °C for 30minutes. The treated film was cooled to 60 °C, and then impregnated

with each solution of the dye compounds 1a to 1c of the present invention which were prepared in the above steps VIII) to X) (0.3 mM dye in ethanol containing 10 mM kenodioxycholic acid). A high temperature melting film (Surllyn 1702, 25 μ m thickness) was placed as
5 a spacer between the dye-absorbed TiO₂ electrode and a platinum-counter electrode, and heated to prepare a sealed sandwich cell. As an electrolyte solution, 0.6 M 3-hexyl-1,2-dimethylimidazolium iodide, 0.04 M I₂, 0.025 M LiI, 0.05 M guanidium thiocyanate and 0.28 M *tert*-butylpyridine dissolved in acetonitrile were used.

10

[Example 3] Measurement of the prepared dye and dye-sensitized solar cell

Absorption and emission spectrums of each of the dye compounds 1a to 1c of the present invention prepared in the above step VIII) to X) in ethanol (1a: solid line, 1b: bar line, 1c: dotted line), and
15 absorption spectrums of the dye compounds supported on TiO₂ layer(1a: bar line-dotted line, 1b: bar line-dotted line-dotted line, 1c: short bar line) were shown in Fig. 1. The emission spectrums were obtained

by exciting the compound 1a at 450nm, the compound 1b at 410 nm, and the compound 1c at 500nm at 298K.

The graphs as shown in Fig. 1 indicate that the absorption spectrum of the compound 1b was blue shifted, and the absorption
5 spectrum of the compound 1c was red shifted, compared to the absorption spectrum of the compound 1a.

Such differences result from the molecular structures of the dye compounds, and the optimized structure of each of the compounds 1a to 1c (TD-DFT computation at B3LYP/3-21G) were shown in Fig. 2 ((a): 1a,
10 (b): 1b, (c): 1c). In Fig. 2 (a) and (b), the angle observed at the upper part is a twist angle between julolidine and thienyl unit, and the angle observed at the lower part is a facial angle between two thienyl units. In Fig. 2 (c), the angle observed at the upper part is a facial angle of julolidine and 3,4-ethylenedioxythiophene, and
15 the angle observed at the lower part is a facial angle of bis(3,4-ethylenedioxythiophene). The molecular structures as shown in Fig. 2 indicate that the compound 1b more twisted, and the compound 1c is less twisted and close to a plane, compared to the compound 1a.

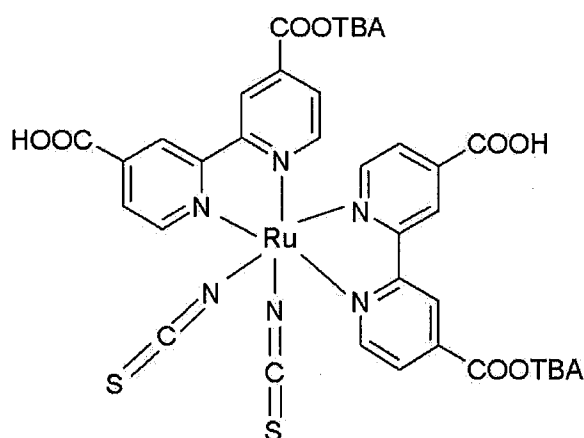
And, the geometrical structures of the compounds 1a and 1c (HOMO and LUMO molecular orbitals, TD-DFT computation at B3LYP/3-21G) were shown in Fig. 3. The structures as shown in Fig. 3 indicate that HOMO-LUMO excitation moves electron distribution from aniline unit to
 5 cyanoacrylic acid, and the change in electron distribution caused by light excitation results in efficient charge separation.

The optical performance and oxidation-reduction performance of each of the dye compounds of 1a to 1c of the present invention, and photoelectrochemical characteristics and IPCE spectrum of the solar
 10 cell prepared using each of the dye compound were shown in Fig. 4, Fig. 5 and the following Table 1.

[Table 1]

Dye	$\lambda_{\text{abs}}^{\text{a}}, \text{nm}$ ($\epsilon, \text{dm}^{-3} \text{mol}^{-1} \text{cm}^{-1}$)	$E_{\text{ox}}^{\text{b}}, \text{V}$	$E_{\text{o-o}}^{\text{c}}, \text{V}$	$E_{\text{LUMO}}^{\text{d}}, \text{V}$	$J_{\text{sc}}, \text{mAcm}^{-2}$	V_{oc}, V	ff	$\eta^{\text{e}}, \%$
1a	462(17,400)	1.34	2.21	-0.87	6.26	0.61	0.64	2.47
1b	422(12,000)	1.37	2.55	-1.18	6.58	0.61	0.73	2.95
1c	506(31,500)	1.10	2.00	-0.90	2.26	0.55	0.59	0.74
N719					16.29	0.75	0.64	7.84

In the above Table 1, N719 is ruthenium-based catalyst used for a dye-sensitized solar cell of the prior art, having the following structure.



5 In the above Table 1, ε is absorption coefficient, E_{ox} is an oxidation potential, E_{0-0} is a voltage at the intersection of absorption and emission spectrums, J_{sc} is a short-circuit photocurrent density, V_{oc} is an open circuit photovoltage, ff is a fill factor, η is total photo-conversion efficiency. And, a means
 10 that an absorption spectrum is measured in an ethanol solution, b means that oxidation-reduction potential of the dye on TiO_2 is measured at a scan ratio of 50 mVs^{-1} (vs. Fc/Fc^+) using $0.1M (n-C_4H_9)_4N^+PF_6^-$ in CH_3CN , c means that E_{0-0} is determined at the intersection of absorption and emission spectrums in ethanol, d means that E_{LUMO} is

calculated by $E_{ox}-E_{0-0}$, e means that the performance of dye-sensitized solar cell is measured on the working area of 0.18cm^2 .

The IPCE graph of a solar cell as shown in Fig. 4 and the photocurrent voltage curve (under AM 1.5 radiation) of a solar cell
5 as shown in Fig. 5 (1a: solid line, 1b: bar line, 1c: dotted line, N719: bar line-dotted line) indicate that IPCE maximum of the compound 1c is lower than those obtained from the compounds 1a and 1b, and total conversion efficiency of the compound 1c is low.

These results indicate that the efficiency of dye largely depends
10 on the condensation degree of dye on TiO_2 layer rather than dye absorption amount, and that it is also related to a twisted non-planar structure of the dye compound of the present invention. Namely, it is suggested that the photoelectric conversion efficiency of dye largely change according to the structural transformation of
15 bithiophene linking moiety, and that the photoelectric conversion efficiency becomes higher as the degree of twist between julolidine and thienyl unit is high.

【Industrial Applicability】

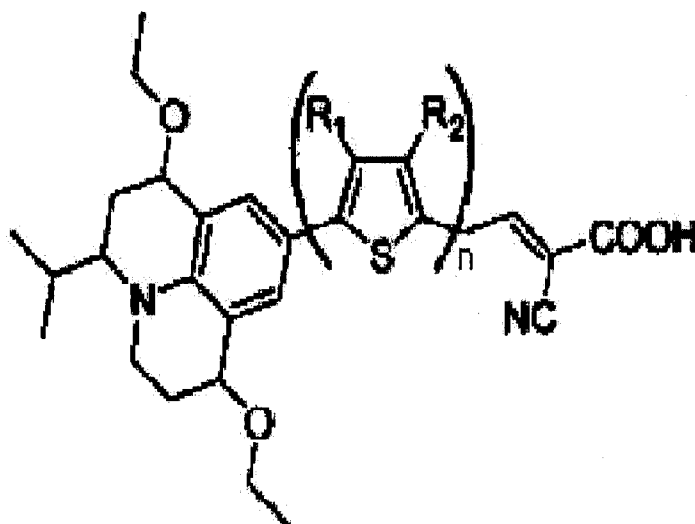
The novel julolidine-based dye of the present invention shows improved molar absorptivity, J_{sc} (short circuit photocurrent density) and photoelectric conversion efficiency, compared to the metal complex dye of the prior art, and thus can largely improve the efficiency of a solar cell. And, it can dramatically decrease dye synthesis cost because it can be purified without using expensive columns.

【CLAIMS】

【Claim 1】

Julolidine-based dye of the following Formula 1:

[Formula 1]



5

wherein, each R_1 and R_2 is independently hydrogen, C_{1-12} alkyl or C_{1-12} alkoxy, and when R_1 or R_2 is C_{1-12} alkoxy, they may be bonded to each other to form an oxygen-containing heterocycle; n is an integer of 2 to 5, and two or more thiophene units can be optionally linked by a vinyl group.

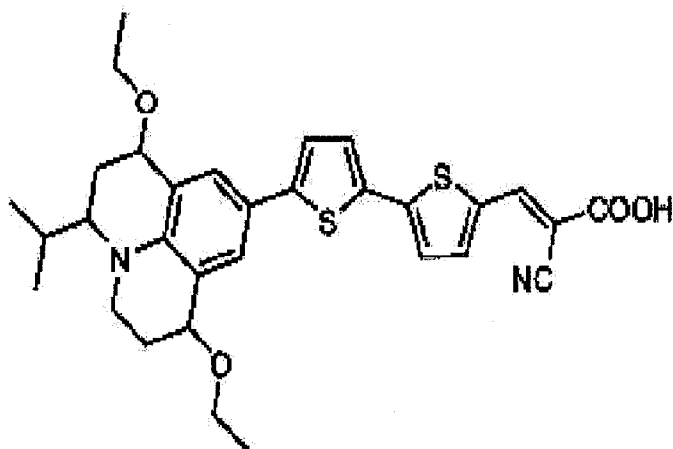
10

【Claim 2】

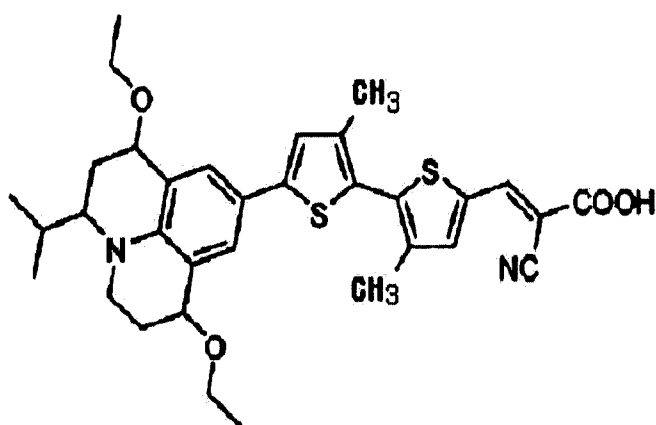
The julolidine-based dye according to claim 1, wherein the dye is represented by one of the following Formula 1a to 1c:

[Formula 1a]

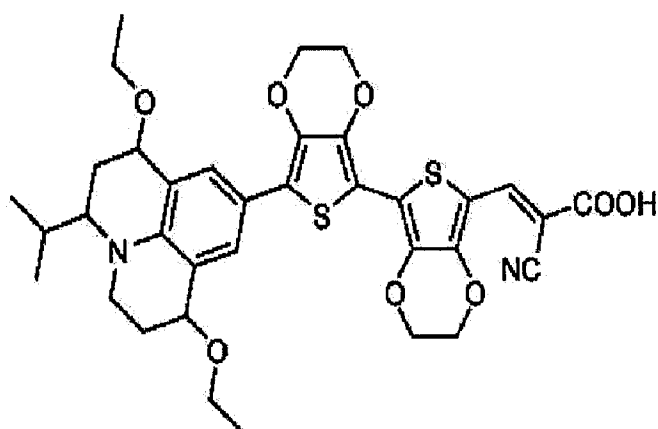
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[Formula 1b]



[Formula 1c]



5

【Claim 3】

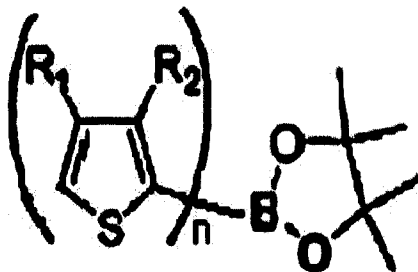
A process for preparing the julolidine-based dye of the Formula 1 as described in claim 1, comprising the steps of:

(1) subjecting bromojulolidine to a Suzuki coupling reaction with a compound of the following Formula 2 to form a compound of the following Formula 3;

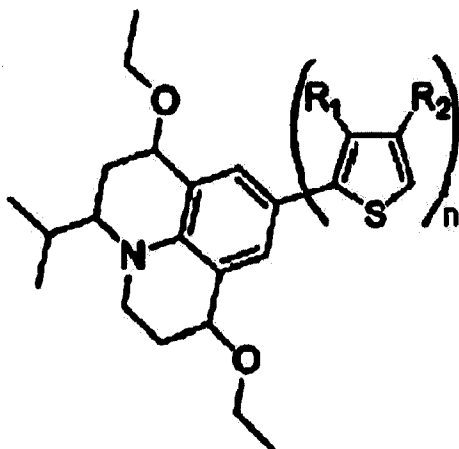
(2) lithiating the compound of the Formula 3 with n-butyllithium, and then continuously cooling it with dimethylformamide to form a compound of the following Formula 4:

(3) reacting the compound of the Formula 4 with cyanoacetic acid in CH₃CN in the presence of piperidine:

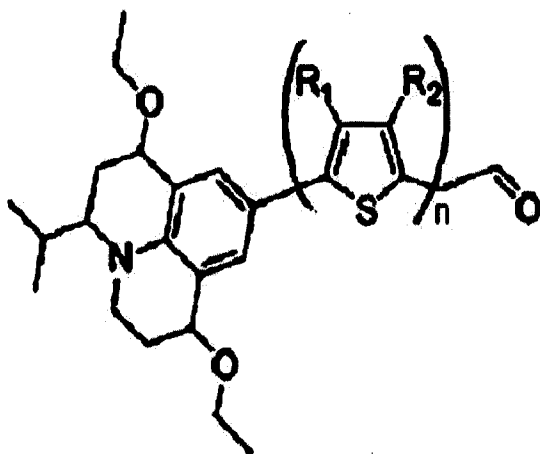
[Formula 2]



[Formula 3]



[Formula 4]



wherein, each R_1 , R_2 and n has the same meaning as defined in
 5 claim 1.

【Claim 4】

A dye-sensitized photoelectric conversion element comprising
 oxide semiconductor particles on which the julolidine-based dye as
 described in claim 1 is supported.

10 **【Claim 5】**

The dye-sensitized photoelectric conversion element according to claim 4, wherein the julolidine-based dye is supported on the oxide semiconductor particles in the presence of an inclusion compound.

【Claim 6】

5 The dye-sensitized photoelectric conversion element according to claim 4, wherein the oxide semiconductor particles comprise titanium dioxide as an essential element.

【Claim 7】

10 The dye-sensitized photoelectric conversion element according to claim 4, wherein the oxide semiconductor particles have an average particle size of 1 ~ 500 nm.

【Claim 8】

15 A dye-sensitized solar cell comprising the dye-sensitized photoelectric conversion element as described in claim 4 as an electrode.

【Claim 9】

The dye-sensitized solar cell according to claim 8, wherein the dye-sensitized solar cell is prepared by a process comprising the steps of:

coating a titanium oxide on a transparent conductive substrate;

subjecting the coated substrate to calcination so as to form a titanium oxide thin film;

impregnating the titanium oxide thin film with a mixed solution
5 in which the dye of the Formula 1 is dissolved, so as to form a dye-
absorbed titanium oxide film electrode;

providing a second glass substrate on which a counter electrode
is formed;

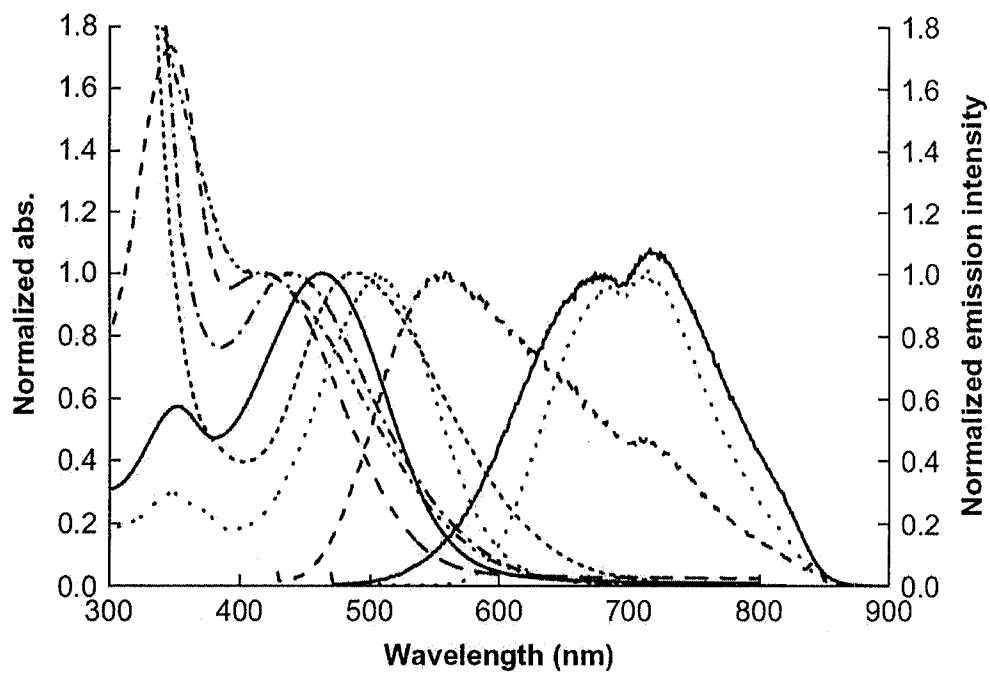
forming a hole through the second glass substrate and the counter
10 electrode;

placing a thermoplastic polymer film between the counter
electrode and the dye-absorbed titanium oxide film electrode, and
conducting heat pressing, so as to join the counter electrode and the
titanium oxide film electrode;

15 injecting an electrolyte in the thermoplastic polymer film placed
between the counter electrode and the titanium oxide film electrode
through the hole; and

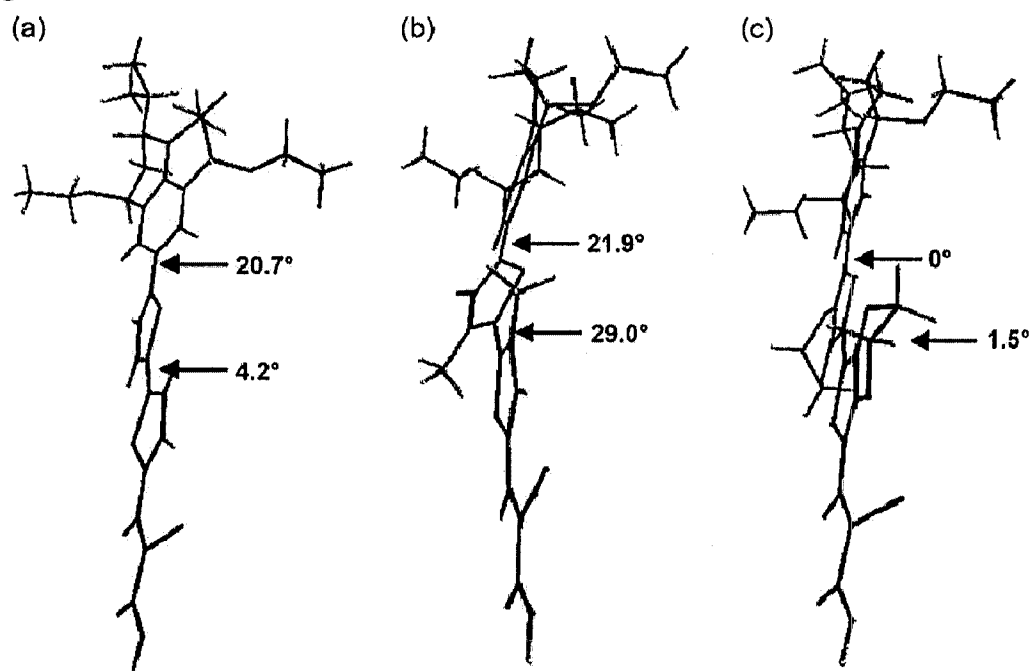
sealing the thermoplastic polymer.

【Figure 1】

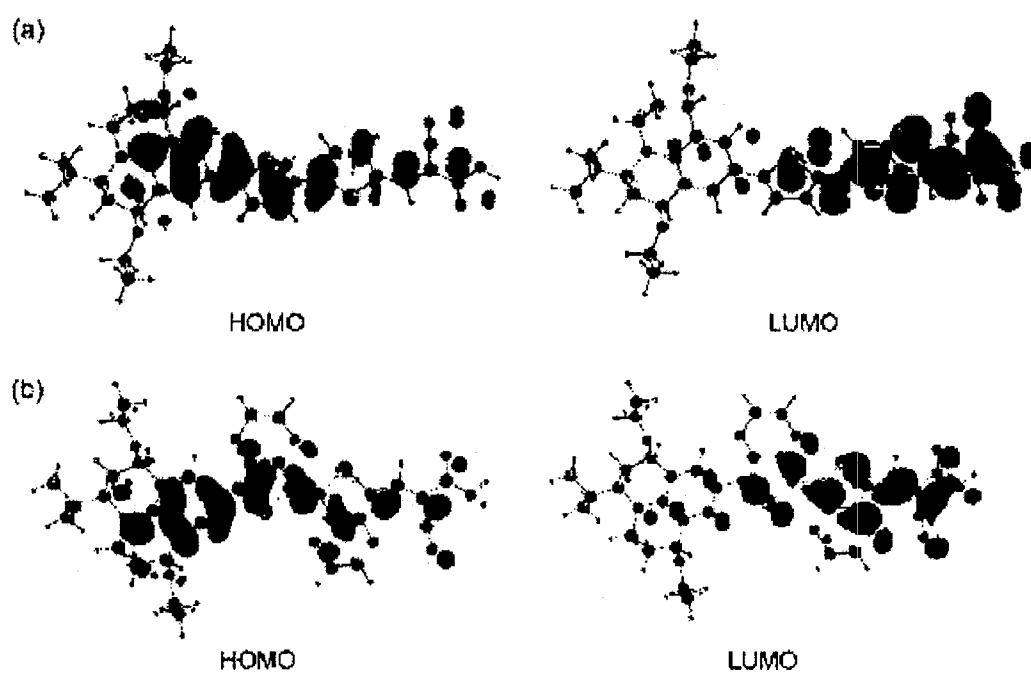


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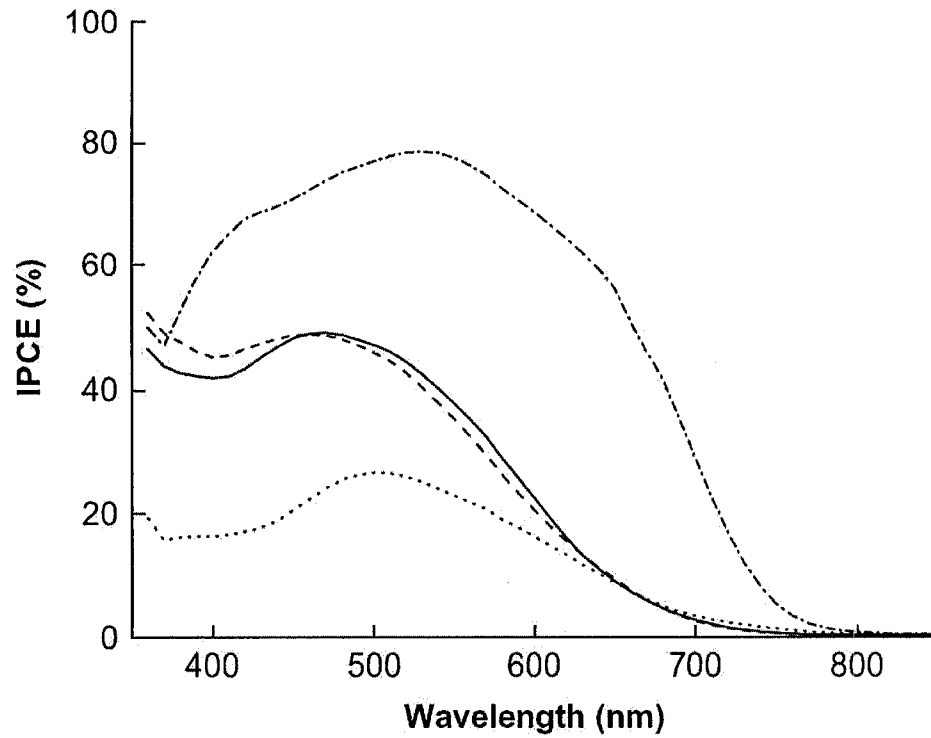
【Figure 2】



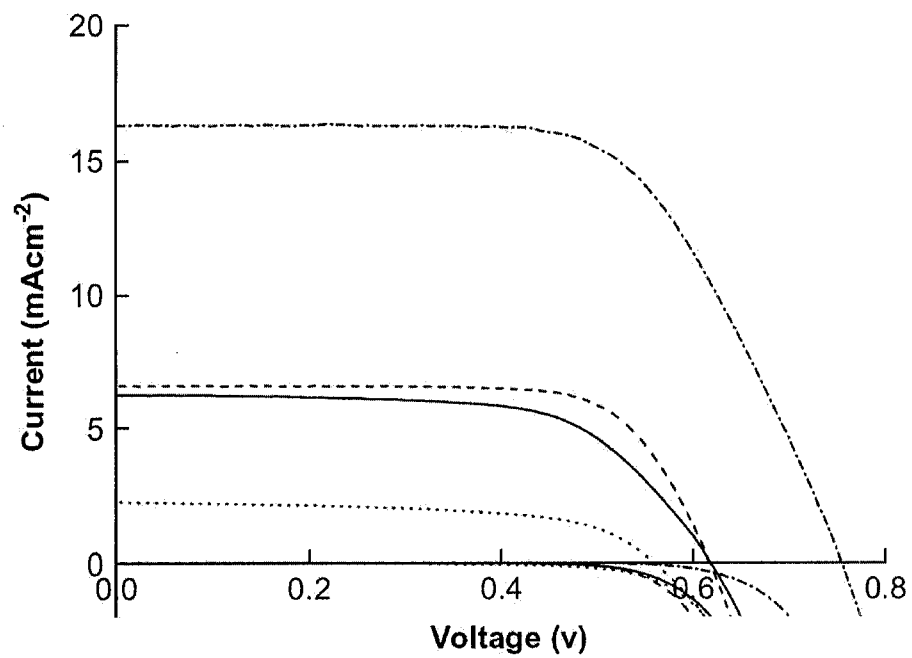
【Figure 3】



【Figure 4】



【Figure 5】



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Paper Copy (NOT for submission)

VIII-5-1	Declaration: Non-prejudicial disclosure or exceptions to lack of novelty Declaration as to non-prejudicial disclosures or exceptions to lack of novelty (Rules 4.17(v) and 51bis.1(a)(v)): Name (LAST, First)	in relation to this international application CHOI, Hyun-bong declares that the subject matter claimed in this international application was disclosed as follows:
VIII-5-1(i)	Kind of disclosure:	publication
VIII-5-1(i)	Date of disclosure:	26 December 2006 (26.12.2006)
VIII-5-1(ii)	Title of disclosure:	Synthesis of new julolidine dyes having bithiophene derivatives for solar cell
VIII-5-1(i)	Place of disclosure:	Tetrahedron 63 (2007) 1553-1559

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VIII-5-2	Declaration: Non-prejudicial disclosure or exceptions to lack of novelty Declaration as to non-prejudicial disclosures or exceptions to lack of novelty (Rules 4.17(v) and 51bis.1(a)(v)): Name (LAST, First)	in relation to this international application KO, Jae-jung declares that the subject matter claimed in this international application was disclosed as follows:
VIII-5-2(i)	Kind of disclosure:	publication
VIII-5-2(i)	Date of disclosure:	26 December 2006 (26.12.2006)
VIII-5-2(i)	Title of disclosure:	Synthesis of new julolidine dyes having bithiophene derivatives for solar cell
VIII-5-2(i)	Place of disclosure:	Tetrahedron 63 (2007) 1553-1559

A. CLASSIFICATION OF SUBJECT MATTER***C09B 49/00(2006.01)i***

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 8 :C09B 49/00

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

Korean Utility Models and Applications for Utility Models since 1975

Japanese Utility Models and Applications for Utility Models since 1975

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

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2005-78888 A (KONICA MINOLTA HOLDINGS INC.) 24 March 2005 See claim 1; page 5, paragraph [32]	1-9
A	JP 2003-109676 A (KONICA CORP.) 11 April 2003 See claim 1; page 4, paragraph [0028]	1-9
A	JP 2003-86257 A (NIPPON KAYAKU CO., LTD.) 20 March 2003 See claim 1; page 3, paragraph [0010]	1-9
A	WO 2004/082061 A1 (NIPPON KAYAKU KABUSHIKI KAISHA) 23 September 2004 See page 7, line 14 - page 10, line 12	1-9
A	JP 2006-134649 A (NIPPON KAYAKU CO., LTD.) 25 May 2006 See claim 1; page 5, paragraph [24]and page 6, paragraph [25]	1-9



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

11 FEBRUARY 2008 (11.02.2008)

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2007/003038

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		EP 1628356A1	22-02-2006
		KR 2005116146A	09-12-2005
		US 20060130249A1	22-06-2006
JP 2006-134649 A	25-05-2006	NONE	