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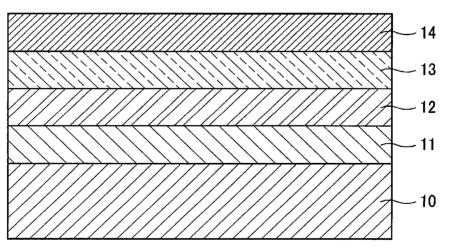
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[Continued on next page]

(54) Title: CONDUCTIVE POLYMER COMPOUND AND ORGANIC PHOTOELECTRIC DEVICE INCLUDING SAME

[FIG. 1a]



(57) Abstract: The present invention relates to a conductive polymer compound and an organic photoelectric device including the same. The conductive polymer compound includes a conductive polymer, and repeating units by of the specific Chemical Formulae. The conductive polymer compound of the present invention can suppress moisture absorption capability and prevent problems that may be caused by high acidity in an organic photoelectric device by decreasing acidity in the presence of a water-soluble polymer. Also, the conductive polymer compound of the present invention can reduce agglomeration between molecules when a water-soluble polymer is mixed with a colloid-type polymer. Thus, it can be used for preparing a conductive polymer compound composition with excellent thin film characteristics and storage stability. Particularly, the conductive polymer compound composition can improve luminous efficiency and life-span characteristics of an organic light emitting diode.



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[Invention Title]

CONDUCTIVE POLYMER COMPOUND AND ORGANIC PHOTOELECTRIC DEVICE INCLUDING SAME

[Technical Field]

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The present invention relates to a conductive polymer compound and an organic photoelectric device including the same. More particularly, the present invention relates to a conductive polymer compound having excellent thin film characteristics and storage stability, and being capable of improving luminous efficiency and life-span characteristics of an organic photoelectric device, and an organic photoelectric device including the same.

[Background Art]

A photoelectric device is a device for transforming photo energy to electrical energy, and conversely, for transforming electrical energy to photo-energy. The photoelectric device may be exemplified by an organic light emitting diode, a solar cell, a transistor, and so on.

Particularly, among these photoelectric devices, the organic light emitting device employing organic light emitting diodes (OLED) has recently drawn attention due to the increase in demand for flat panel displays (FPD).

In the field of photoelectric devices including the organic light emitting diode, researchers are studying the formation of a conductive polymer layer in order to improve efficiency of a photoelectric device by smoothly transferring charges generated in an electrode, that is, holes and electrons, to the photoelectric device.

An organic light emitting diode is an active light emitting display device taking advantage of a phenomenon in which electrons and holes are combined in an organic layer while emitting light when an electrical current flows to a fluorescent or phosphorescent organic compound thin film (hereinafter referred to as an organic layer). The organic light emitting diode does not use a single light emission layer as the organic layer but employs a multi-layer structure including a hole injection layer (HIL) using a conductive polymer, a light emission layer, and an electron injection layer (EIL) to improve efficiency and decrease a driving voltage.

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The multi-layer structure can be simplified by making one layer perform a plurality of functions. One of the simplest OLED structures is a structure where an organic layer performing all functions including the function of a light emission layer is interposed between two electrodes.

However, to substantially increase luminance, an electron injection layer (EIL) or a hole injection layer should be introduced to an electrical light emitting assembly.

The literature discloses many organic compounds capable of transferring charges (which are holes and electrons) to be used by an electron injection layer (EIL) or a hole injection layer (HIL). As examples, European Patent Publication No. 387 715, U.S. Patent No. 4,539,507, U.S. Patent No. 4,720,432, and U.S. Patent No. 4,769,292 disclose organic compounds and their usages.

Particularly, Baytron-P, which is commercially available in the market by the Bayer AG Company, is a representative organic compound capable of

transferring charges and is used for soluble organic electro-luminescence (EL).

Baytron-P is a kind of PEDOT (poly(3,4-ethylene dioxythiophene))-PSS (poly (4-styrene sulfonate)) aqueous solution.

PEDOT-PSS is widely used for fabrication of an organic light emitting diode. It is used to form a hole injection layer (HIL) by spin-coating it on an indium tin oxide (ITO) electrode. The PEDOT-PSS has a structure as shown in the following Chemical Formula A.

[Chemical Formula A]

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The PEDOT-PSS expressed in the above Chemical Formula A is a simple ion composite of a polyacid, which is poly(4-styrene sulfonate) (PSS), and a conductive polymer, which is poly(3,4-ethylenedioxythiophene) (PEDOT). It has a structure in which PEDOT is doped with a water-soluble polyacid.

However, when the hole injection layer (HIL) is formed using the PEDOT-PSS conductive polymer composition, the PSS is deteriorated and dedoped due to its property of absorbing moisture, or a part of the PSS may be decomposed through a reaction with electrons to thereby emit a material such as

a sulfate. The emitted material may be diffused into a neighboring organic layer, such as a light emission layer. The diffusion of a material originating from the hole injection layer (HIL) into the light emission layer causes exciton quenching to thereby decrease the efficiency and life-span of the organic light emitting diode.

To overcome the drawbacks, U.S. Patent Publication No. 2005/0251597 and Korean Patent Publication No. 2006-0120378 disclose using a conductive polymer doped with an ionomer where both main chains and branch chains have substituted fluorine groups.

[Chemical Formula B]

$$\begin{array}{c|c} & & & & \\ & &$$

Such materials shown in the above Chemical Formula B have most of their carbon groups in the main chain and branch chain substituted with fluorine groups. Thus, the time that they are dispersed in water is short, and they form colloid-type particles. When a conductive polymer is prepared by using these materials, the particles agglomerate severely even with a minute increase in the length of the repeating unit of the conductive polymer. Also, when they are used for forming a thin film through a spin coating process, the generated thin film has poor uniformity.

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[Detailed Description]

[Technical Problem]

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An exemplary embodiment of the present invention provides a conductive polymer compound having excellent thin film characteristics and storage stability, and being capable of improving luminous efficiency and life-span characteristics of an organic photoelectric device.

Another embodiment of the present invention provides a conductive polymer compound composition including the conductive polymer compound.

A further embodiment of the present invention provides a polymer organic layer fabricated using the conductive polymer compound.

A further embodiment of the present invention provides an organic photoelectric device including the polymer organic layer, and thereby having excellent high efficiency and a long life-span.

The embodiments of the present invention are not limited to the above technical purposes, and a person of ordinary skill in the art can understand other technical purposes.

[Technical Solution]

According to a first embodiment of the present invention, provided is a conductive polymer compound that includes: a conductive polymer; a first repeating unit of the following Chemical Formula 1; a second repeating unit of the following Formula 2; and a third repeating unit of the following Chemical Formula 3 and/or Chemical Formula 4.

[Chemical Formula 1]

$$A$$
 B

[Chemical Formula 2]

In the above Formulae 1 and 2,

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when the number of moles of Chemical Formula 1 is m1 and the number of moles of Chemical Formula 2 is n1, the ratio of m1 and n1 is $0.0001 \le n1/m1 \le 1$;

A is selected from the group consisting of a substituted or unsubstituted alkyl, a substituted or unsubstituted heteroalkyl, a substituted or unsubstituted alkoxy, a substituted or unsubstituted heteroalkoxy, a substituted or unsubstituted arylalkyl, a substituted or unsubstituted arylalkyl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heteroarylalkyl, a substituted or unsubstituted heteroaryloxy, a substituted or unsubstituted or unsubstituted or unsubstituted heteroaryloxyl, a substituted or unsubstituted or unsubstituted or unsubstituted or unsubstituted or unsubstituted alkylester, a substituted or unsubstituted arylester, and a substituted or unsubstituted heteroarylester;

B is an ion pair of a cation and an anion, where the cation is selected from the group consisting of a metal ion selected from the group consisting of H⁺, Na⁺, K⁺, Li⁺, Mg²⁺, Zn²⁺, and Al³⁺, and NR₃⁺ where R is H or a substituted or unsubstituted alkyl, and an organic ion of CH₃(-CH₂-)_pO⁺, where p ranges from 1 to 50, and the anion is selected from the group consisting of PO₃²⁻, SO₃⁻, COO⁻, I⁻, and CH₃COO⁻; and

C is halogen-containing substituted or unsubstituted hydrocarbon.

[Chemical Formula 3]

$$\begin{array}{c|c} + \text{CF-CF}_2 \\ \hline | & \text{CF}_2 - \text{CF}_2 \\ \hline | & \text{CF}_2 - \text{CF}_2 \\ \hline | & \text{CF}_3 \\ \end{array} \\ \begin{array}{c|c} + \text{CF}_2 - \text{CF}_2 \\ \hline | & \text{N}_1 \\ \hline | & \text{CF}_2 - \text{CF}_2 \\ \hline | & \text{N}_1 \\ \hline | & \text{CF}_3 \\ \end{array}$$

10 [Chemical Formula 4]

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$$\begin{array}{c|c} + \text{CF-CF}_2 \\ \hline + \text{CF-CF}_2 \\ \hline \\ \text{(O-CF}_2 - \text{CF}_2 \\ \hline \\ \text{CF}_3 \\ \end{array} \\ \begin{array}{c|c} \text{(O-CF}_2 - \text{CF}_2 \\ \hline \\ \text{y2} \\ \end{array} \\ \text{Y2} \\ \end{array}$$

In the above Chemical Formulae 3 and 4, $0 < m2 \le 10,000,000, 0 \le n2 < 10,000,000,$

 $0 < m3 \le 10,000,000, 0 \le n3 < 10,000,000,$

x1, x2, y1, and y2 are independently integers ranging from 0 to 20, and
Y1 and Y2 are independently -COO⁻M⁺, -SO₃M⁺, or -PO₃²⁻(M⁺)₂, where
M⁺ is Na⁺, K⁺, Li⁺, H⁺, or NH₄⁺.

According to a second embodiment of the present invention, provided is a conductive polymer compound composition including the conductive polymer

compound, and a solvent.

According to a third embodiment of the present invention, provided is a polymer organic layer fabricated using the conductive polymer compound composition.

According to a fourth embodiment of the present invention, provided is an organic photoelectric device including the polymer organic layer fabricated using the conductive polymer compound composition.

[Advantageous Effects]

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The conductive polymer compound of the present invention can suppress the moisture absorption property, and since the acidity is decreased by the water-soluble polymer, it is possible to prevent a problem that may be caused by high acidity in an organic photoelectric device. Also, since the conductive polymer compound of the present invention can reduce agglomeration among molecules when a water-soluble polymer is mixed with a colloid-type polymer, it is possible to prepare a conductive polymer compound composition with excellent thin film characteristics and storage stability. Therefore, the conductive polymer compound can improve the luminous efficiency and life-span characteristics of an organic light emitting diode that is fabricated therewith.

[Brief Description of the Drawings]

FIGS. 1A to 1D are schematic cross-sectional views of organic light emitting diodes according to the present invention.

FIGS. 2 to FIG. 4 respectively show AFM measurement results of the

organic layers fabricated using the polymer compound compositions according to Example 2 and Comparative Example 1.

FIG. 5 is a graph showing efficiency characteristics of the organic light emitting diode according to Example 3 and Comparative Example 3.

FIG. 6 is a graph showing power characteristics of the organic light emitting diodes according to Example 3 and Comparative Example 3.

<Description of Reference Numerals Indicating Primary Elements in the Drawings>

10: first electrode 11: buffer layer

12: light emission layer 13: hole blocking layer

14: second electrode 15: electron transport layer (ETL)

16: hole transport layer (HTL)

[Best Mode]

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Exemplary embodiments of the present invention will hereinafter be described in detail. However, these embodiments are only exemplary, and the present invention is not limited thereto.

As used herein, when specific definition is not provided, the term "alkyl" refers to a C1-C30 alkyl, the term "heteroalkyl" refers to a C1-C30 heteroalkyl, the term "alkoxy" refers to a C1-C30 alkoxy, the term "heteroalkoxy" refers to a C1-C30 heteroalkoxy, the term "aryl" refers to a C6-C30 aryl, the term "arylalkyl" refers to a C6-C30 arylalkyl, the term "aryloxy" refers to a C6-C30 aryloxy, the term "a heteroaryl" refers to a C2-C30 heteroaryl, the term "heteroarylalkyl" refers to a C2-C30 heteroarylalkyl, the term "heteroaryloxy" refers to a C2-C30

heteroaryloxy, the term "cycloalkyl" refers to a C5-C20 cycloalkyl, the term "heterocycloalkyl" refers to a C2-C30 heterocycloalkyl, the term "alkylester" refers to a C2-C30 alkylester, the term "heteroalkylester" refers to a C1-C30 heteroalkylester, the term "arylester" refers to a C7-C30 arylester, and the term "heteroarylester" refers to a C6-C30 heteroarylester.

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As used herein, when specific definition is not provided, the term "substituted" refers to one substituted with at least a substituent including a halogen (F, Br, Cl, or I), a hydroxy, a nitro, a cyano, an amino (-NH₂, -NH(R), or -N(R')(R"), where R, R', and R" are independently a C1 to C10 alkyl), an amidino, a hydrazine, or a hydrazone, a carboxyl, a substituted or unsubstituted alkyl, a substituted or unsubstituted aryl, a substituted or unsubstituted cycloalkyl, a substituted or unsubstituted heteroaryl, or a substituted or unsubstituted heterocycloalkyl.

An alkyl may be a linear or branched alkyl such as methyl, ethyl, propyl, isobutyl, sec-butyl, tert-butyl, pentyl, iso-amyl, hexyl, and the like.

A heteroalkyl refers to an alkyl including at least one heteroatom, and preferably 1 to 5 heteroatoms such as oxygen (O), sulfur (S), nitrogen (N), phosphorus (P), and the like, in its main chain instead of carbon.

An alkoxy includes methoxy, ethoxy, propoxy, isobutyloxy, sec-butyloxy, pentyloxy, iso-amyloxy, hexyloxy, and the like.

An aryl refers to carbocycle aromatic molecules including at least one of aromatic cycles, and the cycles may be bound as a pendent group or fused. Examples of the aryl include aromatic groups such as phenyl, naphthyl,

tetrahydronaphthyl, and the like.

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An arylalkyl refers to an aryl including a lower alkyl, for example C1 to C5 radicals such as methyl, ethyl, propyl, and the like. Specific examples of the arylalkyl include benzylmethyl, phenylethyl, and the like.

An aryloxy refers to an -O-aryl radical, where the aryl is the same as described above. Examples of the aryloxy include phenoxy, naphthoxy, anthracenyloxy, phenanthrenyloxy, fluorenyloxy, indenyloxy, and the like, and at least one of hydrogen atoms of the aryloxy may be substituted with an alkyl.

A heteroaryl refers to C5 to C30 cyclic aromatic compounds including 1 to 3 hetero atoms selected from the group consisting of N, O, P, and S, with the remaining being carbon atom cycles. The cycles may be bound as a pendent group or fused.

A heteroarylalkyl refers to a heteroaryl including a lower alkyl, and the heteroaryl of the heteroarylalkyl is the same as above-described.

A heteroaryloxy refers to an -O-heteroaryl radical where the heteroaryl is the same as above-described.

A cycloalkyl refers to a C5 to C30 monovalent monocyclic system.

A heterocycloalkyl refers to a C5 to C30 monovalent monocyclic compound that is a cycloalkyl including 1 to 3 heteroatoms selected from N, O, P, or S.

A heteroalkoxy refers to a carbon compound where one side of -O- is connected to 1 to 3 heteroatoms selected from N, O, P, or S.

An alkylester refers to a -COO- alkyl radical where the alkyl is the same

as above-described.

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A heteroalkylester refers to a -COO- heteroalkyl radical where the heteroalkyl is the same as above-described.

An arylester and heteroarylester refer to -COO- aryl or heteroaryl radicals, and the aryl and heteroaryl are the same as above-described. Examples of the heteroarylester include moieties derived from oxadiazole, furan, pyrrol, pyrimidine, and the like.

According to a first embodiment of the present invention, provided is a conductive polymer compound that includes: a conductive polymer; a first repeating unit of the following Chemical Formula 1; a second repeating unit of the following Chemical Formula 2; and a third repeating unit of the following Chemical Formula 3 and/or Chemical Formula 4. The first and second repeating units exist in the form of a copolymer, and the third repeating unit exists in the form of a compound. The copolymer and the third repeating unit compound exist as a mixture, and the copolymer and the third repeating unit compound may be applied to dope the conductive polymer through ion coupling and function as a dopant, individually, or they may be present as a physical mixture with a conductive polymer.

The copolymer may be a block copolymer with a repeating unit repeating regularly, or it may be a random copolymer with a repeating unit repeating randomly.

[Chemical Formula 1]

$$A$$
 B

[Chemical Formula 2]

$$\left\langle \begin{array}{c} \\ \\ \\ \end{array} \right\rangle_{n1}$$

5 In the above Formulae 1 and 2,

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when the number of moles of Chemical Formula 1 is m1 and the number of moles of Chemical Formula 2 is n1, the ratio of m1 and n1 is $0.0001 \le n1/m1 \le 1$;

A is selected from the group consisting of a substituted or unsubstituted alkyl; a substituted or unsubstituted heteroalkyl, a substituted or unsubstituted alkoxy, a substituted or unsubstituted heteroalkoxy, a substituted or unsubstituted arylalkyl, a substituted or unsubstituted arylalkyl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heteroarylalkyl, a substituted or unsubstituted heteroaryloxy, a substituted or unsubstituted or unsubstituted or unsubstituted heteroaryloxy, a substituted or unsubstituted or unsubstituted or unsubstituted or unsubstituted alkylester, a substituted or unsubstituted arylester, and a substituted or unsubstituted heteroalkylester, a substituted or unsubstituted arylester, and a substituted or unsubstituted heteroarylester;

B is ion-pair of a cation and an anion, where the cation is selected from the group consisting of a metal ion selected from the group consisting of H^+ , Na^+ , K^+ , Li^+ , Mg^{2+} , Zn^{2+} , and Al^{3+} , and NR_3^+ where R is H or a substituted or unsubstituted alkyl, and an organic ion of $CH_3(-CH_2-)_pO^+$, where p ranges from 1 to 50, and the anion is selected from the group consisting of PO_3^{2-} , SO_3^- , COO^- , I^- , and CH_3COO^- ; and

C is halogen-containing substituted or unsubstituted hydrocarbon. The hydrocarbon refers to a C2 to C30 hydrocarbon, and the substituent refers to nitrogen, phosphor, sulfur, silicon, or oxygen. The halogen refers to fluorine, chlorine, bromine, iodine, or astatine, and specifically, the halogen refers to fluorine. The C is a structure for applying a morphological change to the polymer copolymer by a dipole-dipole interaction or a hydrophobic group.

The C may be a functional group of the following Chemical Formulae 8 to 12:

[Chemical Formula 8]

[Chemical Formula 9]

-C₆F₁₄

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[Chemical Formula 10]

[Chemical Formula 11]

5 [Chemical Formula 12]

[Chemical Formula 3]

$$+CF-CF_{2}|_{m2}+CF_{2}-CF_{2}|_{n2}$$
 $(O-CF_{2}-CF)_{x1}+(O-CF_{2}-CF_{2})_{y1}$ Y1
 CF_{3}

[Chemical Formula 4]

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$$\begin{array}{c|c} + \text{CF-CF}_2 \middle|_{m3} \middle| \text{CF}_2 - \text{CF}_2 \middle|_{n3} \\ & | \\ \text{O-CF}_2 - \text{CF}_{\frac{1}{2} \times 2} \middle| \text{O-CF}_2 - \text{CF}_2 \middle|_{\frac{1}{2} \times 2} \text{Y2} \end{array}$$

In the above Chemical Formulae 3 and 4, m2 and n2 are independently 0 < m2 \le 10,000,000, 0 \le n2 <10,000,000,

m3 and n3 are independently $0 < m3 \le 10,000,000, 0 \le n3 < 10,000,000,$ x1, x2, y1, and y2 are independently integers ranging from 0 to 20, and Y1 and Y2 are independently $-COO^-M^+$, $-SO_3M^+$, or $-PO_3^{2-}(M^+)_2$, where M^+ is Na^+ , K^+ , Li^+ , H^+ , or NH_4^+ .

The conductive polymer of the conductive polymer compound may be a generally used conductive polymer for an organic photoelectric device. The conductive polymer may a polymer obtained from polymerization of at least one of a monomer selected from: polyphenylene; polyphenylenevinylene; monomers of aniline or derivatives thereof having the following Chemical Formula 5; monomers of pyrrol, thiophene, or derivatives thereof having the following Chemical Formula 6; and cyclic monomers having the following Chemical Formula 7.

[Chemical Formula 5]

$$R_a$$
 R_b
 NH
 R_c
 R_d

[Chemical Formula 6]

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In the above Formulae 5 and 6,

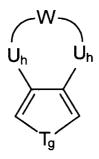
E is NR where R is H, or a C1 to C7 lower alkyl,

R_a, R_b, R_c, and R_d are selected from the group consisting of independently hydrogen; a substituted or unsubstituted alkyl; a substituted or unsubstituted heteroalkyl; a substituted or unsubstituted alkoxy; a substituted or unsubstituted aryl; a substituted or unsubstituted arylalkyl; a substituted or unsubstituted aryloxy; a substituted or unsubstituted arylamine; a substituted or unsubstituted pyrrol; a substituted or unsubstituted or unsubstituted heteroaryl; a substituted or unsubstituted or unsubstituted heteroaryl; a substituted or unsubstituted or unsubstituted or unsubstituted or unsubstituted or unsubstituted or unsubstituted alkylester; a substituted or unsubstituted alkylester; a substituted or unsubstituted o

arylester; and a substituted or unsubstituted heteroarylester, and

 R_e and R_f are independently selected from the group consisting of NR where R is H or a C1 to C7 lower alkyl; a C1-C20 alkyl including a heteroatom selected from the group consisting of N, O, S, and P; a C6-C20 aryl including a heteroatom selected from the group consisting of N, O, S, and P; an alkyl; an aryl; an alkoxy; a C1-C30 heteroalkyl; a heteroalkoxy; an arylalkyl; an aryloxy; a C6-C30 arylamine; a C6-C30 pyrrol; a C6-C30 thiophene; a heteroaryl; a heteroarylalkyl; a heteroaryloxy; a C5-C20 cycloalkyl; a heterocycloalkyl; an alkylester; a heteroalkylester; an arylester; and a heteroarylester.

[Chemical Formula 7]



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In the above Formula 7,

T is NR where R is H or a C1 to C7 lower alkyl; a C1-C20 alkyl including a heteroatom selected from the group consisting of N, O, S, and P; a C6-C20 aryl including a heteroatom selected from the group consisting of N, O, S, and P,

U is NR where R is H or a C1 to C7 lower alkyl; a C1-C20 alkyl including a heteroatom selected from the group consisting of N, O, S, and P; a C6-C20 aryl including a heteroatom selected from the group consisting of N, O, S, and P,

g and h are independently 0 to 9,

W is $-(CH_2)_x$ - CR_gR_h - $(CH_2)_y$ where R_g and R_h are independently selected from the group consisting of H, a C1 to C20 alkyl radical, a C6 to C14 aryl radical, and $-CH_2$ -ORi, where R_i is selected from the group consisting of H, a C1 to C6 alkyl acid, a C1-C6 alkylester, a C1 to --C6 heteroalkyl acid, and a C1 to C6 alkylsulfonic acid, and

x and y are independently 0 to 5.

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For example, the states where the conductive polymers of the Chemical Formulae 5 to 7 are doped with the first repeating unit represented as the Chemical Formula 1, the second repeating unit represented as the Chemical Formula 2, and the third repeating unit represented as the Chemical Formula 3 and/or 4 are the states where the substituent B of Chemical Formula 1 and the substituents Y1 and Y2 of Chemical Formulae 3 and 4 are coupled with NH, E, and T of the Chemical Formulae 5 to 7.

The conductive polymer compound of the present invention including the first repeating unit represented as Chemical Formula 1 and the second repeating unit represented as Chemical Formula 2, and the third repeating unit represented as the Chemical Formula 3 and/or Chemical Formula 4 and the conductive polymer has an advantage of excellent filtering performance and thin film uniformity as the water-soluble repeating units of the Chemical Formulae 1 and 2 inhibit the colloidal structures of the Chemical Formulae 3 and 4 to thereby drastically reduce the agglomeration phenomenon. Also, the conductive polymer compound of the present invention has excellent storage stability because it can reduce the moisture absorption and acidity by using the first and

second repeating units, which are water-soluble polyacids with a substituted halogen structure in their branch chain, and the third repeating unit, which is a polymer ionomer with fluoro groups substituted at more than 70mol%. Also, an organic photoelectric device including the conductive polymer compound of the present invention has high efficiency and a long life-span.

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The mixing ratio of the conductive polymer and the first to third repeating units may range from 50:50 wt% to 1:99 wt%, and more specifically from 1:99 wt% to 20:80 wt%. When the conductive polymer is included in the range of 1 to 50 wt%, the agglomeration phenomenon of the conductive polymer composition can be suppressed and thus no precipitation is generated in a solvent, which is desirable. In other words, the content of the conductive polymer should be at least 1 wt% to acquire conductivity applicable to an organic light emitting diode. When the content of the conductive polymer is less than 1 wt%, the conductivity is too low and the hole injection characteristic becomes drastically deteriorated. Therefore, appropriate dispersion and conductivity can be acquired when the content of the conductive polymer falls in the range of 1 to 50 wt%.

The above structures are only examples presented to help understanding of the present invention, and the above structures do not limit the repeating units shown in Chemical Formulae 1 to 4 and or the conductive polymer of the present invention.

A second embodiment of the present invention provides a conductive polymer compound composition including the conductive compound and

solvent.

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Any solvent that is capable of dissolving the conductive polymer can be used as a solvent for preparing the conductive polymer compound composition of the present invention. The solvent may be at least one selected from the group consisting of water, alcohol, dimethyl formamide (DMF), dimethylsulfoxide, toluene, xylene, and chlorobenzene.

In the conductive polymer compound composition of the present invention, the content of solid components, including a conductive polymer compound and/or a cross-linking agent, may range from 0.5 to 30 wt%, and more specifically from 0.5 to 10 wt%. When the content of the solid components falls in the range, the content of the solid component becomes appropriate and thus the concentration of the composition becomes appropriate as well. Since the concentration is appropriate, a thin film can be formed with a good shape, and this makes the process excellent.

Also, the conductive polymer compound composition of the present invention may further include a cross-linking agent to improve the cross-linking performance of the conductive polymer compound. The cross-linking agent may be a physical and/or chemical cross-linking agent.

The physical cross-linking agent used in the present invention is a material for physically cross-linking polymer chains without chemical coupling. The physical cross-linking agent refers to a low-molecular or polymer compound containing a hydroxyl group (-OH).

Examples of the physical cross-linking agent include low molecular

compounds such as glycerol and butanol, and polymer compounds such as polyvinyl alcohol, polyethyleneglycol. Further, polyethyleneimine and polyvinylpyrrolidone can be used as the physical cross-linking agent.

The content of the added physical cross-linking agent may range from 0.001 to 5 parts by weight with respect to 100 parts by weight of the conductive polymer compound, and more specifically from 0.1 to 3 parts by weight.

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When the content of the physical cross-linking agent falls in the range, the cross-linking agent performs efficiently, and the thin film morphology of the conductive polymer layer can be effectively maintained.

A chemical cross-linking agent is a material for chemically cross-linking polymer chains, and is a chemical material that is available for in-situ polymerization and is capable of forming an interpenetrating polymer network (IPN).

As for the chemical cross-linking agent, silane materials are often used, and for example, tetraethyloxysilane (TEOS) is used as a chemical cross-linking agent. Further, polyaziridine, melamine materials, and epoxy materials can be used as the chemical cross-linking agent.

The content of the chemical cross-linking agent may range from 0.001 to 50 parts by weight with respect to 100 parts by weight of a conductive polymer containing an organic ion salt, and more specifically from 1 to 10 parts by weight.

When the content of the chemical cross-linking agent falls in the range, the cross-linking agent performs effectively and does not affect the conductive polymer to thereby maintain sufficient conductivity.

When a mixture of the physical cross-linking agent and the chemical cross-linking agent is used, the mixture can be prepared properly within their content ranges described above.

The conductive polymer compound composition of the present invention may further include an organic ion salt.

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The organic ion salt transfers electrons of the conductive polymer in a device to thereby improve current stability, life-span, and electrochemical stability. Examples of the organic ion salt include imidazolium salt, thiazolium salt, pyridinum salt, pyrrolidinum salt, and piperidinum salt.

The content of the organic ion salt may range from 0.001 to 10 parts by weight with respect to 100 parts by weight of a conductive polymer compound, and more specifically from 0.01 to 3 parts by weight.

When the content of the organic ion salt falls in the range of 0.001 to 10 parts by weight with respect to 100 parts by weight of a conductive polymer compound, there is an advantage in that the physical properties of the conductive polymer composition are not changed.

When the conductive polymer compound composition of the present invention is used for fabrication of an organic photoelectric device, it is coated on a substrate. Herein, most of its solvent is removed and the conductive polymer compound composition remains as a conductive polymer organic layer. In this way, a third embodiment of the present invention provides a polymer organic layer formed by using the conductive polymer compound composition.

A fourth embodiment of the present invention provides an organic

photoelectric device including a conductive polymer organic layer formed by using a conductive polymer compound composition. The photoelectric device may be exemplified by organic light emitting diodes, organic solar cells, organic transistors, organic memory device, and the like.

Hereafter, the way in which a conductive polymer composition of the present invention is applied to an organic light emitting diode will be described.

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In an organic light emitting diode, the conductive polymer composition is used in a charge injection layer, that is, a hole or electron injection layer (EIL). The light emitting intensity and the efficiency of the organic light emitting diode are increased by uniformly and efficiently injecting holes and electrons.

Also, in case of an organic solar cell, the conductive polymer layer composition of the present invention is used as an electrode or an electrode buffer layer to thereby increase quantum efficiency. In case of an organic transistor, it can be used as an electrode material in a gate and/or source-drain electrode.

Among the organic photoelectric devices described above, a structure of an organic light emitting diode using the conductive polymer layer composition of the present invention and a fabrication method thereof will be described hereafter.

FIGS. 1A to 1D are schematic cross-sectional views of organic light emitting diodes according to the present invention.

The organic light emitting diode of FIG. 1A includes a light emission layer 12 formed above a first electrode 10, a hole injection layer (HIL) 11 including the

conductive polymer composition of the present invention disposed between the first electrode 10 and the light emission layer, a hole blocking layer (HBL) 13 on top of the light emission layer 12, and a second electrode 14 on top of the hole blocking layer (HBL) 13. The hole injection layer (HIL) 11 may be referred to as a buffer layer.

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The organic light emitting diode of FIG. 1B has the same stacking structure as that of FIG. 1A, except that an electron transport layer (ETL) 15 is formed instead of the hole blocking layer (HBL) 13 on top of the light emission layer 12.

The organic light emitting diode of FIG. 1C has the same stacking structure as that of FIG. 1A, except that a dual layer of the hole blocking layer(HBL) 13 and the electron transport layer ETL 15 sequentially stacked therein is formed on top of the light emission layer 12.

The organic light emitting diode of FIG. 1D has the same structure as that of FIG. 1C, except that a hole transport layer (HTL) 16 is formed between the hole injection layer (HIL) 11 and the light emission layer 12. Herein, the hole transport layer (HTL) 16 suppresses permeation of impurities from the hole injection layer (HIL) 11 to the emission layer 12.

The organic light emitting diode having the stacking structure of FIGS. 1A to 1D can be fabricated through a general fabrication method.

First, a patterned first electrode 10 is formed on a substrate (not shown).

The substrate is a generally-used substrate for an organic light emitting diode,
and may be a glass substrate or a transparent plastic substrate having excellent

general transparence, surface smoothness, handling ease, and water repellency. The substrate has a thickness of 0.3 to 1.1 mm.

Materials for forming the first electrode 10 are not specifically limited. When the first electrode is a cathode, the cathode is formed using conductive metals or oxides thereof that easily performs hole injection. Examples of the materials include indium tin oxide (ITO), indium zinc oxide (IZO), nickel (Ni), platinum (Pt), gold (Au), iridium (Ir), and so on.

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The substrate including the first electrode 10 is cleaned and is subjected to UV ozone treatment. An organic solvent such as isopropanol (IPA), acetone, and the like may be used for the cleaning process.

The hole injection layer (HIL) 11, which is a buffer layer including the conductive polymer compound composition of the present invention, is formed on the first electrode 10 of the cleaned substrate. The formation of the hole injection layer (HIL) 11 reduces contact resistance between the first electrode 10 and the light emission layer 12, and at the same time improves hole transfer capability of the first electrode 10 toward the light emission layer 12. Thus, the driving voltage and life-span characteristics of the device can be generally improved.

The hole injection layer HIL 11 is formed by dissolving the conductive polymer compound of the present invention, and optionally a cross-linking agent and/or organic ion salt, in a solvent to thereby prepare a composition for forming a hole injection layer (HIL), coating the upper part of the first electrode 10 with the prepared composition for forming a hole injection layer (HIL) through a

spin-coating process, and drying the composition.

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Herein, the thickness of the hole injection layer (HIL) 11 may range from 5 to 200nm, and more specifically from 20 to 100nm. When the thickness of the hole injection layer (HIL) 11 falls in the range, the hole injection can be sufficiently performed, and the light transmission can be maintained at a good level.

A light emission layer 12 is disposed on the hole injection layer (HIL) 11. The light emission layer material is not specifically limited. Specific examples of the material include an oxadiazole dimer dye (Bis-DAPOXP)), spiro compounds (Spiro-DPVBi, Spiro-6P), triarylamine compounds, bis(styryl)amine (DPVBi, DSA), Flrpic, CzTT, anthracene, TPB, PPCP, DST, TPA, OXD-4, BBOT, and AZM-Zn (blue-emitting); coumarin 6, C545T, quinacridone, and Ir(ppy)3 (green-emitting); DCM1, DCM2, Eu(thenoyltrifluoroacetone)3 (Eu(TTA)3 and 1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran: DCJTB) (red-emitting), and the like.

In addition, polymer light emitting materials may be used. The polymer light emitting materials include polymers such as phenylene-based, phenylene vinylene-based, thiophene-based, fluorine-based, and spiro-fluorene-based polymers or nitrogen-included aromatic compounds, but are not limited thereto.

The thickness of the emission layer 12 may range from 10 to 500nm, and more specifically from 50 to 120nm. When the thickness of the emission layer 12 falls in the range, leakage current amount and driving voltage increase can be appropriately maintained and this effectively increases the life-span.

A dopant may be added to the composition for forming the light emission layer.

The content of the dopant varies according to the material used for forming the light emission layer, but generally the content of the dopant may range from 30 to 80 parts by weight with respect to 100 parts by weight of the material for forming a light emission layer (total weight of host and dopant).

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When the content of the dopant falls in the range, the light emitting characteristics of the EL device can be effectively maintained. Examples of the dopant include an arylamine, peril-based compounds, pyrrol-based compounds, hydrazone-based compounds, carbazole-based compounds, stilbene-based compounds, starburst-based compounds, and oxadiazole-based compounds.

A hole transport layer (HTL) 16 may be selectively formed between the hole injection layer (HIL) 11 and the emission layer 12.

A material for forming the hole transport layer (HTL) is not specifically limited. However, it may include at least one selected from the group consisting of compounds including a carbazole and/or an arylamine, which transport holes, phthalocyanine-based compounds, and triphenylene derivatives.

More specifically, the hole transport layer (HTL) material includes at least one material selected from the group consisting of 1,3,5-tricarbazolylbenzene, 4,4'-biscarbazolylbiphenyl, polyvinylcarbazole, m-biscarbazolylphenyl, 4,4'-biscarbazolyl-2,2'-dimethylbiphenyl, 4,4',4"-tri(N-carbazolyl)triphenylamine, 1,3,5-tri(2-carbazolylphenyl)benzene,

1,3,5-tris(2-carbazolyl-5-methoxyphenyl)benzene, bis (4-carbazolylphenyl)silane, N,N'-bis(3-methylphenyl)-N,N'-diphenyl-[1,1-biphenyl]-4,4'diamine (TPD), $(\alpha-NPD)$, benzidine N,N'-di(naphthalen-1-yl)-N,N'-diphenyl N,N'-diphenyl-N,N'-bis(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB), IDE320 Ltd.) Co., Kosan (Idemitsu poly(9.9-dioctylfluorene-co-N-(4-butylphenyl)diphenylamine) (TFB), and poly(9,9-dioctylfluorene-co-bis-N,N-phenyl-1,4-phenylenediamine) (PFB), but is not limited thereto.

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The hole transport layer (HTL) 16 may have a thickness ranging from 1 to 100 nm, and more specifically from 5 to 50 nm. When the thickness of the hole transport layer (HTL) 16 falls in the range, the hole transport layer (HTL) 16 can maintain sufficient hole transport capability and an appropriate level of driving voltage.

A hole blocking layer 13 and/or an electron transport layer (ETL) 15 may be disposed on the light emission layer 12 through a deposition or spin coating method. The hole blocking layer 13 prevents excitons formed in a light emitting material from transferring to the electron transport layer (ETL) 15, or it prevents holes from transferring to the electron transport layer (ETL) 15.

Examples of a material for forming the hole blocking layer 13 include phenanthroline-based compounds (e.g., BCP of the UDC Company,) represented as Chemical Formula 13, imidazole-based compounds represented as Chemical Formula 14, triazole-based compounds represented as Chemical Formula 15, oxadiazole-based compounds (e.g., a commercial product PBD)

represented as Chemical Formula 16, and an aluminum complex (e.g., BAlq of the UDC Company) represented as Chemical Formula 17.

The thickness of the hole blocking layer may range from 5 to 100 nm, and the thickness of the electron transport layer (ETL) may range from 5 nm to 100 nm. When the thicknesses fall in the above ranges, the electron transport capability and the hole suppression capability can be effectively maintained.

[Chemical Formula 13]

[Chemical Formula 14]

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[Chemical Formula 15]

[Chemical Formula 16]

[Chemical Formula 17]

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The electron transport layer ETL 15 includes a material selected from oxazole-based compounds, isooxazole-based compounds, triazole-based compounds, isothiazole-based compounds, oxadiazole-based compounds, thiadiazole-based compounds, perylene-based compounds of Chemical Formula 18, aluminum complexes (Alq3 (tris(8-quinolinolato)-aluminum)) of

Chemical Formula 19, BAlq of Chemical Formula 20, SAlq of Chemical Formula 21, Almq3 of Chemical Formula 22, gallium complexes (Gaq'2OPiv) of Chemical Formula 23, Gaq'2OAc of Chemical Formula 24, 2(Gaq'2) of Chemical Formula 25, and the like.

5 [Chemical Formula 18]

[Chemical Formula 19]

[Chemical Formula 20]

[Chemical Formula 21]

5 [Chemical Formula 22]

[Chemical Formula 23]

[Chemical Formula 24]

5 [Chemical Formula 25]

The second electrode 14 is disposed on the stacking structure fabricated as above, and the resulting material is sealed to thereby complete the fabrication

of an organic light emitting diode.

The materials for forming the second electrode 14 are not specifically restricted, but the materials may be metals with a small work function, such as Li, Cs, Ba, Ca, Ca/Al, LiF/Ca, LiF/Al, BaF₂/Ca, Mg, Ag, Al, or alloys thereof, or multi-layers thereof. The thickness of the second electrode 14 may range from 50 to 3000 Å.

The fabrication of an organic light emitting diode suggested in the present invention does not require a specific apparatus or method, and the organic light emitting diode of the present invention may be fabricated through an organic light emitting diode fabrication method using a typical conductive polymer composition.

[Mode for Invention]

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Hereinafter, in the following examples and comparative examples, a conductive polymer for an organic photoelectric device according to embodiments of the present invention can suppress moisture absorption, and reduce polyacid concentration in a molecule and intermolecular agglomeration resulting in improvement of thin film characteristics and storage stability and efficiency and life-span characteristics of an organic photoelectric device. A person having ordinary skills in this art can sufficiently understand parts of the present invention that are not specifically described.

<u><Example 1>: Synthesis of Water-Soluble Copolymer</u>

48 gram of sodium stylene sulfonate (SSNa) produced by the Sigma Aldrich Company and 19 gram of pentafluorostyrene (PFS) were completely

dissolved in 0.6 liter of dimethylsulfoxide (DMSO) while being heated.

1 gram of azobisisobutyronitrile (AIBN) was dissolved in dimethylsulfoxide (DMSO) and added in a dropwise fashion for polymerization for more than 24 hours. Through precipitation and filtration, a {P(SSNa-co-PFS)} copolymer with 30 mol% PFS was prepared.

In the same method, P(SSNa-co-PFS)} copolymers with 5, 10, and 20 mol% pentafluorostyrene (PFS) were prepared by varying and reacting 5, 10, and 20 mol% PFS.

A poly(styrenesulfonic acid-perfluorostyrene) copolymer {P(SSA-co-PFS)} aqueous solution represented as the following Chemical Formula 26 was prepared by reacting the above copolymers with a cation-based resin (AmberiteTM R-120) and an anion-based resin (LewatitTM MP62). The prepared copolymer was water-soluble, and the total solid content of the aqueous solution was 1.5 wt%. In the following Chemical formula 26, n1/m1 is 0.25.

[Chemical Formula 26]

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<Example 2>: Preparation of PEDOT Conductive Polymer
Compound Composition

An ionomer where the structure of the following Chemical formula 27 (which is NAFION) exists as a colloid in a 5 wt% mixed solvent of water and 2-propanol at a volume ratio of 45:55 was purchased from the Sigma Aldrich Company.

The copolymer of Chemical Formula 26 prepared in Example 1 and containing 20 mol% of PFS was mixed with the ionomer of Chemical formula 27 at weight ratios of 50:50, 80:20, and 90:10. Then, a mixed solvent of water and alcohol at 50:50 was added to the mixture in such a manner that the entire solids occupied 1.5 wt%. The mixture solution was sufficiently agitated for more than 1 hour.

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3,4-ethylenedioxythiophene (EDOT) was added to the mixture solution and polymerized using an ammoniumpersulfate oxidizing agent under the conditions of Table 1. Salts generated as products or byproducts of the reaction were purified through an ion exchange resin method or a dialysis method. A solution including the conductive polymer compound acquired as above was used as a conductive polymer compound composition. The solution included a solvent of water and 2-propanol at a volume ratio of 45:55. The content ratio of the polymer compound, i.e., the solid content ratio, was in the range of 1.5 to 1.7 wt%. The conductive polymer compound composition was used for fabrication of an organic light emitting diode.

[Chemical Formula 27]

$$\begin{array}{c|c} + CF - CF_2 \Big|_{m2} + CF_2 - CF_2 \Big|_{n2} \\ \hline (O - CF_2 - CF_3) - OCF_2 CF_2 - SO_3 H \\ \hline (CF_3)_{\times 1} \end{array}$$

wherein m2=1, n2=5-11, and x1=1.

(Table 1)

Sample	Compound of Chemical Formula 26 (wt%)	NAFION (wt%)	EDOT (wt%)	Reaction time (hrs)	Filtering capability
S-1	44.5	44.5	11	12	0
S-2	43	43	14	12	0
S-3	40	40	20	12	Х
S-4	71.2	17.8	11	12	0
S-5	68.8	17.2	14	12	0
S-6	64	16	20	12	0
S-7	80.1	8.9	11	12	0
S-8	77.4	8.6	14	12	0
S-9	72	8	20	12	0

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<Comparative Example 1>: Preparation of NAFION/PEDOT

Composition

A NAFION/PEDOT conductive polymer composition was prepared by

using an ionomer of a colloid structure according to U.S. Patent Application Serial No. 10/803,113.

<Comparative Example 2>: Preparation of PEDOT/PSS and NAFION Blended Composition

In accordance with Korean Patent Publication No. 2006-0091220, a conductive polymer composition solution was prepared by simply mixing Baytron-P, which is a commercial product name of PEDOT, with the NAFION ionomer shown in Chemical formula 27 at weight ratios of 1:1, 2:1, and 4:1.

Comparison of Filtering Capability

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Filtering capability of the compositions acquired from Example 2 and Comparative Examples 1 and 2 was measured by using a 0.45um syringe filter formed of a polyvinylidene fluoride material. The results are as shown in the following Table 2.

(Table 2)

		Compound of				
Sample	Copoly	Chemical	Davidson D	NAFION	EDOT	Filtering
Sample	mer	Formula 26	Baytron-P	(wt%)	(wt%)	capability ^a
		(wt%)				
S-2	Ex. 2	43	-	43	14	0
S-3	Ex. 2	40	-	40	20	Х
ref-1	Comp.		_	86	14	x
	Ex. 1	-	-	00	17	^
ref-2	Comp.		_	89	11	х
	Ex. 1	-	-	09	11	^
ref-3	Comp.		50	50	_	Δ
	Ex. 2	-	30	30	-	<i>←</i> 3
ref-4	Comp.	_	67	33	_	0
101-4	Ex. 2		0,			
ref-5	Comp.	_	80	20	_	0
	Ex. 2	_	00	20	_	

Note) filtering capability: 0 (filterable over 3 ml), \triangle (filterable 2 to 3 ml), X (filterable only less than 2 ml)

Filtering capability was not remarkably decreased except for sample S-3 among the samples S-1 to S-9 shown in Table 1 of Example 2. However, Table 2 shows that ref-1 and ref-2 prepared as reference samples in Comparative

Example 1 had poor filtering capability. This is because the ionomer itself was colloidally dispersed in water. Since the dispersion property in water is decreased when the conductive polymer copolymer was prepared, the filtering capability was decreased.

Assessment of Thin Film Characteristic based on AFM

Samples S-2 and ref-3 having the same EDOT content were selected among the compositions prepared in Example 2 and Comparative Example 2, and a thin film was fabricated by using sample ref-5 having the least content of the colloid-type ionomer. The thin film was fabricated by spin-coating the compositions of S-2, ref-3, and ref-5 on an ITO glass substrate at 2000 rpm for 30 seconds with a spin-coating machine, and baking the resulting substrate at 120°C for about 15 minutes. The quality of the thin film was assessed by taking AFM photographs with a Park AFM (atomic force microscopy) system XE-100 (product model name). The results are presented in FIGS. 2 to 4. In addition, surface roughness Ra and Rq were measured and the results are presented in Table 3.

(Table 3)

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Example 2	Comparative Example 2	Comparative		
Example 2	Comparative Example 2	Example 2		
S-2	ref-3	ref-5		
Ra = 0.75 nm	Ra = 5.46 nm	Ra = 1.80 nm		
Rq = 0.95 nm	Rq = 6.94 nm	Rq = 3.60 nm		

As shown in FIG. 2 to FIG. 4 and Table 3, sample S-2 had the best thin film characteristic as a result of the AFM measurement. On the other hand, reference samples ref-3 and ref-5 using only an ionomer or simple blending had inferior thin film planarity to the sample S-2, because the colloid-type ionomers agglomerated during the fabrication of the thin film, as confirmed by the AFM image.

< Example 3>: Fabrication of Organic Light Emitting Diode

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A 15Ψ/cm² 1200Å ITO glass substrate from the Corning Company was cut in a size of width x length x thickness of 50mm x 50mm x 0.7mm, rinsed using ultrasonic waves in isopropyl alcohol and deionized water for 5 minutes, and cleaned with ultraviolet rays and ozone for 30 minutes. The above-prepared substrate was spin-coated with the conductive polymer compound compositions of samples S-2, S-5, and S-8 prepared in Example 2 to thereby form a 70 nm-thick hole injection layer (HIL). A 700 nm-thick light emission layer was formed of a green light emitting polymer in the upper part of the hole injection unit, and a second electrode of LiF at 2 nm and Al at 100 nm was formed on the light emission layer to thereby fabricate an organic light emitting diode. The prepared device samples were marked as D-1, D-2, and D-3, and are presented as in the following Table 4.

(Table 4)

	Conductive		Compound of	-	
Device			Chemical	NAFION	EDOT
	polymer	Example Nos.	Formula 26	(wt%)	(wt%)
	compound		(wt%)		
D-1	S-2	Example 2	43	43	14
D-2	S-5	Example 2	68.8	17.2	14
D-3	S-8	Example 2	77.4	8.6	14

<Comparative Example 3>

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An organic light emitting diode was fabricated according to the same method as Example 5, except that a Baytron-P 4083 PEDOT/PSS aqueous solution of the Bayer Company was used as a material for forming a hole injection layer (HIL). This was named sample Ref-D.

<Comparison of Device Characteristics>

Luminous efficiency of the device samples prepared according to

Example 3 and Comparative Example 3 was measured using a SpectraScan

PR650 spectroradiometer. The results are presented in the following Table 5,

FIG. 5 (efficiency characteristic), and FIG. 6 (power characteristic. Table 5

presents a relative assessment based on the ref-D. In other words, values

were given by assuming the value of the ref-D to be 100%.

(Table 5)

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	Device measurement result					Relative evaluation						
	Voltage and				Mari		Voltage and				Max.	
	efficiency		Max.		efficiency		Von		efficie			
Sample	l	000 n	it	Von	efficiency (max)		(1000 nit		(V)		ncy	
	ref	erenc	e)	(V)			reference)				(max)	
	Vd (V)	cd/A	lm/w		cd/A	lm/w	Vd (V)	cd/A	lm/w	cd	/A	lm/w
ref-D	6.2	7.7	3.9	2.4	9.9	4.0	100%	100%	100%	100%	100%	100%
D-1	6.2	8.2	4.2	2.4	10.2	4.2	100%	106%	106%	100%	103%	105%
D-2	5.0	8.8	5.5	2.4	9.5	8.6	119%	113%	140%	100%	95%	216%
D-3	4.8	13.1	8.6	2.4	14.5	15.1	123%	169%	219%	100%	146%	381%

Table 4 and FIGS. 5 and 6 show that device sample D-3 had the best efficiency among the examples. The current efficiency of device sample D-3 was about 10.9 cd/A, which is 69% higher than reference sample Ref-D, i.e., 7.7 cd/A. Also, it showed an improvement of about 220% in electrical power efficiency.

Table 4 also reveals that other samples except for D-3 had improved efficiency compared to Ref-D. Consequently, it can be seen that the organic light emitting diode of the present invention using the conductive polymer copolymer composition as a hole injection layer (HIL) has excellent luminous efficiency.

The present invention is not limited to the embodiments illustrated with

the drawings and tables, but can be fabricated with various modifications and equivalent arrangements included within the spirit and scope of the appended claims by a person who is ordinarily skilled in this field. Therefore, the aforementioned embodiments should be understood to be exemplary but not limiting the present invention in any way.

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[CLAIMS]

[Claim 1]

A conductive polymer compound comprising:

a conductive polymer;

a first repeating unit of the following Chemical Formula 1;

a second repeating unit of the following Chemical Formula 2; and

a third repeating unit of the following Chemical Formula 3 and/or Chemical Formula 4:

[Chemical Formula 1]

$$A$$
 B

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[Chemical Formula 2]

$$\begin{pmatrix} \\ \\ \\ \\ \\ \\ \end{pmatrix}$$
n1

wherein, in the above Chemical Formulae 1 and 2,

when the number of moles of Chemical Formula 1 is m1 and the number of moles of Chemical Formula 2 is n1, the ratio of m1 and n1 is $0.0001 \le n1/m1 \le 1$,

A is selected from the group consisting of a substituted or unsubstituted alkyl; a substituted or unsubstituted heteroalkyl, a substituted or unsubstituted

alkoxy, a substituted or unsubstituted heteroalkoxy, a substituted or unsubstituted aryl, a substituted or unsubstituted arylalkyl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heteroarylalkyl, a substituted or unsubstituted heteroaryloxy, a substituted or unsubstituted or unsubstituted or unsubstituted heteroaryloxy, a substituted or unsubstituted arylester, a substituted or unsubstituted arylester, and a substituted or unsubstituted heteroarylester,

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B is an ion pair of a cation and an anion, where the cation is selected from the group consisting of a metal ion selected from the group consisting of H⁺; Na⁺, K⁺, Li⁺, Mg²⁺, Zn²⁺, and Al³⁺, and NR₃⁺ where R is H or a substituted or unsubstituted alkyl, and an organic ion of CH₃ (-CH₂-)_pO⁺, where p ranges from 1 to 50, and the anion is selected from the group consisting of PO₃²⁻, SO₃⁻, COO⁻, I⁻, and CH₃COO⁻, and

C is a halogen-containing substituted or unsubstituted hydrocarbon:

[Chemical Formula 3]

$$\begin{array}{c|c}
+ CF - CF_2 \Big|_{m2} \Big\{ CF_2 - CF_2 \Big|_{n2} \\
(O - CF_2 - CF_2 \Big|_{x1} \Big\{ O - CF_2 - CF_2 \Big|_{y1} \\
CF_3
\end{array}$$

[Chemical Formula 4]

$$+CF-CF_{2}|_{m3}|_{CF_{2}-CF_{2}|_{n3}}|_{CF_{2}-CF_{2}|_{x2}(O-CF_{2}-CF_{2})_{y2}}|_{CF_{3}}$$

wherein, in the above Chemical Formulae 3 and 4, $0 < m2 \le 10,000,000$, $0 \le n2 < 10,000,000$,

 $0 < m3 \le 10,000,000, 0 \le n3 < 10,000,000,$

x1, x2, y1, and y2 are independently integers ranging from 0 to 20, and Y1 and Y2 are independently -COO⁻M⁺, -SO₃M⁺, or -PO₃²⁻(M⁺)₂, where M⁺ is Na⁺, K⁺, Li⁺, H⁺, or NH₄⁺.

[Claim 2]

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The conductive polymer compound of claim 1, wherein A is selected from the group consisting of a substituted or unsubstituted C1-C30 alkyl; a substituted or unsubstituted C1-C30 heteroalkyl; a substituted or unsubstituted C1-C30 alkoxy; a substituted or unsubstituted or unsubstituted or unsubstituted or unsubstituted C6-C30 aryl; a substituted or unsubstituted C6-C30 arylalkyl; a substituted or unsubstituted or unsubstituted or unsubstituted or unsubstituted C2-C30 heteroaryl; a substituted or unsubstituted C2-C30 heteroarylalkyl; a substituted or unsubstituted c2-C30 heteroaryloxy; a substituted or unsubstituted c2-C30 heteroaryloxy; a substituted or unsubstituted c2-C30 heteroaryloxy; a substituted c3-C30 heteroa

or unsubstituted C1-C30 heteroalkylester; a substituted or unsubstituted C7-C30 arylester; and a substituted or unsubstituted C2-C30 heteroarylester.

[Claim 3]

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The conductive polymer compound of claim 1, wherein the conductive polymer is a polymer obtained from polymerization of at least one monomer selected from polyphenylene; polyphenylenevinylene; monomers of polyaniline or derivatives thereof having the following Chemical Formula 5; monomers of pyrrol, thiophene, or derivatives thereof having the following Chemical Formula 6; and cyclic monomers having the following Chemical Formula 7:

[Chemical Formula 5]

$$R_a$$
 R_b NH R_c R_d

[Chemical Formula 6]

wherein, in the above Chemical Formulae 5 and 6,

E is NR where R is H, or a C1 to C7 lower alkyl,

R_a, R_b, R_c, and R_d are selected from the group consisting of independently hydrogen; a substituted or unsubstituted alkyl; a substituted or unsubstituted alkoxy; a substituted or unsubstituted heteroalkyl; a substituted or unsubstituted aryl; a substituted or unsubstituted arylalkyl; a substituted or unsubstituted arylalkyl; a substituted or unsubstituted arylalkyl; a substituted or unsubstituted pyrrol; a substituted or unsubstituted or unsubstituted or unsubstituted or unsubstituted heteroaryl; a substituted or unsubstituted heteroaryl; a substituted or unsubstituted or unsubstituted heteroarylalkyl; a substituted or unsubstituted heteroaryloxy; a substituted or unsubstituted alkylester; a substituted or unsubstituted or unsubstituted or unsubstituted arylester; and a substituted or unsubstituted heteroarylester, and

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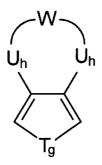
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R_e and R_f are independently selected from the group consisting of NR where R is H or a C1 to C7 lower alkyl; a C1-C20 alkyl including a heteroatom selected from the group consisting of N, O, S, and P; a C6-C20 aryl including a heteroatom selected from the group consisting of N, O, S, and P; an alkyl; an aryl; an alkoxy; a C1-C30 heteroalkyl; a heteroalkoxy; an arylalkyl; an aryloxy; a C6-C30 arylamine; a C6-C30 pyrrol; a C6-C30 thiophene; a heteroaryl; a heteroarylalkyl; a heteroaryloxy; a C5-C20 cycloalkyl; a heterocycloalkyl; an alkylester; a heteroalkylester; an arylester; and a heteroarylester:

[Chemical Formula 7]



wherein, in the above Chemical Formula 7,

T is NR where R is H or a C1 to C7 lower alkyl; a C1-C20 alkyl including a heteroatom selected from the group consisting of N, O, S, and P; a C6-C20 aryl including a heteroatom selected from the group consisting of N, O, S, and P,

U is NR where R is H or a C1 to C7 lower alkyl; a C1-C20 alkyl including a heteroatom selected from the group consisting of N, O, S, and P; a C6-C20 aryl including a heteroatom selected from the group consisting of N, O, S, and P, g and h are independently 0 to 9,

W is $-(CH_2)_x$ - CR_gR_h - $(CH_2)_y$ where R_g and R_h are independently selected from the group consisting of H, a C1-C20 alkyl radical, a C6-C14 aryl radical, and $-CH_2$ - OR_i , where R_i is selected from the group consisting of H, a C1-C6 alkyl acid, a C1-C6 alkylester, a C1-C6 heteroalkyl acid, and a C1-C6 alkylsulfonic acid, and

x and y are independently 0 to 5.

[Claim 4]

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A conductive polymer compound composition comprising:

a conductive polymer compound comprising a conductive polymer, a first repeating unit of the following Chemical Formula 1, a second repeating unit of the following Chemical Formula 2, and a third repeating unit of the following Chemical Formula 3 and/or Chemical Formula 4; and

5 a solvent:

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[Chemical Formula 1]

[Chemical Formula 2]

$$\begin{pmatrix} \\ \\ \\ \\ \\ \\ \end{pmatrix}$$

wherein, in the above Chemical Formulae 1 and 2:

when the number of moles of Chemical Formula 1 is m1 and the number of moles of Chemical Formula 2 is n1, the ratio of m1 and n1 is $0.0001 \le n1/m1 \le 1$;

A is selected from the group consisting of a substituted or unsubstituted alkyl, a substituted or unsubstituted heteroalkyl, a substituted or unsubstituted alkoxy, a substituted or unsubstituted heteroalkoxy, a substituted or unsubstituted arylalkyl, a substituted or unsubstituted arylalkyl, a substituted or unsubstituted arylalkyl, a substituted or unsubstituted heteroaryl, a substituted or

unsubstituted heteroarylalkyl, a substituted or unsubstituted heteroaryloxy, a substituted or unsubstituted cycloalkyl, a substituted or unsubstituted heterocycloalkyl, a substituted or unsubstituted alkylester, a substituted or unsubstituted arylester, and a substituted or unsubstituted heteroarylester;

B is an ion pair of a cation and an anion, where the cation is selected from the group consisting of a metal ion selected from the group consisting of H⁺; Na⁺, K⁺, Li⁺, Mg²⁺, Zn²⁺, and Al³⁺, and NR₃⁺ where R is H or a substituted or unsubstituted alkyl, and an organic ion of CH₃(-CH₂-)_pO⁺ where p ranges from 1 to 50, and the anion is selected from the group consisting of PO₃²⁻, SO₃⁻, COO⁻, I⁻, and CH₃COO⁻; and

C is a halogen-containing substituted or unsubstituted hydrocarbon, [Chemical Formula 3]

$$\begin{array}{c|c}
+ CF - CF_2 + CF_2 - CF_2 + CF_2 - CF_2 + CF_2 - CF_2 -$$

15 [Chemical Formula 4]

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$$\begin{array}{c|c}
+CF-CF_2 & CF_2 - CF_2 \\
\hline
 & (O-CF_2 - CF_2 - CF_2) \\
\hline
 & CF_3
\end{array}$$

wherein, in the above Chemical Formulae 3 and 4, $0 < m2 \le 10,000,000$, $0 \le n2 < 10,000,000$,

 $0 < m3 \le 10,000,000, 0 \le n3 < 10,000,000,$

x1, x2, y1, and y2 are independently integers ranging from 0 to 20, and Y1 and Y2 are independently -COO⁻M⁺, -SO₃M⁺, or -PO₃²⁻(M⁺)₂, where M⁺ is Na⁺, K⁺, Li⁺, H⁺, or NH₄⁺.

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[Claim 5]

The conductive polymer compound composition of claim 4, wherein the conductive polymer is a polymer obtained from polymerization of at least two monomers selected from polyphenylene; polyphenylenevinylene; monomers of polyaniline or derivatives thereof having the following Chemical Formula 5; monomers of pyrrol, thiophene, or derivatives thereof having the following Chemical Formula 6; and cyclic monomers having the following Chemical Formula 7:

[Chemical Formula 5]

$$R_{c}$$
 R_{b}
 NH

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[Chemical Formula 6]

wherein, in the above Chemical Formulae 5 and 6, E is NR where R is H, or a C1 to C7 lower alkyl,

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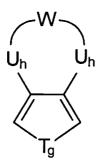
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R_a, R_b, R_c, and R_d are selected from the group consisting of independently hydrogen; a substituted or unsubstituted alkyl; a substituted or unsubstituted heteroalkyl; a substituted or unsubstituted alkoxy; a substituted or unsubstituted aryl; a substituted or unsubstituted arylalkyl; a substituted or unsubstituted aryloxy; a substituted or unsubstituted arylamine; a substituted or unsubstituted pyrrol; a substituted or unsubstituted or unsubstituted heteroaryl; a substituted or unsubstituted or unsubstituted heteroaryl; a substituted or unsubstituted or unsubstituted heteroarylalkyl; a substituted or unsubstituted heteroaryloxy; a substituted or unsubstituted alkylester; a substituted or unsubstituted or unsubstituted or unsubstituted arylester; and a substituted or unsubstituted heteroarylester, and

R_e and R_f are independently selected from the group consisting of NR where R is H or a C1 to C7 lower alkyl; a C1-C20 alkyl including a heteroatom selected from the group consisting of N, O, S, and P; a C6-C20 aryl including a heteroatom selected from the group consisting of N, O, S, and P; an alkyl; an aryl; an alkoxy; a C1-C30 heteroalkyl; a heteroalkoxy; an arylalkyl; an aryloxy; a C6-C30 arylamine; a C6-C30 pyrrol; a C6-C30 thiophene; a heteroaryl; a heteroarylalkyl; a heteroaryloxy; a C5-C20 cycloalkyl; a heterocycloalkyl; an alkylester; a heteroalkylester; an arylester; and a heteroarylester.

[Chemical Formula 7]



wherein, in the above Chemical Formula 7,

T is NR where R is H or a C1 to C7 lower alkyl; a C1-C20 alkyl including a heteroatom selected from the group consisting of N, O, S, and P; a C6-C20 aryl including a heteroatom selected from the group consisting of N, O, S, and P,

U is NR where R is H or a C1 to C7 lower alkyl; a C1-C20 alkyl including a heteroatom selected from the group consisting of N, O, S, and P; a C6-C20 aryl including a heteroatom selected from the group consisting of N, O, S, and P, g and h are independently 0 to 9,

W is $-(CH_2)_x$ - CR_gR_h - $(CH_2)_y$ where R_g and R_h are independently selected from the group consisting of H, a C1-C20 alkyl radical, a C6-C14 aryl radical, and $-CH_2$ -ORi, where R_i is selected from the group consisting of H, a C1-C6 alkyl acid, a C1-C6 alkylester, a C1-C6 heteroalkyl acid, and a C1-C6 alkylsulfonic acid, and

x and y are independently 0 to 5.

[Claim 6]

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The conductive polymer compound composition of claim 4, wherein the

conductive polymer compound composition further comprises a cross-linking agent selected from the group consisting of a physical cross-linking agent, a chemical cross-linking agent, and a combination thereof.

5 [Claim 7]

The conductive polymer compound composition of claim 1, wherein the conductive polymer compound composition comprises a physical cross-linking agent in an amount of 0.001 to 5 parts by weight based on 100 parts by weight of the conductive polymer.

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[Claim 8]

The conductive polymer compound composition of claim 1, wherein the conductive polymer compound composition comprises a chemical cross-linking agent in an amount of 0.001 to 50 parts by weight based on 100 parts by weight of the conductive polymer.

[Claim 9]

The conductive polymer compound composition of claim 6, wherein the physical cross-linking agent is selected from the group consisting of glycerol, butanol, polyvinylalcohol, polyethyleneglycol, polyethyleneimine, polyvinylpyrrolidone, and combinations thereof.

[Claim 10]

The conductive polymer compound composition of claim 6, wherein the chemical cross-linking agent is selected from the group consisting of tetraethyloxysilane, polyaziridine, a melamine-based polymer, an epoxy-based polymer, and combinations thereof.

[Claim 11]

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The conductive polymer compound composition of claim 4, wherein the solvent is selected from the group consisting of water, alcohol, dimethyl formamide (DMF), dimethylsulfoxide, toluene, xylene, chlorobenzene, and combinations thereof.

[Claim 12]

A conductive polymer organic layer made using the conductive polymer composition according to one of claims 4 to 11.

[Claim 13]

An organic photoelectric device comprising a conductive polymer organic layer made using the conductive polymer composition according to one of claims 4 to 11.

[Claim 14]

The organic photoelectric device of claim 13, wherein the organic

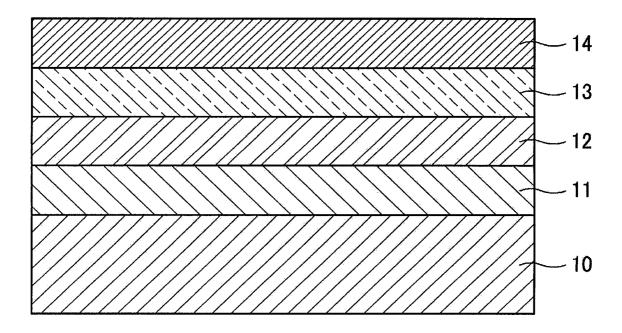
photoelectric device is an organic light emitting diode.

[Claim 15]

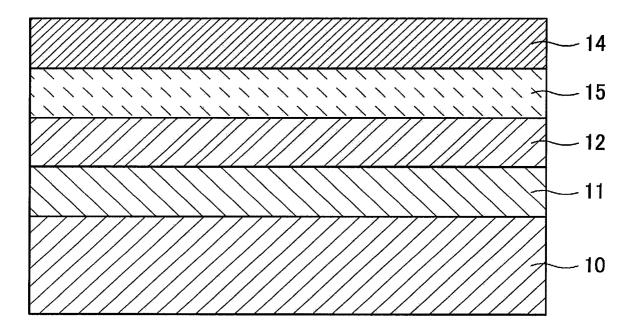
The organic photoelectric device of claim 13, wherein the conductive polymer organic layer is a hole or electron injection layer (EIL).

[DRAWINGS]

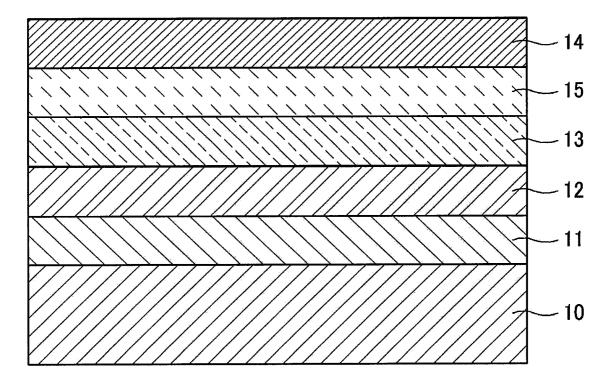
【FIG. 1a】



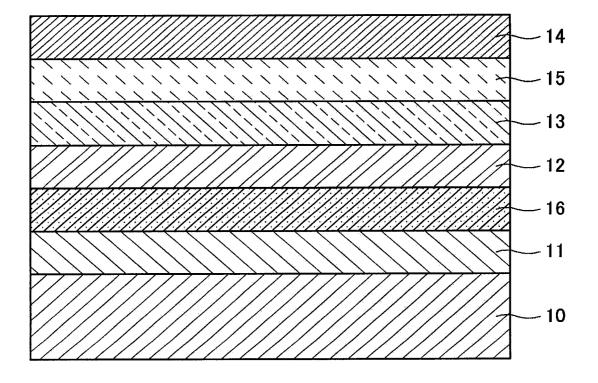
[FIG. 1b]



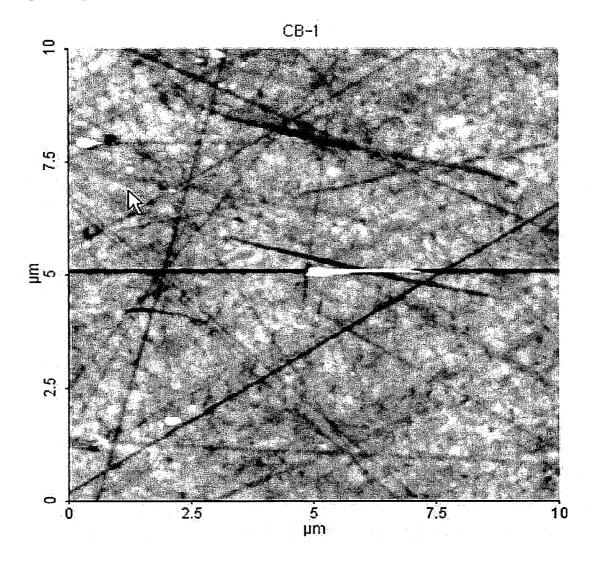
[FIG. 1c]



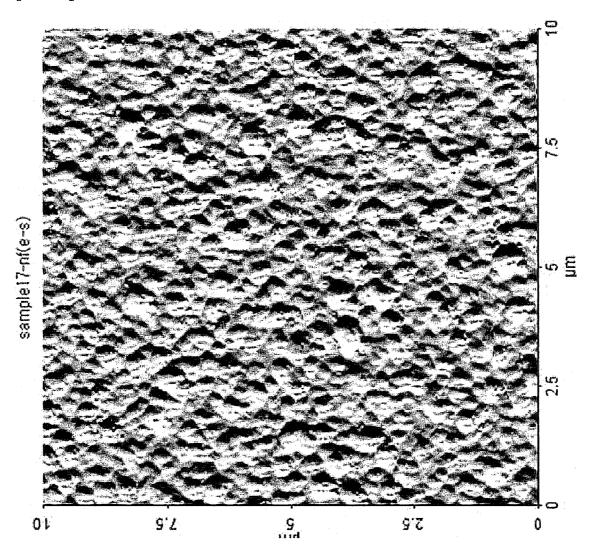
[FIG. 1d]



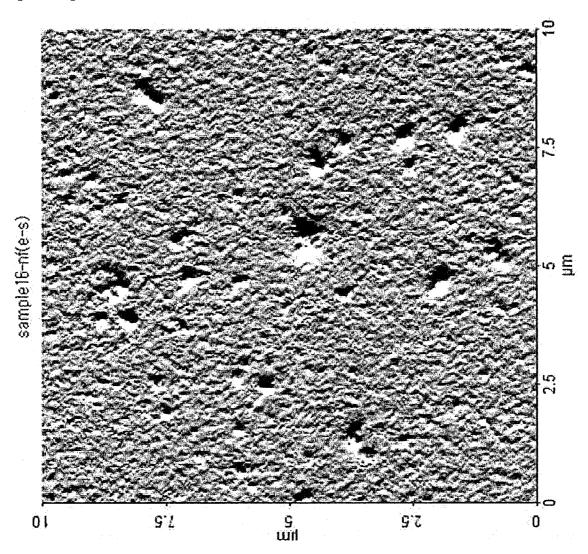
[FIG. 2]



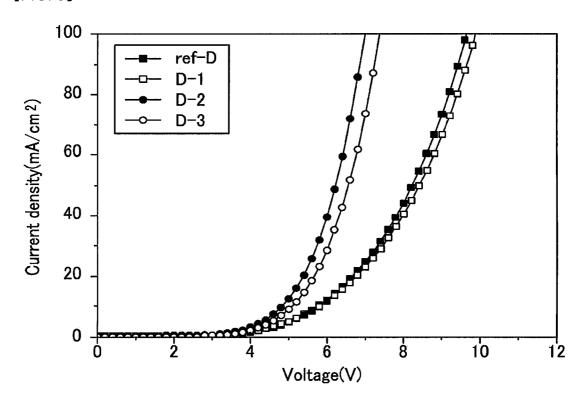
[FIG. 3]



[FIG. 4]







[FIG. 6]

