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(54) **LIQUID ORGANIC SEMICONDUCTOR MATERIAL**

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(57) **ABSTRACT**

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An organic material having at least one aromatic conjugated π -electron system is selected. The purity of the organic material is improved by purification, and a conduction mechanism of the organic material is confirmed by a time-of-flight method, whereby a liquid phase of the organic material is usable as an organic semiconductor. A method that enables the usage of a liquid phase of an organic material as an organic semiconductor is provided. The method involves confirming the electronic conduction of the organic material having at least one aromatic conjugated π -electron system by evaluation of a charge transport property using a time-of-flight method, and by evaluation of a dilution effect caused by addition of a diluent.

Related U.S. Application Data

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(30) **Foreign Application Priority Data**

Sep. 16, 2009 (JP) 2009-214717

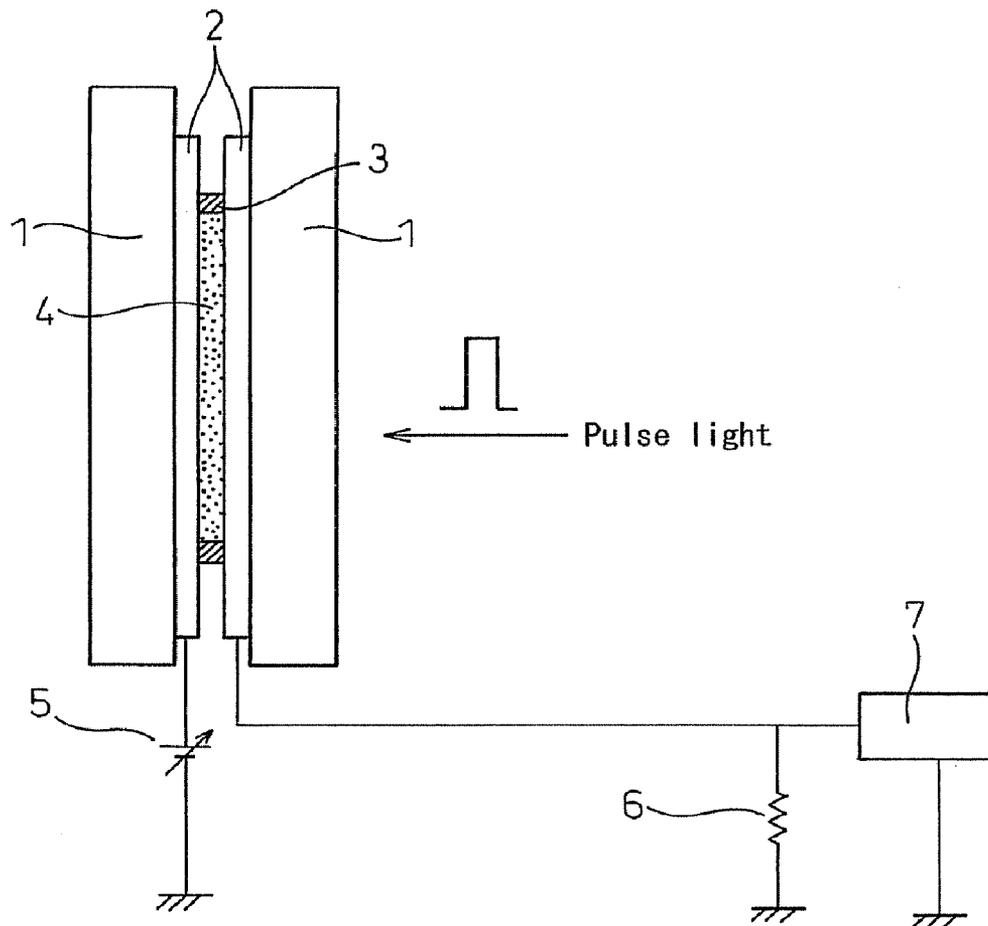


Fig.1

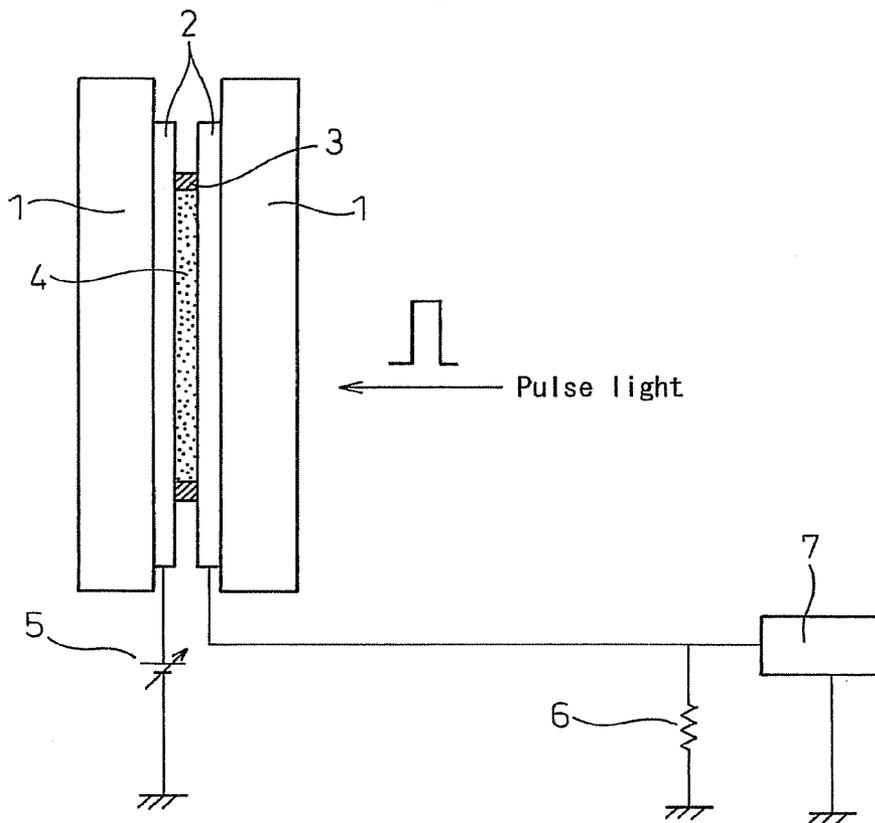


Fig.2

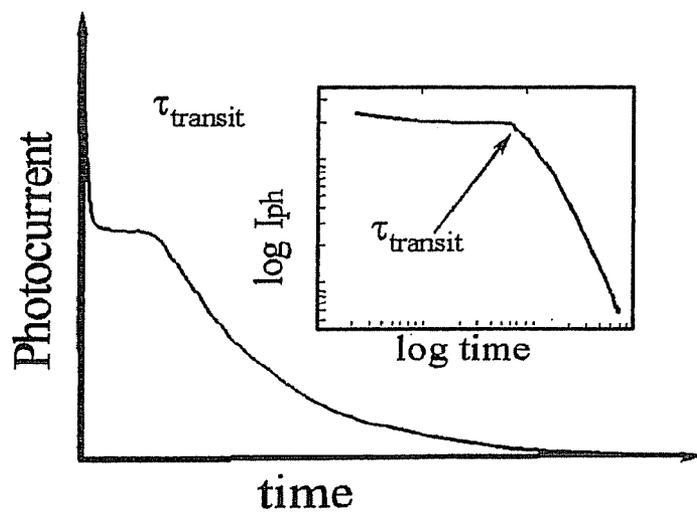


Fig.3

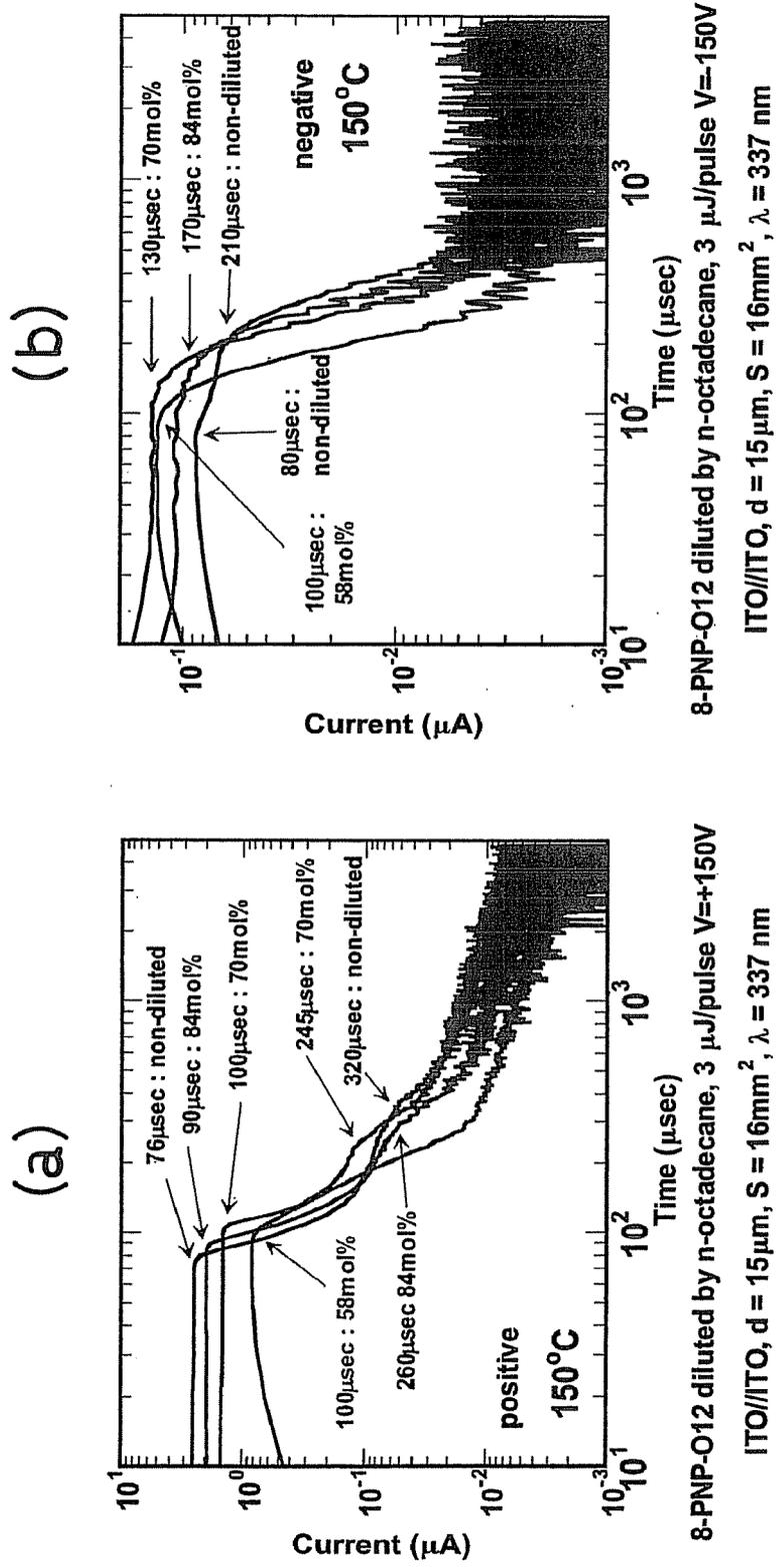


Fig.4

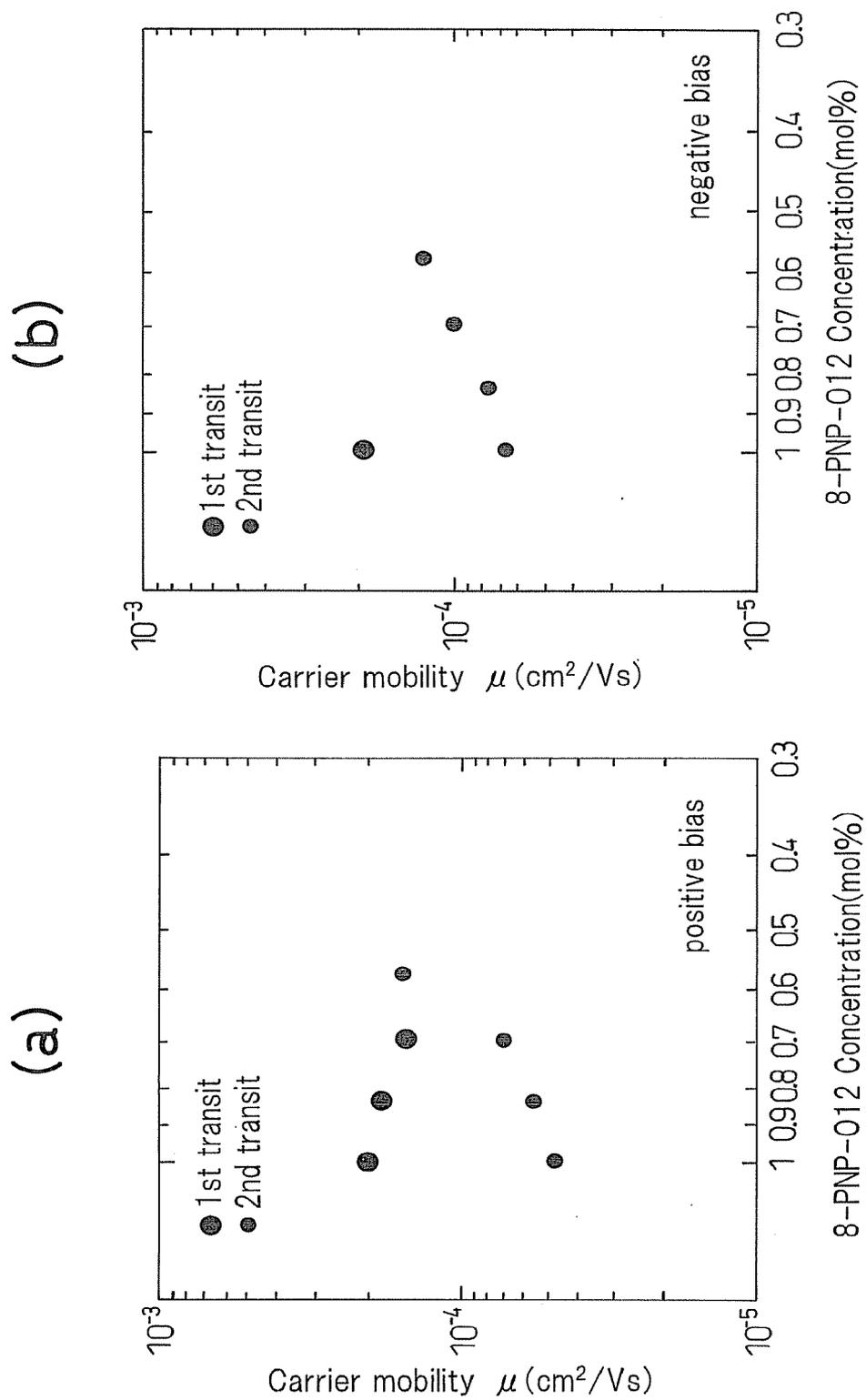
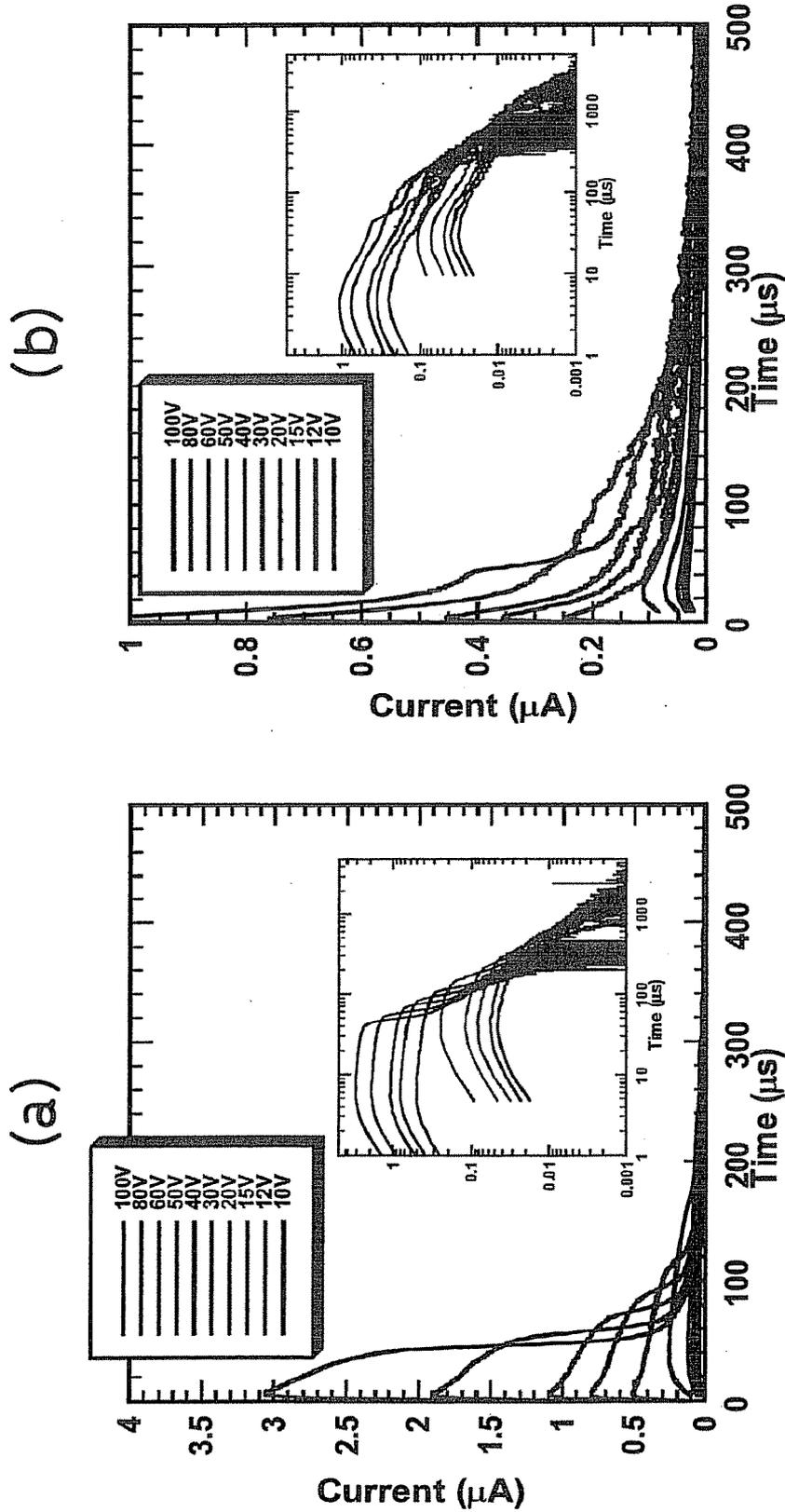


Fig.5



PNP, 7z04-1, S2, 105°C, Iso phase, -bias,
ITO//ITO, d=16.31 μm , S = 16mm², λ = 337 nm

PNP, 7z04-1, S2, 105°C, Iso phase, +bias,
ITO//ITO, d=16.31 μm , S = 16mm², λ = 337 nm

Fig.6

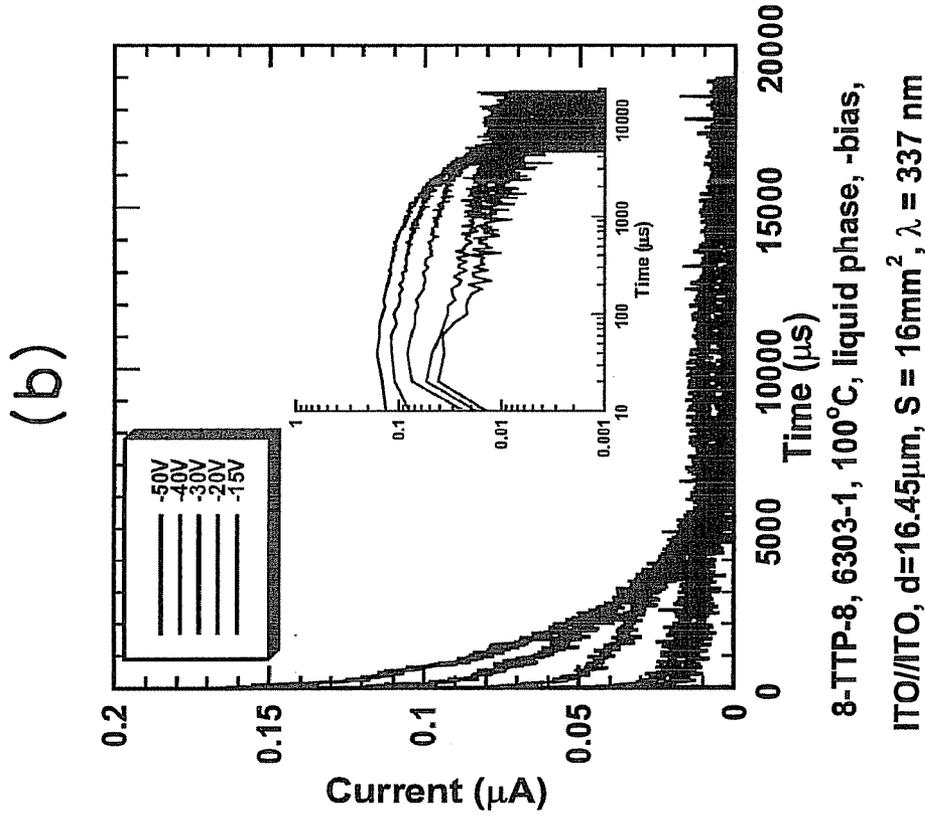
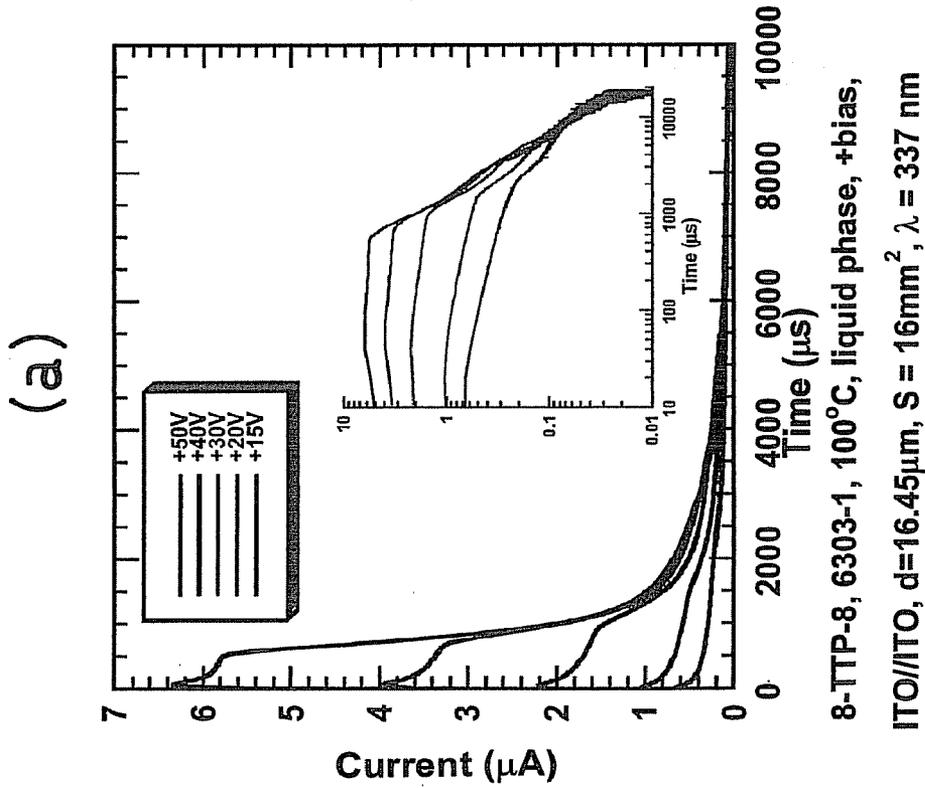
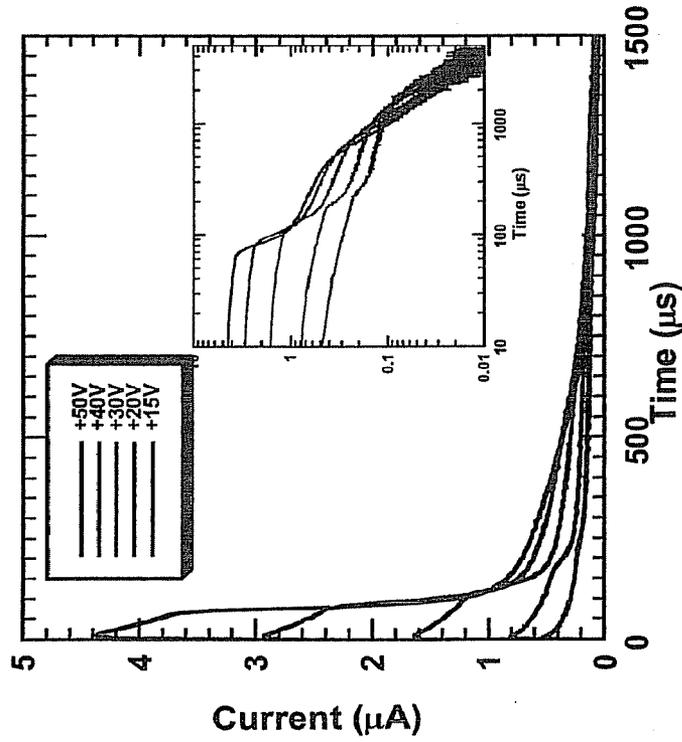


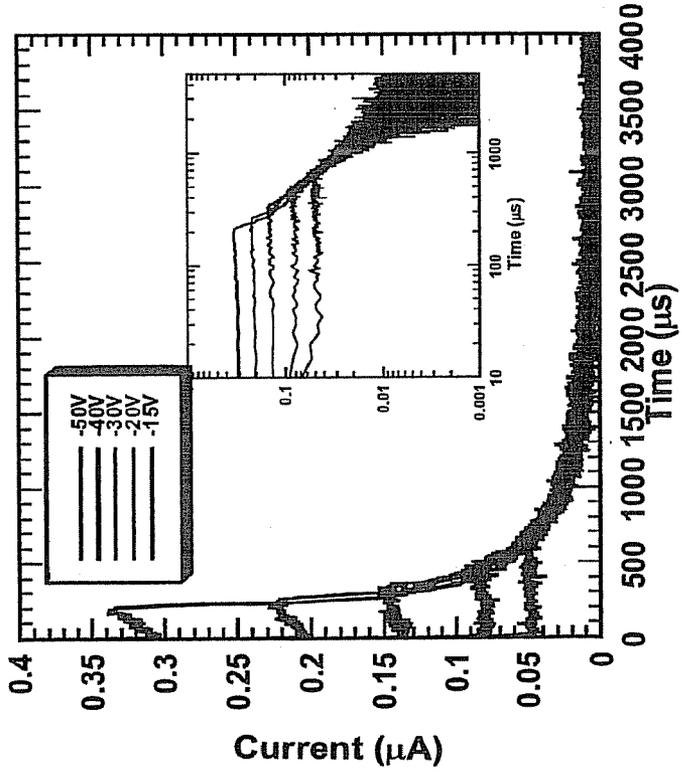
Fig.7

(a)



6-QTP-6, 7719-2, 200°C, liquid phase, +bias,
ITO//ITO, d=13.88μm, S = 16mm², λ = 337 nm

(b)



6-QTP-6, 7719-2, 200°C, liquid phase, -bias,
ITO//ITO, d=13.88μm, S = 16mm², λ = 337 nm

Fig.8

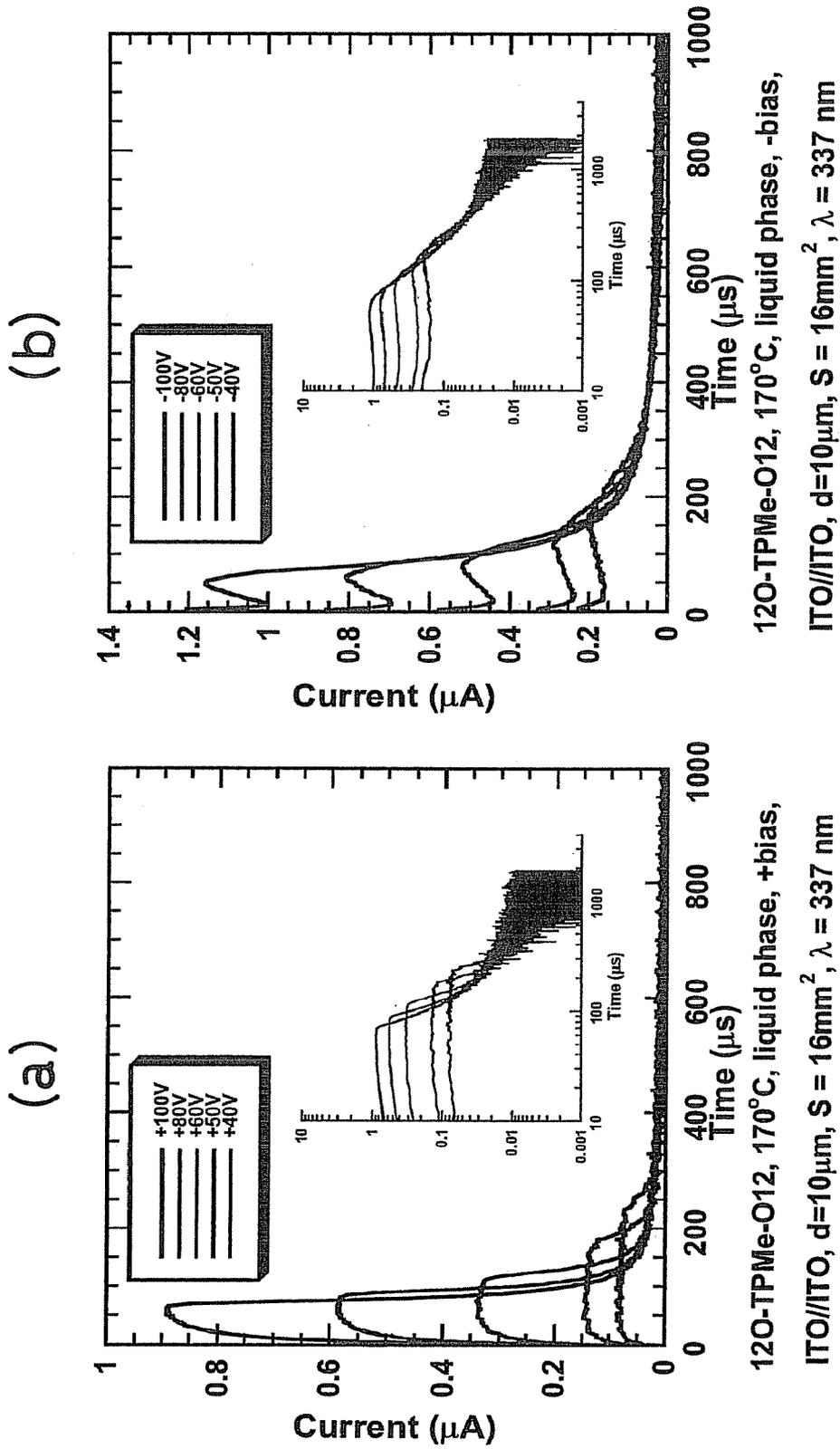


Fig.9

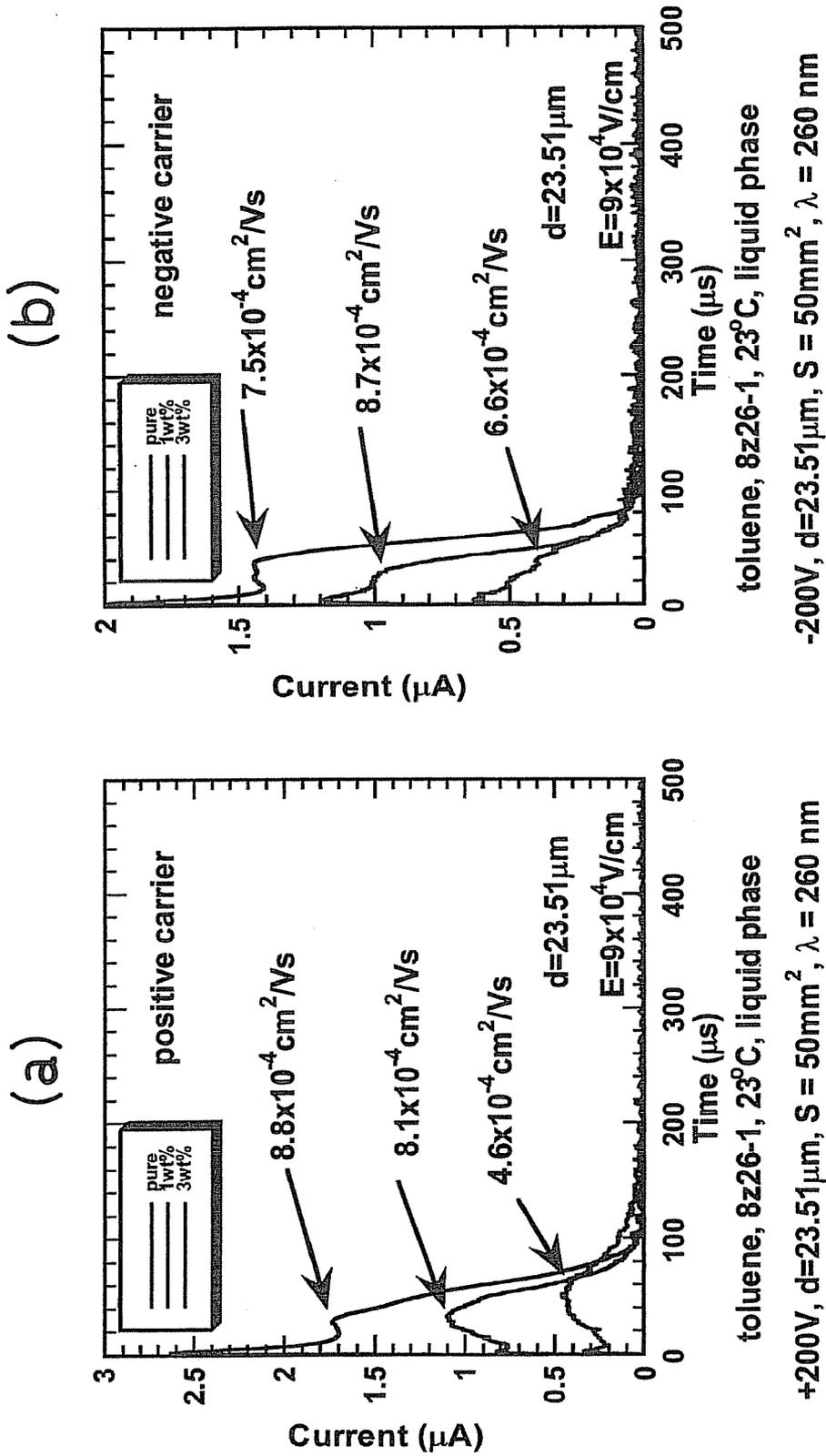
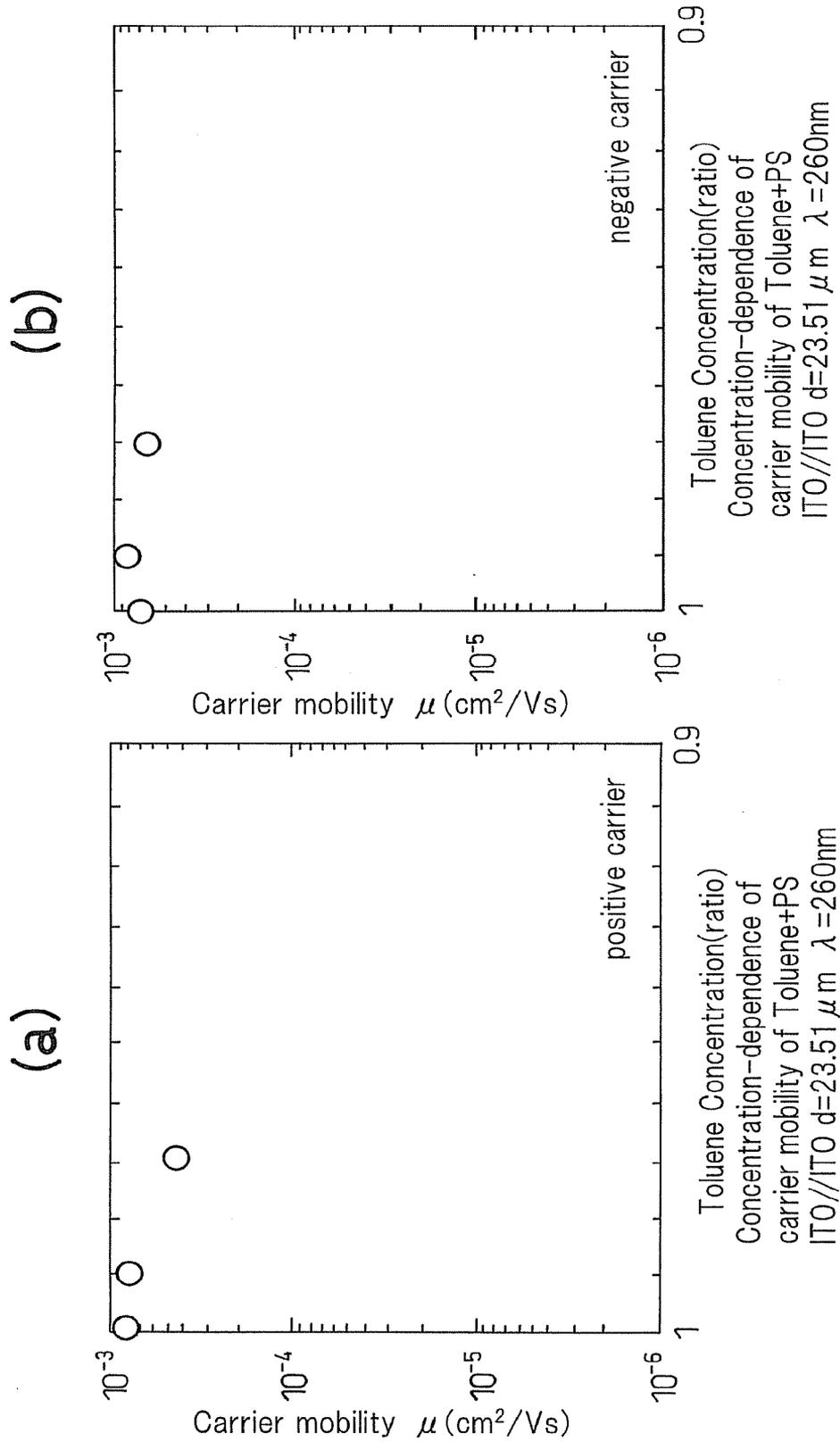


Fig.10



LIQUID ORGANIC SEMICONDUCTOR MATERIAL

TECHNICAL FIELD

[0001] The present invention relates to an organic material capable of exhibiting an electronic conduction. The liquid organic semiconductor material according to the present invention can be applied to various wide fields, and can achieve a new process for producing an organic electronic device, or a new form thereof. Specific examples of such an organic electronic device may include: optical sensor, organic EL (electro-luminescence) device, organic transistor, organic solar cell, or organic semiconductor memory.

BACKGROUND ART

[0002] An organic semiconductor material is a material which can be used for an optical sensor, an organic photo-receptor, an organic EL element, an organic transistor, an organic solar cell, an organic semiconductor memory, and the like. Specific examples of the organic semiconductor material which have heretofore been used may include: for example, an amorphous thin film or polycrystalline thin film which has been formed on a by using vacuum deposition of an organic semiconductor substance, or by applying a solution containing an organic semiconductor substance onto a substrate. The organic semiconductor material may be, for example, a thin film material formed by dispersing the organic semiconductor substance into a polymer material or the like and applying the dispersed semiconductor substance onto a substrate; or a single-crystal material of the organic semiconductor material (that is, a semiconductor material which is a solid in a temperature range wherein a device using the semiconductor material can be driven). This is because, in order to produce an organic electronic device, the function of such a device should be achieved by utilizing the electronic conductivity exhibited by the organic semiconductor. From this point, it has been considered that it is necessary to use an amorphous material, a polycrystalline material, a single-crystal material or the like, which has been hitherto considered as the material which can achieve the electronic conduction.

[0003] On the other hand, in recent years, it has been found that a liquid crystal material capable of providing a molecular orientation having a higher viscosity, compared to that of a general liquid material, can also exhibit the electronic conduction in the nematic phase, in the smectic phase, in the columnar phase thereof, or the like. It has also been found that such a liquid crystal material which can be used as the organic semiconductor material, and accordingly, the applications of the liquid crystal material to organic electronic devices have also been studied.

[0004] The conduction of a low-molecular-weight non-liquid crystal organic compound in an isotropic phase (i.e., liquid phase) is considered to show the ion conduction, because its viscosity is generally low. An example in which the electronic conduction in such a material is recognized, has been reported only in a extremely specific system. An example thereof is such that high-energy electrons are generated by the application of a high-energy electron beam, an X ray, or a short-wavelength light to a hydrocarbon, such as methane or ethane, and the conduction of the high-energy

electrons is confirmed by using a time-of-flight method or the like (IEEE Transaction on Electrical Insulation vol. EI-19, No. 5, 390-418).

[0005] It is considered that the conduction of high-energy electrons, which have been generated in the above manner, is similar to the conduction of free electrons which are weakly bound to a molecule. Further, it has also been found that the mobility of the high-energy electron in the above-mentioned organic compound is much more than that in a general organic solid, and that some high-energy electrons show a mobility exceeding several tens cm^2/Vs . Among the liquid crystal substances, a phthalocyanine liquid crystal in an isotropic phase, which is one of discotic liquid crystals with a high viscosity, shows an electronic conduction, which has been confirmed by using the time-of-flight method (Extended Abstract of the 54th Meeting of The Japan Society of Applied Physics and Related Societies, 2007, p 1333). However, at present, it is considered that the conduction in a rod-like non-polymeric liquid crystal substance or the conduction in a liquid phase (isotropic phase) of a non-liquid crystal substance is the ionic conduction, and there has been no example wherein an electronic conduction of such a substance is experimentally confirmed. Accordingly, the electronic conduction of such a substance has never been confirmed.

[0006] In general, it has been considered that the conduction of the so-called liquid (i.e., the liquid state in an isotropic phase) is the ionic conduction. That is, it has been considered that the organic material in the liquid state cannot achieve any organic electronic device using the electronic conduction. In other words, in the prior art, in order to achieve the function of the device using the electronic conduction, the organic semiconductor material to be used for the organic electronic device is required to be an amorphous solid or crystal, or a liquid crystal phase of a liquid crystal material, the electronic conduction of which has already been confirmed, in a temperature range wherein the device can be driven.

PRIOR ART DOCUMENTS

Patent Documents

- [0007]** [Non-Patent Document 1] IEEE Transaction on Electrical Insulation vol. EI-19, No. 5 390-418
[0008] [Non-Patent Document 2] Extended Abstract of the 54th Meeting of The Japan Society of Applied Physics and Related Societies, 2007, p 1333

SUMMARY OF INVENTION

Problems to be Solved by the Invention

[0009] An object of the present invention is to provide a new type organic semiconductor material which can solve the above problem encountered in the prior art.

[0010] Another object of the present invention is to provide a new organic semiconductor material which can achieve an electronic device using a liquid.

Means for Solving the Problem

[0011] As a result of earnest study, the present inventors have found a material capable of showing an isotropic phase and a fluidity, which exhibits an electron and/or hole conduction.

[0012] The organic semiconductor material according to the present invention has been accomplished based on the above discovery.

Effects of the Invention

[0013] As described above, the present invention provides an organic semiconductor material which shows a liquid state at a temperature whereat the semiconductor material is operable. The organic semiconductor material according to the present invention can be applied to various fields, to which a conventional organic semiconductor material can be applied. That is, for example, the organic semiconductor material according to the present invention is applicable to an optical sensor, an organic optical receptor, an organic EL diode, an organic transistor, an organic solar cell, an organic semiconductor memory, and the like, without particular limitation.

[0014] More specifically, the present invention can achieve the organic electronic device by using the electron conduction in a liquid state, which is difficult to be utilized in the prior art. Accordingly, the present invention can achieve a new device structure, form, and function of the organic electronic device, which is free from the limitation of the solid-state device in the prior art. Further, the organic semiconductor material according to the present invention enables the application and selection of any of techniques in producing, manufacturing or fabrication processes, which is free from the limitation of those processes in the prior art. The organic semiconductor material according to the present invention is especially effective for a device requiring a large area. This is also effective in increasing the application range of the device, and in reducing the production costs of the devices.

[0015] Further, in view of the material according to the present invention, the present invention enables the selection of a material which is free from the limitation of the conventional concept of the organic semiconductor material. Accordingly, the present invention can increase the range of selection of the material, which is suitable for various properties to be required for the device.

BRIEF DESCRIPTION OF DRAWINGS

[0016] FIG. 1 is a schematic sectional view showing the structure of a time-of-flight measuring device which is usable in the present invention.

[0017] FIG. 2 is a schematic diagram of a waveform of a typical transient photocurrent which can be measured by using the above device shown in FIG. 1.

[0018] FIG. 3 is a graph showing the change of waveform of the transient photocurrent obtained in Example 2 appearing hereinafter.

[0019] FIG. 4 is a graph which has been obtained by plotting the mobilities calculated from the "two transit times" (two stepped or shoulder portions) in Example 2, against the concentration of n-octadecane.

[0020] FIG. 5 is a graph showing another example of "two stepped portions" corresponding to two different transit times which had been obtained in Example 3.

[0021] FIG. 6 is a graph showing one example of the waveforms of the transient photocurrent which had been obtained in Example 4.

[0022] FIG. 7 is a graph showing one example of the waveform of the transient photocurrent which had been obtained in Example 5.

[0023] FIG. 8 is a graph showing one example of the waveform of the transient photocurrent which had been obtained in Example 6.

[0024] FIG. 9 is a graph showing one example of the results which had been obtained by an experiment using a dilution with n-hexane in Example 7, which is similar to Example 2.

[0025] FIG. 10 is a graph showing one example of the results which had been obtained by measuring the transient photocurrent by the addition of toluene to polystyrene in Example 8.

MODES FOR CARRYING OUT THE INVENTION

[0026] Hereinbelow, the present invention will be specifically described with reference to the accompanying drawings, as desired. In the following description, the "part" and "%" representing the amounts and ratios are based on the mass, unless otherwise noted specifically (it should be noted that a "mol %", for example, is clearly expressed in other cases).

(Mechanism of Present Invention)

[0027] According to the knowledge and investigations by the present inventors, the mechanism of the electron and/or hole conduction in the organic semiconductor material according to the present invention may be presumed in the following manner.

[0028] The present inventors have made it clear that the ionic conduction, which is often observed in liquid crystal substances, can be induced not only by an ionic substance which is contained as an impurity in the liquid crystal substance, but also by the ionization of impurity molecules capable of providing an electrically trap level. The impurity molecule has its LUMO or HOMO level which are positioned between the HOMO level and LUMO level of a substance serving as a base for the liquid crystal substance. Based on these discoveries, the present inventors have also found that, even in the case of a "general organic substance" in a liquid state (i.e., liquid in an isotropic phase), the electric conduction of which is considered to be ionic conduction, a conduction mechanism satisfying a condition appearing hereinafter can be confirmed, and that such an organic substance can be used as an organic semiconductor, because of the electronic conduction in the organic substance.

[0029] Basically, the present invention may have three aspects. These aspects may include the selection of a material, purification of the material, and confirmation of the conduction mechanism in the material.

(Selection of Material)

[0030] In the case of the selection of a substance, it is necessary to choose an energy level associated with the transport of charges in the material in view of the function of a device, the operating condition of the device, the selection of an electrode material therefor, the environment for the device to be used, and the like. Accordingly, as the material to be used for a semiconductor according to the present invention, it is necessary to use an organic substance

having at least one aromatic conjugated π -electron system in the chemical structure of the organic substance.

(Preferred Organic Substance)

[0031] The “organic substance having at least one aromatic conjugated π -electron system” which is usable in the present invention is not specifically limited. In view of the optical characteristic, it is preferred to use a substance having an optical absorption peak (i.e., ϵ_{Max}), for example, in a wavelength range of 260 nm or more.

[0032] Further, in view of the chemical property of the substance, the so-called aprotic substance may preferably be used. When the semiconductor material according to the present invention is a mixture, in general, each of the components constituting the mixture may preferably be aprotic. In the present invention, the term “aprotic” substance refers to a substance which does not have any “hydrogen atom” in its chemical structural formula such that the hydrogen atom would produce a hydrogen gas by the reaction of the substance with a metal Na. More actually, the term “aromatic” substance in the present invention refers to a substance which does give the stoichiometric production of hydrogen gas even in the case of the reaction thereof with metal Na in a “dried state” at a lower limit temperature in the operable temperature range for the semiconductor substance. It should be noted that, in the present invention, ethanol, for example, is not “aprotic”.

(Mixture)

[0033] In the present invention, the organic semiconductor material may be a single material (for example, a compound), or may be in the form of a “mixture”. The form of the mixture is not specifically limited, but may be preferably be homogeneous or uniform such that the mixture does not cause a phase separation at the lower limit temperature in the operable temperature range for the semiconductor material. The mixture can also be in the form of, for example, a solution or gel.

(Solution)

[0034] In an embodiment wherein the organic semiconductor material in the form of a “solution”, it is possible to use the following solutes and solvents.

(Solute)

[0035] The solute is not specifically limited, as long as the solute is an organic material having a property of semiconductor. For example, it is possible to use any of various materials which have hitherto been used as an organic semiconductor (i.e., so-called “OPC”) photoconductive material, for example, in the field of electrophotography. Such organic semiconductors can be those disclosed, for example, in the following document (with respect to the details of the organic semiconductor, documents such as Paul M. Borsenberger & David S. Weiss “Organic Photoreceptors for Xerography”, Marcel Dekker Inc., New York, Basel, Hongkong, ISBN 0-8247-0173-9, 1998 may be referred to, as desired).

(Solvent)

[0036] In combination with the solute as described above, the solvent to be used providing the organic semiconductor

material according to the present invention is not specifically limited. It is preferred to use an “aprotic” solvent, for example, as the above “solvent”. In the present invention, the term “aprotic” substance refers to a substance which does not have any “hydrogen atom” in its chemical structural formula such that the hydrogen atom would produce a hydrogen gas by the reaction of the substance with a metal Na. More actually, the term “aromatic” substance in the present invention refers to a substance which does give the stoichiometric production of hydrogen gas even in the case of the reaction thereof with metal Na in a “dried state” at a lower limit temperature in the operable temperature range for the semiconductor substance. It should be noted that, in the present invention, ethanol, for example, is not “aprotic”.

(Confirmation of Semiconductor Property)

[0037] The property of the “semiconductor” in the organic semiconductor material according to the present invention can be confirmed by observing the conduction (electronic conduction) due to at least one of hole and electron by use of a time-of-flight method.

(Operable Temperature Range)

[0038] In the present invention, the operable temperature range is not specifically limited. In view of the use of the organic semiconductor material according to the present invention in an ordinary and normal environment, the “operable temperature range” may be preferably in a range of about -60 to $+300^\circ\text{C}$., and more preferably in a range of about -200 to $+200^\circ\text{C}$., particularly preferably about -20 to $+120^\circ\text{C}$..

(Isotropic Phase)

[0039] The fact that the organic semiconductor material according to the present invention is in the “isotropic phase” can be confirmed by using the following method.

[0040] In general, when a texture of the liquid is observed with a polarized optical microscope, the liquid in the isotropic phase, which does not exhibit an orientation, light does not pass through the liquid so as to provide a “black” field of view in the microscope, because the liquid does not exhibit a polarization property in a cross-Nicol arrangement. In the actual observation, a sample is sandwiched between a slide glass and a cover glass or injected into a liquid crystal cell in capillary action, and then heated, as desired. In this way, the organic semiconductor in the “isotropic phase” may be confirmed by observing the liquid state of the sample with the polarized optical microscope so as to confirm the blocking of the transmission of light in a cross-Nicol arrangement, i.e., to confirm the black visual field.

(Electron and/or Hole Conduction)

[0041] The fact that the organic semiconductor material according to the present invention exhibits the “electron and/or hole conduction” can be confirmed, for example, by measuring the mobility by using a “dilution method” to be described later.

(Suitable Mobility)

[0042] The “mobility” of the organic semiconductor material according to the present invention may preferably be $10^{-7}\text{ cm}^2/\text{Vs}$ or more, more preferably $10^{-5}\text{ cm}^2/\text{Vs}$ or more, and particularly preferably $10^{-5}\text{ cm}^2/\text{Vs}$ or more (especially, $10^{-4}\text{ cm}^2/\text{Vs}$).

(Fluidity)

[0043] The fact that the organic semiconductor material according to the present invention has a “fluidity” can be confirmed by using the following method. In the present invention, the term “fluidity” as used herein is not necessarily complete fluidity, but the organic semiconductor material according to the present invention may also be a sludgy material such as coal tar.

[0044] Accordingly, the term “fluidity” as used in the present invention refers to a state satisfying any one of the following condition.

[0045] (a) The organic semiconductor material does not have a shape-retaining property.

[0046] (b) A material to be tested (for example, a material, the appearance of which is temporarily viewed so as to have a shape-retaining property) is molded into a rectangular parallelepiped shape with a base of 1×1 cm (w×d) and a height (h) of 10 cm, and is left standing for one week under normal temperature and normal pressure. In this case, when the material to be tested has a height of 9 cm or less (that is, the ratio of the height at this time with respect to the original height is 0.9 or less), the presence of the “fluid” property (that is, the fact that the organic semiconductor material does not substantially have a shape-retaining property) is confirmed. The fluid property is measured at the lower limit temperature in the operable temperature range.

(Shape-Retaining Property)

[0047] Accordingly, the organic semiconductor material according to the present invention can be distinguished from a “merely solid”, because the semiconductor material does not substantially have a shape-retaining property in the operable temperature range.

(Purification of Material so as to Provide Higher Purity)

[0048] In order to purify the material so as to provide a higher purity, it is essential not only to reduce an ionic impurity but also to reduce impurity molecules for electrically providing the trap level in the organic semiconductor material. That is, in general, it is essential to reduce the substance (impurity molecules) having its LUMO level in a case where the transport of electrons is intended, or the material having its HOMO level in a case where the transport of holes is intended, between a HOMO level and a LUMO level of a base material for the organic semiconductor material. In general, it is necessary to reduce the concentration of the impurity molecules to 100 ppm or less. Even by use of normal instrumental analysis, in many cases, it is difficult to determine the structure of the impurity molecules, and even the detection thereof.

[0049] The purpose of application of the impurity is to provide the application of the organic semiconductor in the present invention, as clearly described above, the undesired impurity should clearly be an ionic impurity and a substance which electrically provides a trap level with respect to the organic semiconductor material. In other words, when an impurity is a substance which does not electrically provide the trap level with respect to the organic semiconductor material, such an impurity can serve only as a diluent therefor, and accordingly the basic property of the organic semiconductor is not impaired substantially. That is, when the organic material according to the present invention is used as an organic semiconductor, the chemical purity of the

material does not become problematic, but the electrical purity of the material becomes important, because the mixing of the “electrically active impurity” will impair the function of the organic semiconductor. According to the studies performed by the present inventors, it is considered that the concentration of the electrically active impurity should be reduced to 100 ppm or less.

[0050] This is because, when the concentration of such an impurity is high, the electronic conduction disappears so as to induce the ionic conduction due to the ionization of the impurity.

[0051] For the purpose of purifying the intended material, it is possible to use conventional purifying methods for organic chemicals, such as distillation, recrystallization, sublimation, various types of chromatography, zone melting, vapor crystal growth, and the like. It is particularly preferred to use a combination of these methods.

[0052] As to the degree of the purification, the chemical purity may preferably be as high as possible. However, as described above, in view of the use thereof as semiconductor, the chemical purity itself is not important, but the concentration of the electrically active impurity is very important. Accordingly, as will be described later, the purification of the electrically active impurity needs to be determined according to a method of evaluating the impurity appearing hereinafter.

(Evaluation of Electrically Active Impurity)

[0053] Now, there will be described a method of evaluating the electrically active impurity in an organic liquid, which is another important aspect concerning the present invention.

[0054] In general, the ionic conduction may be a conduction in which ionized molecules or atoms (i.e., ions) are moved in a medium. As a result, the mobility thereof depends on both the ionic radius and the viscosity of the medium. As the ionic radius becomes larger, the mobility becomes smaller. As the viscosity becomes higher, the mobility also becomes smaller. The above relationship is known as the Walden rule. The mobility of ionic conduction in an ordinary organic liquid is 10^{-5} cm²/Vs or less.

(Electron Conduction of Non-Crystalline Substance)

[0055] The electronic conduction of the non-crystalline organic substance is hopping conduction in which charges moves from a molecular to another molecular. The mobility may be governed by the intermolecular distance as a site for the hopping, or the difference in the energy level between these sites. For an ordinary pure substance, its mobility is 10^{-4} cm²/Vs or more in many cases. In the case of a substance having a structure providing a large dipole, or a substance containing a small amount of an impurity providing a shallow trap level, the mobility is often 10^{-5} cm²/Vs or less in some cases. Accordingly, when the absolute value of the mobility is 10^{-4} cm²/Vs or less, it is generally difficult to determine the conduction mechanism from the value thereof. Both of the electronic conduction and the ionic conduction may be co-existent depending on the concentration of the impurity to be contained in the substance. In any case, the difference in conduction mechanism is essentially confirmed by use of the transient photocurrent measurement using the time-of-flight method and/or a method of determining the mechanism appearing hereinafter.

(Discrimination Between Electron Conduction and Ionic Conduction)

[0056] One effective method for discriminating the electronic conduction of an organic liquid from the ionic conduction thereof involves determination from the mobility and the dependence thereof on electric field and temperature. When the temperature for measuring the mobility is 200° C. or lower, the conduction with a mobility of 10^{-5} cm²/Vs or more is highly possibly the electronic conduction. The conduction with a mobility of the order of 10^{-4} cm²/Vs is highly possibly the electronic conduction, but the confirmation thereof is necessary.

[0057] In the conduction in the liquid phase (isotropic phase) due to electronic, the mobility may generally depend on the electric field in many cases, whereas in the ionic conduction, the mobility may not generally depend on the electric field. The activation energy in the ionic conduction may be generally governed by the temperature dependence of the viscosity, which differs from the activation energy in the electronic conduction. By use of these phenomena, the comparison between the temperature dependence of the viscosity and the temperature dependence of the mobility serves as a reference for the determination of the conduction. The difference in this characteristic, however, serves only as a guide, and does not provide a strict confirmation method.

(Addition of Diluent)

[0058] A simple method for surely determining whether the conduction mechanism is the electronic conduction or ionic conduction comprises: adding a substance (diluent) not serving as an electronic trap, and confirming the resultant change in the mobility between before and after the dilution.

[0059] When the substance of interest is diluted with a diluent with a smaller viscosity than that of the substance of interest, the viscosity of the substance after the dilution is decreased, and at the same time the intermolecular distance therein is increased by the dilution. In this case, when the conduction observed before the dilution is the electronic conduction, the mobility is decreased. On the other hand, when the conduction observed before the dilution is the ionic conduction, the mobility after the dilution is increased due to the decrease of the viscosity.

[0060] In some cases, depending on the concentration of an impurity serving as the trap, a plurality of signals representing the coexistence of the electronic conduction and the ionic conduction can be observed. In this case, when the sample of interest is subjected to a dilution test as described hereinabove, a decrease in the mobility is observed in the case of the electronic conduction, while an increase in the mobility is observed in the case of the ionic conduction. The degree of the decrease or increase in the mobility depends on the concentration of the diluent, and on the degree of the difference in the viscosity between the diluent and the substance of interest. Accordingly, the selection of the diluent does not necessarily cause a noticeable change in the mobility of one of the substances. In such a case, it is possible to easily determine the type of conduction mechanism, by selecting the diluent while taking the viscosity thereof into consideration, or the concentration of the diluent is changed so as to systematically measure a change in the mobility of the substance.

[0061] On the other hand, when the substance of interest has a low viscosity, and the diluent having a low viscosity

is limited, and the viscosity of the substance after the dilution is not considerably different from that before the dilution. In this case, a substance having a higher viscosity is further used as another diluent, so as to confirm the conduction mechanism. In such a case, the mobilities in the electronic conduction and in the ionic conduction will be decreased by the dilution at the same time. Even the addition of polymeric substance in a small amount, for example, 10 mol % or less can largely increase the viscosity, and thus is very effective. Such an addition of the diluent may change the viscosity of the substance largely, as compared to a change in the average intermolecular distance at the time of the addition of the diluent, whereby the difference between the conduction mechanisms can easily be determined.

[0062] Based on the above method and principle, the conduction in the liquid phase of the substance of interest is evaluated by using the time-of-flight method to determine whether the conduction is the electronic conduction or the ionic conduction. Accordingly, it can be determined whether or not the substance is usable for the organic semiconductor.

(Concentration of Impurity Serving as Trap)

[0063] In general, when the degree of the purification of the substance of interest is increased, the concentration of the impurity serving as the trap may gradually be decreased. When the concentration of the impurity is high, only a signal based on the ionic conduction is observed in terms of the waveform of the transient photocurrent observed by the time-of-flight method. However, after the degree of the purification is increased, a signal representing the electronic conduction starts to appear. As a result, the signal caused by the ionic conduction and the signal caused by the electronic conduction can simultaneously be observed. When the signals based on the two conduction mechanisms of the electronic conduction and the ionic conduction are observed in terms of the waveform of the transient photocurrent, the contribution of the electronic conduction and the ionic conduction to the total conduction can be evaluated in the following way. That is, the contribution can be evaluated by a method wherein the waveforms of the transient photocurrent to the electronic conduction and the ionic conduction are separated from each other and assigned to the respective conduction mechanisms, and the amounts of charges are determined from the time integral values of the current in these conduction mechanisms (with respect to the details of such a measuring method, as desired, the documents: Chemical Physics Letters 397, 2004, 319-323; Japanese Journal of Applied Physics Vol. 44, No. 6A, 2005, pp. 3764-3768; J. Phys. Chem. B 2005, 109, 22120-22125; Physical Review B 72, 193203, 2005; and Journal of Applied Physics, 102, 2007, 093718 may be referred to). When the degree of the purification is increased, finally, the signal based on the ionic conduction disappears, and only the signal representing the electronic conduction is observed.

(One Example of Method of Measuring Mobility)

[0064] Now, a "method of measuring mobility" which is usable in the present invention will be described below.

[0065] In general, the mobility of a substance can be determined by measuring the hole effect thereof, measuring the transient photocurrent by use of the time-of-flight method, analyzing the characteristic of a device such as transistor, and the like. However, most of the organic semi-

conductor materials according to the present invention have a small conductivity which is similar to that exhibited by an insulator, have a very small carrier concentration, so that most of the organic semiconductor materials hardly show an ohmic contact with an electrode. Accordingly, in order to measure the mobility of a bulk material, the measurement of the transient photocurrent by the time-of-flight method is the most effective measure to be used therefor.

(Mobility of Electron Conduction)

[0066] In general the mobility of a pure substance in the electronic conduction may be larger than that in the ionic conduction due to the movement of an ionized substance. Accordingly, when such a behavior is observed in the waveform of the transient photocurrent together with the purification of the material, the signal appearing in a region at a shorter transit time together with the purification can be assigned to that due to the electronic conduction, whereas the signal in a region at a longer transit time can be assigned to that due to the ionic conduction caused by an impurity.

[0067] When the conduction mechanism is determined by using the above method, a substance having a small viscosity tends to show a larger mobility due to the ionic conduction, and in such a case, it is often difficult to distinguish the mobility due to the ionic conduction from that due to the electronic conduction. Accordingly, in a case where the substance has already been purified sufficiently as to show a high purity, and only a signal caused by one kind of conduction is observed from the beginning in the waveform of the transient photocurrent obtained by the time-of-flight method, it is necessary to totally determine the conduction mechanism from the absolute value of mobility thereof, the temperature and electric field dependence thereof, and the change in the mobility thereof caused by a diluent. In this case, a method of evaluating a change in the mobility due to the addition of a diluent is very effective. Particularly, it is very effective to examine the behavior of the mobility in the substance of interest before and after the dilution, by adding a substance having a larger viscosity and by adding a substance having a small viscosity as compared to the viscosity of the substance of interest.

[0068] In order to determine the conduction mechanism of the substance of interest, it is basically possible to determine the conduction mechanism by using the method as described hereinabove, wherein the degree of the purification is increased, and the waveform of the transient photocurrent is measured by using the time-of-flight method. However, in some cases, the determination of the conduction mechanism becomes difficult exceptionally, even by use of the evaluation involving the addition of a diluent as described above. In this case, it is possible to determine the conduction mechanism of a substance before the addition of an impurity thereto, by selecting the impurity serving as a trap with reference to the HOMO and LUMO levels of the substance of interest, measuring the transient photocurrent of a sample of the substance, to which the impurity has been added, by using the time-of-flight method, and observing the ionic conduction due to the added impurity. In this case, with respect to the substance to be added as the impurity, it is important to select a substance so as to give a not so large difference of the ionic radiuses between the impurity and the substance of interest. Further, it is also important to use the impurity in a concentration, such as about 0.01 to 1 mol %, so that the impurity in the low concentration may not serve

as a diluent. It is important to select the impurity so as to provide a small change in the viscosity of the substance of interest before and after the addition of the impurity. The measurement under such a condition can provide the value of the ionic conduction in the substances of interest, even with a difference in ionic radius, if any. Accordingly, such a method is very useful for the determination of the conduction mechanism.

[0069] For example, in such a case, it is possible to observe only one signal due to one conduction mechanism in the waveform of the transient photocurrent of the substance of interest. In a case where another signal due to a new conduction appears in a region at a later time in the waveform of the transient photocurrent after the above addition of the impurity, the value of the mobility can be determined while taking the difference in ionic radius into consideration, so as to determine whether the conduction mechanism in the substance of interest before the addition of the impurity is electronic conduction or ionic conduction.

[0070] The organic substance in a liquid phase (isotropic phase), in which the impurity has been reduced by the purification thereof and the electronic conduction has been confirmed, is usable as an organic semiconductor. When the thus obtained organic semiconductor is used in an embodiment wherein the organic semiconductor is used in a specific application form or shape, the organic substance is also usable after the dilution thereof with the diluent as described above. In particular, when the organic semiconductor substance is diluted with the polymer substance, even the addition of the polymer substance in a small amount does not lead to a large decrease in mobility, but can increase the viscosity of the substance. The addition is very effective for the applications, and has the effect of suppressing the ionic conduction.

[0071] In the present invention, the impurity causing the ionic conduction of the organic substance is reduced to suppress the ionic conduction, so that the inherent electronic conduction can be basically achieved. For this reason, in order to reduce the impurity causing the ionic conduction, it is apparently important to perform purification of the substance. It is essential to confirm that the conduction mechanism of the refined substance is not the ionic conduction, but the electronic conduction. The confirmation can be performed by measurement of the transient photocurrent by the time-of-flight method. Alternatively, the confirmation can be performed by measuring a change in transit time of charges by addition of the diluent that increases or can increase the viscosity of the substance as compared to the viscosity of pure substance. Alternatively, the confirmation can be performed by comparison with the ionic conduction of the substance doped with a substance electrically providing the trap level in a very small amount. Otherwise, the confirmation can be performed by a combination of the above methods.

EXAMPLES

[0072] The present invention will be described in detail below by way of Examples, and is not limited thereto.

Measurement Example 1

[0073] Now, the present invention will be described below by showing cautions about the measurement of transient photocurrent by the time-of-flight method for distinguishing

the electronic conduction from the ionic conduction, the structure of a sample used for the measurement, and the waveform of the transient photocurrent actually observed.

[0074] The time-of-flight method used for evaluation in the present invention involves applying an electric field to a sample for measurement, generating charges eccentrically located near an electrode, and measuring a displacement current as a function of time by using an oscilloscope or the like when the charges reach an opposite electrode. Suppose that the charge moves at a certain velocity toward the opposite electrode, the electric field across the sample can be set uniform, and the traveling distance of the charge can be set to the thickness of the sample. In this case, a time required for the charge to reach the opposite electrode, which is, a transit time of the charge is estimated from the current waveform, so that the mobility of the sample can be determined from the thickness of the sample, the strength of the electric field, and the transit time of the charge.

[0075] In order to ensure the measurement of the mobility based on the above principle, the measurement performs the following method of generating charges eccentrically located near the electrode. That is, the generating method involves applying a pulse light with a short time width of one tenth or less of the transit time of a charge using as an excitation light, a light having a large absorption coefficient and a depth of light penetration of one tenth or less of the thickness of the sample. It is essential to set not only the conditions for application of light used as the charge formation means (light wavelength, light intensity, light application time), but also the measurement conditions sufficiently taking into consideration the following factors. That is, the measurement conditions are set taking into consideration the thickness of a sample, the selection of an electrode for ensuring the blocking contact, the level of an external resistance used for measuring a current, a time constant of a measurement system, and the like.

[0076] FIG. 1 shows an example of a sample structure and a measurement system which are usable for the above measurement.

[0077] The exact thickness of a liquid crystal cell used for the measurement is important to determine the mobility. Accordingly, it is necessary to accurately determine the thickness of the liquid crystal cell together with measurement of an electric capacitance and measurement of an interference pattern by measuring the optical characteristic. The measurement is also effectively performed using the same cell. It is necessary to pay attention to the deformation of the cell when a high electric field is applied.

[0078] A cell is formed by fixing two glass or crystal substrates with electrodes via a spacer in a certain thickness, and a liquid is charged as a sample into the cell. The cell is used for the measurement. At this time, attention should be paid to the fact that an impurity would be dissolved from a component used for producing the spacer or the cell into the sample. Taking into consideration the depth of light penetration with the wavelength of an irradiation light into the sample, the cell may be generally used whose thickness is about ten times as large as that of the sample. The electrode of the sample cell is used to irradiate light, and is a semi-transparent metal electrode made by vapor deposition or sputtering, or a transparent electrode, like the ITO, such that its one side becomes semi-transparent. In this case, attention needs to be paid so as to form the blocking contact which can suppress the injection of charges from the elec-

trode into the sample. It is apparent that the measurement of the transient photocurrent selects the measurement conditions according to the measurement time region, taking into consideration an electric capacitance of the measurement cell, a resistance of the measurement sample, a resistance to be coupled, and a time constant of the measurement system.

[0079] A pulse light is irradiated by applying a voltage to the sample, and using a nitrogen pulse laser or a harmonic or the like of a YAG laser to thereby photo-produce charges. In this case, it is necessary that the amount of charges produced by irradiation of the light is reduced within 10% or less of the amount of charges determined by both a geometric capacitance of the sample and an applied voltage to suppress the influence due to a space charge.

[0080] The light irradiation time has to be short enough to be ignorable as compared to the transit time of the charge. As a light source, a pulse light (having a pulse width of several tens ns or less), such as a nitrogen laser or a YAG laser, is usable.

[0081] FIG. 1 is a diagram showing the structure of a time-of-flight measurement device. FIG. 2 is a schematic diagram of a waveform of a typical transient photocurrent measured. As to the typical waveform of the photocurrent measured by the time-of-flight method, the measurement waveform of an organic liquid may generally have a shoulder representing a transit time when plotted in a normal scale as shown on the left side of the figure.

[0082] In order to determine the transit time of the charge, it is necessary to confirm the shoulder shown in FIG. 2 in the normal scale and the position of the stepped part systematically changing according to the intensity of the electric field.

[0083] In general, the waveform of the organic liquid having a high purity and measured by the time-of-flight method may be of the so-called non-dispersive type. When the photocurrent is plotted in the linear scale against the measurement time, a clear shoulder representing a transit time is observed. A mobility is determined from the following equation: $\mu = d^2 / \tau V$ where τ is the transit time, μ is a mobility, d is a thickness of the sample, and V is a voltage. In this case, it needs to be confirmed that when the applied voltage is changed to change the moving velocity of the charge, the transit time is changed together with the above change, and that the stepped part observed really represents the transit time.

(Applications of Liquid Organic Semiconductor Material)

[0084] The organic semiconductor material may not be generally defined strictly, unlike an inorganic semiconductor material, such as Si. The "organic material which can use the function for allowing a current to flow through the material to serve as an electron device" is called the organic semiconductor.

[0085] Most of the organic semiconductor materials have the small concentration of a carrier thermally formed (hole or electron), and thus are categorized as the insulator in view of conductivity. However, the carrier (hole or electron) can be transported. By use of the generation of carriers by the irradiation of the light, or the implantation of the carriers from the electrode, the carriers are introduced into the organic semiconductor. The function exhibited by the transport or recombination of the carriers is usable to manufacture various electron devices, such as an optical sensor, an EL device, a transistor, or a solar cell. This does not depend

on the provides of materials, such as solid or liquid, as long as the electronic conduction is basically caused in the material.

[0086] Actually, many examples using a liquid crystal material having a liquid property for the optical sensor, the organic EL device, and the solar cell are reported. For example, Appl. Phys. Lett., 74, pp. 2584-2586 (1999), Appl. Phys. Lett., 73, pp. 1595-1597 (1998) have respectively reported examples in which the optical sensor and the organic EL device were produced. As an example using a non-liquid crystal liquid, Appl. Phys. Lett., 95, pp 053304 (2009) reports an example of manufacturing the organic EL device.

[0087] According to a method disclosed in the present specification, the property of the liquid material as the organic semiconductor can be ensured, so that various electron devices can be manufactured using the liquid organic semiconductor based on the example described above.

Example 1

[0088] (The mobility of the material is 10^{-3} cm²/Vs or more, and thus the material does not need to be considered as one that causes the ionic conduction.)

[0089] A purified TPD (N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-diphenyl]-4,4'-diamine) was injected into a liquid crystal cell at the temperature of the isotropic phase. The transient photocurrent was measured by the above time-of-flight method to determine a mobility of the material from the transit time of the charge. The mobilities of a positive charge and a negative charge obtained at a measurement temperature of 150° C. were 4×10^{-3} cm²/Vs and 4×10^{-3} cm²/Vs, respectively. From the mobilities, the conduction can be determined to be not the ionic conduction, but the electronic conduction caused by each of the hole and the electron.

[0090] In the same manner, in the purified TTA(tritolyllamine), the mobilities of the positive charge and the negative charge at 100° C. were determined to be 4×10^{-3} cm²/Vs and 9×10^{-5} cm²/Vs, respectively. Accordingly, the conduction of at least the positive charge can be determined to be the electronic conduction caused by the hole.

Example 2

[0091] A 6-(4'-octylphenyl)-2-dodecyloxynaphthalene(8-PNP-012) was injected in an isotropic phase (liquid phase: in a thickness of the sample of 15 μm) into a glass cell having an ITO electrode (4 mm square) positioned therein. A 337 nm nitrogen laser pulsed light (pulse width: 600 ps, 3 μJ/pulse) was radiated to apply voltages of +150 V or -150 V to the electrode on the light irradiation side, so that the transient photocurrent observed was measured by a digital oscilloscope. The wave profiles (in black) shown in FIG. 5 (whose left side illustrated the waveform of a transient photocurrent of the positive charge, and whose right side illustrated the waveform of a transient photocurrent of the negative charge) had two shoulders corresponding to transit times in different time regions. In order to clarify the conduction, the dilution experiment using an n-octadecane was performed. When the concentration of the n-octadecane was changed from 16 mol % to 42 mol %, the change of

waveform of the transient photocurrent was shown in FIG. 5 (in green for 42 mol %, in red for 30 mol %, and in blue for 16 mol %).

[0092] The stepped part appearing in the short or early time region among two transient photocurrent wave profiles of the positive and negative charges is shifted to the late time region with increasing concentration of the n-octadecane. The stepped part appearing in the late time region is shifted to the earlier time region. From this aspect, the shoulder appearing in the early time region can be attributed to the electronic conduction, and another shoulder appearing in the late time region can be attributed to the ionic conduction. FIG. 4 shows the mobilities determined from two transit times plotted based on the concentration of the n-octadecane. In the change of two mobilities of 8-PNP-O12 by dilution (left: positive charge, right: negative charge), the "black" part represents the mobility determined from the transit time of the charge in the early time region, and the "red" part represents the mobility determined from the transit time of the charge in the late time region. The mobility of the electronic conduction represented by the "black" part is decreased together with the dilution. In contrast, the mobility of the ionic conduction represented by the "red" part is increased together with the dilution.

[0093] According to the result, the mobilities of the hole and electron at 130° C. were determined to be 1.1×10^{-4} cm²/Vs, and 1.1×10^{-4} cm²/Vs, respectively. The mobilities of the positive ion and the negative ion were determined to be 2.7×10^{-5} cm²/Vs, and 4.6×10^{-5} cm²/Vs, respectively.

Example 3

[0094] A 2-phenylnaphthalene in an isotropic phase (liquid phase: in a thickness of the sample of 16.31 μm) was charged into a glass cell having an ITO electrode (4 mm square) positioned therein in the same manner as in Example 2. A 337 nm nitrogen laser pulsed light (pulse width: 600 ps, 3 μJ/pulse) was radiated at 105° C. to apply voltages of +10 to 100 V or -10 to 100 V to the electrode on the light irradiation side, so that the transient photocurrent was observed and measured by a digital oscilloscope. The waveform of the transient photocurrent was shown in FIG. 5. The waveform of the positive charge has one stepped part representing a charge travelling in an early time region. The waveform of the negative charge has "two shoulders" corresponding to two different travelling time regions.

[0095] In the same manner as in Example 2, According to the result of the dilution experiment, the mobilities of the hole and electron were determined to be 8.9×10^{-4} cm²/Vs, and 8.8×10^{-4} cm²/Vs, respectively. The mobility of a negative ion was determined to be 2.1×10^{-5} cm²/Vs.

Example 4

[0096] A ω,ω'-dioctylterthiophene in an isotropic phase (liquid phase: in a thickness of the sample of 16.45 μm) was charged into a glass cell having an ITO electrode (4 mm square) positioned therein in the same manner as in Example 2. A 337 nm nitrogen laser pulsed light (pulse width: 600 ps, 3 μJ/pulse) was radiated at 100° C. to apply voltages of +15 to 50 V or -15 to 50 V to the electrode on the light irradiation side, so that the transient photocurrent was observed and measured by the digital oscilloscope. The waveform of the transient photocurrent was observed as shown in FIG. 6. The wave provides the transient photocurrents of the positive

electrode and the negative electrode have two stepped portions corresponding to two different travelling times.

[0097] In the same manner as in Example 2, According to the result of the dilution experiment, the mobilities of the hole and electron were determined to be 9.3×10^{-5} cm²/Vs. The mobilities of the positive ion and the negative ion were determined to be 2.0×10^{-5} cm²/Vs and 2.9×10^{-5} cm²/Vs, respectively.

Example 5

[0098] A ω, ω' -dihexylcyquaterthiophene in an isotropic phase (liquid phase: in a thickness of the sample of 13.86 μ m) was charged into a glass cell having an ITO electrode (4 mm square) positioned therein in the same manner as in Example 2. A 337 nm nitrogen laser pulsed light (pulse width: 600 ps) was radiated at 200° C. to apply voltages of +15 to 50 V or -15 to 50 V to the electrode on the light irradiation side, so that the transient photocurrent observed was measured by the digital oscilloscope. The waveform of the transient photocurrent was observed as shown in FIG. 7. The waveform of the positive charge has two shoulders corresponding to two different transit times, and the waveform of the negative charge transit has one shoulder.

[0099] In the same manner as in Example 2, According to the result of the dilution experiment (the absolute value), the mobilities of the hole and electron were determined to be 5.5×10^{-4} cm²/Vs, and 1.8×10^{-4} cm²/Vs, respectively. The mobilities of the positive ion and the negative ion were determined to be 8.0×10^{-5} cm²/Vs and 8.4×10^{-5} cm²/Vs, respectively.

Example 6

[0100] A ω, ω' -didodecyloxy-2-methylterphenyl (12O-TPMe-O12) in an isotropic phase (liquid phase: in a thickness of the sample of 10 μ m) was charged into a glass cell having an ITO electrode (4 mm square) positioned therein in the same manner as in Example 2. A 337 nm nitrogen laser pulsed light (pulse width: 600 ps) was radiated at 170° C. to apply voltages of +40 to 100 V or -40 to 100 V to the electrode on the light irradiation side, so that the transient photocurrent observed was measured by the digital oscilloscope. The waveform of the transient photocurrent was observed as shown in FIG. 8. The waveform of the positive charge has one shoulder corresponding to one transit time.

[0101] In the same manner as in Example 2, According to the result of the dilution experiment, the mobilities of the hole and electron were determined to be 9.7×10^{-5} cm²/Vs, and 1.0×10^{-4} cm²/Vs, respectively.

Example 7

[0102] A toluene was charged at room temperature into a crystal cell (liquid phase: in a thickness of the sample of 23.51 μ m) having an ITO electrode (4 mm square) positioned therein in the same manner as in Example 2. A 260 nm YAG laser pulsed light was radiated at 23° C. to apply voltages of +200 V or -200 V to the electrode on the light irradiation side, so that the transient photocurrent was observed and measured by the digital oscilloscope. The waveform of the transient photocurrent was observed as shown in FIG. 9. The wave profiles of the positive and negative charges have respective shoulders corresponding to the transit times. In the same manner as in Example 2, the

dilution experiment using n-Hexane was performed. As a result, as shown in FIG. 9, the slight decrease in mobility was observed.

Example 8

[0103] A change in Example 7 was not clear. Accordingly, a styrene monomer sufficiently purified was thermally polymerized without any catalyst. In the same manner, the thus-obtained polystyrene was added to the toluene. The transient photocurrent of the material was measured to determine the mobility thereof as shown in FIG. 10.

[0104] According to the result, the toluene containing polystyrene has its viscosity increased largely, but its mobility does not change so much. Accordingly, the mobilities of the hole and electron of the toluene were determined to be 8×10^{-4} cm²/Vs, and 8×10^{-4} cm²/Vs, respectively.

EXPLANATION OF LETTERS OR NUMERALS

- [0105] 1 Substrate
- [0106] 2 Electrode
- [0107] 3 Spacer
- [0108] 4 Sample
- [0109] 5 Power supply (having positive and negative polarities)
- [0110] 6 External resistor
- [0111] 7 Digital oscilloscope

1. A method for measuring characteristics of an organic substance, comprising:

- (a) disposing the organic substance to be measured between a pair of electrodes;
- (b) injecting charges into the organic substance and measuring a transient current in an isotropic liquid phase of the organic substance using a time-of-flight method;
- (c) separating the transient current into a current by electronic conduction and a current by ionic conduction; and
- (d) measuring a charge amount corresponding to each separated current,

wherein purity of the organic substance is evaluated based on the charge amount corresponding to each separated current.

2. The method according to claim 1, wherein the charge injection into the organic substance is conducted by applying a pulse voltage or a pulse light to the organic substance.

3. The method according to claim 1, wherein the organic substance is purified to the extent that the organic substance exhibits electron conduction and/or hole conduction.

4. The method according to claim 1, wherein the organic substance is an organic semiconductor material, and a semiconductor property of the organic semiconductor material is evaluated based on the charge amount corresponding to each separated current.

5. The method according to claim 4, wherein the semiconductor property is purity of the organic semiconductor material as an electronic material, wherein the purity of the organic semiconductor material as an electronic material is relative concentration of a substance serving as an electronic trap.

6. The method according to claim 4, wherein the semiconductor property is mobility, and whether the conduction mechanism, in the organic semiconductor material, is electronic conduction or ionic conduction is determined based on a value of mobility measured.

7. The method according to claim 6, wherein when the mobility measured is mobility of 10^{-3} cm²/Vs, the conduction in the organic semiconductor material is evaluated as electronic conduction.

8. The method according to claim 6 or 7, wherein whether the conduction mechanism is electronic conduction or ionic conduction is determined based on a change in the mobility due to a change in viscosity of the organic substance or a change in an intermolecular distance of the organic substance between before and after adding a diluent.

9. The method according to claim 8, wherein the diluent is a substance having HOMO and LUMO levels, the HOMO and LUMO levels being not providing an electronic trap level with respect to HOMO and LUMO levels of the organic substance.

10. The method according to claim 1, wherein the organic substance is a mixture.

11. The method according to claim 10, wherein the organic substance is in the form of solution.

12. The method according to claim 1, wherein the pair of electrodes are respectively disposed on a pair of substrates, and a charge injection means for injecting charges into the organic substance is provided.

13. The method according to claim 12, wherein the pair of substrates, the pair of electrodes and the charge injection means form a cell for measuring electronic conduction and/or ionic conduction.

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