

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets

(11)



EP 1 251 720 A2

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:

23.10.2002 Bulletin 2002/43

(51) Int Cl. 7: H05B 33/08, H01L 51/20

(21) Application number: 02252144.7

(22) Date of filing: 25.03.2002

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 26.03.2001 JP 2001087133

(71) Applicant: Pioneer Corporation  
Meguro-ku, Tokyo (JP)

(72) Inventors:

- Wakimoto, Takeo, c/o Pioneer Corporation  
Tsurugashima-shi, Saitama 350-2288 (JP)
- Nakamura, Kenji, c/o Pioneer Corporation  
Tsurugashima-shi, Saitama 350-2288 (JP)

(74) Representative:

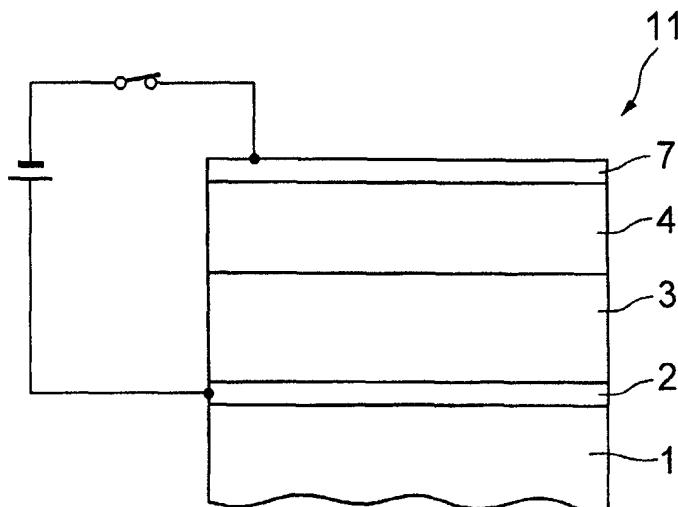
Luckhurst, Anthony Henry William  
MARKS & CLERK,  
57-60 Lincoln's Inn Fields  
London WC2A 3LS (GB)

### (54) Organic semiconductor diode and organic electroluminescence element display device

(57) An organic semiconductor diode includes at least one hole transport layer which is arranged on an anode side and formed of an organic compound having a hole transport capability, and at least one electron transport layer which is arranged on a cathode side and formed of an organic compound having an electron transport capability. The at least one hole transport layer and the at least one electron transport layer are lami-

nated one upon another. The organic semiconductor diode exhibits nonlinear current-voltage characteristics when a voltage is applied between the hole transport layer and the electron transport layer in contact with each other. The hole transport layer at an anode-side end has an ionization potential larger than an electron affinity of the electron transport layer at a cathode side end.

### FIG. 2



EP 1 251 720 A2

**Description**BACKGROUND OF THE INVENTION

## 5 1. Field of the Invention

**[0001]** The present invention relates to an organic semiconductor, i.e. a two-terminal element diode which exhibits a nonlinear current-voltage characteristics by the movement of electrons and holes supplied to the junction of thin films made of organic compounds having electrical characteristics different from each other and to an organic electroluminescence element display device using the same.

## 10 2. Description of the Related Art

**[0002]** An organic electroluminescence element (hereinafter also referred to as "organic EL element") is known which makes use of electroluminescence (hereinafter also referred to as "EL") of an organic compound that emits light by injection of electric current and includes a light-emitting layer formed by a thin layer of such an organic compound. Now, an organic EL element display device formed by arranging a plurality of the above organic EL elements in a matrix form is receiving attention as a display device capable of achieving low power consumption, high display quality, and thickness reduction. As shown in FIG. 1, each organic EL element 200 is comprised of a transparent substrate 1, such as a glass plate or the like, a transparent anode electrode 201 formed on the substrate, at least one organic material layer 202 which is comprised of an electron transport layer, a light-emitting layer, and a hole transport layer, and a metal cathode electrode 203, all of which are laminated in the mentioned order. When a positive voltage is applied to the transparent anode electrode 201, and a negative voltage is applied to the metal cathode electrode 203, that is, when a direct current is caused to flow between the transparent electrode and the metal electrode, the light-emitting layer in the organic material layer 202 emits light.

**[0003]** The organic EL element is considered as a capacitive light-emitting element. When a direct current driving voltage for causing light emission is applied between the electrodes, an electric charge is accumulated in a capacity component. Then, when the driving voltage exceeds a light-emitting threshold voltage of the EL element, a current starts to flow in the organic material layer to cause the organic EL element to emit light at a luminous intensity approximately proportional to the current.

**[0004]** The organic EL element display device is a light-emitting apparatus composed of a plurality of light-emitting pixels, that is, organic EL elements, in an image display layout in which the organic EL elements are disposed at respective points of intersection of horizontal lines and vertical lines, i.e. in a so-called matrix form. An example of the method of driving the organic EL element display device is a so-called simple matrix driving method. A display apparatus based on the simple matrix driving method has a plurality of anode lines and cathode lines arranged in the form of a matrix (grid), with organic EL elements connected at respective points of the intersection of the anode lines and the cathode lines. Either of the anode lines and the cathode lines are sequentially selected at predetermined time intervals for scanning, and the other lines are driven by a drive source in synchronism with the scanning, to cause organic EL elements arranged at desired points of intersection of the lines to emit light. In this method, each organic EL element is lighted only during an access time period, and hence to increase the size of a display screen of the apparatus, a large current and a high voltage are required.

**[0005]** To increase the size of the display screen of the organic EL element display device, an active matrix driving method may be considered, besides the simple matrix driving method. The active matrix driving method uses a thin film transistor (TFT) arranged at each point of the intersection (of the anode lines and the cathode lines), and supplies a current to each pixel by switching operation to cause the associated organic EL element to emit light. The TFT can be formed with using an element formed by p-Si or a-Si. Further, it is also possible to form the TFT by using a MOS-FET (Metal Oxide Semiconductor Field Effect Transistor) in place of the above element. Accordingly, the active matrix driving method requires a large number of switching circuit substrates, and inorganic materials have to be laminated on substrates of the circuits. Therefore, a high temperature process is employed for manufacturing the switching circuits.

50 OBJECT AND SUMMARY OF THE INVENTION

**[0006]** To reduce the instantaneous brightness of light-emitting elements to prevent deterioration or breakdown of both of the driving methods above mentioned, it is required to apply reverse voltage to them when light is not emitted, i.e. the scanning is inhibited. Therefore, it is proposed to provide a rectifier connected in series to the light-emitting element.

**[0007]** Therefore, an object of the present invention is to provide an organic semiconductor diode which can be produced at a relatively low temperature, and another object of the present invention is to provide an organic EL element

display device having the organic semiconductor diodes formed on a common substrate.

[0008] An organic semiconductor diode according to a first aspect of the present invention comprises:

5 at least one hole transport layer which is arranged on an anode side and formed of an organic compound having a hole transport capability; and

at least one electron transport layer which is arranged on a cathode side and formed of an organic compound having an electron transport capability, said at least one hole transport layer and said at least one electron transport layer being laminated one upon another,

10 wherein said hole transport layer at an anode-side end has an ionization potential larger than an electron affinity of said electron transport layer at a cathode side end, whereby the organic semiconductor diode exhibiting nonlinear current-voltage characteristics when a voltage is applied between said hole transport layer and said electron transport layer in contact with each other.

15 [0009] In another aspect of the present invention of the organic semiconductor diode, as to all of two adjacent layers of said at least one hole transport layer, a hole transport layer on the anode side has a smaller ionization potential than that of another hole transport layer.

[0010] In a further aspect of the present invention of the organic semiconductor diode, as to all of two adjacent layers of said at least one electron transport layer, an electron transport layer on the cathode side has a larger electron affinity than that of another electron transport layer.

20 [0011] An organic electroluminescence element display device having plural light-emitting portions arranged in a display layout according to a second aspect of the present invention comprises:

25 a plurality of organic electroluminescence elements arranged therein as the light-emitting portions, said plurality of organic electroluminescence elements each including an anode, and a cathode, as well as a light-emitting layer having a light-emitting function and formed of an organic compound having at least an electron transport capability or a hole transport capability, and a carrier transport layer formed of an organic compound having at least a hole transport capability or an electron transport capability; and

30 respective organic semiconductor diodes each arranged adjacent to and at the same time connected in series to an associated one of said plurality of organic electroluminescence elements,

35 wherein each of said organic semiconductor diodes has a hole transport thin film layer which is arranged on an anode side and formed of an organic compound having a hole transport capability, and an electron transport thin film layer which is arranged on a cathode side and formed of an organic compound having an electron transport capability, the hole transport layer and the electron transport layer being laminated one upon another, said organic semiconductor diode exhibiting nonlinear current-voltage characteristics when a voltage is applied between the hole transport layer and the electron transport layer in contact with each other.

40 [0012] In another aspect of the present invention of the organic electroluminescence element display device, at least one of said hole transport layer and said electron transport layer of said organic semiconductor diode is formed of the same organic compound as that of at least one of said light-emitting layer and said carrier transport layer.

[0013] In a further aspect of the present invention of the organic electroluminescence element display device, said organic semiconductor diode and said organic electroluminescence element are laminated one upon another.

#### BRIEF DESCRIPTION OF THE DRAWINGS

45 [0014]

FIG. 1 is a sectional view schematically showing the construction of an organic EL element;

FIG. 2 is a sectional view schematically showing the construction of an organic semiconductor diode;

FIG. 3 is a diagram showing energy levels of an organic semiconductor diode having a two-layer structure;

50 FIG. 4 is a diagram showing energy levels of an organic semiconductor diode having a multi-layer structure;

FIG. 5 is a graph showing the current-voltage characteristics of an organic semiconductor diode according to an embodiment of the present invention;

FIG. 6 is a partial plan view showing a portion of a display panel for an organic EL element display device based on the simple matrix driving method;

55 FIG. 7 is a sectional view schematically showing the construction of the organic semiconductor diode and the organic EL element, which are connected in series to each other; and

FIG. 8 is a sectional view schematically showing the construction of an organic semiconductor diode and an organic EL element, which are connected in series to each other, as another embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0015] The present invention will now be described in detail with reference to the drawings showing embodiments thereof.

[0016] FIG. 2 shows an organic semiconductor diode according to an embodiment. As shown in the figure, the organic semiconductor diode 11 includes an insulating substrate 1 of glass or the like, an anode 2 formed on the insulating substrate 1, a hole transport layer 3 which is formed of an organic compound, an electron transport layer 4 which is formed of an organic compound, the hole transport layer 3 and the electron transport layer 4 having formed on the anode 2 such that they are in contact with each other, and a cathode 7 is laminated on the electron transport layer 4. The cathode 7 cooperates with the anode 2 opposed thereto to apply an electric field to the junction of the hole transport layer 3 and the electron transport layer 4. More specifically, the cathode 7 injects electrons into the electron transport layer 4 having an electron transporting property, whereas the anode 2 injects holes into the hole transport layer 3 having a hole transporting property.

[0017] Further, the organic semiconductor diode 11 is only required to be composed of a hole transport layer on the anode side and an electron transport layer on the cathode side, which are laminated one upon the other. The organic semiconductor diode 11 may have the components laminated on the substrate in the reverse order to that of the example illustrated in FIG. 2, that is, in the order of the cathode, the electron transport layer, the hole transport layer, and the anode. The hole transport layer is formed of an organic compound having a hole transport capability, and the electron transport layer is formed of an organic compound having an electron transport capability. The ionization potential of the hole transport layer on the anode side is larger than the electron affinity of the electron transport layer on the cathode side. The hole transport layer and the electron transport layer can be constructed such that they have multi-layer structures formed by thin films of organic compounds having a hole transport capability and an electron transport capability, respectively. The organic semiconductor diode exhibits nonlinear current-voltage characteristics when a voltage is applied between the hole transport layer and the electron transport layer in contact with each other. The cathode has a work function close to or smaller than the electron affinity of the electron transport layer, while the anode has a work function larger than that of the cathode. It should be noted that as shown in FIG. 3, the electron affinity  $E_a$  is an energy measured from a vacuum level as the reference energy level of 0 eV to a lowest unoccupied molecular orbital (LUMO) level at a lower edge of a conduction band CB. The ionization potential  $I_p$  is an energy value measured from the vacuum level to a highest occupied molecular orbital (HOMO) level at an upper edge of a valence electron band VB. The work functions  $W_f A$  and  $W_f C$  at the respective anode and cathode are energies measured from the vacuum level (0 eV) to respective Fermi levels, concerning a metal material and a metal oxide material.

[0018] It is preferred that an anode material (ANODE) used for the organic semiconductor diode according to the present invention has a work function  $W_f A$  as high as possible. For instance, it is preferable to use gold, platinum, palladium, indium tin oxide (hereinafter referred to as "ITO"), iridium zinc oxide, zinc oxide, or an alloy of selected ones of these metals, or further tin oxide, selenium, copper iodide or nickel, each of which has a work function of 4.5 eV or more. Further, it is also possible to employ a conductive polymer, such as poly (3-methylthiophene), polyphenylene sulfide, or polyaniline. These materials can be used separately or by laminating two or more kinds of them one upon the other, for instance, by laminating a polyaniline film on ITO film.

[0019] On the other hand, as a cathode material (CATHODE), there is used a metal or a compound having a low work function  $W_f C$ , for instance, an alkali metal, such as silver, lead, tin, aluminum, calcium, indium, chromium, or lithium, an alkaline-earth metal, such as magnesium, or an alloy of selected ones of these metals, or further an alkali metal compound, or an alkaline-earth metal compound, each of which has a work function lower than 4.5 eV.

[0020] The electron transport material of the electron transport layer, which has an electron transport capability, is selected from organic compounds represented by the following formulas (1) to (35). When the electron transport layer is configured to have a multi-layer structure, as shown in FIG. 4, the electron transport material (N-TYPE ORGANICS) is selected such that a layer of the material closer to the interface between the electron transport layers and the hole transport layers has a smaller electron affinity  $E_a$  ( $E_a 1 < E_a 2$ ). In other words, out of two electron transport layers adjacent to each other, an electron transport layer on the cathode side has a larger electron affinity than that of an electron transport layer on the anode side.

5

10

15

20

25

30

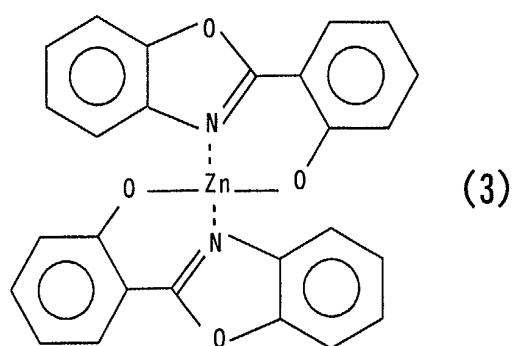
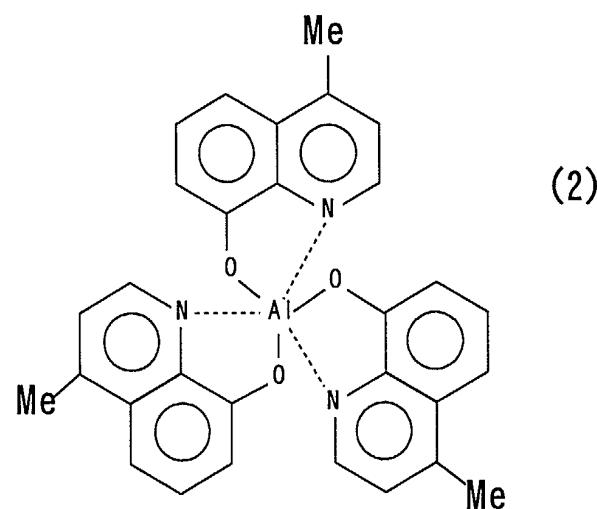
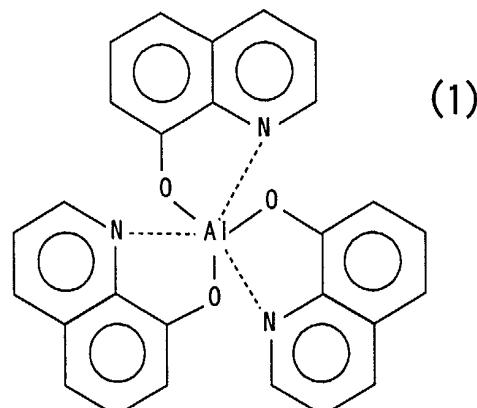
35

40

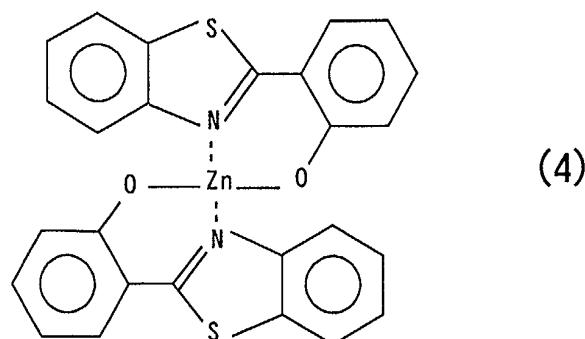
45

50

55



5



10

15

20

25

30

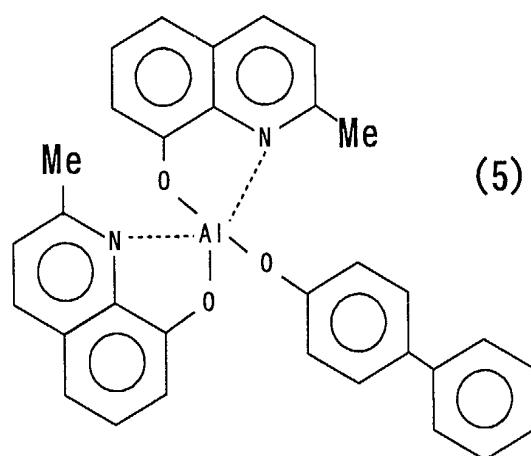
35

40

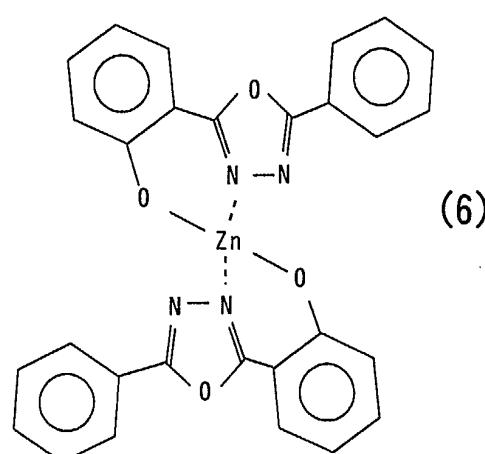
45

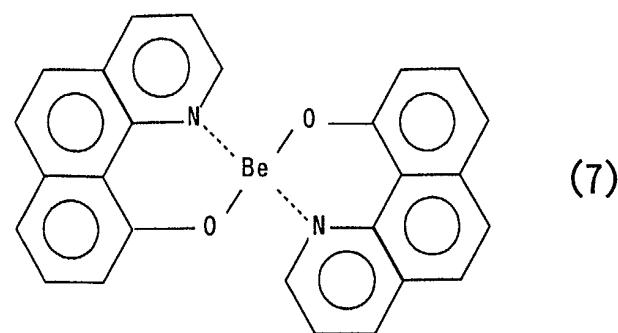
50

55

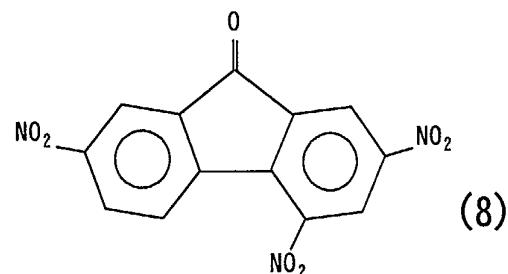


(6)

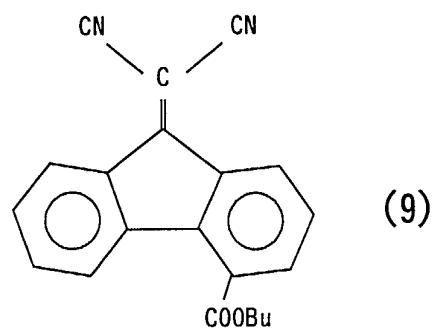




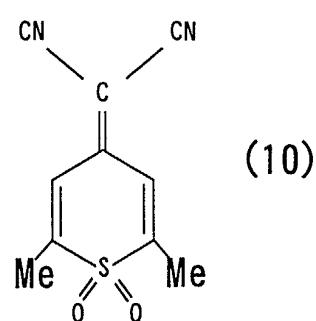
15



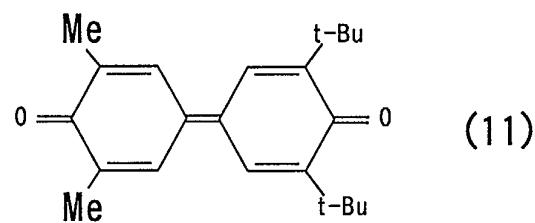
30



45

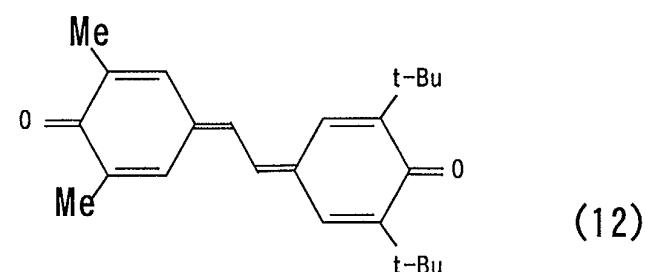


5



10

15



20

25

30

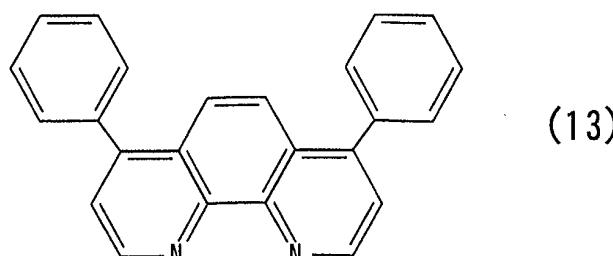
35

40

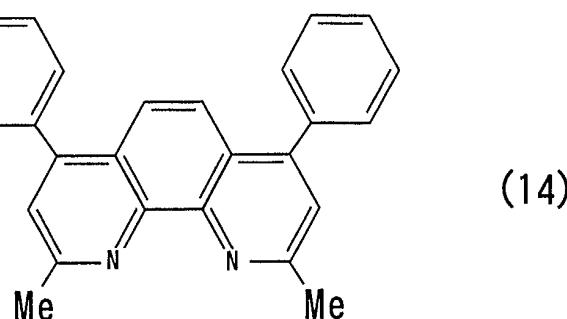
45

50

55

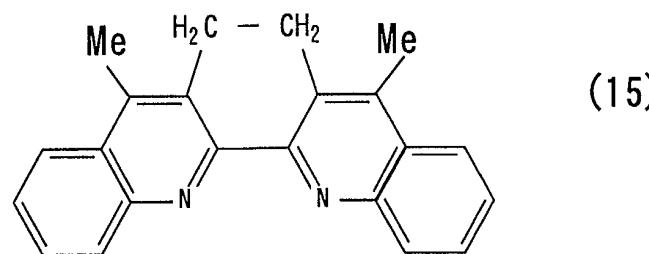


(13)



(14)

5



10

15

20

25

30

35

40

45

50

55

5

10

15

20

25

30

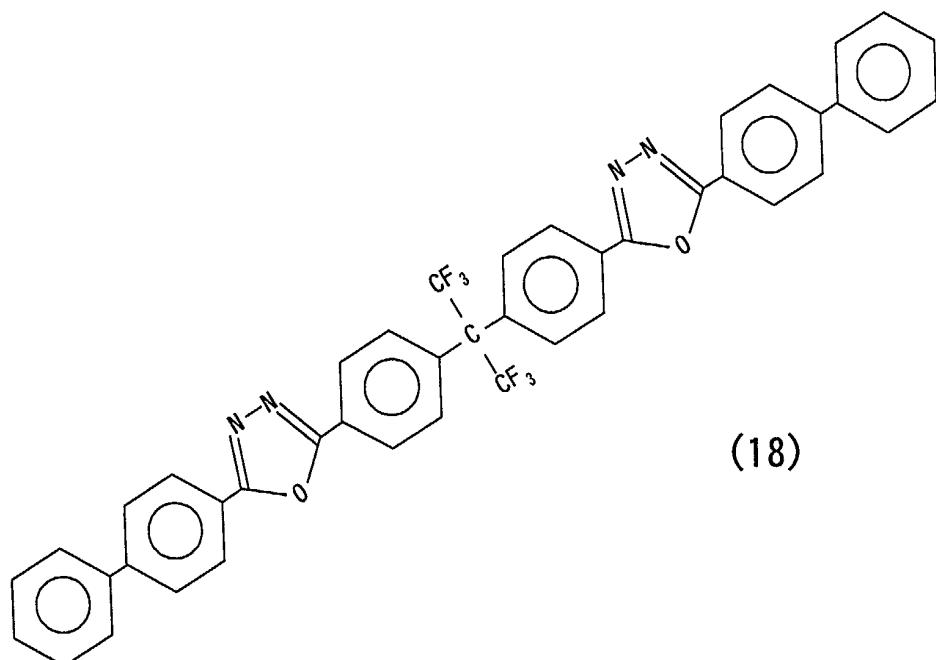
35

40

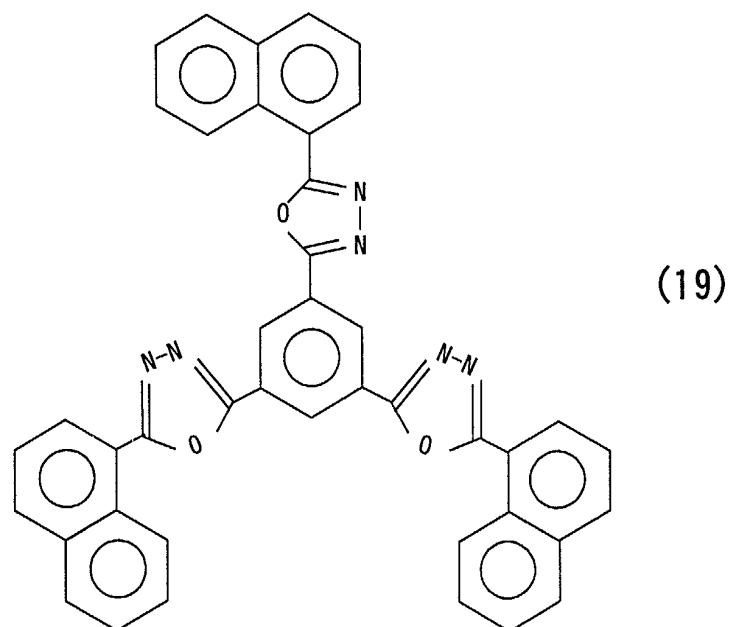
45

50

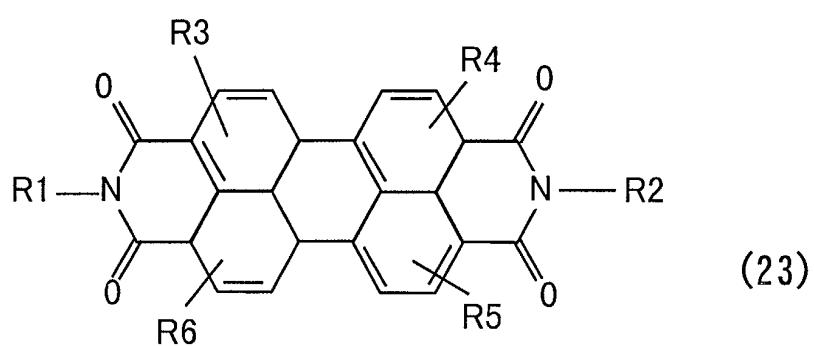
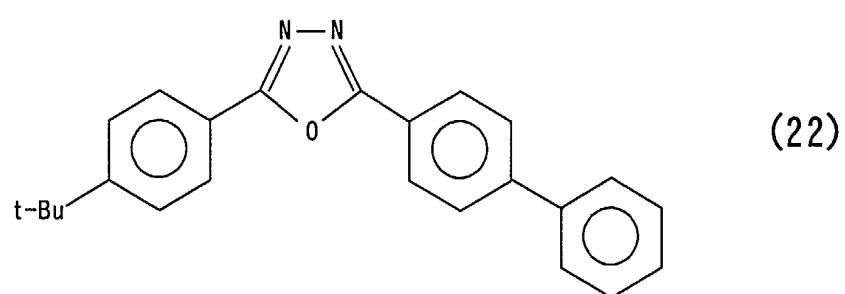
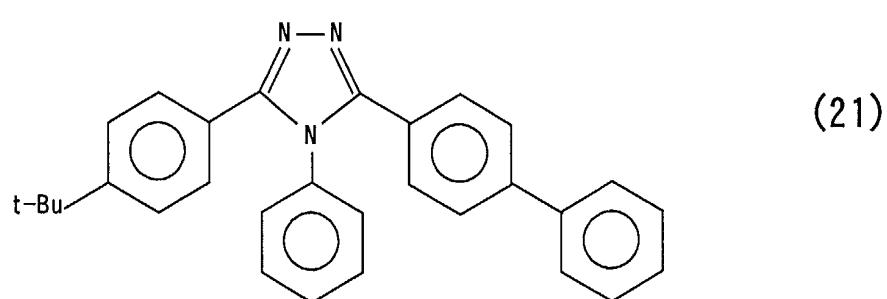
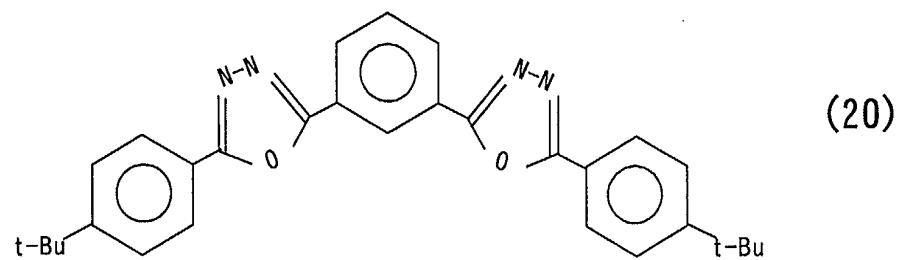
55



(18)



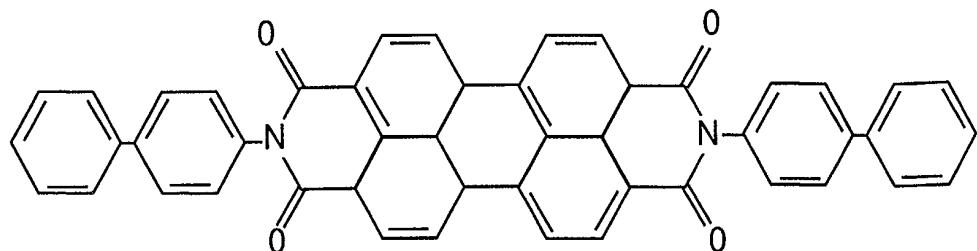
(19)



wherein R1 to R6 each independently represent hydrogen, an alkyl or alkoxy group having a carbon number of 1 to

12, an aryl or aryloxy group having a carbon number of 6 to 14, a heterocyclic compound group, a cyano group, a halogen group, a halogenated alkyl group, or a nitro group.

5

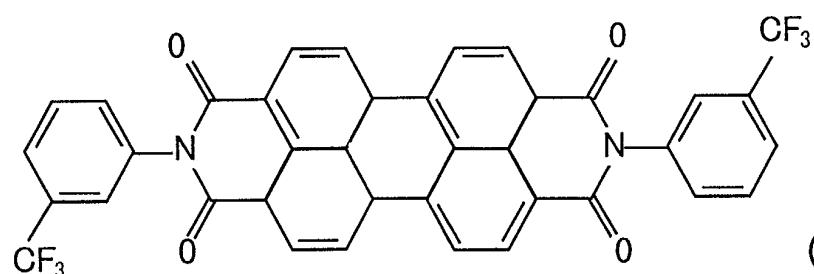


(24)

15

20

25

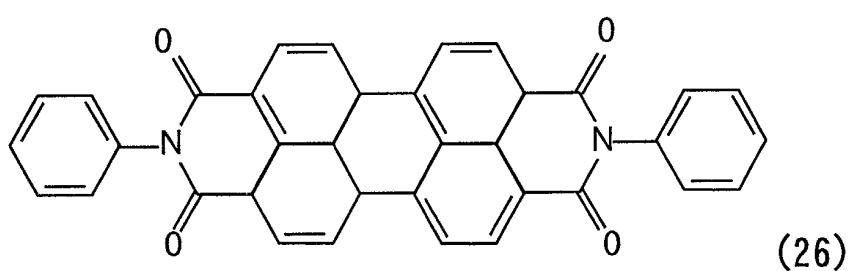


30

35

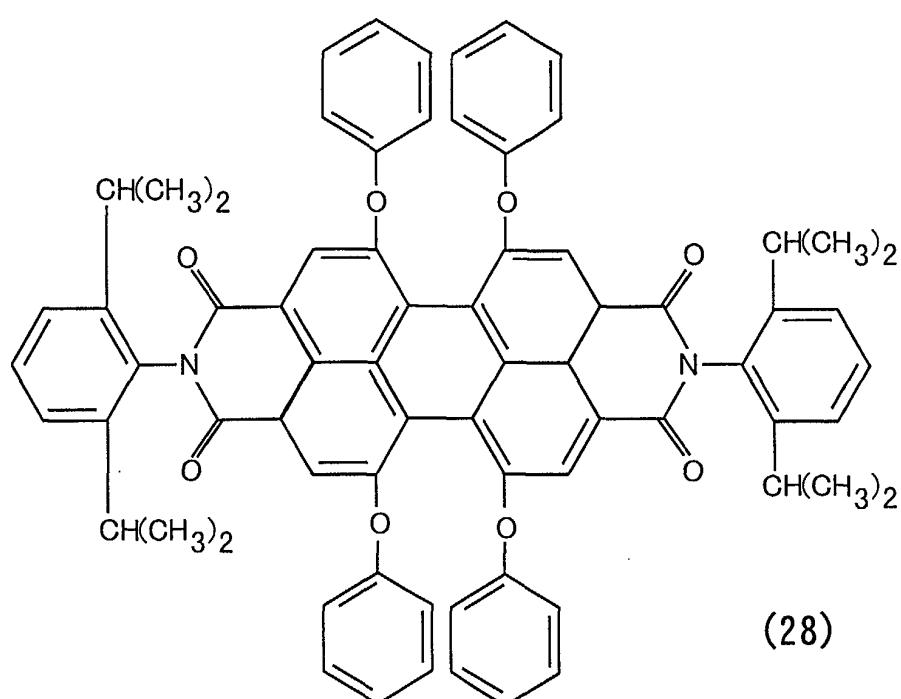
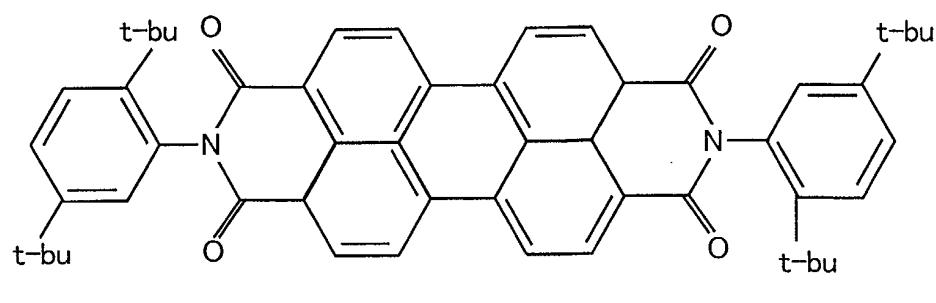
40

45

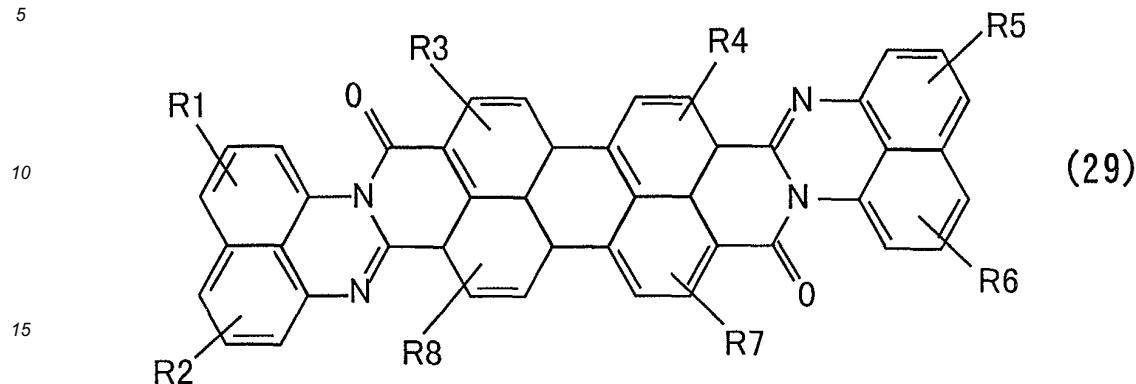


50

55

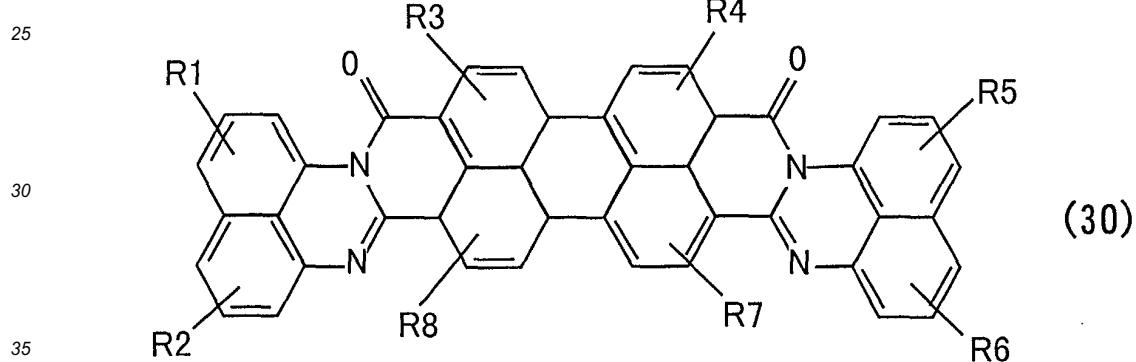


5



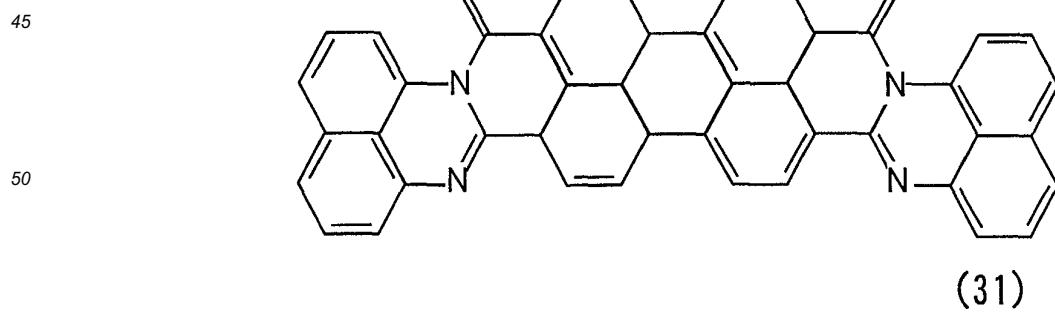
wherein R1 to R8 each independently represent hydrogen, an alkyl or alkoxy group having a carbon number of 1 to 20 12, an aryl or aryloxy group having a carbon number of 6 to 14, a heterocyclic compound group, a cyano group, a halogen group, a halogenated alkyl group, or a nitro group.

25

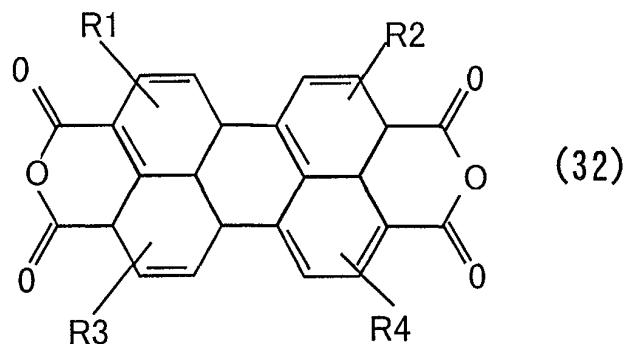


wherein R1 to R8 each independently represent hydrogen, an alkyl or alkoxy group having a carbon number of 1 to 40 12, an aryl or aryloxy group having a carbon number of 6 to 14, a heterocyclic compound group, a cyano group, a halogen group, a halogenated alkyl group, or a nitro group.

45

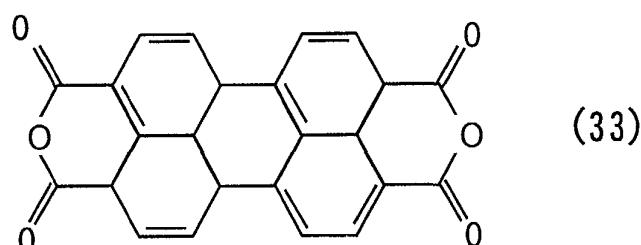


55



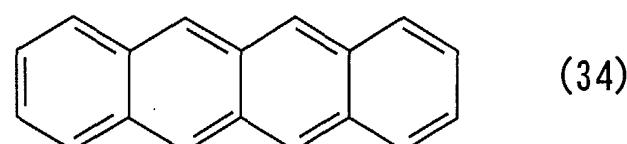
15 wherein R1 to R4 each independently represent hydrogen, an alkyl or alkoxy group having a carbon number of 1 to 12, an aryl or aryloxy group having a carbon number of 6 to 14, a heterocyclic compound group, a cyano group, a halogen group, a halogenated alkyl group, or a nitro group.

20



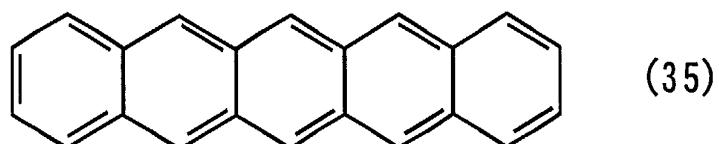
30

35



45

50

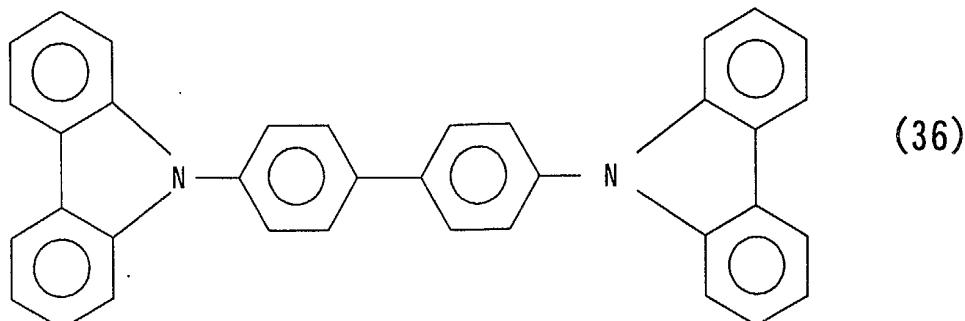


55 [0021] Further, condensed ring compounds, such as a perylene derivative or the like, shown in the above formulas (23) to (35) are preferably used as materials having an electron transport capability, of the electron transport layer.

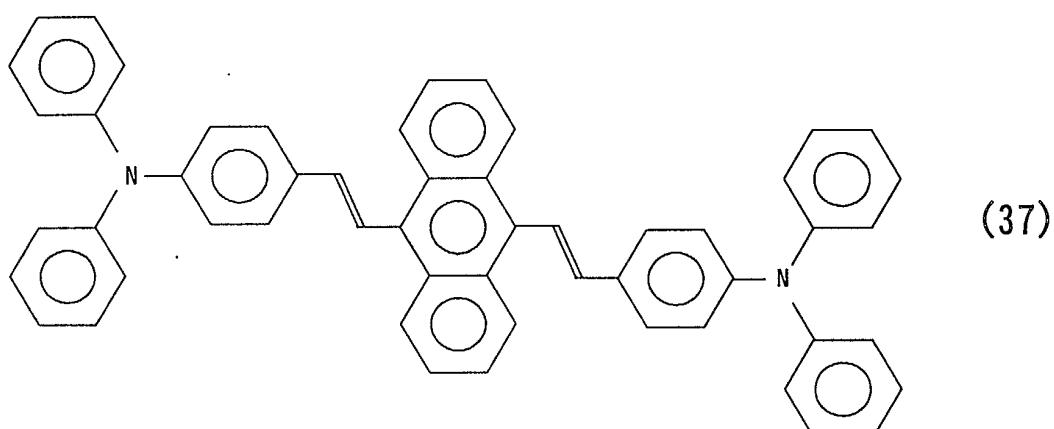
[0022] The hole transport material of the hole transport layer, which has a hole transport capability, is selected from organic compounds represented by the following formulas (36) to (64). When the hole transport layer is configured to

have a multi-layer structure, as shown in FIG. 4, the hole transport material (P-TYPE ORGANICS) is selected such that a layer of the material closer to the interface between the hole transport layers and the electron transport layers has a higher ionization potential  $I_p$  ( $I_p1 < I_p2 < I_p3$ ). In other words, out of two hole transport layers adjacent to each other, a hole transport layer on the anode side has a smaller ionization potential than that of a hole transport layer on the cathode side.

5



20

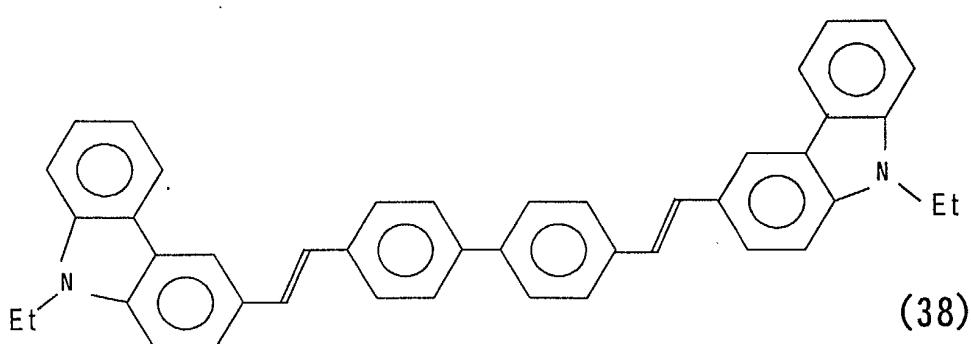


35

40

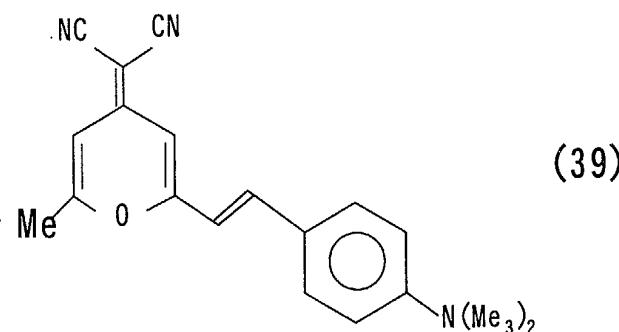
45

50



55

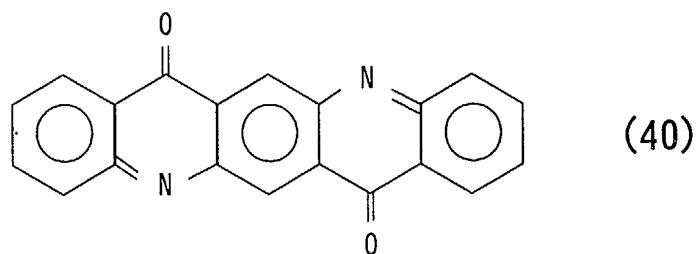
5



(39)

10

15



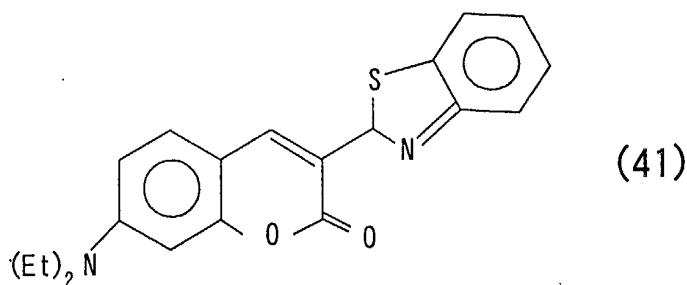
(40)

20

25

30

35



(41)

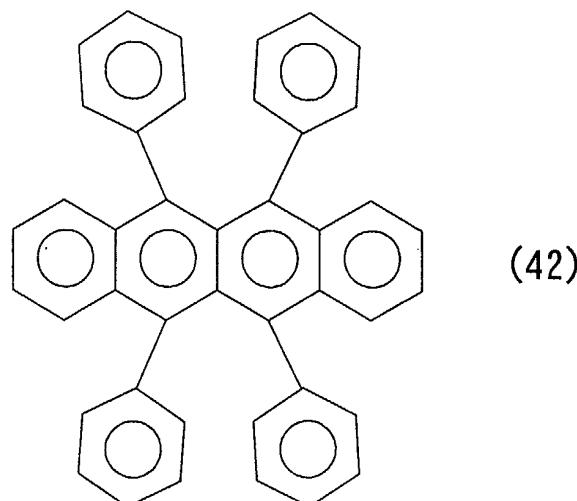
40

45

50

55

5



(42)

10

15

20

25

30

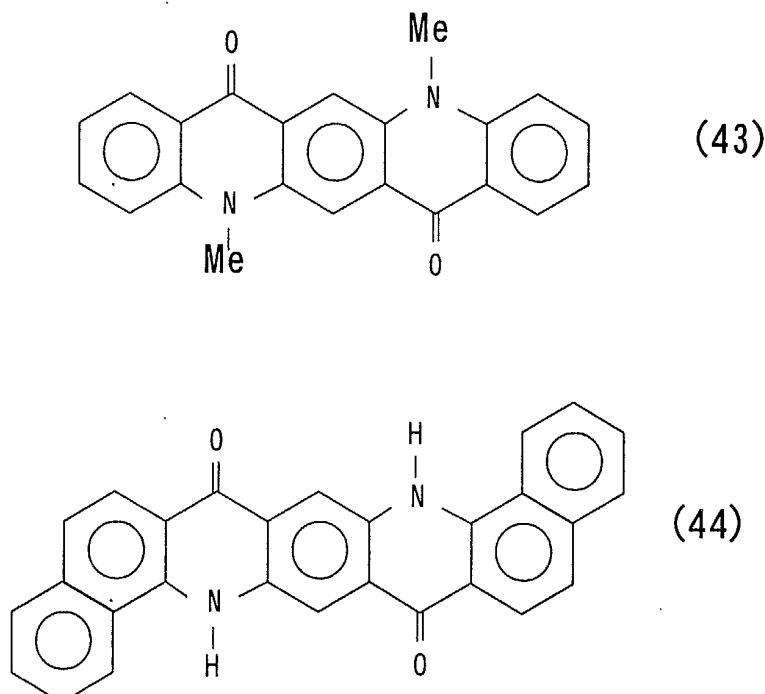
35

40

45

50

55



(43)

(44)

5

10

15

20

25

30

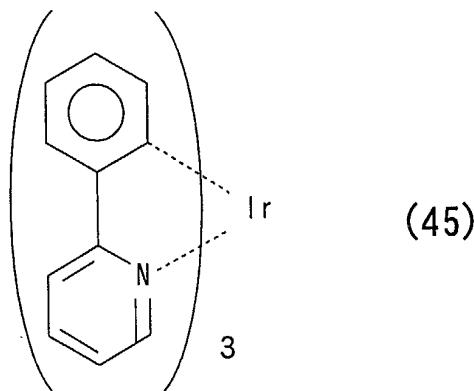
35

40

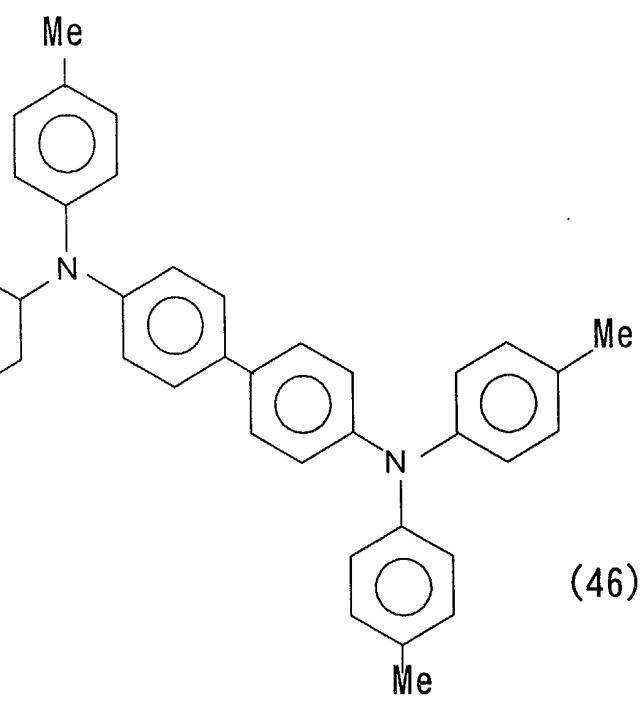
45

50

55



(45)



(46)

5

10

15

20

25

30

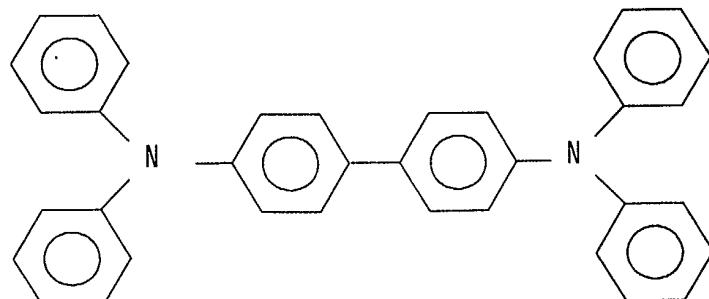
35

40

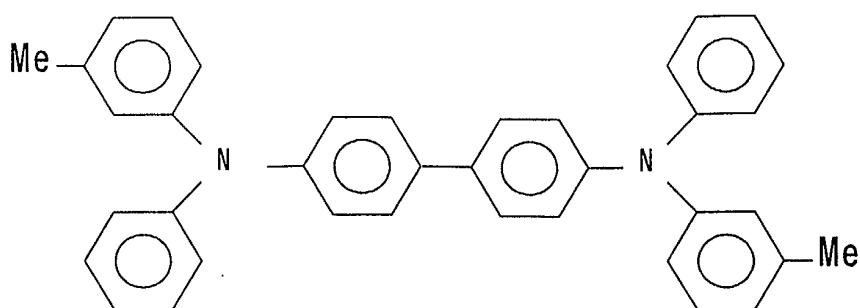
45

50

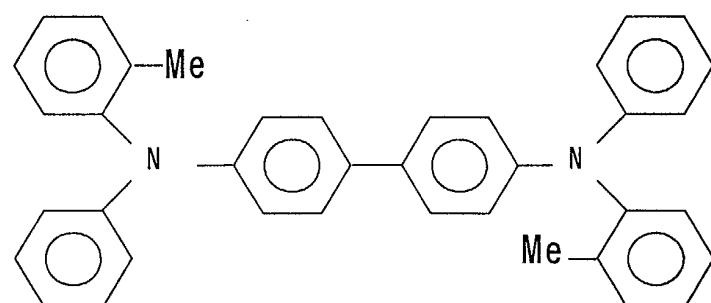
55



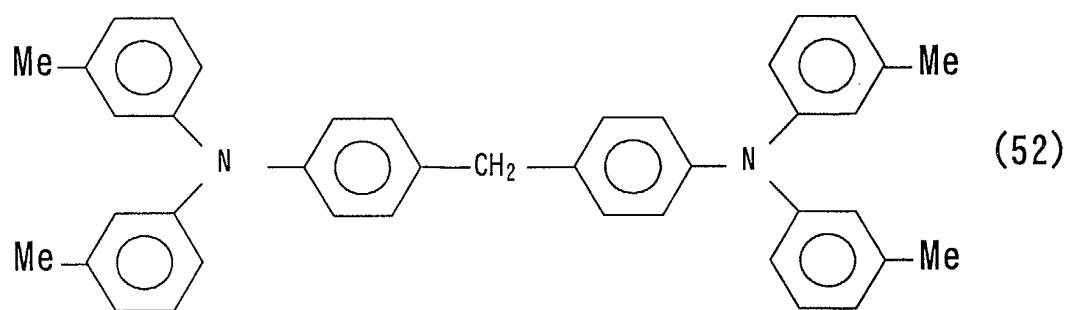
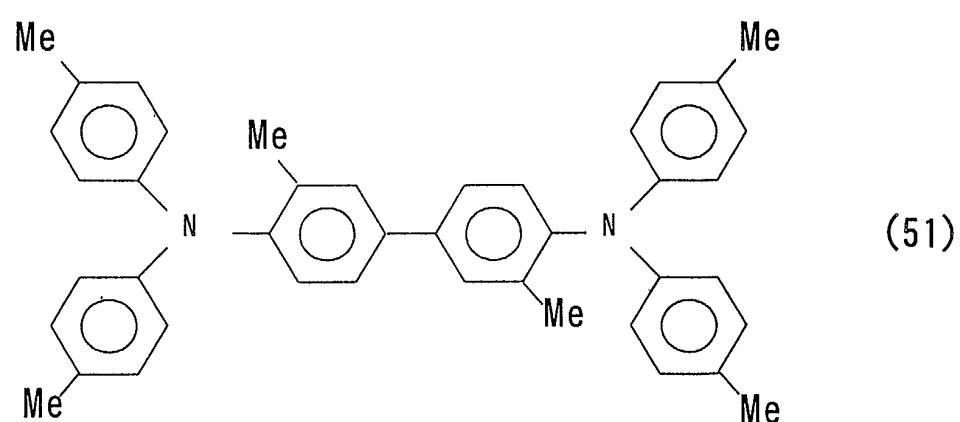
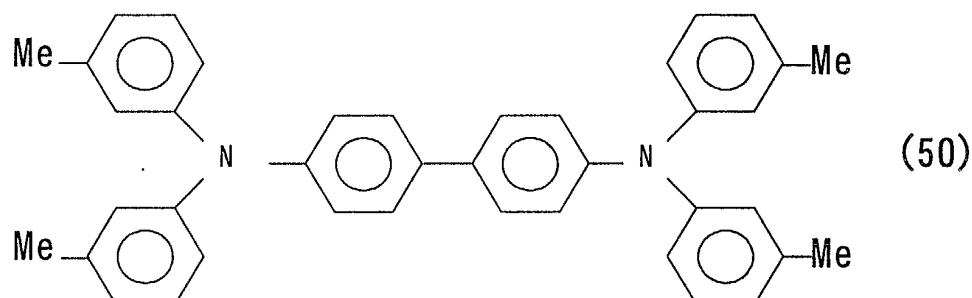
(47)

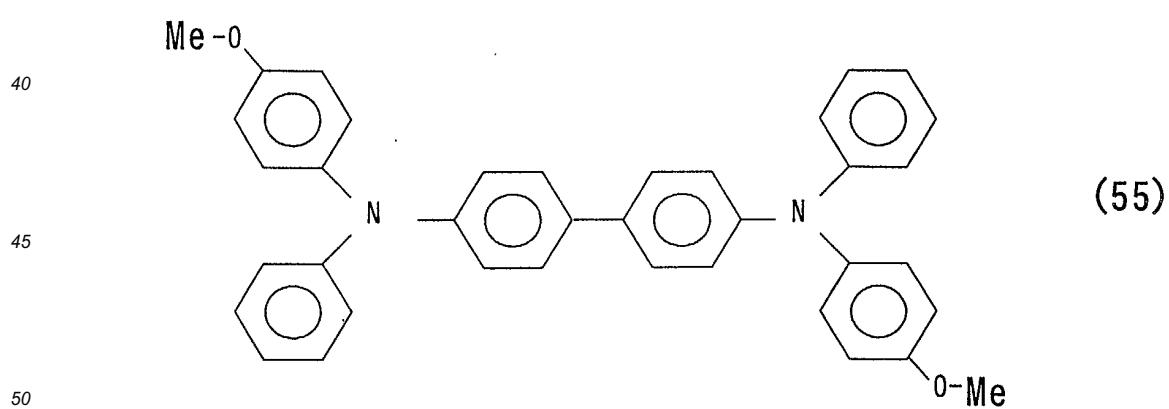
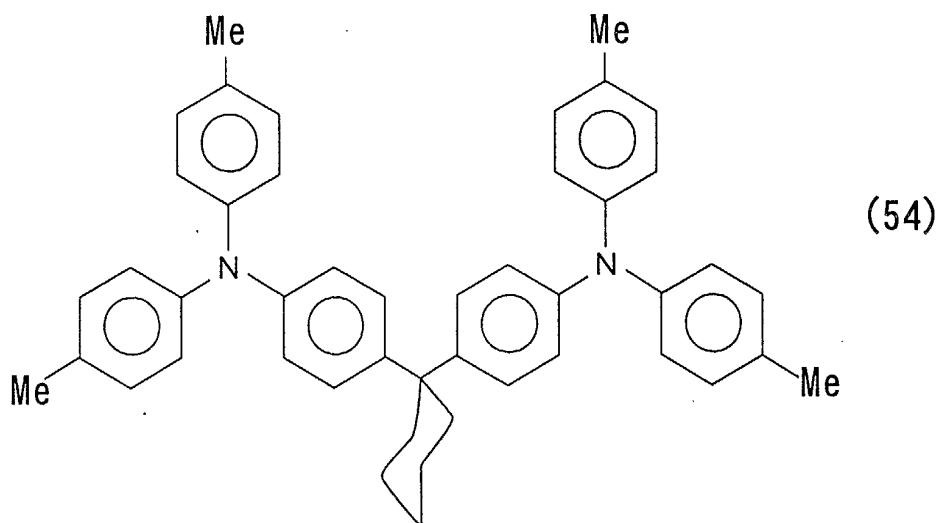
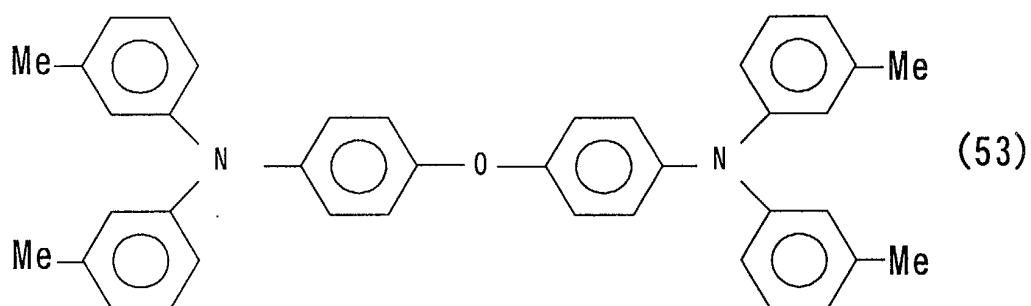


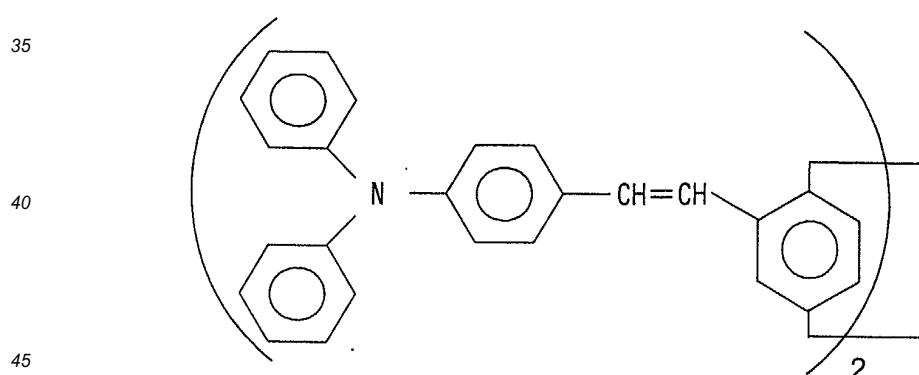
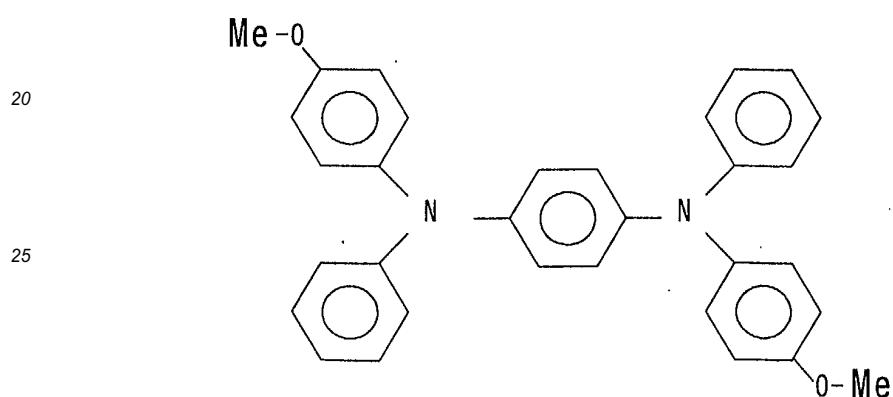
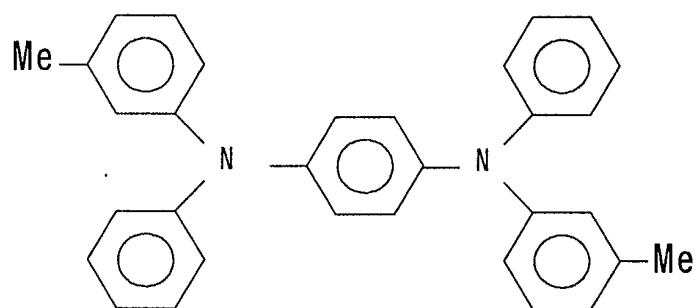
(48)



(49)

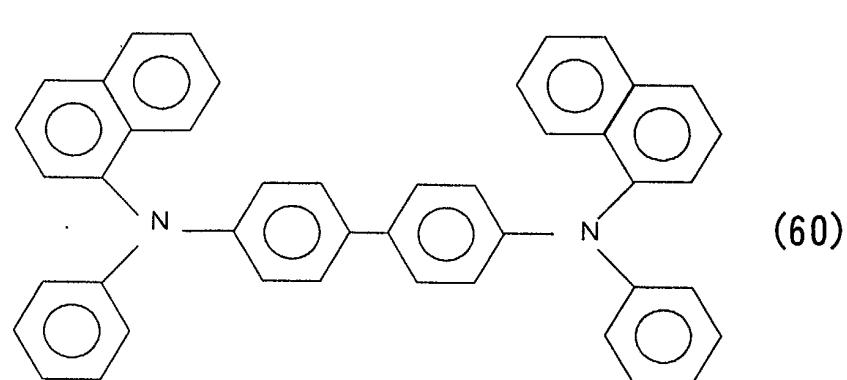
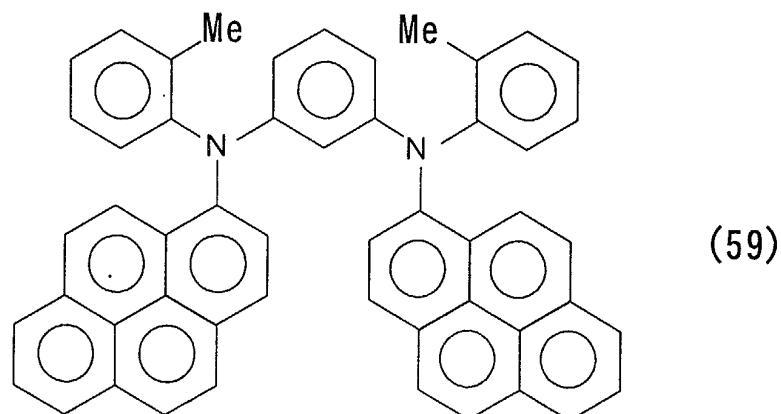






50

55



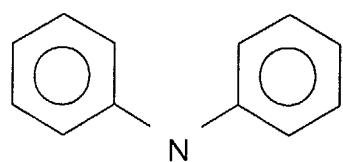
40

45

50

55

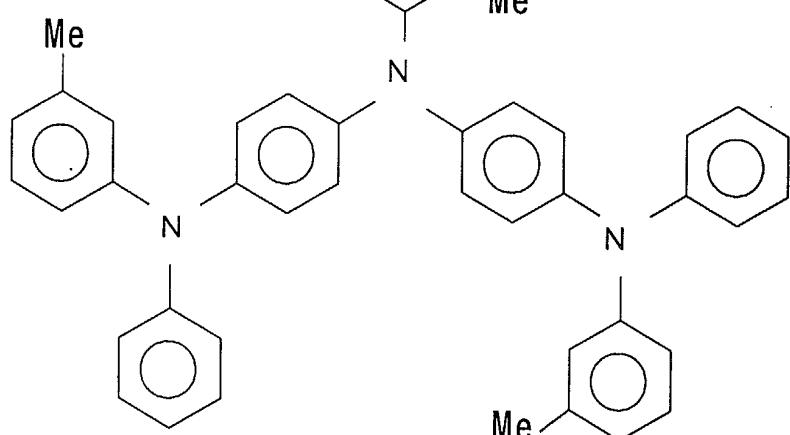
5



10



15



20

25

30

35

40

45

50

55

(61)

(62)

5

10

15

20

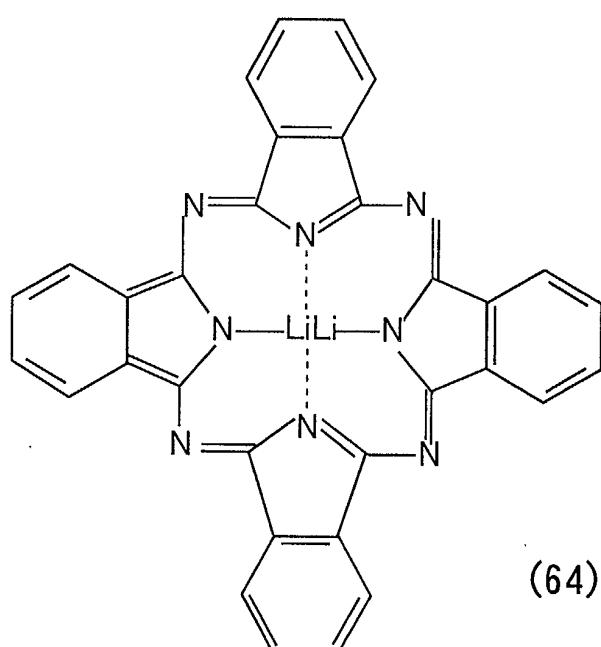
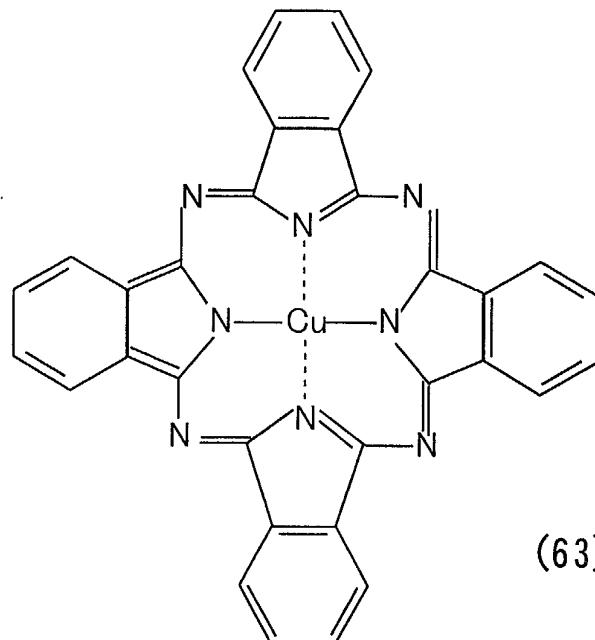
25

30

35

40

45



**[0023]** It should be noted that in the above formulas (1) to (64), Me designates a methyl group, Et designates an ethyl group, Bu designates a butyl group, and t-Bu designates a tertiary butyl group.

**[0024]** The formula (63) represents copper phthalocyanine, that is called CuPc, having a hole transport capability, which is included in porphyrin derivatives. The porphyrin derivatives include the following materials which can be employed as hole transport layers:

55

porphine,  
 1,10,15,20-tetraphenyl-21H,23H-porphine copper (II),  
 1,10,15,20-tetraphenyl-21H,23H-porphine zinc (II),  
 5,10,15,20-tetrakis(pentafluorophenyl)-21H,23H-porphine,

5        silicon phthalocyanine oxide,  
 aluminum phthalocyanine chloride,  
 phthalocyanine (metal-free),  
 dilithium phthalocyanine,  
 copper tetramethyl phthalocyanine,  
 chromium phthalocyanine,  
 zinc phthalocyanine,  
 lead phthalocyanine,  
 10      titanium phthalocyanine oxide,  
 magnesium phthalocyanine,  
 copper octamethyl phthalocyanine  
 chromium phthalocyanine fluoride.

15      **[0025]** It should be noted that a material other than the compounds represented by the above-mentioned formulas may be included in the hole transport layer or the electron transport layer. For instance, the layers may be doped with a fluorescence material or a phosphorescence material. Further, they may be doped with an inorganic or organic material for enhancing the carrier density of each layer.

20      **[0026]** Further, the hole transport layer or the electron transport layer may be formed by co-deposition as a mixture layer composed of a plurality of materials each of which is formed of an organic compound and has a transport capability.

25      Further, the hole transport layer or the electron transport layer may be configured to have one or more mixture layers.

30      **[0027]** The hole transport layer and the electron transport layer each composed of an organic compound are kinds of semiconductors which can be regarded as a p-type organic semiconductor material and an n-type organic semiconductor material (hereinafter also simply referred to as "the p-type material" and "the n-type material"), respectively. The inventors have found that it is possible to properly form an organic p-n junction by taking into account the electron affinity, ionization potential, electron energy band gap, Fermi level, and (carrier) mobility of each of the above organic transport materials as well as the thickness of each of thin films of the organic compounds, and obtain an organic semiconductor diode by using such an organic p-n junction.

35      **[0028]** The electrical characteristics of laminate layers of thin films made of the above organic compounds different in electrical characteristics, that is, the electrical characteristics of the junction interface depend on the ionization potential, electron energy band gap, Fermi level and carrier mobility, and work functions at the anode and cathode, of each organic thin film layer, and determine the characteristics of the element itself. The organic p-n junction is formed by laminating two kinds of adjacent organic compound thin films different in energy band gap, one upon the other. During thermal equilibrium, the two kinds of organic compound materials have constant Fermi levels as a whole. The thermal equilibrium is achieved by diffusion of the carriers of free electrons and holes through the junction interface, and as a result, an inner electric field is generated within the junction. The inner electric field causes the vacuum level to move, and the end of the energy band to bend. An inner electric field generated between the conduction bands of the p-type material and the n-type organic material serves as a potential barrier for preventing electrons oozing out of the region of the n-type material from moving into the region of the p-type material. Further, an inner electric field generated between the valence bands of the same serves as another potential barrier for preventing holes from moving from the region of the p-type material to the region of the n-type material.

40      **[0029]** When a forward bias voltage is applied to the organic p-n junction, electrons are injected from the cathode into the n-type material whereas holes are injected from the anode into the p-type material.

45      **[0030]** The injected electrons and holes are accumulated on the junction interface. When the bias voltage exceeds a predetermined threshold, the electrons overcome the potential barrier to move from the region of the n-type material of the p-n junction into the region of the p-type material of the same, and are diffused and recombined with the holes to be lost. The injection of these carriers causes a current to flow to an external circuit e.g. of the organic EL element.

50      **[0031]** If at least one of the hole transport layer and the electron transport layer is configured to have a multi-layer structure, since electrons move toward a lower energy level, the electrons injected from the cathode sequentially travel via the lowest unoccupied molecular orbital (LUMO) level of each of the electron transport layers made of the n-type materials to reach a hole transport layer made of the p-type material. On the other hand, since holes move toward a higher energy level, the holes injected from the anode sequentially travel via the highest occupied molecular orbital (HOMO) level of each of the hole transport layers made of the p-type materials to reach an electron transport layer made of the n-type material. Accordingly, when the hole transport layer is configured to have a multi-layer structure, the p-type materials of respective hole transport layers are selected such that a layer closer to the anode has a smaller ionization potential. Further, when the electron transport layer is configured to have a multi-layer structure, the n-type materials of respective electron transport layers are selected such that a layer closer to the cathode has a larger electron affinity.

55      **[0032]** The thin films of the p-type organic semiconductor and n-type organic semiconductor which form the p-n

junction and are used in the organic semiconductor diode according to the present invention can be formed by a well-known method, such as a vacuum vapor deposition method, a spin-coating method, a sputtering method, or a sol-gel method. The thickness of each organic semiconductor thin film is preferably 500 nm or less, and more preferably, 10 to 200 nm. Therefore, the thickness of an organic p-n junction is only required to be 1000 nm or less, and preferably 5 1 to 500 nm, and more preferably 20 to 400 nm.

**[0033]** In the organic semiconductor diode element according to the present invention, there is not used an inorganic insulating material which requires a high temperature process, so that the element can be manufactured at a relatively low temperature, and is suitable for control of organic functional elements, such as current control of organic EL elements, or the like.

**[0034]** As examples, organic semiconductor diodes are made by using a porphyrin derivative for a hole transport layer and a perylene derivative for an electron transport layer, and the characteristics of the diode are evaluated.

<Example 1>

**[0035]** Thin films defined as described below were laminated on a glass substrate which is formed with an anode made of an ITO film having a film thickness of 1100 Å, by the vacuum vapor deposition method at a vacuum level of  $5.0 \times 10^{-6}$  Torr.

**[0036]** First, a thin film of a porphyrin derivative (hereinafter referred to as "the LiPc") represented by the formula (64) was formed on the ITO film as a first hole transport layer at a vapor deposition rate of 3 Å/sec. to have a thickness of 50 nm.

**[0037]** Next, a thin film of the above-mentioned CuPc was formed on the first hole transport layer as a second hole transport layer at a vapor deposition rate of 3 Å/sec. to have a thickness of 50 nm.

**[0038]** Then, a thin film of the so-called TPD (triphenylamine) represented by the formula (48) was formed on the second hole transport layer as a third hole transport layer at a vapor deposition rate of 3 Å/sec. to have a thickness of 50 nm.

**[0039]** After that, a thin film of a perylene derivative (hereinafter simply referred to as "the Pery-1") represented by the formula (27) was deposited on the third hole transport layer as a first electron transport layer at a vapor deposition rate of 3 Å/sec. such that the Pery-1 thin film layer has a thickness of 50 nm.

**[0040]** Next, a thin film of a perylene derivative (hereinafter simply referred to as "the Pery-2") represented by the formula (28) was formed on the first electron transport layer as a second electron transport layer at a vapor deposition rate of 3 Å/sec. such that the Pery-2 thin film layer has a thickness of 50 nm.

**[0041]** Further, a thin film of magnesium (Mg) was laminated on the second electron transport layer as a cathode at a vapor deposition rate of 10 Å/sec. such that the Mg thin film layer has a thickness of 100 nm, to thereby complete the preparation of the organic semiconductor diode.

<Example 2>

**[0042]** An organic semiconductor diode according to Example 2 was produced which is identical to the organic semiconductor diode of Example 1 except that layers of the LiPc and the TPD, which were used in Example 1 as the materials of the first hole transport layer and the third hole transport layer respectively, were formed by changing the order of the two layers, and that respective layers of the Pery-1 and the Pery-2, which were used as the materials of the first electron transport layer and the second electron transport layer respectively, were formed by changing the order of the two layers.

<Example 3>

**[0043]** An organic semiconductor diode according to Example 3 was produced which is identical to the organic semiconductor diode of Example 1 except that layers of the Pery-1 and the Pery-2 respectively, which were used as the materials of the first electron transport layer and the second electron transport layer, were formed by changing the order of the two layers.

**[0044]** When the organic semiconductor diodes obtained as above were each driven at a fixed current value of 0.1 mA/mm<sup>2</sup>, current-voltage characteristics indicated by respective curved lines in FIG. 5 were exhibited. The ionization potentials  $I_p$  of the first to third hole transport layers are  $I_p$  (LiPc) = 4.9 eV,  $I_p$  (CuPc) = 5.1 eV,  $I_p$  (TPD) = 5.4 eV, respectively, and the electron affinities  $E_a$  of the materials of the first and second electron transport layers are  $E_a$  (Pery-1) = 3.67 eV,  $E_a$  (Pery-2) = 3.85 eV. Therefore, as clearly shown in FIG. 5, if, as to all the two adjacent hole transport layers, a hole transport layer on the anode side has a smaller ionization potential than that of a hole transport layer on the cathode side, it is possible to obtain excellent rectification characteristics. Further, it is shown that if, as to all the two adjacent electron transport layers, an electron transport layer on the cathode has a larger electron affinity than

that of an electron transport layer on the anode side, it is possible to obtain excellent rectification characteristics.

<Further Example>

5 [0045] FIG. 6 shows part of a display panel of an organic EL element display device based on the simple matrix driving method. The display panel 109 is comprised of a plurality of light-emitting pixels 111 arranged in a matrix form. Each light-emitting pixel 111 is composed of three light-emitting portions (organic EL elements) for emitting a red color R, a green color G and a blue color B. One light-emitting portion is comprised of a rectifier circuit formed by one organic semiconductor diode 11, and an organic EL element 200 connected in series to the organic semiconductor diode 11. Such a combination unit of a light-emitting portion for each of the above three colors is formed in each pixel, that is, each pixel has such combination units of a light emitting portion in the number of all the pixels (three). The combination units of the light-emitting portion are arranged at respective locations close to points of the intersection of anode lines 21 and cathode lines 71 orthogonal to each other, such that an organic EL element of each light-emitting portion is connected to an anode line 21 and an organic semiconductor diode 11 is connected to a cathode line 71.

10 [0046] Each organic EL element of the organic EL element display device has a three-layer structure laminated on a transparent substrate 1, such as glass or the like. The three-layer structure is formed by an anode, a cathode, and organic material layers (hole transport layer, light-emitting layer, electron transport layer) sandwiched between the cathode and the anode. The anode is made of a transparent material having a high work function, the hole transport layer and the light-emitting layer as well as the electron transport layer are composed of respective organic compounds, 15 and the cathode has a low work function.

20 [0047] Further, the organic EL element may have a two-layer structure without the hole transport layer so long as the light-emitting layer is made of a luminescent material having a hole transporting property. Further, the organic EL element may have a two-layer structure without the electron transport layer so long as the light-emitting layer is made of a luminescent material having an electron transport property. On the other hand, it is possible to cause the organic 25 EL element to have a multi-layer structure by configuring the hole transport layer, the light-emitting layer, and the electron transport layer such that they are each formed of a plurality of layers. Accordingly, the organic EL element is required to be comprised of an anode, and a cathode, as well as a light-emitting layer having a light-emitting function and formed of an organic compound having at least an electron transport capability or a hole transport capability, and a carrier transport layer formed of an organic compound having at least a hole transport capability or an electron 30 transport capability, which are laminated between the anode and the cathode.

35 [0048] As shown in FIG. 6, the organic semiconductor diodes are island-shaped and formed electrically independently of the organic EL elements, but these two are electrically connected to each other by an electrode connection section 81 as shown in FIG. 7. This enables the organic semiconductor diodes 11 and the organic EL elements 200 connected in series to the organic semiconductor diodes 11 to be arranged together on the substrate. As a result, according to the present invention, it is possible to form organic semiconductor diodes and organic EL elements together 40 in a manner arranged in the form of an array. More specifically, in the organic EL element display device, at least one of the hole transport layer and electron transport layer of the organic semiconductor diode can be formed of the same organic compound as that of at least one of the light-emitting layer and carrier transport layer of the organic EL element. For instance, the hole transport layer of the organic EL element and that of the organic semiconductor diode can be 45 formed of a common compound.

45 [0049] Further, as shown in FIG. 8, each organic EL element and each organic semiconductor diode can be arranged adjacent to each other, and configured in a manner such that they are laminated one upon the other. Here, although it is preferred that the area of an electrode of an organic semiconductor diode for forming an organic thin film diode on an organic EL element be minimized to reduce the capacity of the organic semiconductor diode, the area of the electrode is required to be large enough to prevent degradation of the rectifying action of the diode.

50 [0050] Further, in the organic EL element display device according to the present invention, by changing the film thickness of each layer of an organic EL element in each light-emitting portion, the film thickness of each layer of an organic semiconductor diode connected in series to the EL element, and the areas of the electrodes of the EL element and the diode, the organic semiconductor diode can be formed such that it has a smaller electrostatic capacity than that of the organic EL element. Therefore, it is possible to increase a light-emitting time period in one scanning by the amount of residual luminescence performed by electric charge emission corresponding to the capacity. Therefore, even if momentary brightness is reduced, sufficient luminescence brightness can be obtained to prevent deterioration of light-emitting portions. This makes it possible to increase the service life of a light-emitting panel.

55 [0051] As described hereinabove, according to the present invention, it is possible to obtain organic semiconductor diodes which can be manufactured by a low temperature process. By combining organic EL elements and organic semiconductor diodes, a display panel can be produced by an organic thin film-laminating process alone. Since diode elements can be formed by organic thin films without using a silicon substrate, a large-sized full color display of an organic EL element display device based on the matrix driving method can be manufactured by a simple process for

manufacturing an organic EL panel.

[0052] It is understood that the foregoing description and accompanying drawings set forth the preferred embodiments of the invention at the present time. Various modifications, additions and alternative designs will, of course, become apparent to those skilled in the art in light of the foregoing teachings without departing from the spirit and scope of the disclosed invention. Thus, it should be appreciated that the invention is not limited to the disclosed embodiments but may be practiced within the full scope of the appended claims.

## Claims

10

1. An organic semiconductor diode comprising:

at least one hole transport layer which is arranged on an anode side and formed of an organic compound having a hole transport capability; and

15 at least one electron transport layer which is arranged on a cathode side and formed of an organic compound having an electron transport capability, said at least one hole transport layer and said at least one electron transport layer being laminated one upon another,

20 wherein said hole transport layer at an anode-side end has an ionization potential larger than an electron affinity of said electron transport layer at a cathode side end, whereby the organic semiconductor diode exhibiting nonlinear current-voltage characteristics when a voltage is applied between said hole transport layer and said electron transport layer in contact with each other.

25

2. The organic semiconductor diode according to Claim 1, wherein as to all of two adjacent layers of said at least one hole transport layer, a hole transport layer on the anode side has a smaller ionization potential than that of another hole transport layer.

30

3. The organic semiconductor diode according to Claim 1 or 2, wherein as to all of two adjacent layers of said at least one electron transport layer, an electron transport layer on the cathode side has a larger electron affinity than that of another electron transport layer.

35

4. An organic electroluminescence element display device having plural light-emitting portions arranged in a display layout comprising:

a plurality of organic electroluminescence elements arranged therein as the light-emitting portions, said plurality of organic electroluminescence elements each including an anode, and a cathode, as well as a light-emitting layer having a light-emitting function and formed of an organic compound having at least an electron transport capability or a hole transport capability, and a carrier transport layer formed of an organic compound having at least a hole transport capability or an electron transport capability; and

40 respective organic semiconductor diodes each arranged adjacent to and at the same time connected in series to an associated one of said plurality of organic electroluminescence elements,

45 wherein each of said organic semiconductor diodes has a hole transport thin film layer which is arranged on an anode side and formed of an organic compound having a hole transport capability, and an electron transport thin film layer which is arranged on a cathode side and formed of an organic compound having an electron transport capability, the hole transport layer and the electron transport layer being laminated one upon another, said organic semiconductor diode exhibiting nonlinear current-voltage characteristics when a voltage is applied between the hole transport layer and the electron transport layer in contact with each other.

50

5. The organic electroluminescence element display device according to Claim 4, wherein at least one of said hole transport layer and said electron transport layer of said organic semiconductor diode is formed of the same organic compound as that of at least one of said light-emitting layer and said carrier transport layer.

55

6. The organic electroluminescence element display device according to Claim 4, wherein said organic semiconductor diode and said organic electroluminescence element are laminated one upon another.

FIG. 1

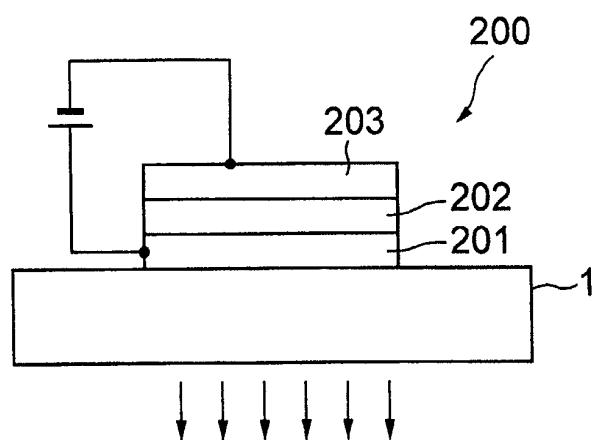


FIG. 2

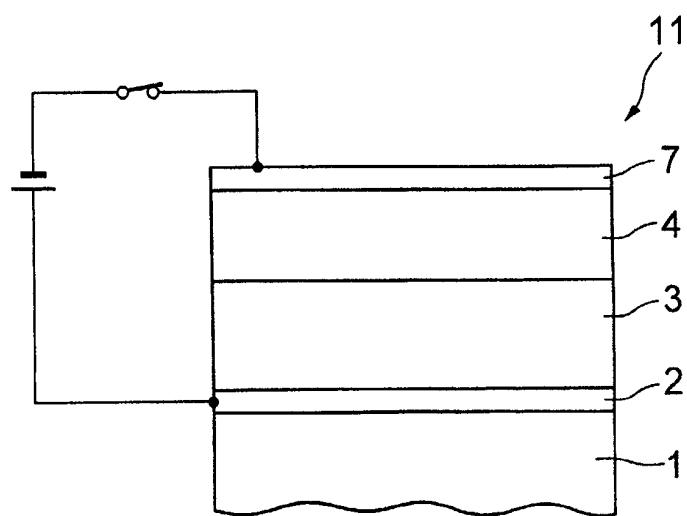


FIG. 3

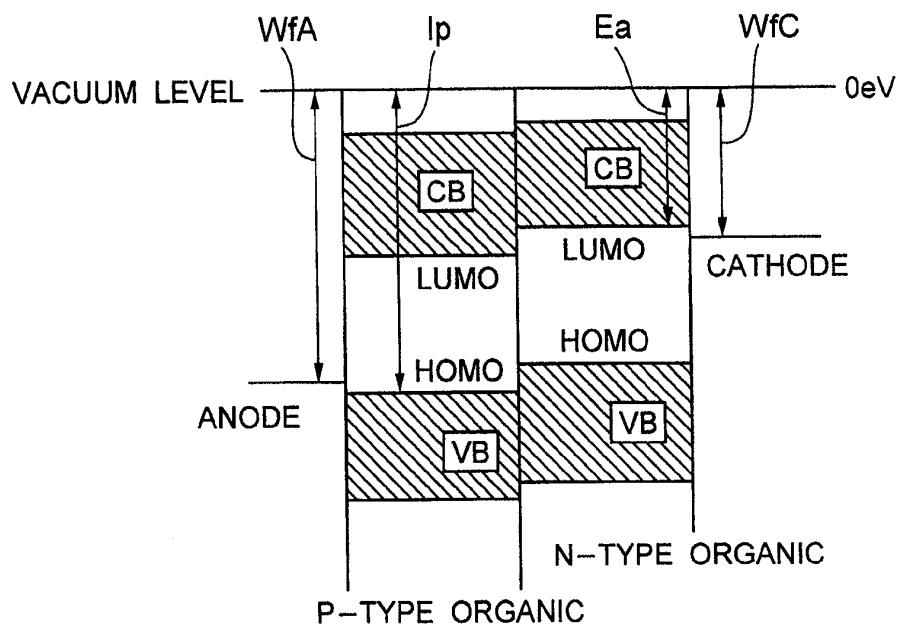


FIG. 4

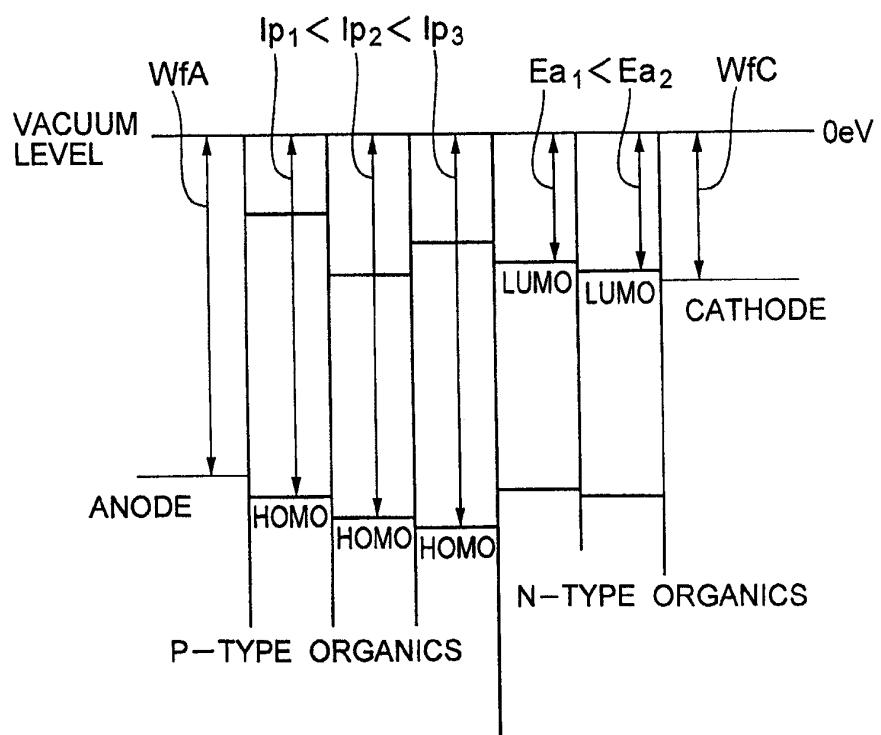


FIG.5

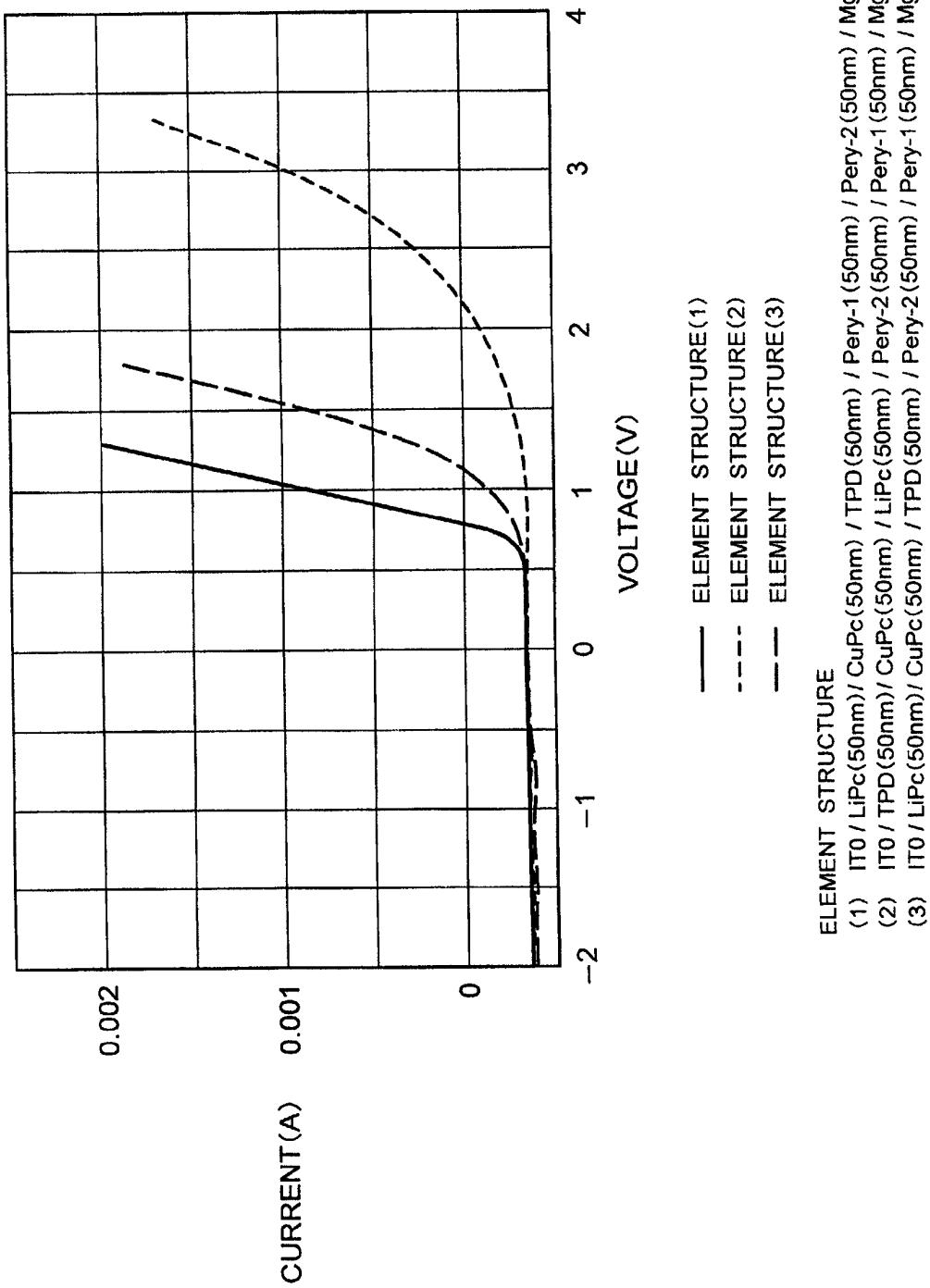


FIG. 6

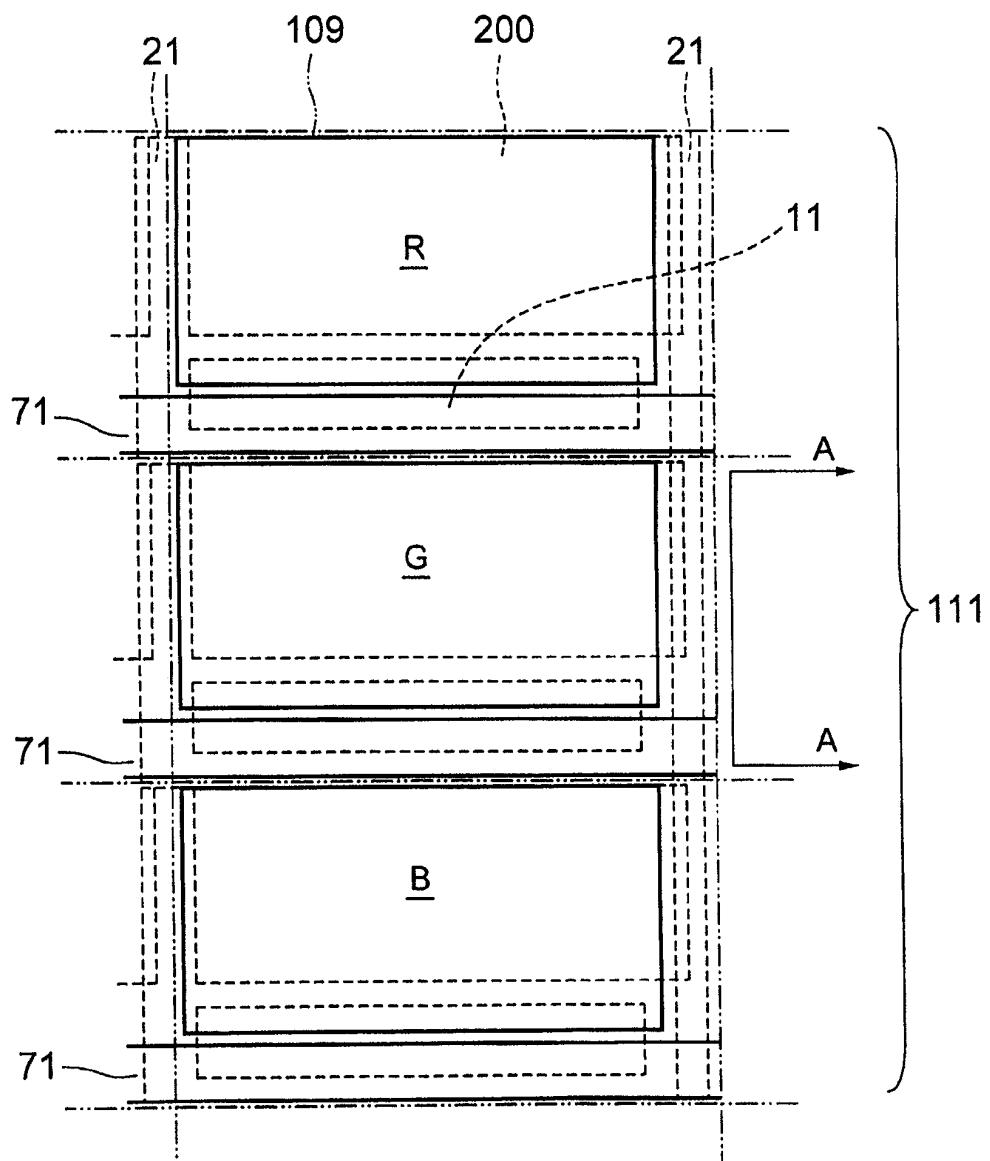


FIG. 7

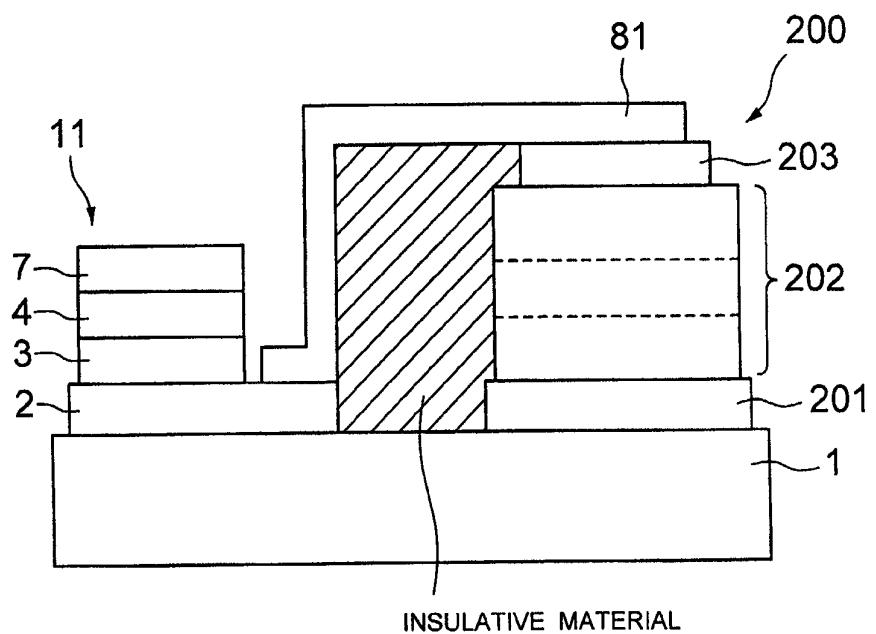
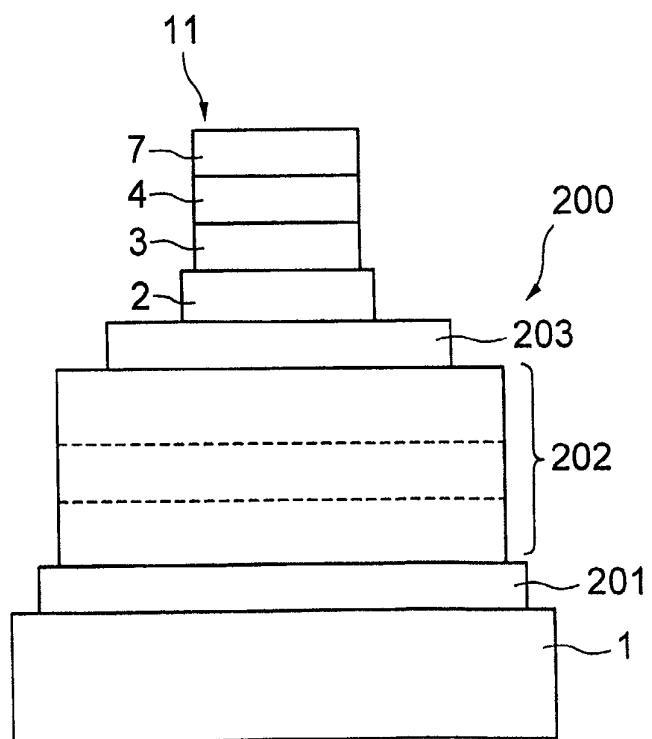


FIG. 8



专利名称(译)	有机半导体二极管和有机电致发光元件显示装置		
公开(公告)号	<a href="#">EP1251720A2</a>	公开(公告)日	2002-10-23
申请号	EP2002252144	申请日	2002-03-25
[标]申请(专利权)人(译)	日本先锋公司		
申请(专利权)人(译)	先锋公司		
当前申请(专利权)人(译)	先锋公司		
发明人	WAKIMOTO, TAKEO, C/O PIONEER CORPORATION NAKAMURA, KENJI, C/O PIONEER CORPORATION		
IPC分类号	H01L51/50 H01L27/32 H01L29/861 H01L35/24 H01L51/00 H01L51/05 H01L51/30 H05B33/08 H05B33/12		
CPC分类号	H01L27/3281 H01L51/005 H01L51/0052 H01L51/0053 H01L51/0059 H01L51/0077 H01L51/0078 H01L51/0081 H01L51/0583 H01L2924/0002		
代理机构(译)	LUCKHURST , ANTHONY HENRY WILLIAM		
优先权	2001087133 2001-03-26 JP		
其他公开文献	EP1251720A3		
外部链接	<a href="#">Espacenet</a>		

## 摘要(译)

有机半导体二极管包括至少一个空穴传输层和至少一个电子传输层，所述空穴传输层设置在阳极侧并由具有空穴传输能力的有机化合物形成，所述电子传输层设置在阴极侧并由有机化合物形成具有电子传输能力。至少一个空穴传输层和至少一个电子传输层彼此层叠。当在空穴传输层和电子传输层之间施加彼此接触的电压时，有机半导体二极管表现出非线性电流 - 电压特性。阳极侧端部的空穴传输层的电离电位大于阴极侧端部的电子传输层的电子亲和势。

FIG. 2

