

(19)



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(11)

EP 1 158 839 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

28.11.2001 Bulletin 2001/48(51) Int Cl.⁷: **H05B 33/14**, C08F 38/00(21) Application number: **01303861.7**(22) Date of filing: **27.04.2001**

(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:

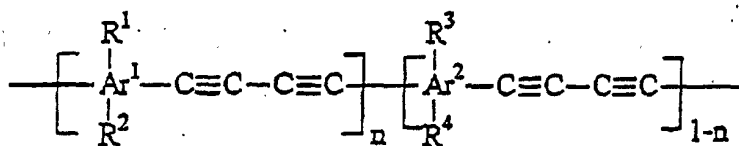
AL LT LV MK RO SI(30) Priority: **27.04.2000 JP 2000128364****22.09.2000 JP 2000288692****24.04.2001 JP 2001125359**(71) Applicant: **FUJITSU LIMITED****Kawasaki-shi, Kanagawa 211-8588 (JP)**

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(57) An organic EL device employing polymer material includes a structure in which a luminous layer formed of a polymer indicated by



is put between a lower electrode and an upper electrode.

In the above formula, Ar¹, Ar², which can be the same or different, denote arylene groups, R¹, R², R³, R⁴ denote substituents, and n denotes the copolymerization ratio. The flatness of the luminous layer can be improved and the solubility of the luminous layer constituent material can be enhanced.

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Description

[0001] The present invention relates to an organic luminous material and an organic light-emitting device and, more particularly, to an organic light-emitting device like an organic electroluminescence (EL) device employing such material.

[0002] In recent years, the research and development of an organic EL device applied to a flat display panel, a mobile display device, etc. has been vigorously pursued. A display device employing an organic EL device can provide high brightness and full color display by low voltage driving.

[0003] In addition, a display device consisting of an organic EL devices has features different from a liquid crystal display (LCD). For example, there can be provided a light weight and low cost product that has no viewing angle dependence because it is a spontaneously emissive display, does not need back lights because of the high contrast, has a quick response speed, has an easy film formation characteristic, and withstands impact since the overall device is constructed from solid state elements.

[0004] An organic EL device has a structure made up of lower electrode formed of transparent conductive material, an organic thin film (luminous layer), and an upper electrode formed of magnesium, potassium, etc. formed in sequence on the glass substrate, for example. The thickness of the overall structure can be reduced up to about several mm. Then, light is emitted from the luminous layer by applying a DC voltage between the lower electrode and the upper electrode, and this light is passed through the lower electrode and the glass substrate to output to the outside. The organic EL device is an injection electroluminescence device that increases the number of carriers in operation by injecting the carriers from the electrode to thus emit light by recombination. Sometimes the organic EL device is also called an organic LED.

[0005] As the luminous material employed in the organic thin film of the organic EL device, there are used monomer materials and polymer materials. Normally a film of monomer material is formed by the vacuum evaporation method, and normally a film of polymer material is formed by a coating method. Coating methods are practical in device formation because expensive equipment is not needed.

[0006] It is known to employ PPV (poly p-phenylenevinylene) as the polymer material. An EL device employing such material is set forth in Patent Application Publication (KOKAI) Hei 10-326675, for example.

[0007] A conjugated polymer material such as PPV employed as the luminous layer in the prior art is in a highly crystalline state at normal temperature, unlike a normal polymer material.

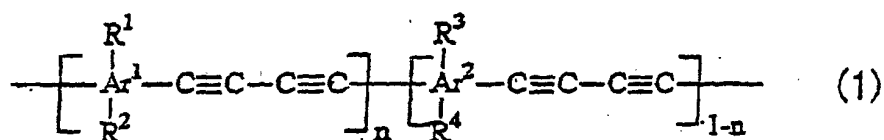
[0008] Accordingly, if such conjugated polymer material is formed on the substrate, unevenness readily occurs on the surface of the luminous layer made of the polymer.

[0009] If a voltage is applied between the lower electrode and the upper electrode under conditions such that unevenness is present on the surface of the luminous layer, the electric field is readily concentrated in the concave portion of the surface of the luminous layer. Thus, there is the possibility that the luminous layer is destroyed by the electric field, and then a short-circuit is caused between the lower electrode and the upper electrode.

[0010] Also, since the luminous polymer layer in the prior art, which is readily crystallised, is insoluble in the organic solvent, treatment must be applied, e.g., the polymer must be mixed into the organic solvent while being heated, when the polymer is coated on the substrate, and thus it is not easy to handle the polymer. In addition, even if the conjugated polymer in the prior art is dissolved in the organic solvent, such polymer is still readily crystallized after cooling.

[0011] It is an object of the present invention to provide a light-emitting device having a luminous layer formed of polymer material that can be highly planarized and has a solubility in organic solvents higher than that of polymer film material in the prior art.

[0012] According to the present invention, there is provided an organic light-emitting device which comprises a lower electrode; a luminous layer formed on the lower electrode and made of polymer of formula:



where Ar¹ and Ar² denote first and second arylene groups which can be the same or different, R¹, R², R³ and R⁴ are substituents which can be the same or different or some of which can be the same and other(s) different, and n denotes the copolymerization ratio; and

an upper electrode formed on the luminous layer.

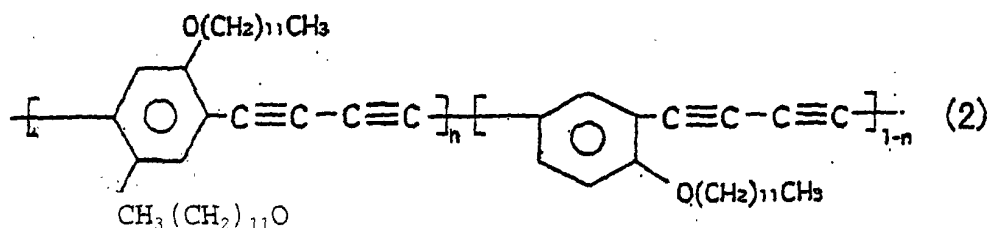
[0013] It is preferable that n is set to 0<n<0.9. The terms "aryl" and "aromatic ring" used herein, unless otherwise indicated, denotes both carbocyclic and heterocyclic optionally substituted single and fused ring systems.

[0014] According to the present invention, the polymer employed as the luminous layer of the organic light-emitting device and given by the chemical formula (1) has low crystallinity at ambient temperature and has better solubility in organic solvents than polymers for the luminous layer in the prior art.

[0015] A polymer given by the chemical formula (1) is deposited as a flat film by coating on a substrate after such polymer has been dissolved in the solvent, and then the solvent is removed.

[0016] As a result, if an organic light-emitting device is constructed by putting a polymer given by the chemical formula (1) between the upper electrode and the lower electrode, a local electric field concentration is hard to achieve, a short-circuit between the upper electrode and the lower electrode is hard to achieve, and the yield of the device can be improved.

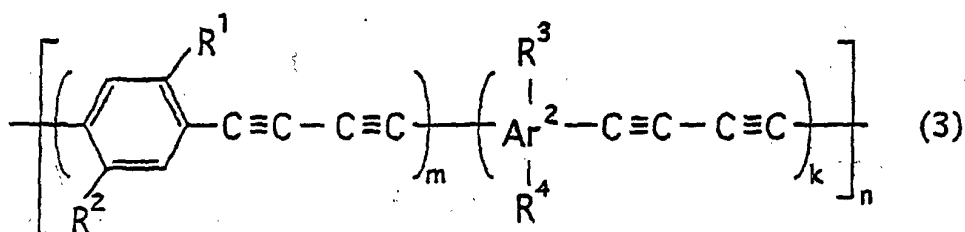
[0017] If the first arylene group of the polymer is a paraphenylene group and the second arylene group is a meta-phenylene group, and the polymer in the organic light-emitting device may be that given by



a difference in the luminous intensity of the luminous layer may be achieved by changing the value of n in the polymer given by the chemical formula (2) under the conditions at which structures other than the luminous layer are formed identically. If n is 0.66, or n has a value to satisfy $n:(1-n)=2:1$, the highest luminous intensity can be achieved.

[0018] The chemical formula (2) is for a material that can emit light in or near the green color wavelength band. In order to utilise a luminous material in a full color display device, a material that can emit light in or near the red color wavelength band or the material that can emit light in or near the blue color wavelength band is needed.

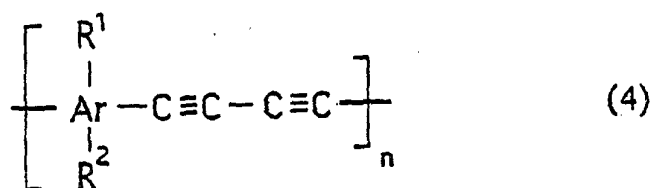
[0019] A luminous material that emits light in or near the red color luminous wavelength band is an organic luminous material given by



in which a benzene ring is utilized as the aromatic ring constituting the first arylene group in the chemical formula (1).

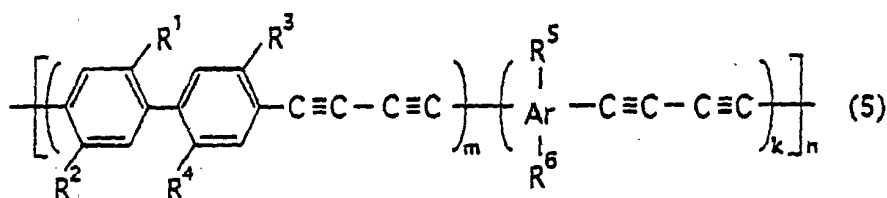
[0020] In the chemical formula (3), in addition, Ar^2 denotes an arylene group, R^1 , R^2 , R^3 and R^4 denotes substituents, which can be the same or different or some of which can be the same and other(s) different and m and k together denote the copolymerization ratio and n denotes the degree of polymerisation. The aromatic ring constituting the arylene group can be any one of thiophene, anthracene, pyridine, phenol, aniline, and derivatives thereof. Also, the respective substituents R^1 , R^2 , R^3 and R^4 can be any one of hydrogen, alkyl, alkoxy, carboxyl, cyano, phenyl, biphenyl, and cyclohexylphenyl.

[0021] Also, usable as a luminous material that emits light in the red or near red color wavelength band is an organic luminous material given by



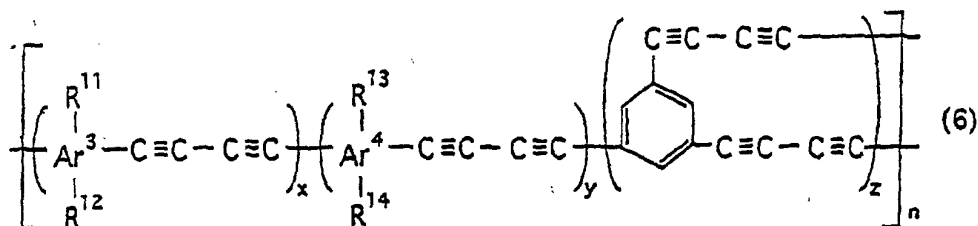
In the chemical formula (4), Ar denotes an arylene group, R¹ and R² denotes first and second substituents, and n denotes the degree of polymerisation. The aromatic ring constituting the arylene group can be any one of thiophene, anthracene, pyridine, phenol, aniline derivatives thereof. As indicated above, the respective substituents, in this case R¹ and R², can consist of any one of hydrogen, alkyl, alkoxy, carboxyl, cyano, phenol, biphenyl, and cyclohexylphenyl.

[0022] In addition, as a luminous material that can emit light in the blue or near blue color wavelength band, there is the organic luminous material



[0023] In the chemical formula (5), Ar denotes an arylene group, R¹, R², R³, R⁴, R⁵ and R⁶, denote substituents which can be the same or different or some of which can be the same and other(s) different, m and k denote the copolymerization ratio and n denotes the degree of polymerisation. The aromatic ring constituting the arylene group can be any one of benzene, pyrrole, thiophene, carbazole, furan, fluorene, naphthalene, anthracene or a derivative thereof. Also, the respective groups R¹ to R⁶, can have any of the meanings already given for substituents R¹ to R⁴.

[0024] Other luminous material that can emit light in the blue or near blue color wavelength band is the organic luminous material.



[0025] In the chemical formula (6), Ar³ denotes a first arylene group, Ar⁴ denotes a second arylene group, R¹¹, R¹², R¹³ and R¹⁴ are substituents which can be the same or different or some of which can be the same and other(s) different, x, y, z denote copolymerization ratios and n denotes the degree of polymerisation. The aromatic rings constituting the first and second arylene groups can be any one of benzene, pyrrole, thiophene, carbazole, furan, fluorene, naphthalene, anthracene, and derivatives thereof. The substituents R¹¹ to R¹⁴ can have any of the meanings given earlier herein for substituents R¹ to R⁴.

[0026] For a better understanding of the invention, and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawings, in which:-

FIGS.1A to 1D are sectional views showing steps in manufacturing an organic EL device according to a first embodiment of the present invention;

FIG.2 is a graph showing the change of fluorescent spectrum of a luminous layer employed in an organic EL device during the manufacturing process according to the first embodiment of the present invention;

FIG.3 is a graph showing the EL spectrum change with respect to the luminous wavelength emitted by the luminous layer employed in an organic EL device produced according to the first embodiment of the present invention, and FIG.4 is a graph showing the fluorescent spectrum of a red color luminous layer employed in an organic EL device according to the first embodiment of the present invention;

FIG.5 is a graph showing the fluorescent spectrum of a red color luminous layer employed in an organic EL device according to a second embodiment of the present invention;

FIG.6 is a graph showing the fluorescent spectrum of a blue color luminous layer employed in an organic EL device according to a third embodiment of the present invention; and

FIG.7 is a graph showing the fluorescent spectrum of a blue color luminous layer employed in an organic EL device according to a fourth embodiment of the present invention.

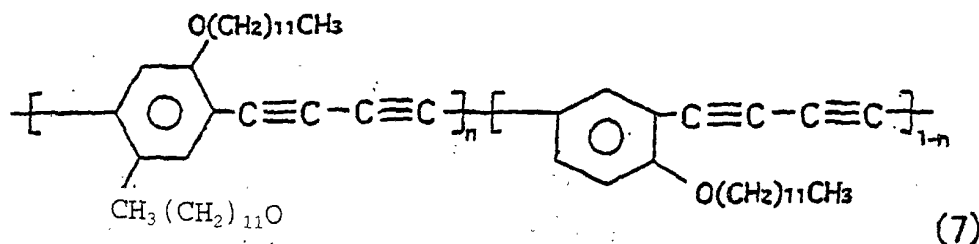
[0027] An embodiment of the present invention will be explained, with reference to the accompanying drawings hereinafter.

[0028] FIGS. 1A to 1D are sectional views showing steps in manufacturing an organic EL device embodying the present invention.

[0029] In FIG. 1A, an ITO (indium tin oxide) film of 200 nm thickness is formed on a glass (transparent) substrate 1 as a lower electrode (anode) 2 by the sputtering method. The ITO Film is exposed to oxygen, an ozone plasma, or the like to clean the surface.

[0030] The constituent material of the lower electrode 2 is not limited to ITO. Transparent conductive materials such as IDIXO (indium zinc oxide) and others may be employed.

[0031] Then, the polymer given by a following chemical formula (7) is formed as a luminous layer 3 on the lower electrode 2 by the spin coating method to have a thickness of 150 nm, for example. For example, in the chemical formula (7), $n=0.5$.



[0032] In the spin coating of the polymer, a solution is prepared by dissolving the polymer in a solvent, e.g., chloroform (CHCl_3) at ambient temperature. Then, as shown in FIG. 1B, the solution 3a is coated on the lower electrode 2, and then the solvent is removed by drying. The drying temperature is set to more than the vaporisation temperature of the solvent but less than 150°C . If the solvent is removed at 150°C , the drying time is set to about 30 minutes. The preferable drying conditions are drying temperature of 90°C and drying time of 60 minutes.

[0033] As shown in FIG. 1C, the polymer left on the lower electrode 2 and having the chemical formula (7) is employed as the luminous layer 3.

[0034] Then, as shown in FIG. 1D, a magnesium silver (MgAg) layer of 300 nm thickness is formed as an upper electrode (cathode) 4 on the luminous layer 3 by the co-evaporation method. This co-evaporation method used to form the magnesium silver is such that separate evaporation sources for each constituent element are arranged in the evaporation chamber and the elements are evaporated toward the same substrate to form the alloy. In this embodiment, the upper electrode 4 is formed of a MgAg film in which the magnesium and the silver are alloyed at the ratio of 1:10. In this case, the upper electrode 4 may be grown during the evaporation while effecting patterning of the upper electrode 4 by placing a metal mask between the evaporation sources and the substrate. In addition, as the material of the upper electrode 4, alkali metals and alkaline earth metals, singly or in combinations with each other or other metals such as Na, NaK, Mg, Li, CaMg/Cu mixture, Mg/In alloy, etc. may be employed.

[0035] When producing the light-emitting device by the above steps, if the current is supplied by applying a voltage while setting the lower electrode 2 to the positive side and the upper electrode 4 to the negative side, green light is emitted from the light-emitting device. The light is passed through the lower electrode 2 and the glass substrate 1 and then emitted to the outside.

[0036] In the above embodiment, since the polymer of chemical formula (7) has low crystallinity at ambient temperature and has good solubility in solvent used, the surface of the polymer left after drying is flat unlike in the prior art. Thus, short-circuiting between the upper electrode and the lower electrode can be prevented and the yield of the device can be improved.

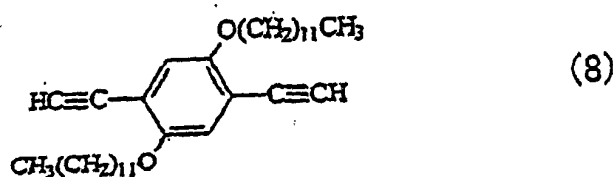
[0037] The fluorescent spectrum produced when the polymer of chemical formula (7) is dissolved in the chloroform has a profile indicated by a broken line in FIG. 2, and the fluorescent spectrum of the polymer in the film state after the chloroform is removed has a profile indicated by a solid line in FIG. 2. In other words, it is to be understood that the polymer in the film state can emit light in the range of 500 to 550 nm.

[0038] A method of synthesizing the polymer given by the chemical formula (7) will be explained hereunder.

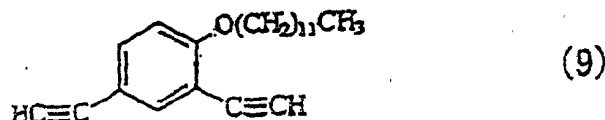
[0039] First, 150 mg (1.5 mmol) of copper (I) chloride and 180 mg (1.5 mmol) of N,N,N',N'-tetramethylethylenediamine (TMEDA) are added in 180ml of tetrahydrofuran (THF). Then, the catalyst is formed by supplying oxygen to the mixture for 10 minutes.

[0040] 1.48 g (3 mmol) of 2,5-didodecyloxy-1,4-diethynylbenzene and 0.93 g (3 mmol) 4-dodecyloxy-1,3-diethynylbenzene are dissolved in 180ml tetrahydrofuran solution, and then this resultant solution is added to the THF solution containing the above catalyst. Then, substances in the resulting mixture are caused to react with each other under an oxygen atmosphere for two days. This reaction is an oxidative condensation polymerisation reaction.

[0041] The 2,5-didodecyloxy-1,4-diethynylbenzene is indicated by a following chemical formula (8).



[0042] The 4-dodecyloxy-1,3-diethynylbenzene is given by a following chemical formula (9).



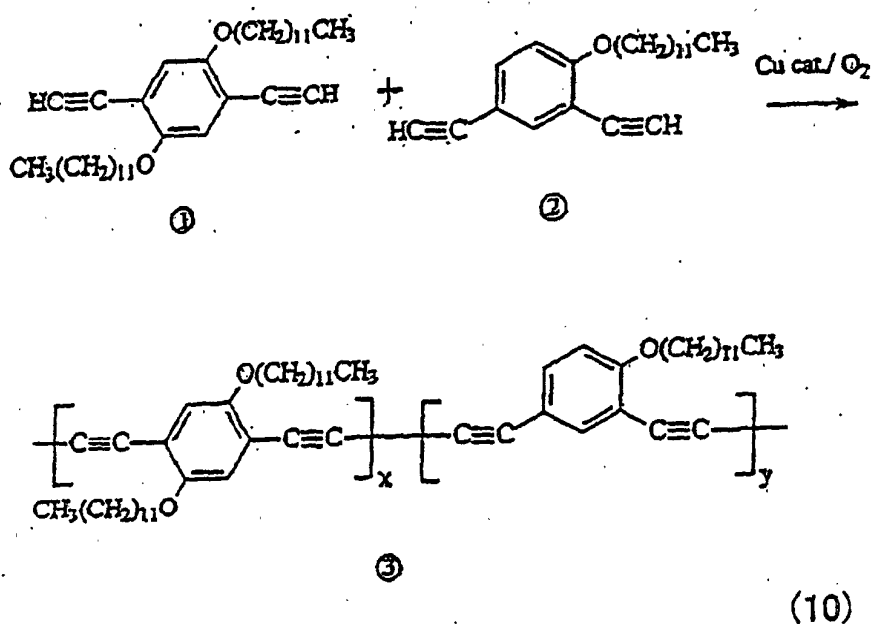
[0043] The THF reactive solution obtained by the oxidative condensation polymerisation reaction is concentrated to about 10 ml, and then the concentrate is dropped into 1-litre of 2N-HCl/MeOH solution that is hardly stirred. Then, the polymer generated by the oxidative condensation polymerisation reaction is precipitated in the 2N-HCl/MeOH solution, the catalyst is removed, and the polymer is purified.

[0044] Then, the precipitated polymer is recovered by using a glass filter, and a small amount of the polymer is dissolved once again in 10ml of the THF solution and then the polymer is reprecipitated by dropping such polymer into a large amount, e.g., 1 litre, of MeOH liquid. The MeOH liquid is strongly stirred.

[0045] The product is again refined by filtration of the reprecipitated polymer by using a glass filter. Then, the polymer is dried by the vacuum drying. The yield was 95%.

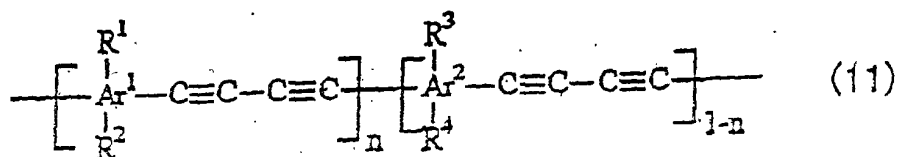
[0046] Equation (10) shows the reaction between the above 2,5-didodecyloxy-1,4-diethynylbenzene and the 4-dodecyloxy-1,3-diethynylbenzene to obtain the intended polymer.

[0047] In the reaction formula, "cat." denotes the catalyst. The copolymerization ratio of the polymer is given as x:y=1:1 similarly to the ratio of supply of the substances of chemical formulae (7), (8) as confirmed by the yield, and thus a polymer in which n the chemical formula (7) is 0.5 can be obtained.



[0048] The polymer indicated by ③ in the reaction formula (10) is the structure obtained in the synthesis, and is the same substance as the polymer of chemical formula (7).

[0049] In the above example, the polymer given by the chemical formula (7) is employed as the luminous layer 3 of the organic EL device. A general formula for the polymer can be given by the following chemical formula (11).



[0050] In the chemical formula (11), Ar¹ and Ar² each denote an arylene group (bivalent aromatic ring). Examples of the aromatic ring comprised by the term arylene group are benzene, pyrrole, thiophene, carbazole, furan, fluorene, naphthalene, anthracene, and derivatives thereof. The first unit which includes Ar¹ has two carbon-carbon triple bonds, and the second unit which includes Ar² also has two carbon-carbon triple bonds.

[0051] Specific arylene groups can be, for example, biphenyl, terphenyl, perylene, coumarin, diphenylamine, triphenylamine, phenanthrene, phenanthridine, phenanthroline, phenylazobenzene, diphenylazobenzene, anthraquinone, acridinone, quinacridone, stilbene, and derivatives of them.

[0052] The simplest arylene groups Ar¹ will be based on benzene and naphthalene as with 1,4-phenylene and 1,5-naphthalene groups, the latter enhancing the rigidity of the polymer. With Ar², the arylene group can be 1,3-phenylene or 1,2-naphthalene group, the latter having a structure to reduce the rigidity of the polymer.

[0053] R¹, R², R³, R⁴ are substituents such as hydrogen, alkyl, alkoxy, carboxyl, cyano, phenyl, biphenyl and cyclohexylphenyl. Also, R¹, R², R³, R⁴ can be the same or different or just some can be the same.

[0054] n in the chemical formula (11) is a copolymerization ratio and preferably n is set to 0 < n ≤ 0.9. As a polymer having n=1, for example, there is polyarylene butadienylene. In this case, it has been confirmed that the crystallinity at ambient temperature is relatively low and the solubility relatively high compared to the prior art.

[0055] The emission wavelength of the luminous layer 3 is changed by selecting R¹, R², R³, R⁴, Ar¹, Ar² appropriately. Accordingly, if a color image is needed, a pattern in which the structure of the polymer is changed for every pixel of the image is formed.

[0056] In order to finely adjust the luminous color of the luminous layer 3, a plurality of kinds of polymer may be contained.

[0057] In the chemical formula (11), the first unit can be defined as A and the second unit can be defined as B. Then, if A and B have the structures given by the chemical formula (7), i.e., if unit A has the structure of the para-substitution product and unit B has the structure of the meta-substitution product, a relationship between the copolymerization ratio n of the polymer constituting the luminous layer 3 given by the chemical formula (7) and the luminous intensity of the luminous layer 3 exists which has been examined experimentally. As a result, it has been found that, if the film thickness of the polymer and the forming steps are not changed, the luminous intensity differs according to difference in the value of n. In the case of n=0.66, or n:(1-n)=2:1, the luminous intensity of the luminous layer 3 was the highest.

[0058] When the luminous intensities of the luminous layers 3 formed by the polymer of chemical formula (7) obtained when n:(1-n)=2:1 and that obtained when n:(1-n)=1:1 is set in the chemical are compared with each other, the EL spectrum shown in FIG.3 was derived. The profile showing the relationship between the luminous wavelength and the EL intensity is reflective of a profile of the fluorescent spectrum shown in FIG.2.

[0059] In FIG.3, the driving voltage of the luminous layer 3 formed of the polymer of n=0.5 is set to 40 V and the driving voltage of the luminous layer 3 formed of the polymer of n=0.66 is set to 26 V. Although there exists such difference in the driving voltage, the polymer of n=0.66 could provide an emission that is about 40 times as strong as that of the polymer of n=0.5.

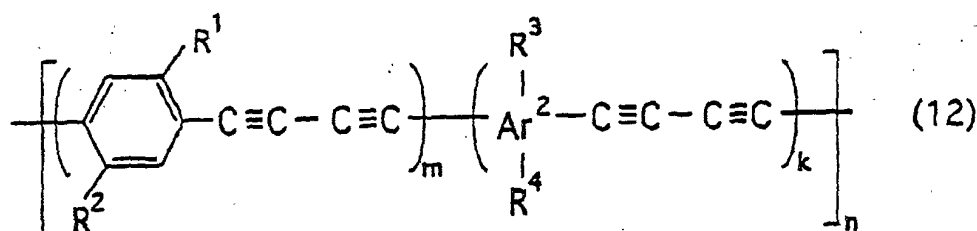
[0060] In order to get n=0.66 in the chemical formula (7), i.e. to set x=2, y=1 in the chemical formula (10), 2.96 g (6 mmol) of the para-product indicated by a symbol ① in the chemical formula (10) and 0.93g (3 mmol) of the meta-product indicated by a symbol ② in the chemical formula (10) as the ratio of supply are dissolved in the tetrahydrofuran solution to cause the oxidative condensation polymerisation reaction. Then, like the case where the polymer of n=0.5 is formed, processes such as catalyst removal, polymer refinement, filtration/recovery, polymer reprecipitation, filtration/recovery, vacuum drying, etc. are carried out sequentially as before.

[0061] In the above organic EL device, a structure that outputs the light from the glass substrate side is employed. In contrast, the light may also be outputted from the upper side by reversing the structure of the electrodes and forming the light transparent conductive film on the upper side. Also, in the above organic EL device, a structure in which the luminous layer is directly put between a pair of electrodes is shown. In this case, an organic electron transmitting layer may be formed between the luminous layer and the negative side electrode, otherwise an organic hole transmitting layer may be formed between the luminous layer and the positive side electrode.

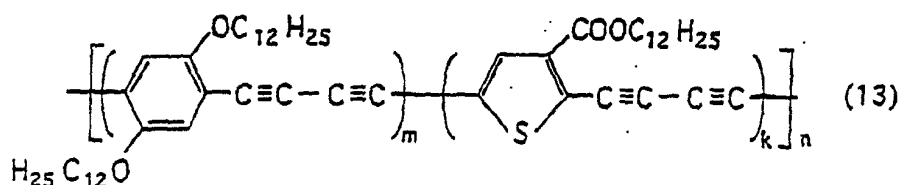
[0062] In the meanwhile, the polymer given by the chemical formula (7) can emit light in the emitting wavelength range of 500 to 550 nm, i.e., at green or near green color wavelengths.

[0063] In order to display a full color image on the display device, polymers that can emit red color light and blue color light are also required. A polymer that can emit light in the red color wavelength band will now be explained.

[0064] First, the copolymerized polymer used as red color luminous layer 3 is given by the chemical formula (12). In the copolymerized polymer in the chemical formula (12), the aromatic ring Ar¹ in the chemical formula (11) now denotes a benzene ring, substituent R⁴ denotes a hydrogen atom, and Ar² denotes an arylene group, in which the aromatic ring is any one of thiophene, anthracene, pyridine, phenol, aniline, and derivatives thereof. In the chemical formula (12), R¹, R², R³, and R⁴ generally can be any one of hydrogen, alkyl, alkoxy, carboxyl, cyano, phenyl, biphenyl, and cyclohexylphenyl. As before, m and k denote copolymerisation ratio, and n denotes degree of polymerisation.



[0065] A polymer of chemical formula (12) in which R¹, R² are both alkoxy groups, the aromatic ring constituting Ar² is thiophene, R³ is carboxyl group, and R⁴ is hydrogen is copoly(2,5-didodecyloxy-1,4-phenylenebutadiynylene)(3-dodecyloxycarbonylthienylenebutadiynylene)(2: 1), and is given by (13)

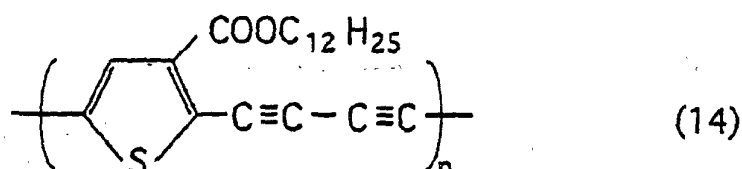


[0066] A luminous layer 3 formed of this copolymer given by the chemical formula (3) has the spectrum shown in FIG.4, and the peak in the luminous wavelength band is 574 nm.

[0067] The polymer given by the chemical formula (13) can be synthesised in the same manner as mentioned above by using 3-dodecyloxycarbonyl-2,5-bis(trimethylsilylethynyl)thiophene in place of 4-dodecyloxy-1,3-diethynylbenzene having the chemical formula (9).

(Second Embodiment)

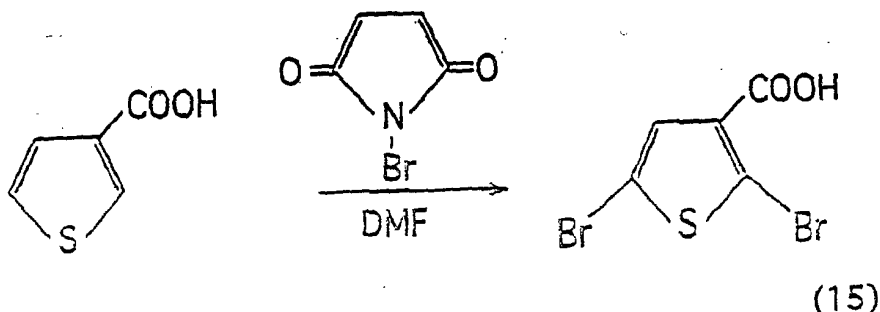
[0068] An alternative material constituting a red color luminous layer 3 is a homopolymer of general formula (4) hereinabove and this can be used in place of the above copolymer. A typical homopolymer, is poly(3-dodecyloxycarbonyl-2,5-thienylenebutadiynylene) given by the chemical formula (14). The spectrum of the homopolymer of chemical formula (14) is shown in FIG.5; the spectrum has a peak at 596 nm in the luminous wavelength band.



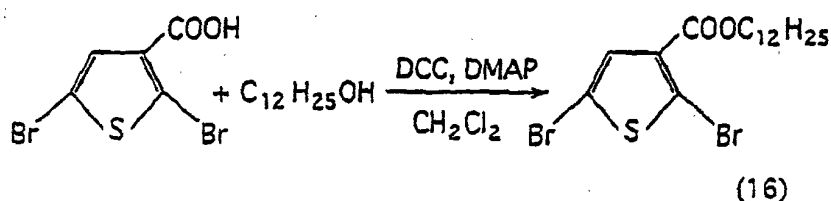
[0069] The homopolymer given by the formula (14) can be synthesised as follows.

[0070] First, under a light-shielded argon atmosphere. 5.12 g (40 mmol) of 3-thenoic acid, also called thiophenecarboxylic acid, are added to 50ml of dimethylformamide (DMF) and then 14.6 g (82 mmol) of N-bromosuccinimide is added.

[0071] The reaction solution obtained is stirred overnight to enable the reaction of equation (15) to proceed. The reaction solution is then injected into a mixture of 100ml of saturated sodium sulfate solution and 600ml water of 600 ml, and the resulting deposit is recovered. 9.38g of white needle-like crystals are obtained as a yield of 82.0% by recrystallising the deposit from an ethanol/water mixed solution. The white needle-like crystals are crystals of 2,5-dibromo-3-thenoic acid shown on the right side of the reaction equation (15).



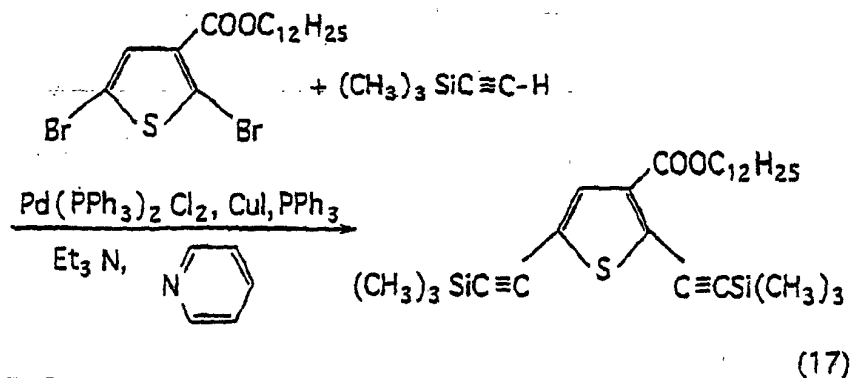
[0072] Then, 4.13 g (20 mmol) of dicyclohexylcarbodiimide (DCC) and 2.44 g (20 mmol) of dimethylaminopyridine (DMAP) are well vacuum-dried, and dichloromethane (CH_2Cl_2) is added to the resultant mixture under the argon atmosphere. When 5.72 g (20 mmol) of 2,5-dibromo-3-thenoic acid and 3.73 g (20 mmol) of dodecanol ($\text{C}_{12}\text{H}_{25}\text{OH}$) are added to the mixture and then stirred for three days, the reaction shown in the reaction equation (16) takes place.



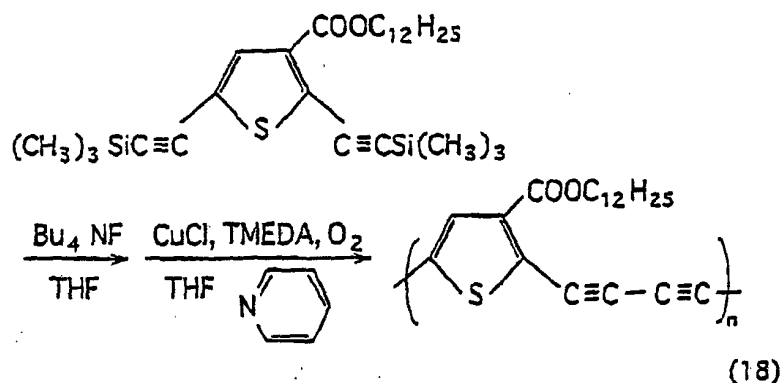
[0073] Then, 8.56 g (18.8 mmol) of white crystals are obtained as a yield 94.2% by filtering the reaction salt, and then purifying the dichloromethane by using a silica gel column employed as a developing solvent. The white crystals are the crystals of 2,5-dibromo-3-dodecyloxycarbonylthiophene, i.e., dodecyl 2,5-dibromo-3-thenoate or 3-dodecylester-2,5-dibromothiophene, shown on the right side of the chemical equation (16).

[0074] Then, 6.81 g (15 mmol) of the 3-dodecylester-2,5-dibromothiophene, 103 mg (0.54 mmol) of copper iodide (CuI) and 210 mg (0.8 mmol) of triphenylphosphine (PPh_3) are added to a mixed solution of 27 ml triethylamine (Et_3N) and 18 ml pyridine under the argon atmosphere. Then, this solution is stirred for twenty minutes while bubbling argon therethrough. Then, 3.44 g (35 mmol) of trimethylsilylacetylene ($(\text{CH}_3)_3\text{SiC}\equiv\text{C-H}$) and 105 mg (0.15 mmol) of bis(triphenylphosphine)palladium dichloride ($\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$) are added to the resultant solution. Then, this solution is stirred overnight while holding at 85°C , and then extraction is executed by using dichloromethane and then water. 5.93 g (11.8 mmol) of a yellow oil are obtained as a yield of 78.9 % by purifying the resultant oily layer in a silica gel column using a developing solvent that contains dichloromethane and hexane in ratio of 1:3 respectively.

[0075] The yellow oil is 3-dodecyloxycarbonyl-2,5-bis(trimethylsilylethynyl)thiophene, i.e., dodecyl-2,5-bis(trimethylsilylethynyl)-3-thenoate, that is obtained by the reaction given by the reaction equation (17).

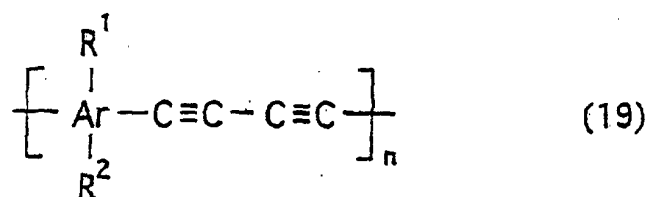


[0076] Then, 0.500 g (1 mmol) of the yellow oil is dissolved in 20mg of THF and then 0.5 ml (0.5 mmol) of tetrabutylammonium fluoride (Bu_4NF) in more THF is added. This solution is then stirred for five minutes, and then the purified product is obtained from the THF by passage through a silica gel column used as the developing solvent. Then, a catalyst solution is formed by adding 10 mg (0.1 mmol) of copper (I) chloride, 12 mg (0.1 mmol) of N,N,N',N'-tetramethylethylenediamine (TMEDA), 8mg THF and 2ml pyridine to another vessel, and then supplying oxygen to the liquid in this vessel. 10 ml of THF containing the above purified product are added in the catalyst solution, and then the reaction given by the reaction equation (18) is generated by stirring this solution for two days under an oxygen atmosphere.



[0077] The solution in which reaction has taken place is dropped into 500ml of 2-normal (N) methanol/hydrochloric acid, and then the resultant precipitate is recovered. 203 g (0.59 mmol) of a red powder is obtained as a yield of 59.5% by dissolving this precipitate in chloroform, then dropping this liquid into 500ml methanol, and then recovering the resultant precipitate. This red powder is the product substance in chemical equation (18), i.e., the homopolymer given by the chemical formula (14).

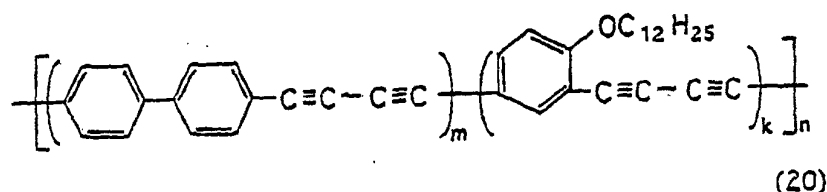
[0078] The general formula of the homopolymer that can emit the light in the red color wavelength band and its near emission wavelength band, according to the present embodiment, is given by the formula (19). In the equation (19), the aromatic ring constituting Ar can be any one of thiophene, anthracene, pyridine, phenol, aniline, and derivatives thereof. R₁ and R₂ denote substituents which can be the same or different and can be hydrogen, alkyl, alkoxy, carboxyl, cyano, phenyl, biphenyl, or cyclohexylphenyl group respectively. n denotes the degree of polymerisation



(Third Embodiment)

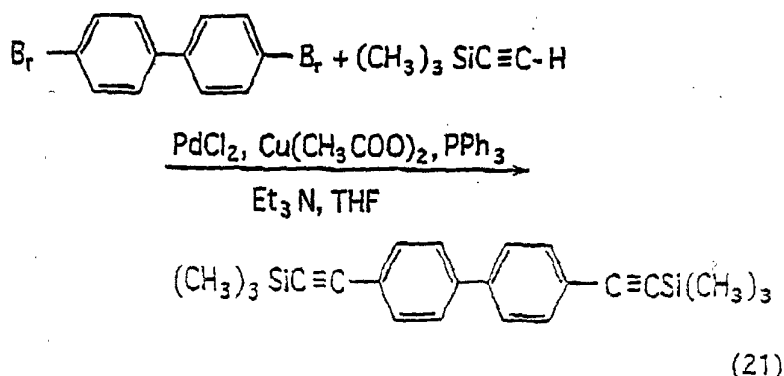
[0079] In the first and second embodiments, polymers that can emit light in the green or near green color wavelength band and in the red or near red color wavelength band are explained. In order to display a full color image on the organic EL display device, a polymer that can emit blue color light is further required. Therefore, polymers that can emit light in the blue color wavelength band will be explained hereunder.

[0080] Copoly(4,4'-biphenylenebutadiynylene)(4-dodecyloxy-m-phenylenebutadiynylene) as given by the chemical formula (20) is an example of a copolymerized polymer for constituting a blue color luminous layer 3. The spectrum of the polymer having the formula (20) is shown in FIG.6 and has peaks at 428 nm and 450 nm in



[0081] The polymer having the chemical formula (20) is synthesised as follows.

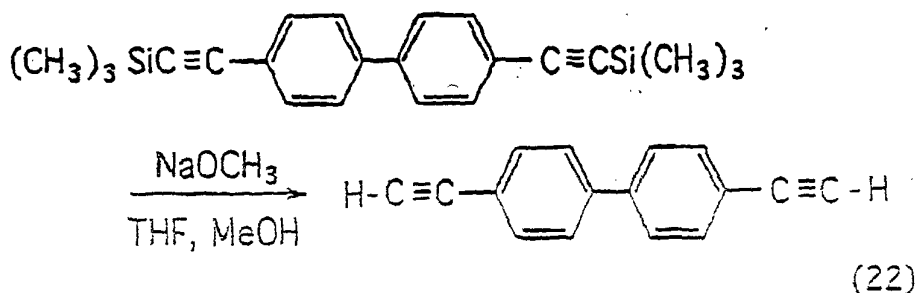
[0082] First, 4,4'-bis(trimethylsilylethynyl)biphenyl is synthesised by the reaction (21).



[0083] More particularly, reaction (21) is brought about by adding 6.24 g (20 mmol) of 4,4'-dibromobiphenyl, 354 mg (2 mmol) of palladium chloride, 364 mg (2 mmol) of copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$), 1.73 g (6.6 mmol) of triphenylphosphine and 3.24 g (3.3 mmol) of trimethylsilylacetylene to a liquid that contains 100ml of triethylamine and 130 ml of THF under an argon atmosphere, and then refluxing this liquid at 85°C overnight. Then, 5.90 g (17 mmol) of white plate-like crystals are obtained as a yield of 85.0% by extracting the liquid with dichloromethane and water, then processing the resultant oily layer using silica gel column chromatography using the dichloromethane as developing solvent, and then purifying the oil obtained by recrystallisation from methanol.

[0084] The white plate-like crystals of 4'-bis(trimethylsilylethynyl)biphenyl have the formula shown on the right side of reaction (21).

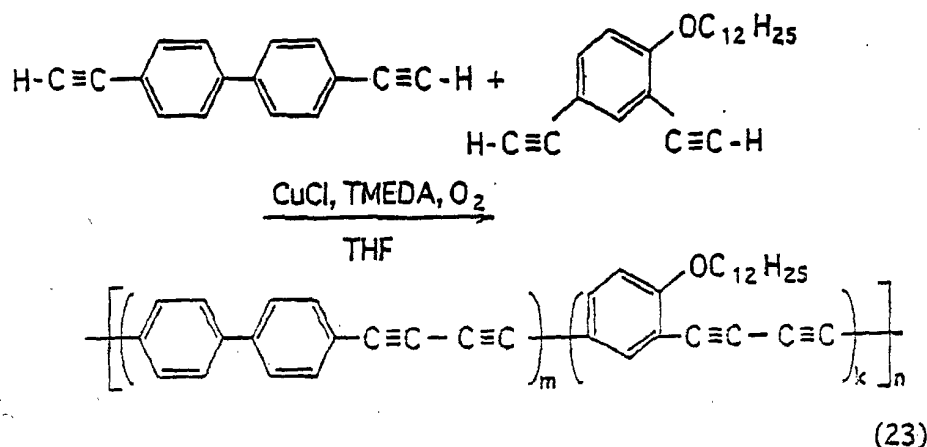
[0085] Then, 4,4'-diethynylbiphenyl is synthesised from this reaction product by the reaction(22).



[0086] In other words, 5.9 g (17 mmol) of the white plate-like crystals are dissolved in 10ml of THF, then 1.83 g (17 mmol) of sodium methoxide (NaOCH₃) dissolved in the 6ml of methanol (CH₃OH; MeOH) are added to this solution, and then they are reacted at ambient temperature for three hours. Then, an oily layer is obtained by extraction using dichloromethane and 10% hydrochloric acid aqueous solution.

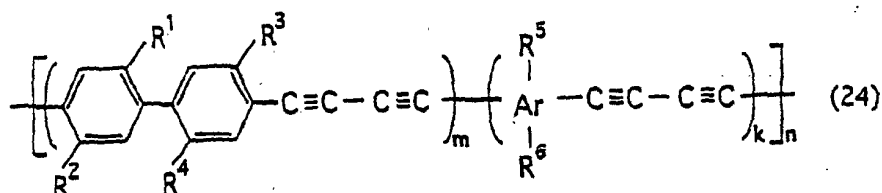
[0087] The oily layer is purified using a silica gel column employing developing solvent that contains dichloromethane and hexane at a ratio of 1:1, whereby a 1.20 g (5.9 mmol) of a white powder is obtained as a yield of 34.8%. This white powder is 4,4'-diethynylbiphenyl shown on the right side of reaction (22).

[0088] Then, copoly(4,4'-biphenylenebutadiynylene) (4-dodecyloxy-m-phenylenebutadiynylene)) is synthesised by reaction (23) using the white powder as starting material.



[0089] More particularly, a catalyst solution is formed by putting 20 mg (0.2 mmol) of copper (I) chloride, 24mg (0.2 mmol) of TMEDA, and 40 ml of THF into a vessel to react with each other, and then supplying oxygen to this reaction solution. Then, 4,4'-diethynylbiphenyl and 311 mg (1 mmol) of 4-dodecyloxy-m-diethynylbenzene, each dissolved in 40 ml THF, are added to the catalyst solution, and then they are stirred under the oxygen atmosphere for two days. The 4-dodecyloxy-m-diethynylbenzene is expressed by the second chemical structural formula appearing in reaction (23). Reaction (23) progresses during this stirring, then the resultant reaction solution is dropped into 500 ml of 2-normal methanol/hydrochloric acid, and then the resultant precipitate is recovered. Then, this precipitate is dissolved in chloroform to remove the insoluble component, then this solution is dropped into 500 ml of methanol, and then the resultant precipitate is recovered, whereby 248 g (0.98 mmol) of white powder are obtained as a yield of 48.7 %. This white powder is the polymer given by the formula (20). When this polymer is employed as a luminous layer 3 as in the first embodiment, the luminous layer 3 emits a blue light or a light close to blue.

[0090] A general formula for the polymer (20) is expressed by the formula (24),



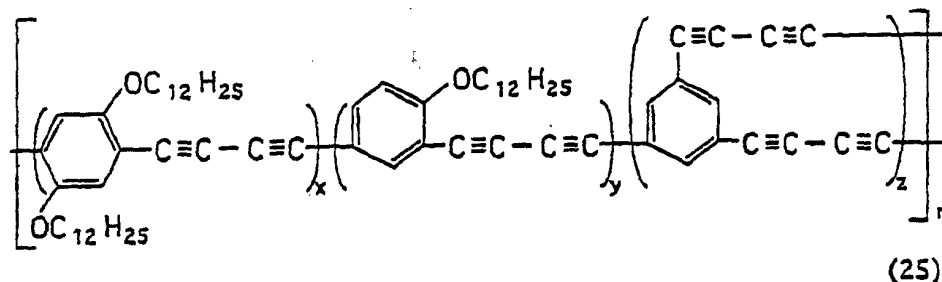
[0091] In the formula (24), Ar denotes an arylene group that can be any one of benzene, pyrrole, thiophene, carbazole, furan, fluorene, naphthalene, anthracene or each derivative of them. Also, R¹, R², R³, R⁴, R⁵ and R⁶ can be the same or different and can be any one of hydrogen, alkyl, alkoxy, carboxyl, cyano, phenyl, biphenyl, and cyclohexylphenyl. Again, m and k denote the co-polymerization ratio, and n denotes the degree of polymerization.

(Fourth Embodiment)

[0092] A polymer for emitting blue color light, that is different from the polymer discussed in the third embodiment, will be explained hereunder.

[0093] A copolymerized polymer providing a blue color luminous layer has, for example, the structure of formula

(25). The spectrum of the polymer given by the formula (25) is shown in FIG.7 and has peaks at 405 nm, 495 nm, and 512 nm in the luminous wavelength band. In the chemical formula. $x : y : z$ is 6 : 3 : 1.

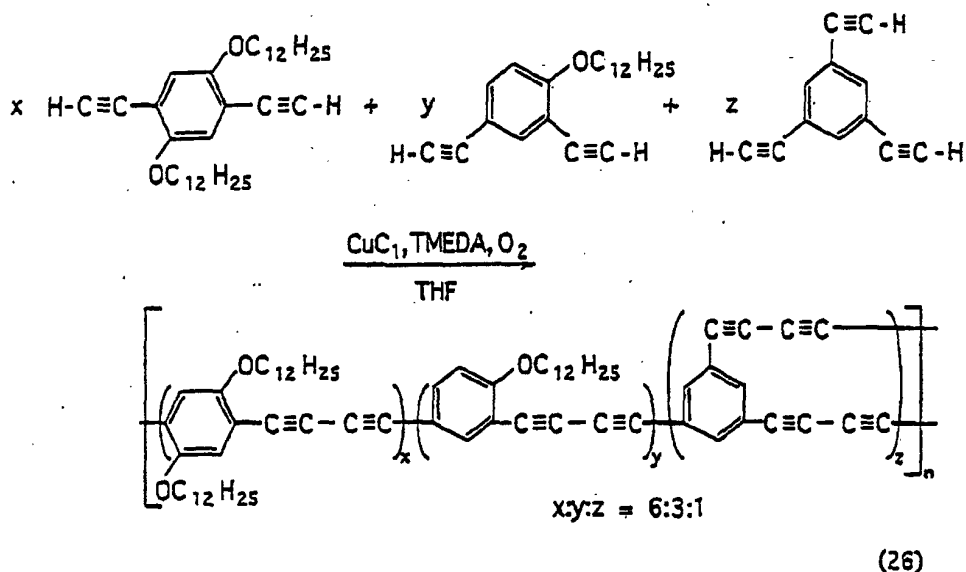


[0094] The polymer given by the chemical formula (25) is synthesised as follows.

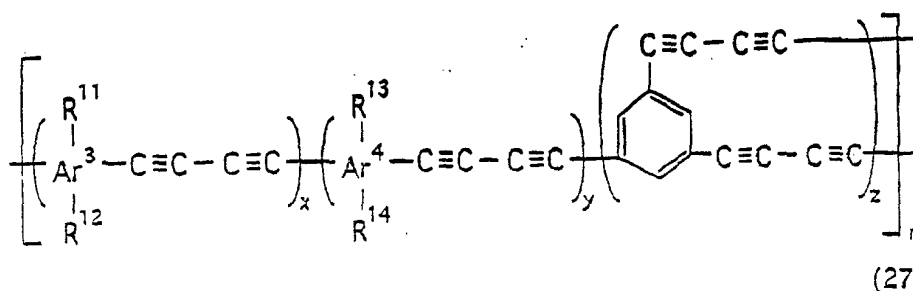
[0095] First, a catalyst solution is formed by supplying oxygen to a reaction solution in which 10 mg (0.1 mmol) of copper (I) chloride, 12 mg (0.1 mmol) of TMEDA, and 20 ml of THF are mixed. Then, 297 mg (0.6 mmol) of 2,5-didodecyloxy-p-diethynylbenzene, 93 mg (0.3 mmol) of 4-dodecyloxy-m-diethynylbenzene, and 15 mg (0.1 mmol) of 1,3,5-triethynylbenzene are added to THF and this solution is added to the above catalyst solution, and then the resultant solution is stirred under an oxygen atmosphere for two days.

[0096] Reaction (26) then takes place.

[0097] The reaction solution is then dropped into 500ml of 2-normal methanol hydrochloride, and the resultant precipitate is recovered. Then, this precipitate is dissolved in chloroform, the insoluble component is removed from this solution and the solution is dropped into 500 ml of methanol, and then the resultant precipitate is recovered, 304g of a yellow powder are obtained as a yield of 75.4 %.



[0098] The general formula of the copolymerized polymer according to the present embodiment, that emits light in the blue and near blue color wavelength band, is expressed by the formula (27). In the formula (27), Ar^3 and Ar^4 both denote an arylene group (dihydric aromatic ring). The aromatic ring providing the arylene group can be a benzene, pyrrole, thiophene, carbazole, furan, fluorene, naphthalene, or anthracene ring or a derivative thereof.



[0099] In general, the arylene group can be, for example, biphenyl, terphenyl, perylene, coumarin, diphenylamine, triphenylamine, phenanthrene, phenanthridine, phenanthroline, phenylazobenzene, anthraquinone, acridinone, quinacridone, stilbene or a derivative thereof.

[0100] R^{11} , R^{12} , R^{13} , R^{14} are substituents which can be the same or different and can be hydrogen, alkyl, alkoxy, carboxyl, cyano, phenyl, biphenyl or cyclohexylphenyl. In addition, R^{11} , R^{12} , R^{13} , R^{14} can all be different types, or some of them are the same types, or R^{11} , R^{12} , R^{13} , R^{14} are all same types. x , y , z denote the copolymerization ratio, and n denotes the degree of polymerization.

[0101] As described above, according to the present invention, a luminous layer made of one or more of the polymers of formula (11), (12), (19), (24), and (27) is formed between the lower electrode and the upper electrode. In contrast to the polymers employed as the luminous layer the prior art, such polymer is hard to crystallize at ambient temperature and has a high solubility in solvents.

[0102] Accordingly, if one or more of these polymers is employed as the luminous layer, planarization of the luminous layer can be facilitated, short-circuiting between the upper electrode and the lower electrode hardly occurs, and the yield of the device can be improved.

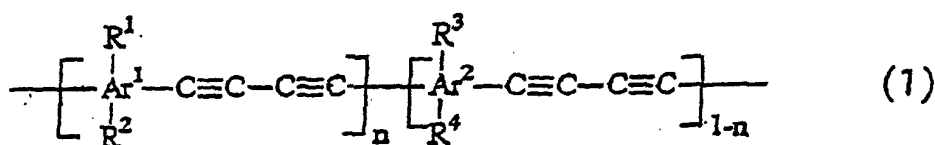
[0103] Also, if a polymer is synthesised such that the substitution ratio of the para-product and the meta-product is set to $x : y = 2 : 1$ in the chemical formula (10), a luminous layer that can provide a particularly strong emission can be obtained.

Claims

1. An organic light-emitting device comprising;

a lower electrode;

a luminous layer formed on the lower electrode and made of polymer indicated by (1)



where Ar^1 and Ar^2 denote first and second arylene groups which can be the same or different, R^1 , R^2 , R^3 and R^4 are substituents which can be the same or different or some of which can be the same and other(s) different, and n denotes the copolymerization ratio; and an upper electrode formed on the luminous layer.

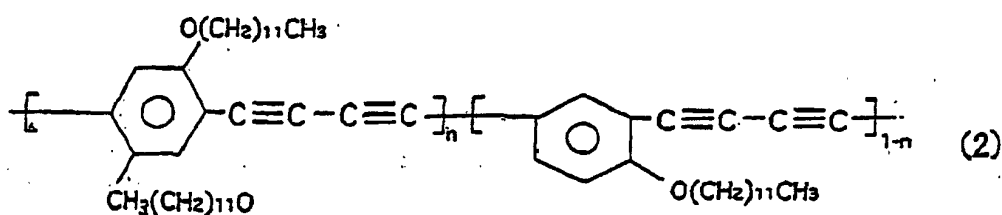
2. An organic light-emitting device according to claim 1, wherein one of the upper electrode and the lower electrode is formed of light transparent conductive material.

3. An organic light-emitting device according to claim 2, wherein the other of the upper electrode and the lower electrode is formed of alkali metal or alkaline earth metal, or contains such metal.

4. An organic light-emitting device according to any preceding claim, wherein the aromatic ring constituting the first arylene group or the second arylene group is any one of benzene, pyrrole, thiophene, carbazole, furan, fluorene,

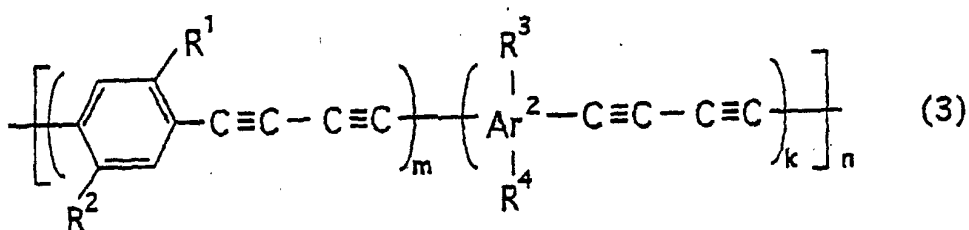
naphthalene, anthracene, and derivatives thereof.

5. An organic light-emitting device according to any one of claims 1 to 3, wherein the first arylene group is a para-phenylene group, and the second arylene group is a metaphenylene group.
6. An organic light-emitting device according to any one of claims 1 to 3, wherein the substituents R¹ to R⁴ are independently selected from hydrogen, alkyl, alkoxy, carboxyl, cyano, phenyl, biphenyl and cyclohexylphenyl.
7. An organic light-emitting device according to any one of claims 1 to 3, wherein R¹, R² and Ar¹ constitute a para-product and R³, R⁴ and Ar² constitute a meta-product in the chemical formula (1).
8. An organic light-emitting device according to any one of claims 1 to 3, wherein the first arylene group of the polymer is a paraphenylene group and the second arylene group is a metaphenylene group, and the polymer is given by the formula.



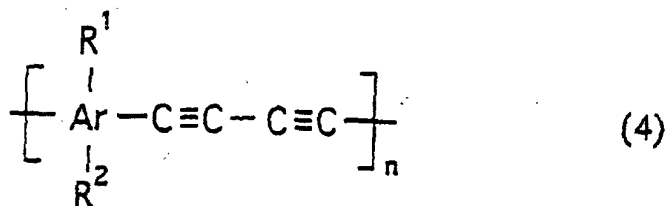
wherein n denotes the copolymerisation ratio.

9. An organic light-emitting device according to claim 8, wherein n is 0.66 or n is a value to satisfy n:(1-n)=2:1.
10. An organic light-emitting device according to claim 1, 2, 3 or 6, wherein n is 0<n≤0.9.
11. An organic luminous material having the general formula



where Ar² denotes an arylene group, R¹, R², R³ and R⁴ denotes substituents, which can be the same or different or some of which can be the same and other(s) different and m and k together denote the copolymerization ratio and n denotes the degree of polymerisation.

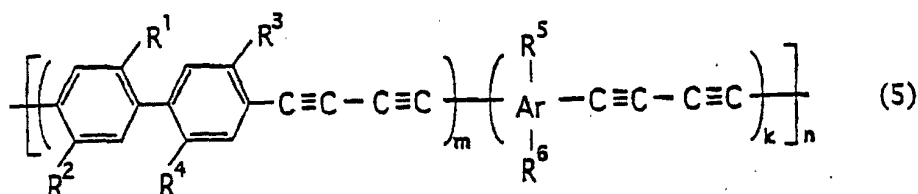
12. An organic luminous material according to claim 11, wherein an aromatic ring comprised by the arylene group is any one of thiophene, anthracene, pyridine, phenol, aniline and derivatives thereof, and the said substituents are selected from hydrogen, alkyl, alkoxy, carboxyl, cyano, phenyl, biphenyl and cyclohexylphenyl.
13. An organic luminous material having the general formula



where Ar denotes an arylene group, R^1 and R^2 denote substituents which can be the same or different and n denotes the degree of polymerisation.

14. An organic luminous material according to claim 13, wherein an aromatic ring comprised by the arylene group is any one of thiophene, anthracene, pyridine, phenol, aniline and derivatives thereof, and the said substituents are selected from hydrogen, alkyl, alkoxy, carboxyl, cyano, phenyl, biphenyl and cyclohexylphenyl.

15. An organic luminous material having the general formula

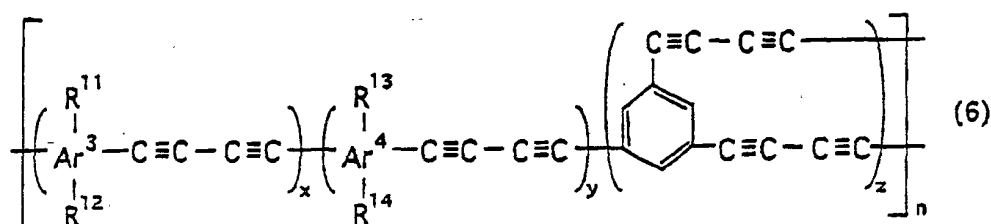


where Ar denotes an arylene group, R^1 , R^2 , R^3 , R^4 , R^5 and R^6 , denotes substituents which can be the same or different or some of which can be the same and other(s) different, m and k denote the copolymerization ratio and n denotes the degree of polymerisation.

16. An organic luminous material according to claim 15, wherein an aromatic ring constituting the arylene group is any one of benzene, pyrrole, thiophene, carbazole, furan, fluorene, naphthalene, anthracene and derivatives thereof.

17. An organic luminous material according to claim 16, wherein the said substituents are selected from hydrogen, alkyl, alkoxy, carboxyl, cyano, phenyl, biphenyl and cyclohexylphenyl.

18. An organic luminous material having the general formula



where Ar^3 denotes a first arylene group, Ar^4 denotes a second arylene group, R^{11} , R^{12} , R^{13} and R^{14} are substituents which can be the same or different or some of which can be the same and other(s) different, x , y , z denote copolymerization ratios and n denotes the degree of polymerisation.

19. An organic luminous material according to claim 18, wherein the aromatic rings constituting the first and second arylene groups are the same or different and selected from benzene, pyrrole, thiophene, carbazole, furan, fluorene, naphthalene and anthracene and derivatives thereof.

20. An organic luminous material according to claim 18 or 19, wherein the said substituents are selected from hydrogen, alkyl, alkoxy, carboxyl, cyano, phenol, biphenyl and cyclohexylphenyl.

- 21.** An organic light-emitting device as claimed in any one of claims 1 to 3 in which the organic luminous material is a material as claimed in any one of claims 11 to 20.

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FIG.1A

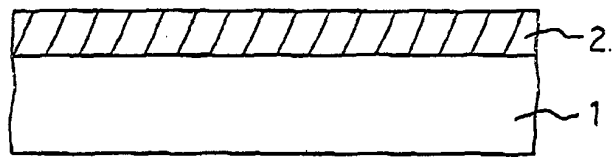


FIG.1B

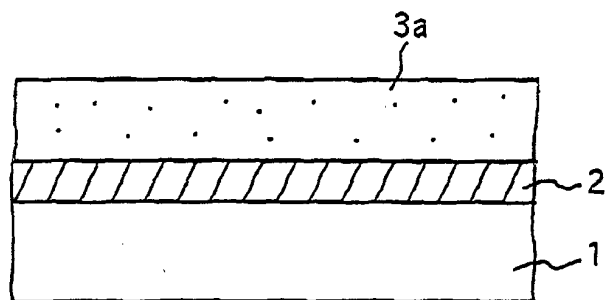


FIG.1C

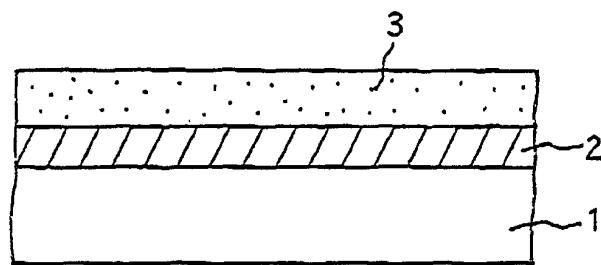


FIG.1D

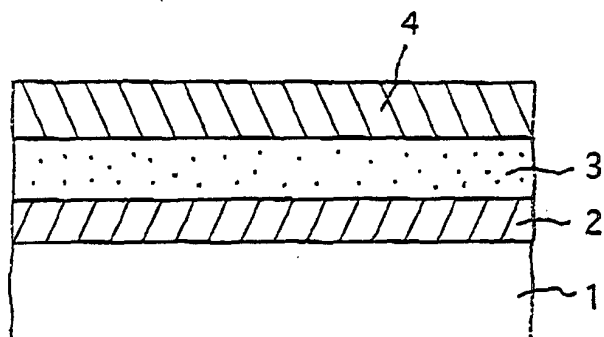


FIG.2

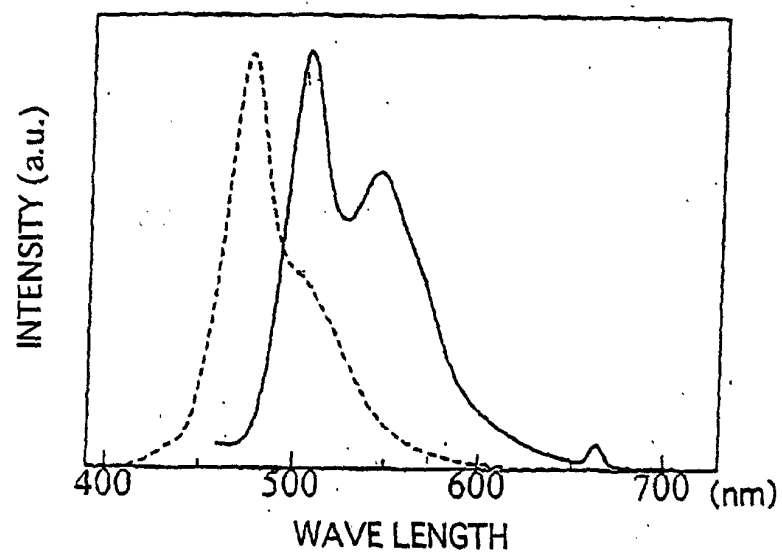


FIG.3

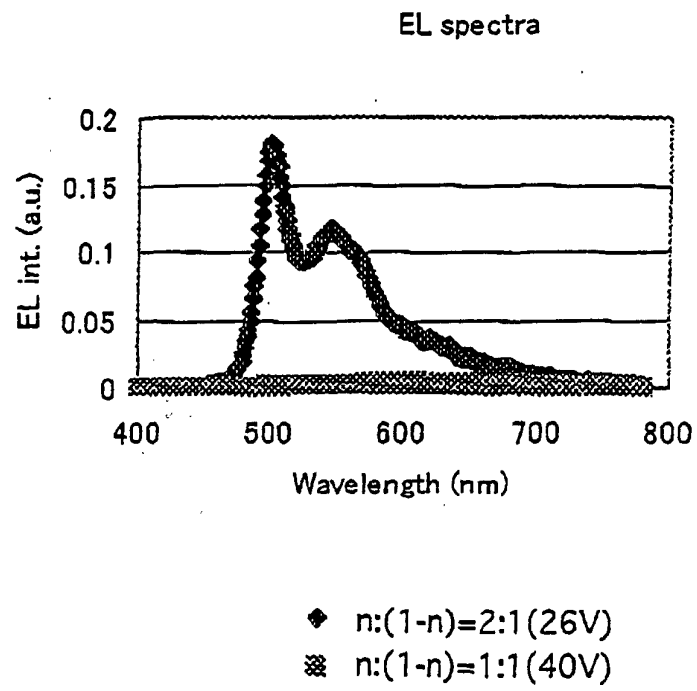


FIG. 4

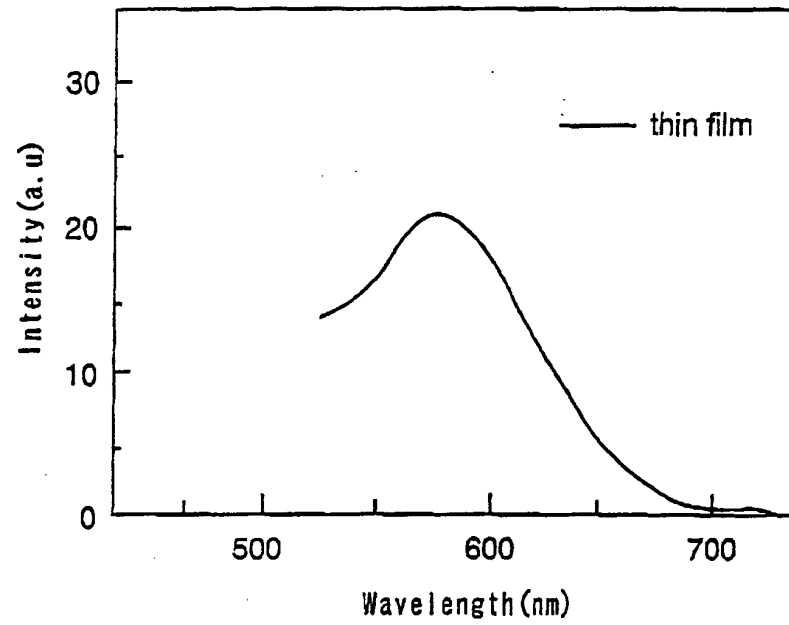


FIG. 5

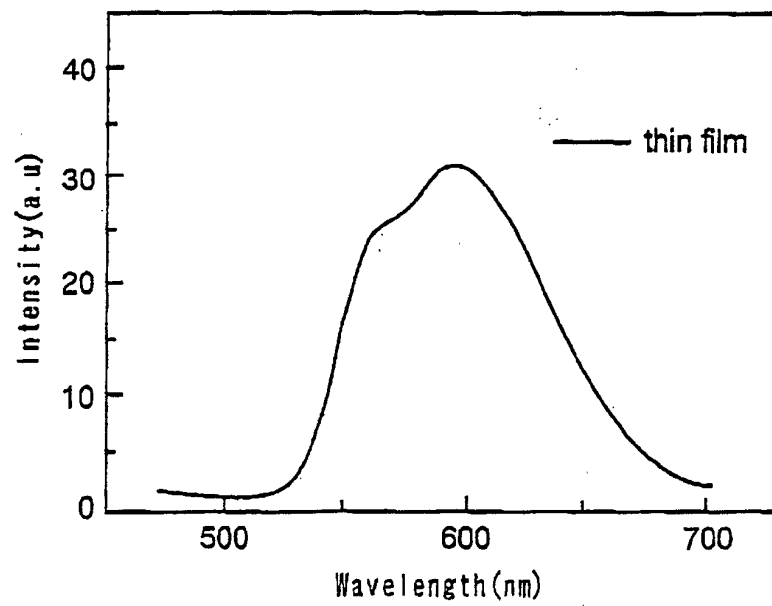


FIG. 6

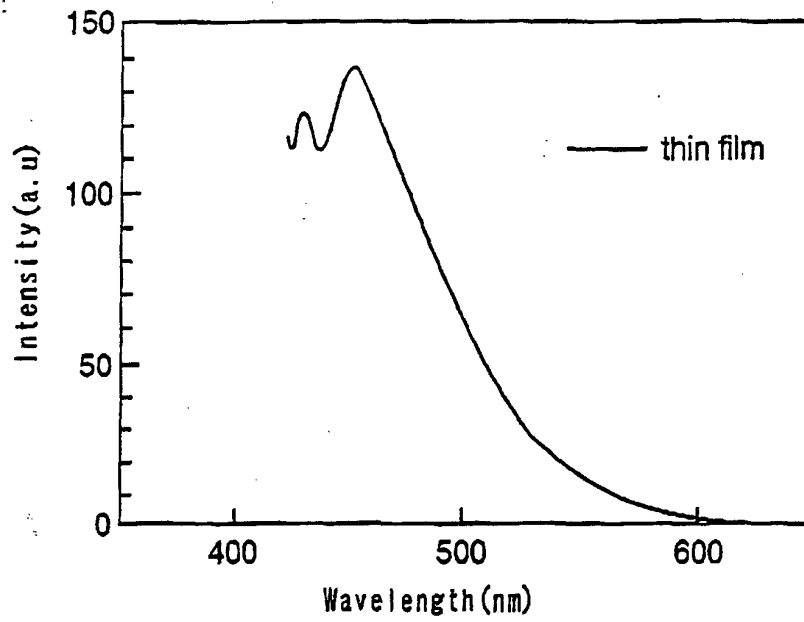
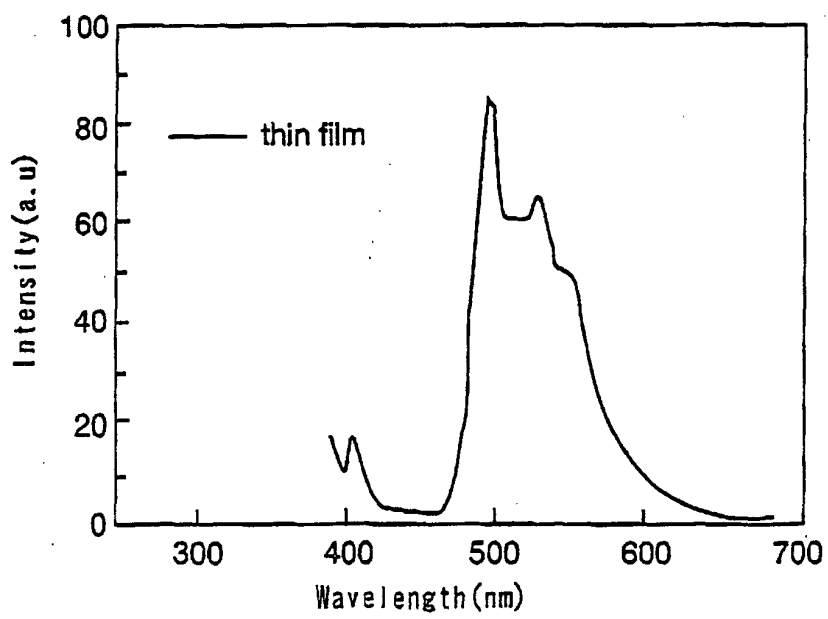


FIG. 7



专利名称(译)	有机发光材料和有机发光器件		
公开(公告)号	EP1158839A2	公开(公告)日	2001-11-28
申请号	EP2001303861	申请日	2001-04-27
[标]申请(专利权)人(译)	富士通株式会社		
申请(专利权)人(译)	FUJITSU LIMITED		
当前申请(专利权)人(译)	FUJITSU LIMITED		
[标]发明人	YOSHIKAWA KOTA C O FUJITSU LIMITED KIJIMA MASASHI SHIRAKAWA HIDEKI KINOSHITA IKUO		
发明人	YOSHIKAWA, KOTA, C/O FUJITSU LIMITED KIJIMA, MASASHI SHIRAKAWA, HIDEKI KINOSHITA, IKUO		
IPC分类号	H01L51/50 C08F38/00 C08G61/02 C09K11/06 H01L51/30 H05B33/14		
CPC分类号	C08F38/00 C08G61/02 C09K11/06 C09K2211/1092 C09K2211/1425 H01L51/0035 H01L51/0043 H01L51/5012 Y10S428/917		
代理机构(译)	西尔弗曼，沃伦		
优先权	2000128364 2000-04-27 JP 2000288692 2000-09-22 JP 2001125359 2001-04-24 JP		
其他公开文献	EP1158839A3 EP1158839B1		
外部链接	Espacenet		

摘要(译)

采用聚合物材料的有机EL器件包括这样的结构，其中由所示聚合物形成的发光层置于下电极和上电极之间。在上式中，Ar 1，Ar 2可以相同或不同，表示亚芳基，R 1，R 2，R 3，R 4表示取代基，n表示共聚比。可以改善发光层的平坦度，并且可以提高发光层构成材料的溶解性。

(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: 27.04.2000 JP 2000128364

22.09.2000 JP 2000288692

24.04.2001 JP 2001125359

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