(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 170 273 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
09.01.2002 Bulletin 2002/02

(21) Application number: **01100286.2**

(22) Date of filing: **04.01.2001**

(51) Int Cl.^{7}: **C07C 13/567**, C07C 211/54, C07D 271/06, C07D 333/18, C07C 15/28, C08F 2/48, H05B 33/02

(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: **03.07.2000 KR 2000037784**

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(54) Alkynic compounds, their use as monomers in vacuum deposition polymerisation, thin films formed from these polymers and their use in electroluminescent devices

(57) The present invention relates to an organic compound having acetylene group(s), a thin film formed by vacuum deposition polymerization using said organic compound, vacuum deposition polymerization to form said thin film, and an electroluminescence device containing said thin film. More particularly, the present invention relates to an organic compound having at least one acetylene groups, vacuum deposition polymerization in which said organic compound is deposited on the substrate and simultaneously or then polymerized by heat treatment or UV irradiation to form a polymer thin film. and an electroluminescence device using at least one layer of said thin film.

Printed by Jouve, 75001 PARIS (FR)

Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to an organic compound having acetylene group(s), a thin film formed by vacuum deposition polymerization using said organic compound, vacuum deposition polymerization to form said thin film, and an electroluminescence device containing said thin film. More particularly, the present invention relates to an organic compound having at least one acetylene groups, vacuum deposition polymerization in which said organic compound is deposited on the substrate and simultaneously or then polymerized by thermal and/or UV radiation curing to form a polymer thin film, and an electroluminescence device using at least one layer of said thin film.

[0002] Organic functional thin film is recently used in Thin Film Transistor-Liquid Crystal Device (TFT-LCD), organic polymer electroluminescence devices, piezoelectric devices, optical materials and the like because it is applicable for portable electronics. Conventional organic thin film can be prepared by wet process such as dip coating or spin coating but it has disadvantages in that a certain polymer which is insoluble in a solvent requires an additional process of coating a precursor and heating to form a thin film. Further, wet process results in problems including easy contamination by a solvent, difficulty in controlling film thickness and film uniformity below 100nm. Also wet process is not favorable for a following process such as a manufacturing process of semiconductors which requires dry process.

[0003] On the other hand, a deposition polymerization is a method to produce an organic thin film by direct polymerization on the substrate by vaporizing a precursor with heat energy under high vacuum. Said deposition polymerization can i)produce a thin film through a simple vacuum device without using a catalyst or a solvent, ii)prevent from contamination of impurities, iii)control molecular sequences and film thickness, iv)provide easy preparing of a thin film of inprocessible polymer, and v)form a pattern by using a mask. Therefore, it is very important to develop thin film forming technology by vacuum deposition polymerization which is expected to be essential to various electronic devices in future information industries.

[0004] There are two types of deposition polymerizations to form a thin film which are radical deposition polymerization and condensation polymerization. Radical deposition polymerization is a method to prepare a thin film on the substrate by polymerizing radicals generated by chemical reactions of precursors by thermal and/or UV radiation after vaporizing precursors. Different thin films such as poly(*p*-xylylene) (A. Greiner, Trends in Polymer, 5(1997), 12), poly (naphthalene) (D. W. Smith et al., J. Am. Chem. Soc., 120(1998), 9078), poly(benzocyclobutene) or poly(p-phenylenevinylene) (K. M. Vaeth et al., Macromolecules, 31(1998), 6789), and Teflon (T. C. Nason et al., Appl. Phys. Lett., 60 (1992), 1866), are prepared by radical deposition polymerization. Thin films prepared by said radical deposition polymerization provide excellent thermal stability and low dielectric constant and thus, they are very attractive for applications as interlayer dielectrics of semiconductors.

[0005] On the other hand, condensation polymerization is a method to prepare a thin film by condensation polymerization after two kinds of precursors are simultaneously deposited on the substrate. Thin films such as polyimide (Ukishima et al., Thin Solid Films, 308-309(1997), 479), polyamide (A. Kubono et al., Thin Solid Films, 289(1996), 107), and polyurea (F. Fukuda, Key Eng. Mater., 92-93(1994), 143), polyazomethane (S. Tatsuura et al., Appl. Phys. Lett., 62(1993), 2182), are prepared by condensation polymerization. Thin films prepared by said condensation polymerization provide excellent electrical and optical properties such as piezoelectricity, non-linear optical property and conductivity and thus, they call the high attention as high-functional materials.

[0006] However, said radical deposition polymerization has to generate radicals by decomposing precursors at a high temperature over 400°C which is not suitable for the device manufacturing process. And said condensation polymerization has also disadvantages for producing by-products during condensation polymerization. Therefore, it is urgent to develop vacuum deposition polymerization which does not require thermal curing at a high temperature for decomposing precursors as well as does not produce by-products during polymerization and further, an appropriate precursor for vacuum deposition polymerization.

SUMMARY OF THE INVENTION

[0007] An object of the present invention is to provide an organic compound having at least one acetylene group which can be easily polymerized by thermal curing at relatively low temperature or UV irradiation.

[0008] Another object of the present invention is to provide a vacuum deposition polymerization to obtain a thin film having uniform thickness without generating by-products by using said organic compound.

[0009] Another object of the present invention is to provide a thin film prepared by vacuum deposition polymerization having an improved thermal stability.

[0010] Another object of the present invention is to provide an electroluminescent device fabricated by using said thin film.

Brief Description of the Drawings

[0011]

Fig. 1 represents a schematic view of vacuum deposition chamber for thermal and UV radiation curing.
Fig. 2 represents a schematic view of electroluminescence device.
Fig. 3 represents NMR spectrum of 2-ethynylfluorene.
Fig. 4 represents DSC thermograms of 2-ethynylfluorene and 2,7-diethynylfluorene.
Fig. 5 represents TGA thermograms of 2-ethynylfluorene and 2,7-diethynylfluorene after thermal curing.
Fig. 6 represents IR spectra of 2-ethynylfluorene before and after thermal curing.
Fig. 7 represents IR spectra of 2,7-diethynylfluorene before and after thermal curing.
Fig. 8 represents changes of UV absorption spectra of 2,7-diethynylfluorene with UV irradiation.
Fig. 9 represents NMR spectrum of tri(4-ethynylphenyl)amine.
Fig. 10 represents DSC thermogram of tri(4-ethynylphenyl)amine.
Fig. 11 represents TGA thermogram of tri(4-ethynylphenyl)amine after thermal curing.
Fig. 12 represents changes of IR spectra of tri(4-ethynylphenyl)amine with UV irradiation.
Fig. 13 represents changes of UV absorption spectra of tri(4-ethynylphenyl)amine with UV irradiation.
Fig. 14 represents picture of a pattern formed on the thin film of tri(4-ethynylphenyl)amine by UV irradiation through photomask.
Fig. 15 represents electrophotoluminescene spectra from ITO/ tri(4-ethynylphenyl)amine/Alq_3/ Al device.

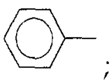
Detailed Description of the Invention

[0012] The present invention is described in detail as set forth hereunder.

[0013] Organic compounds having acetylene groups of the present invention is represented in the following formula 1,

$$\left[R_1 - \equiv - R_2 \right]_n R \qquad (1)$$

wherein R_1 is a hydrogen atom or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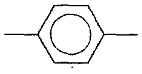
R2 is bond or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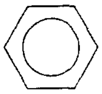
n is a natural number of 1 or above; and R is selected from the group consisting of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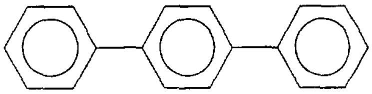
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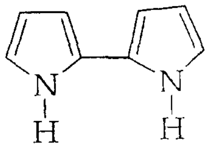
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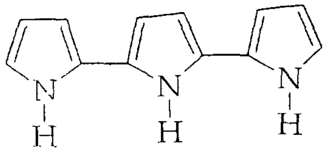
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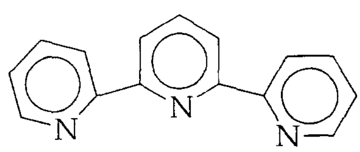
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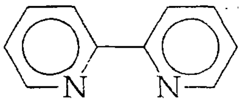
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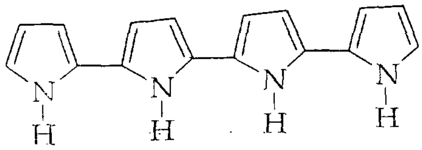
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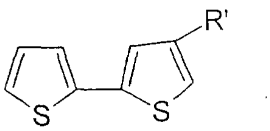
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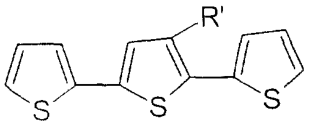
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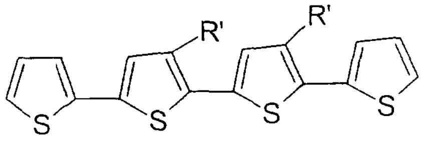
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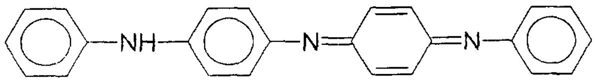
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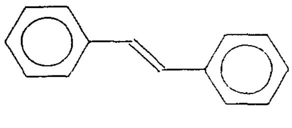

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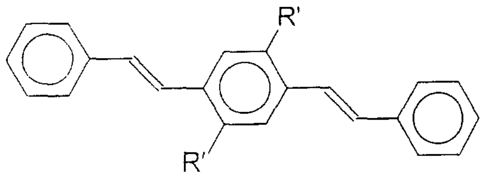
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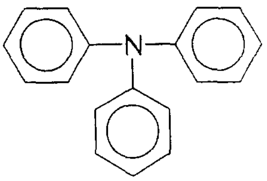
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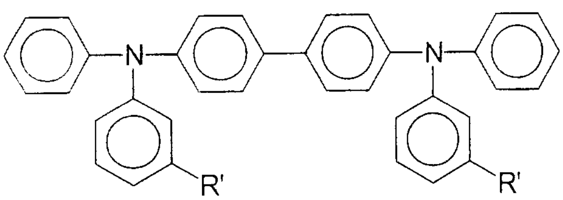
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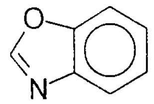
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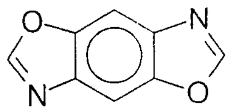
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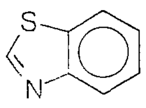
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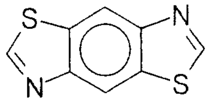
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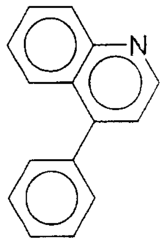
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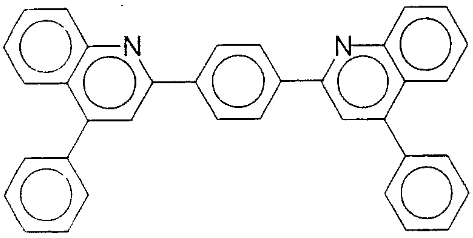
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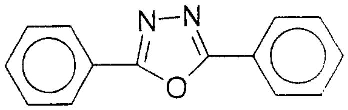
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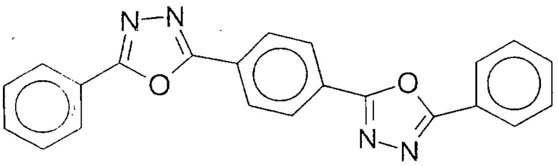
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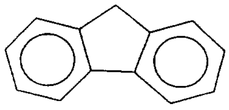
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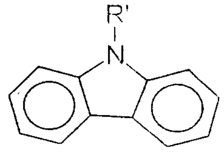
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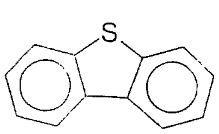
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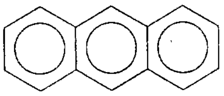
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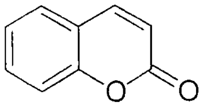
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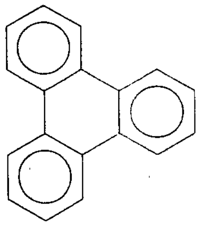
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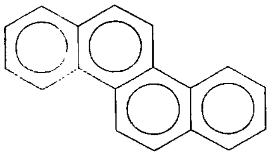
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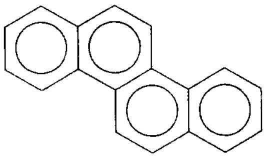
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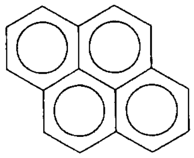
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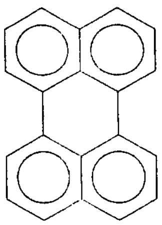

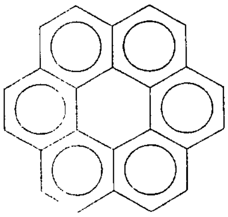
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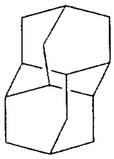
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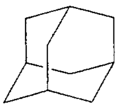
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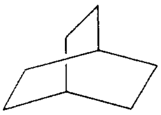
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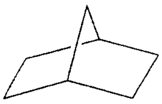
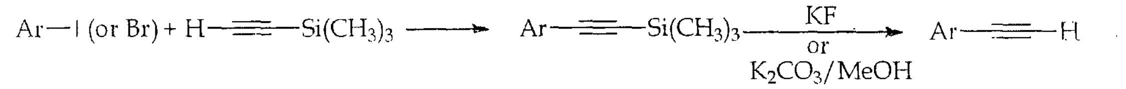


where R' is selected from the group consisting of a hydrogen atom and C_1-C_{12} hydrocarbons.

[0014] Generally, as shown in scheme 1, an aromatic compound having acetylene group(s) is prepared by removal of trimethylsilyl group of an aromatic compound substituted with trimethylsilyl acetylene in the presence of a base or fluoro ion where said aromatic compound substituted with trimethylsilyl acetylene is prepared by reacting aryl iodide (ArI) or aryl bromide (ArBr) with trimethylsilyl acetylene in the presence of palladium catalyst.

Scheme 1



[0015] Most of compounds of formula 1 can be easily prepared from mono, di, tri, or tetra bromo (or iodo) compounds as shown in Scheme 1.

[0016] Because the compound of formula 1 having acetylene group(s) is easily cured (or polymerized) by heat treatment or UV radiation, deposition and thermal or UV radiation curing can be performed simultaneously or thermal or UV radiation curing can be performed after deposition in a process for preparing organic thin film by vacuum deposition polymerization.

[0017] Therefore, in vacuum deposition polymerization of the compound of formula 1 to prepare a polymer thin film on the substrate such as glass or silicon wafer by using vacuum deposition chamber, said polymer thin film can be prepared by deposition and simultaneous polymerization by heat treatment or UV irradiation or by deposition and then polymerization. If necessary, thermal curing can be performed again after UV irradiation to complete polymerization. Fig. 1 represents a vacuum deposition chamber which is used for deposition polymerization. Because the vacuum deposition chamber is equipped with a heater and a UV lamp for direct heating, a thin film of an organic compound can be obtained by simultaneous deposition and polymerization or sequential deposition and polymerization. It is also possible to deposit simultaneously more than two organic compounds with this vacuum deposition chamber.

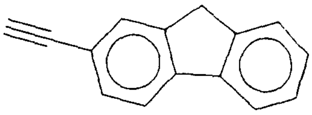
[0018] In the formation of a polymer by exposing UV light according to the present invention, pattern can be easily formed by using a mask. The only exposed area through the mask can be cured and the unexposed area is removed under the vacuum or by dissolving in a solvent so that it is possible to form the pattern wanted.

[0019] The thin film formed by vacuum deposition polymerization of the present invention provides improved thermal stability and thus, it can be applied in various fields such as interlayer dielectrics of semiconductors, hole transport layer and emission layer of electroluminescence device, solar cells, drum of copy machine and laser printer, and various sensors.

[0020] As shown in Fig. 2 which represents an electroluminescence device prepared by using deposition polymerized thin film, it basically includes ITO electrode, emission layer and metal electrode. Said emission layer is a thin film prepared by means of vacuum deposition polymerization of the compound of formula 1 having at least one acetylene group. An electroluminescence device can have a hole transport layer under an emission layer. At least either a hole transport layer or an emission layer can be prepared by vacuum deposition polymerization of the present invention. And further, an electroluminescence device can, additionally, have an electron transport layer on the emission layer. Among an emission layer, a hole transport layer and an electron transport layer, at least one layer is prepared by vacuum deposition polymerization of the present invention.

Example 1: Preparation of 2-Ethynylfluorene

[0021]



(1)

[0022] 10g (0.06mol) of fluorene and 15.23g (0.06mol) of iodine were added into 300ml of acetic acid and stirred. 1.2ml of nitric acid and 12ml of sulfuric acid were added dropwise into the reaction mixture. After the reaction mixture was stirred 35°C for 2 h, 2L of distilled water was added to it. Unreacted fluorene was washed out with 100ml of cold acetic acid. Remaining precipitates were washed with 100ml of 5% potassium iodide solution, 100ml of 5% sodium thiosulfate solution and distilled water, successively. Washed precipitates were dried in the air and extracted by petroleum ether soxhlet. Extracted solution was cooled to obtain 7.89g (45%) of yellow needle shape 2-iodofluorene.

[0023] Thereafter, to 150ml of triethylamine were added 7.89g of 2-iodofluorene, 379mg (0.54mmol) of bis[triphenylphosphine]palladium dichloride and 51mg (0.27mmol) of copper iodide. 4.2ml (29.7mmol) of trimethylsilylacetylene was added slowly to the reaction mixture. After the reaction was stirred for 8 h at room temperature, solvent was removed under reduced pressure. The residue was extracted with benzene and the benzene layer was washed with distilled water. The washed benzene layer was concentrated to give 6.02g (85%) of 2-trimethylsilylethynyl fluorene.

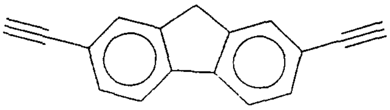
[0024] After 6.02g (22.9mmol) of 2-trimethylsilylethynylfluorene was added to 100ml of methanol, 25ml of 1N potassium hydroxide was added dropwise thereto. The reaction mixture was stirred for 3 h at room temperature and solvent was removed under the reduced pressure. The residue was extracted with ether and the ether layer was washed with distilled water. The washed ether layer was dried over anhydrous sodium sulfate and concentrated under the reduced pressure to give crude product. The crude product was purified by column chromatography on silica gel by eluting hexane/ethylacetate(15/1) and further purified by sublimation at 60°C/2torr to give 3.71g (87%) of 2-ethynylfluorene. Fig. 3 represents NMR spectrum of the final product, 2-ethynylfluorene, and mp was measured to be 85°C.

[0025] The DSC thermogram of 2-ethynyl fluorene as shown in Fig.4 reveals that polymerization of 2-ethynyl fluorene having one acetylene group was started at around 230°C. It indicated that deposition on the substrate and polymerization of 2-ethynylfluorene can be performed simultaneously by controlling a temperature at 230°C.

[0026] Thermal stability of 2-ethynylfluorene after thermal curing was examined by TGA analysis and the result was shown in Fig. 5. As shown in Fig. 5, a polymer prepared by polymerizing 2-ethynylfluorene by thermal curing at 230°C under N_2 was stable up to 260°C.

Example 2: Preparation of 2,7-DiethynylFluorene

[0027]



(2)

[0028] To 100ml of propylene carbonate were added 10g (0.06mol) of fluorene and 22.43g (0.126mol) of N-bromosuccinimide (NBS). After the reaction mixture was stirred at 75°C for 6 h, 200ml of distilled water was added to obtain precipitate. The obtained precipitate was recrystallized from ethylacetate several times to give 10.89g (56%) of 2,7-dibromofluorene.

[0029] Thereafter, to 150ml of diisopropylamine were dissolved 10.89g (33.6mmol) of 2,7-dibromofluorene obtained above, 941mg (0.67mmol) of bis[triphenylphosphine]palladium dichloride, and 128mg (0.67mmol) of copper iodide. After the reaction mixture was stirred for 2 h at room temperature, 10.45ml (73.9mmol) of trimethylsilyl acetylene was added dropwise to it. The reaction mixture was refluxed for 8 h and cooled. Solvent was removed under reduced pressure. The residue was extracted with benzene and the benzene layer was washed with distilled water. The washed benzene layer was concentrated to give 10.12g(85%) of 2,7-di(trimethylsilylethynyl)fluorene.

[0030] Thereafter, 60ml of 1N potassium hydroxide solution was slowly added to 10.12g(28.2mmol) of 2,7-di(trimethylsilylethynyl)fluorene dissolved in 150ml of methanol. The reaction mixture was stirred for 3 h at room temperature and solvent was removed. Residue was extracted with ether and the ether layer was washed with distilled water. The washed ether layer was concentrated. The crude product was purified by column chromatography on silica gel by eluting with hexane/ethylacetate (15/1) to give 1.35g (72%) of 2,7-diethynylfluorene of which mp was 125°C.

[0031] The DSC thermogram of 2,7-diethynylfluorene, as shown in Fig.4, reveals that polymerization of 2,7-diethynylfluorene having two acetylene groups was started at around 198°C. It indicated that deposition on the substrate and polymerization of 2,7-diethynylfluorene can be simultaneously performed by controlling a temperature around 200°C.

[0032] Thermal stability of 2,7-diethynylfluorene after thermal curing was examined by TGA analysis as shown in Fig. 5. In Fig. 5 a polymer prepared by polymerizing 2,7-diethynylfluorene by thermal curing at 198°C for 3 h under N_2 was stable up to 385°C.

Experimental Example 1: Thermal Curing

[0033] 2-Ethynylfluorene prepared from Example 1 and 2,7-diethynylfluorene prepared from Example 2 were deposited on silicon wafer by vacuum deposition chamber of Fig. 1 in order to confirm by IR spectra whether those compounds having (an) acetylene group(s) were polymerized by heat treatment. During deposition, vacuum level was 2×10^{-4} torr and deposited thickness was about 1500 Å. IR spectra of 2-ethynylfluorene and 2,7-diethynylfluorene before and after thermal curing under N_2 were examined and shown in Figs. 6 and 7. Thermal curing of each 2-ethynylfluorene and 2,7-diethynylfluorene was carried out at 230°C and at 198°C, respectively, for 30 min. In Figs. 6 and 7, both 2-ethynylfluorene and 2,7-diethynylfluorene show strong peak of stretching vibration at 3283 cm^{-1} for $\equiv$ C-H and a weak peak of stretching vibration at 2099 cm^{-1} for C $\equiv$ C before thermal curing. After thermal curing for 30 min, both stretching peaks for $\equiv$ C-H and C $\equiv$ C were disappeared and a peak of stretching vibration at between 1600 and 1700 cm^{-1} for

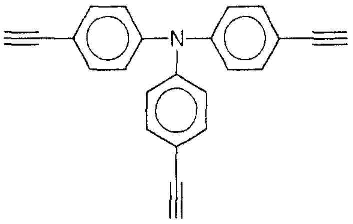
C=C was appeared. This indicated that after thermal curing both 2-ethynylfluorene and 2,7-diethynylfluorene having (an) acetylene group(s) were polymerized by changing a triple bond, C ≡ C, to a double bond, C=C.

Experimental Example 2 : Polymerization by UV Irradiation

[0034] 2,7-Diethynylfluorene prepared from Example 2 was deposited on the glass using vacuum deposition chamber of Fig. 1, and was examined UV absorption spectrum during UV irradiation. During deposition, vacuum level was 2 x 10^{-4} torr and deposited thickness was about 300 Å. Fig. 8 represents changes of UV absorption spectra at different irradiation time. As exposure of UV light increased, the width of maximum absorption peak at 340nm was getting broader and the peak shifted toward longer wavelength. It indicated that the length of double bond was getting increased, that is, a triple bond of the compound having acetylene groups was changed into a double bond by polymerization with UV irradiation.

Example 3 : Preparation of Tri(4-ethynylphenyl)amine

[0035]



(3)

[0036] 10g (0.0408mol) of triphenylamine was added to 150ml of chloroform with stirring. 19.54g (0.122mol) of bromine dissolved in chloroform was added to the reaction mixture and stirred for 2 h at room temperature. 400ml of hot ethanol was added to the reaction mixture and left at room temperature to produce precipitates. Said precipitates was extracted by methanol soxhlet to give 15.54g (79%) of tri(4-bromophenyl)amine

[0037] Thereafter, to 200ml of diisopropylamine were added 15.54g (0.032mol) of tri(4-bromophenyl)amine, 1.35g (1.92mmol) of bis[triphenylphosphin]palladium dichloride and 9.43g (0.96mmol) of copper iodide. After the reaction mixture was stirred for 2 h at room temperature, 9.43g (96mmol) of trimethylsilyl acetylene was slowly added to the reaction mixture. The reaction mixture was refluxed for 8 h and cooled. Solvent was removed under the reduced pressure. The residue was extracted with benzene and the benzene layer was washed with distilled water. The washed benzene layer was concentrated to give 13.84g (81%) of tri(4-trimethylsilylethynylphenyl)amine.

[0038] To a mixture of 180ml of tetrahydrofuran (THF) and 240ml of methanol were added 13.84g (0.026mol) of tri (4-trimethylsilylethynylphenyl)amine and 4.53g (0.078mol) of potassium fluoride. The reaction mixture was heated at 50°C for 5 h, cooled down to room temperature, and solvent was removed under the reduced pressure. The residue was extracted with ether and the ether layer was washed with distilled water. The washed ether layer was concentrated to give crude product. The crude product was purified by column chromatography on silica gel by eluting with hexane to give 6.182g (75%) of tri(4-ethynylphenyl)amine of which NMR spectrum was shown in Fig. 9 and mp was 115°C.

[0039] The DSC thermogram of tri(4-ethynylphenyl)amine, as shown in Fig. 10, revealed that polymerization of tri (4-ethynylphenyl)amine having three acetylene groups was started at 185 °C. It indicated that deposition on the substrate and polymerization of 2,7-diethynylfluorene can be simultaneously carried out by controlling a temperature around 185°C.

[0040] Thermal stability of tri(4-ethynylphenyl)amine after thermal curing was examined by TGA analysis and the result was shown in Fig. 11. In Fig. 11 a polymer prepared by polymerizing tri(4-ethynylphenyl)amine by thermal curing at 185 °C under N_2 for 30 min was stable up to 375°C.

Experimental Example 3 : Polymerization by UV Irradiation

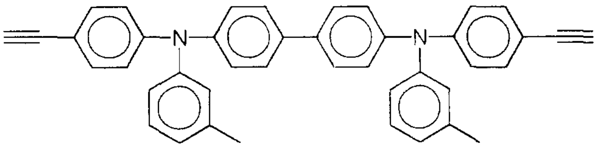
[0041] Tri(4-ethynylphenyl)amine prepared from Example 3 was deposited on silicon wafer in the vacuum deposition chamber of Fig. 1 to examine by IR spectrum whether those compound having three acetylene groups was polymerized by UV irradiation. During deposition, vacuum level was 2 x 10^{-5} torr and deposited thickness was about 1500 Å. IR spectra of tri(4-ethynylphenyl)amine were examined during UV irradiation and shown in Fig. 12. In Fig. 12, tri(4-ethynylphenyl)amine showed a strong peak of stretching vibration at 3277 cm^{-1} for ≡ C-H and a weak peak of stretching vibration at 2102 cm^{-1} for C ≡ C before thermal curing. After thermal curing, both peaks for ≡ C-H and C ≡ C were disappeared and a peak of stretching vibration at between 1600 and 1700 cm^{-1} for C=C was appeared. This indicated that tri(4-ethynylphenyl)amine having three acetylene groups was polymerized with UV irradiation by changing a triple bond, C≡ C, to a double bond, C=C.

[0042] And polymerization of tri(4-ethynylphenyl)amine with UV light was also clarified by UV absorption spectrum. During deposition, vacuum level was 2×10^{-4} torr and deposited thickness was about 300 Å. Fig. 13 showed changes of UV absorption spectra with irradiation time. As exposure time of UV light increased, the width of maximum absorption peat at 340nm was getting broader and the peak was shifted toward longer wavelength. It indicated that the length of double bond was getting increased, that is, a triple bond of the compound having acetylene group was changed to a double bond by polymerization with UV light.

[0043] On the other hand, after exposing UV light at 254 nm or 320nm of wavelength by using a mask on the substrate of the glass deposited with tri(4-ethynylphenyl)amine, a pattern was formed by dissolving the unexposed area in chloroform and the picture thereof was shown in Fig. 14. The compounds having acetylene groups can be cured by UV irradiation and a pattern thereof using a mask can be also formed. The organic compounds of the present invention can be used for preparing a thin film by vacuum deposition polymerization which is appropriate to negative-type photoresists.

Example 4 : Preparation of N,N-Bis(3-Methylphenyl)-N,N-(4-Ethynyl)Benzidine

[0044]



(4)

[0045] To 50ml of diisopropylamine were added 3.3g (4.89mmol) of N,N-bis(3-methylphenyl)-N,N-di(4-bromophenyl) benzidine, 137mg (0.196mmol) of bis[triphenylphosphine]palladium dichloride and 18.7mg (0.098mmol) of copper iodide. After the reaction mixture was stirred for 2 h at room temperature, 0.96mg (9.78mmol) of trimethylsilylacetylene was slowly added to it. The reaction mixture was refluxed for 8 h. The solvent was removed under the reduced pressure. The residue was extracted with benzene and the benzene layer was washed with distilled water. The washed benzene layer was concentrated to dryness to give 2.705g (78%) of N,N-bis(3-methylphenyl)-N,N-di(4-trimethylsilylethynylphenyl)benzidine.

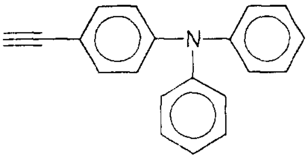
[0046] To a mixture of 60ml of THF and 80ml of methanol were dissolved 2.705g (3.814mmol) of N,N-bis(3-methylphenyl)-N,N-di(4-trimethylsilylethynylphenyl)benzidine and 0.443g(7.628mmol) of KF. After the reaction mixture was stirred for 5 h at 50°C, it was cooled to room temperature and the solvent was removed to dryness. The residue was extracted with chloroform and the chloroform layer was washed with distilled water. The washed chloroform layer was concentrated to dryness to give crude product which was further purified by column chromatography on silica gel by eluting with hexane/ethylacetate (9/1) to give 1.852g (86%) of N,N-bis(3-methylphenyl)-N,N-di(4-ethynylphenyl)benzidine.

Table 1:

Elemental Analysis of N,N-bis(3-methylphenyl)-N,N-di(4-ethynylphenyl)benzidine			
	C	H	N
Found	89.27%	5.77%	4.94%
Calculated	89.33%	5.71%	4.96%

Example 5 : Preparation of (4-ethynyl)diphenylamine

[0047]



(5)

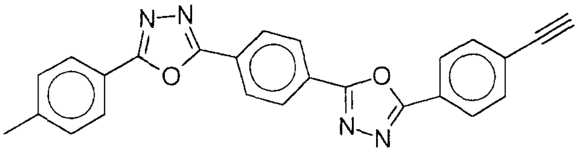
[0048] 1.503g (71%) of 4-(ethynylphenyl)diphnylamine was prepared by the same procedure of Example 4 with using 3.0g (9.25mmol) of (4-bromophenyl)diphenylamine(4-bromophenyl)diphenylamine instead of N,N'-bis(3-methylphenyl)-N,N'-di(4-bromophenyl)benzidine.

Table 2:

Elemental Analysis *of* 4-(ethynylphenyl)diphenylamine			
	C	H	N
Found	89.16%	5.70%	5.14%
Calculated	89.19%	5.61%	5.20%

Example 6 : Preparation of 1,3-di(5-(4-ethynylphenyl)-1,3,4-oxadiazole)benzene

[0049]



(6)

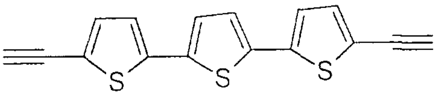
[0050] 1.75g (65%) of 1,3-di(5-(4-ethynylphenyl)-1,3,4-oxadiazole)benzene was prepared by the same procedure of Example 4 with using 5.0g (9.54mmol) of 1,3-di(5-(4-bromophenyl)-1,3,4-oxadiazole)benzene instead of N,N'-bis (3-methylphenyl)-N,N'-di(4-bromophenyl)benzidine.

Table 3:

Elemental Analysis of 1,3-di(5-(4-ethynylphenyl)-1,3,4-oxadiazole)benzene			
	C	H	N
Found	75.29%	3.44%	13.49%
Calculated	76.65%	3.41%	13.52%

Example 7 : Preparation of 5,5-Diethynyl-2,2:5,2-Terthiophene

[0051]



(7)

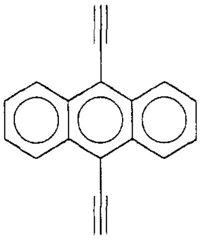
[0052] 2.37g (65%) of 5,5-diethynyl-2,2:5,2-terthiophene was prepared by the same procedure of Example 4 with using 5.0g (12.3mmol) of 5,5-dibromo-2,2:5,2-terthiophene instead of N,N'-bis(3-methylphenyl)-N,N'-di(4-bromophenyl)benzidine.

Table 4:

Elemental Analysis of 5,5-diethynyl-2,2:5,2-terthiophene		
	C	H
Found	64.8 %	2.76%
Calculated	64.83%	2.72%

Example 8 : Preparation of 9,10-diethynylanthracene

[0053]



(8)

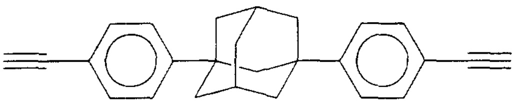
[0054] 2.42g (72%) of 9,10-diethynylanthracene was prepared by the same procedure of Example 4 with using 5.0g (14.9mmol) of 9,10-dibromoanthracene instead of N,N'-bis(3-methylphenyl)-N,N'-di(4-bromophenyl)benzidine.

Table 5:

Elemental Analysis of 9,10-diethynylanthracene		
	C	H
Found	95.53%	4.47%
Calculated	95.55 %	4.45 %

Example 9 : Preparation of 1,4-Di(4-ethynylphenyl)adamantine

[0055]



(9)

[0056] 2.63g (70%) of 1,4-di(4-ethynylphenyl)adamantine was prepared by the same procedure of Example 4 with using 5.0g (14.9mmol) of 1,4-di(4-bromophenyl)adamantine, prepared by reacting 5.0g (21.9mmol) of 1,4-diphenyladamantane and bromine, instead of N,N'-bis(3-methylphenyl)-N,N'-di(4-bromophenyl)benzidine.

Table 6:

Elemental Analysis of 1,4-di(4-ethynylphenyl)adamantine		
	C	H
Found	92.78%	7.22%
Calculated	92.81%	7.19%

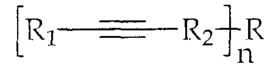
Example 10

[0057] Electroluminescence device was fabricated by using a thin film formed by means of vacuum deposition polymerization of tri(4-ethynylphenyl)amine prepared from Example 3 as a hole transport layer and tris(8-hydroxyquinolinato)aluminum (Alq_3) as an emission layer. ITO glass electrode was placed into a mixture of acetone and isopropyl alcohol and washed several times with ultrasonic cleaner. Tri(4-ethynylphenyl)amine was deposited on the ITO electrode by a deposition chamber of Fig. 1 under 2.0×10^{-5} torr of vacuum level and with 0.5 Å /sec of rate to form a thin film having 80 Å of thickness. During deposition, a hole transport layer was prepared by polymerizing a monomer of tri(4-ethynylphenyl)amine with UV irradiation. After polymerization, an emission layer having 500 Å of thickness was formed by depositing Alq_3 on the hole transport layer with a deposition chamber under 2.0×10^{-5} torr of vacuum level and with 2.0 Å /sec of rate. Thereafter, aluminum was deposited on the emission layer with a deposition chamber under 2.0×10^{-5} torr of vacuum level and with 5.0 Å /sec of rate to form a metal electrode layer having 1,500 Å of thickness. Fig. 5 showed an electroluminescence spectra of ITO/tri(4-ethynylphenyl)amine/ Alq_3/Al electroluminescence device. Said ITO was connected with anode and said Al electrode was connected with cathode and also an operating voltage was 3.5V and an electric current was 0.5mA.

[0058] As described above in detail, the present invention provides an organic thin film of an organic compound having at least one acetylene group formed by deposition under the vacuum and simultaneous or then polymerization by heat treatment or UV irradiation. The process of the present invention does not require high temperature process and does not produce by-products. The thin film formed by vacuum deposition polymerization has uniform thickness and excellent thermal stability and further, be applied in various fields such as interlayer dielectric film of semiconductors, electroluminescence devices, solar cells, drum of copy machine and laser printer, and various sensors.

Claims

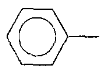
1. An organic compound having acetylene group expressed in formula 1,



$$\left[R_1 - \equiv - R_2 \right]_n R \qquad (1)$$

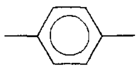
wherein

R$_1$ is a hydrogen atom or



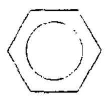
;

R$_2$ is bond or



;

n is a natural number of 1 or above; and
R is selected from the group consisting of



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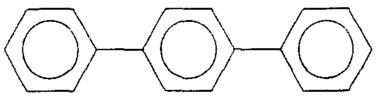

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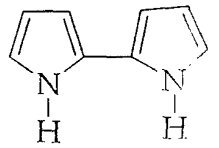

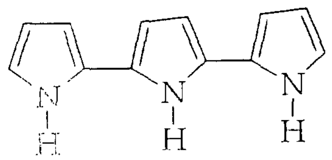
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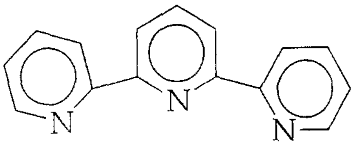
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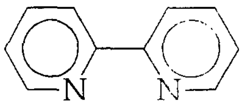
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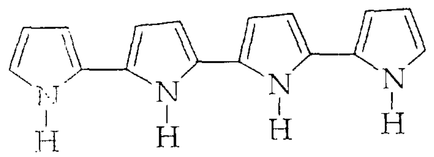
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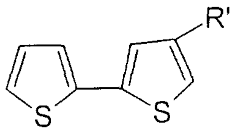
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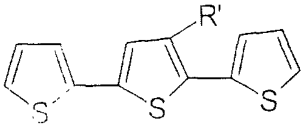
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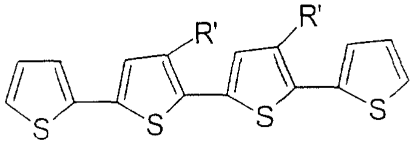
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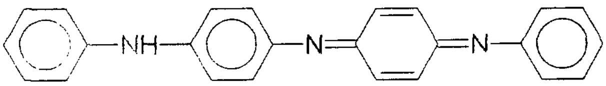
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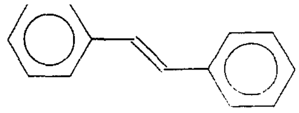

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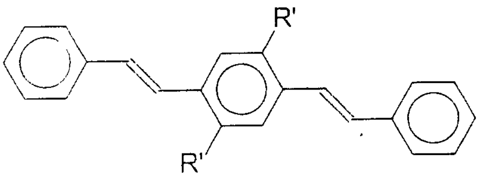
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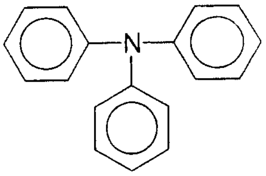
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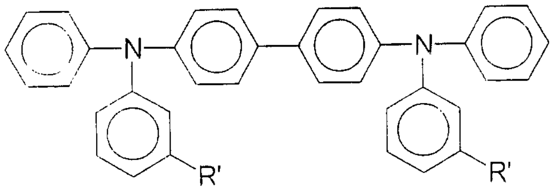
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R'

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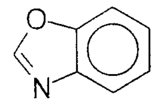
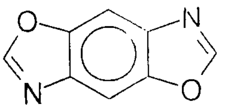
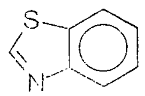

O
N

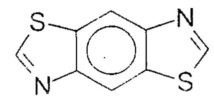
,


O
N
N
O

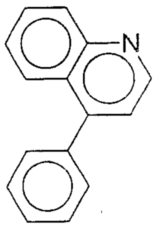
,


S
N

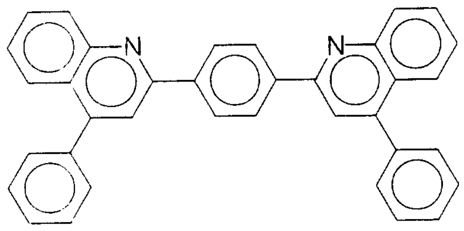
,


S
N
N
S

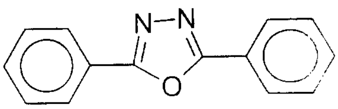
,


N

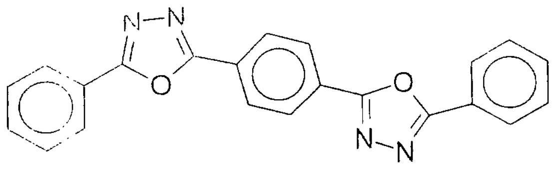
,


N
N

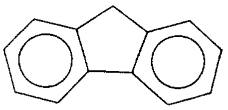
,


N
N
O

.


N
N
O
O
N
N

,



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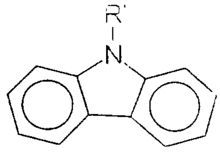
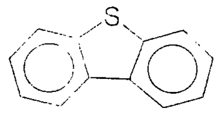
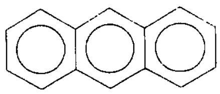

R'
N

,


S

,



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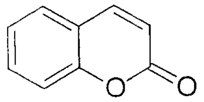
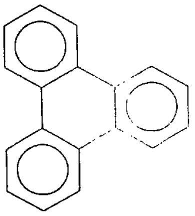

O
O

,



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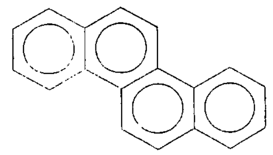

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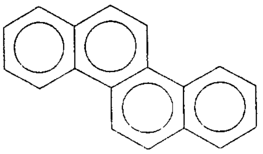

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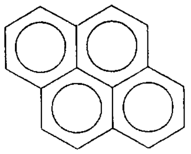

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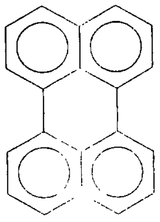

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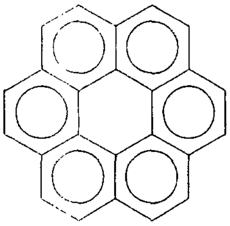

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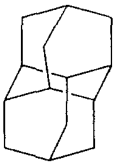

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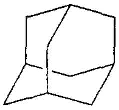

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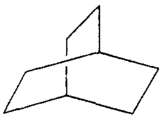

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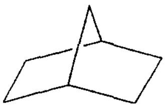


where R' is selected from the group consisting of a hydrogen atom and C_1-C_{12} hydrocarbons.

2. A vacuum deposition polymerization in which at least one of said organic compounds of claim 1 is/are deposited on the substrate and simultaneously or then polymerized by heat treatment and/or UV irradiation to form a polymer thin film.

3. The vacuum deposition polymerization according to claim 2, wherein additional thermal curing is performed after said UV irradiation.

4. The vacuum deposition polymerization according to claims 2 and 3, wherein said UV light is exposed through a patterned photo mask to form pattern by removing an unexposed area.

5. A thin film formed by depositing at least one of said organic compound having acetylene group of claim 1 on the substrate under vacuum and simultaneously or then polymerizing by means of heat treatment or UV irradiation.

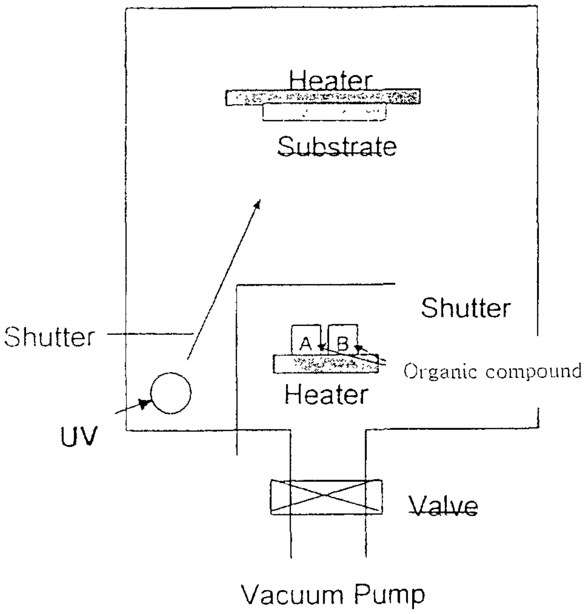
6. The thin film according to claim 5, wherein an additional thermal curing is performed after said UV irradiation.

7. An electroluminescence device comprising ITO electrode layer, emission layer and metal electrode layer, wherein said emission layer is a thin film formed by depositing at least one of said organic compounds of claim 1 on the substrate and simultaneously or then polymerizing by heat treatment and/or UV irradiation.

8. An electroluminescence device comprising ITO electrode layer, hole transport layer, emission layer and metal electrode layer, wherein at least one of said hole transport layer and said emission layer is/are thin film(s) formed by depositing at least one of said organic compounds of claim 1 on the substrate and simultaneously or then polymerizing by heat treatment or UV irradiation.

9. An electroluminescence device comprising ITO electrode layer, hole transport layer, emission layer, electron transport layer and metal electrode layer, wherein at least one of said hole transport layer, said emission layer and said electron transport layer is/are thin film(s) formed by depositing at least one of said organic compounds of claim 1 on the substrate and simultaneously or then polymerizing by heat treatment or UV irradiation.

【Fig. 1】



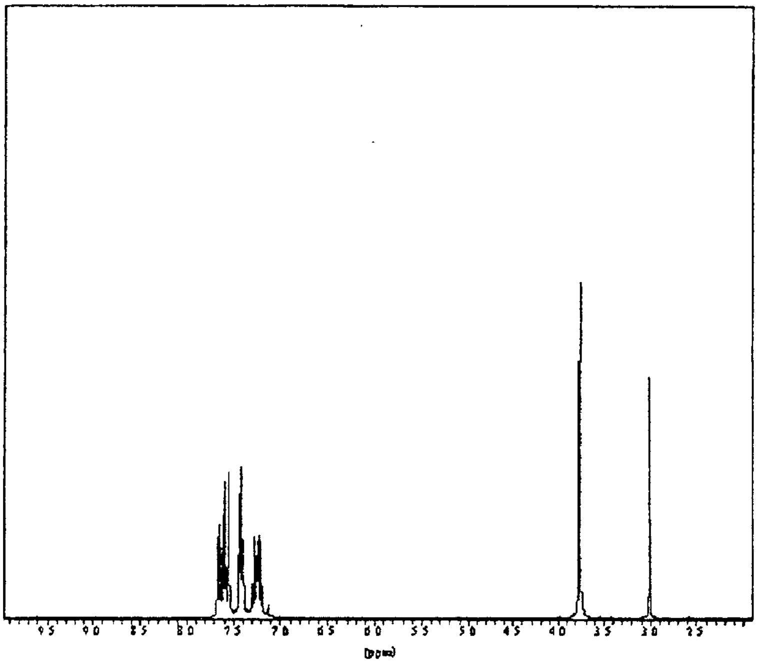
【Fig.2】

Metal electrode
Emission layer
ITO electrode

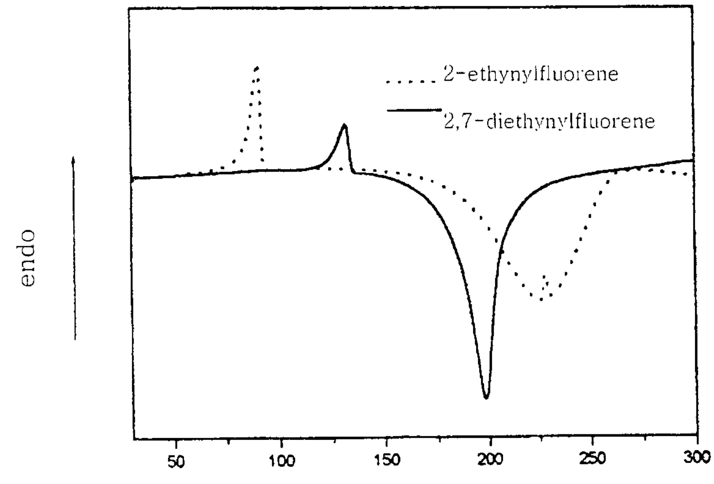
Metal electrode
Emission layer
Hole transport layer
ITO electrode

Metal electrode
Electron transport layer
Emission layer
Hole transport layer
ITO electrode

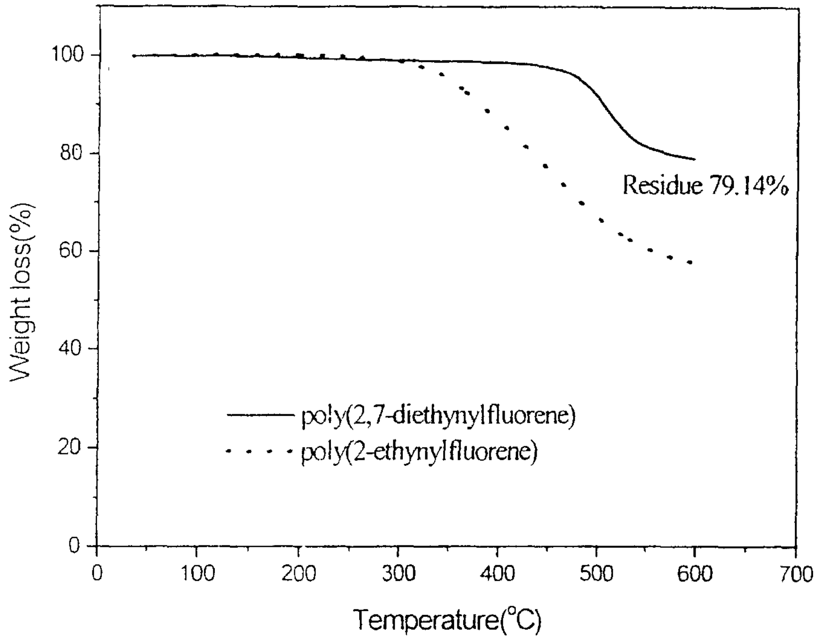
【Fig. 3】


95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
(ppm)

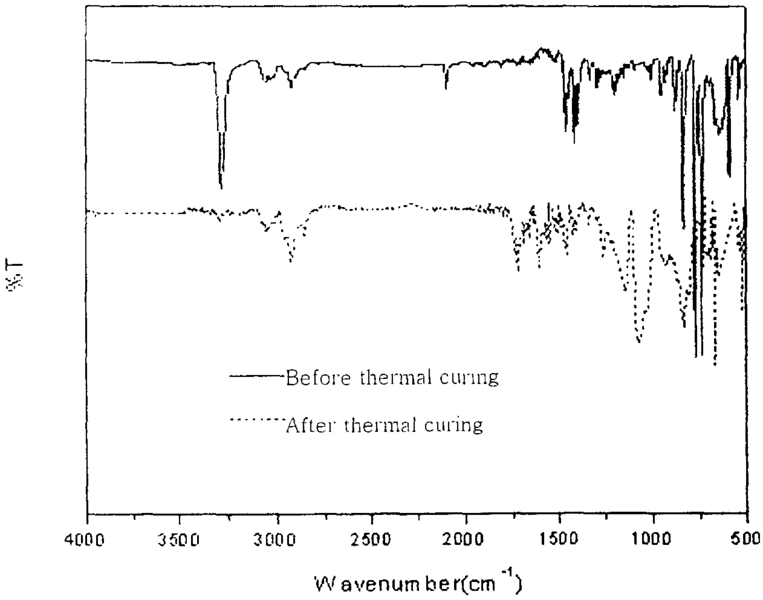
【Fig. 4】


..... 2-ethynylfluorene
2,7-diethynylfluorene
endo
50
100
150
200
250
300
Temperature (℃)

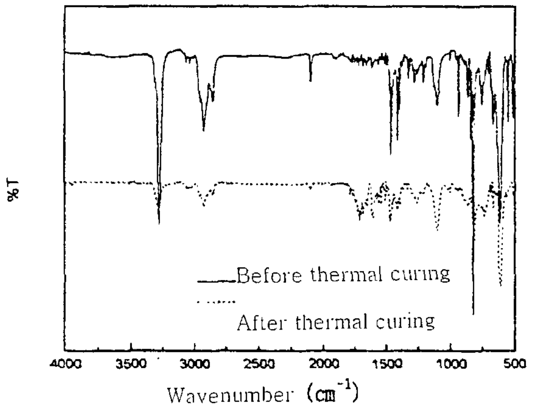
【Fig. 5】


Weight loss(%)
100
80
60
40
20
0
Temperature(°C)
0
100
200
300
400
500
600
700
Residue 79.14%
poly(2,7-diethynylfluorene)
poly(2-ethynylfluorene)

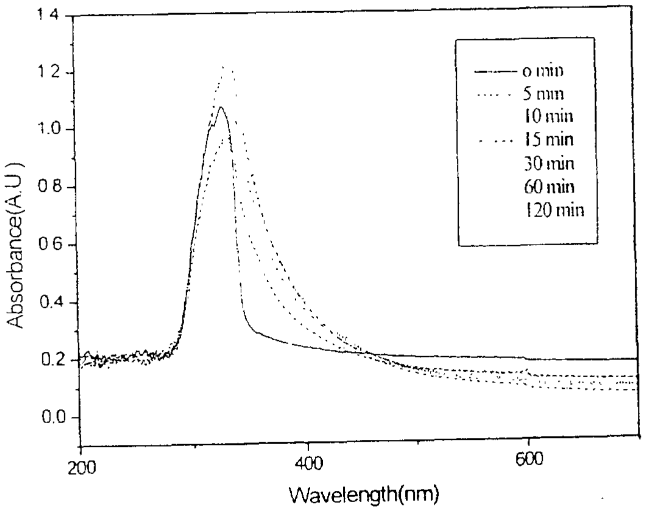
【Fig. 6】


%T
Before thermal curing
After thermal curing
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm^{-1})

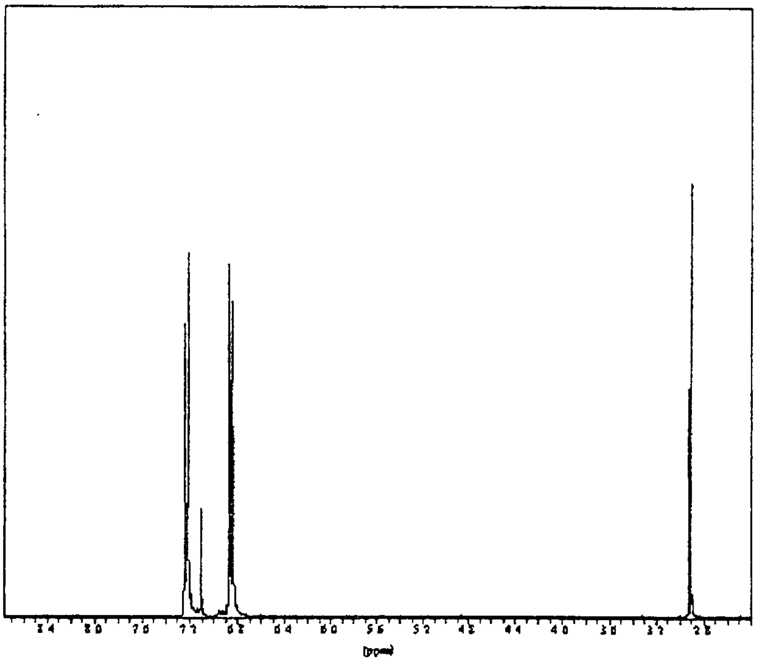
【Fig. 7】


%T
Before thermal curing
After thermal curing
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm⁻¹)

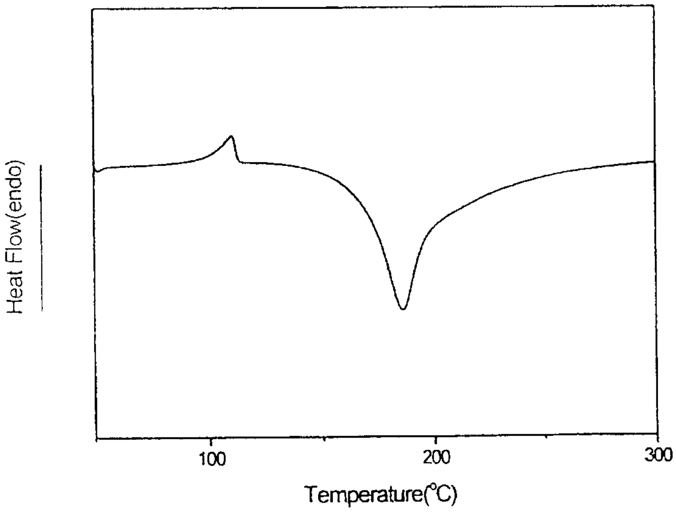
【Fig. 8】


1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Absorbance(A.U.)
0 min
5 min
10 min
15 min
30 min
60 min
120 min
200
400
600
Wavelength(nm)

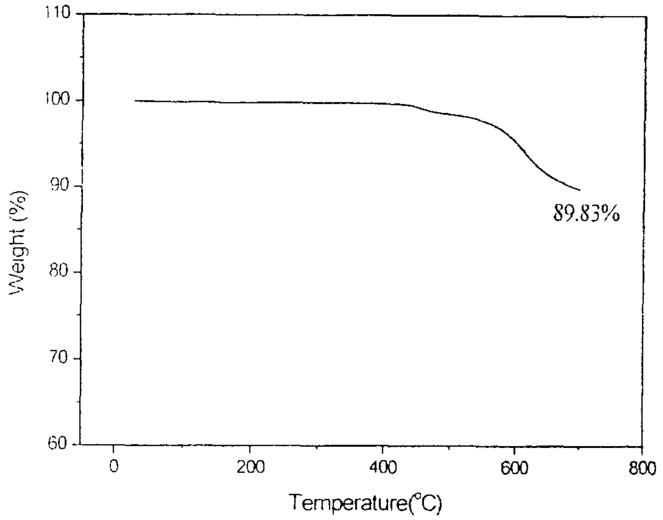
【Fig. 9】


84
80
76
72
68
64
60
56
52
48
44
40
36
32
28
(ppm)

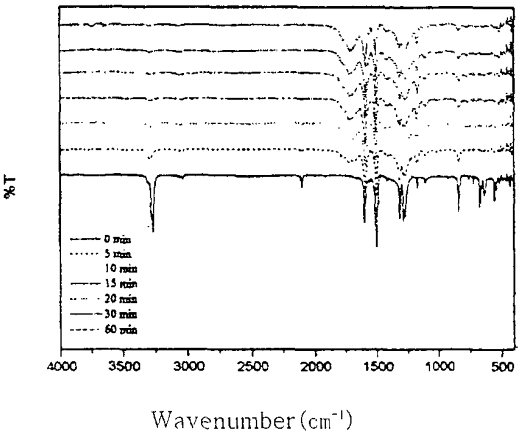
【Fig. 10】


Heat Flow(endo)
100
200
300
Temperature(°C)

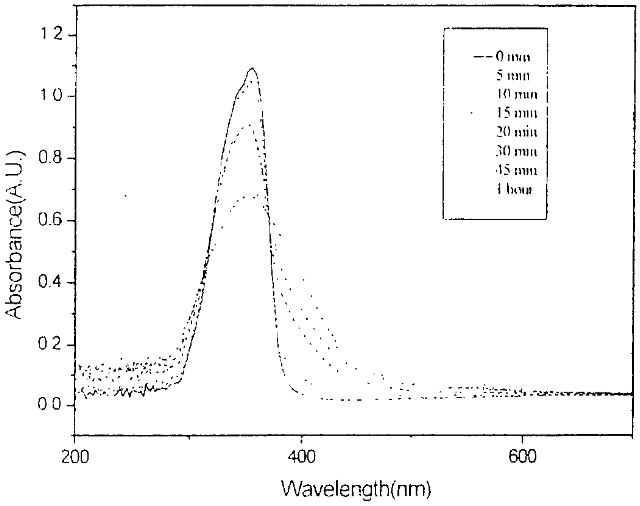
【Fig. 11】


110
100
90
80
70
60
Weight (%)
89.83%
0
200
400
600
800
Temperature(°C)

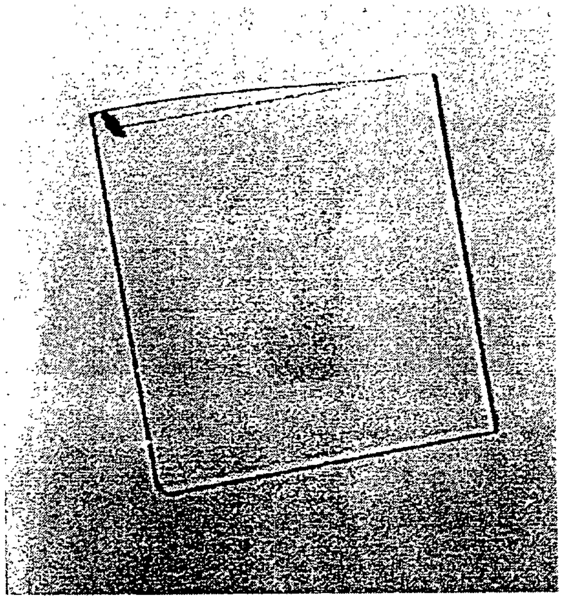
【Fig. 12】


%T
0 min
5 min
10 min
15 min
20 min
30 min
60 min
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

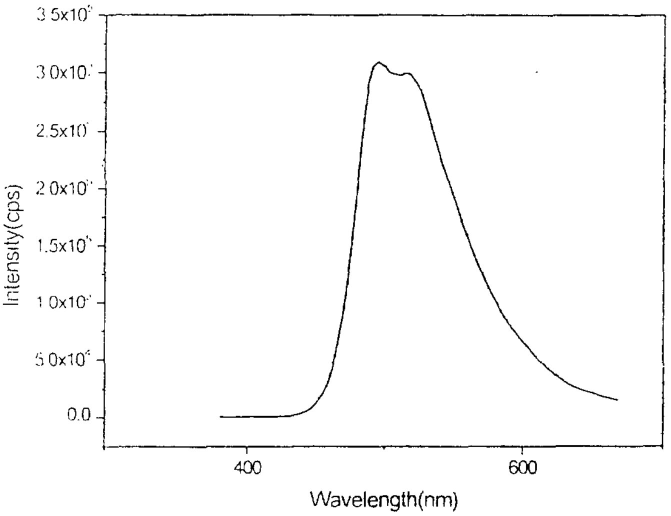
【Fig. 13】


1.2
1.0
0.8
0.6
0.4
0.2
0.0
Absorbance(A.U.)
200
400
600
Wavelength(nm)
0 min
5 min
10 min
15 min
20 min
30 min
45 min
1 hour

【Fig. 14】



【Fig. 15】


Intensity(cps)
3.5x10^5
3.0x10^5
2.5x10^5
2.0x10^5
1.5x10^5
1.0x10^5
5.0x10^4
0.0
400
600
Wavelength(nm)

European Patent Office

PARTIAL EUROPEAN SEARCH REPORT

which under Rule 45 of the European Patent Convention shall be considered, for the purposes of subsequent proceedings, as the European search report

Application Number
EP 01 10 0286

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	"The Merck Index (12th edition)" 1996 , MERCK & CO , WHITEHOUSE STATION XP002178237 * page 654, right-hand column, paragraph 3906 * ---	1	C07C13/567 C07C211/54 C07D271/06 C07D333/18 C07C15/28 C08F2/48 H05B33/02
X	H. TANI ET AL: "Oligomers and Polymers Containing Triple Bonds. I. Derivatives of Ethynylbiphenyl and Ethynylfluorene" BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN., vol. 36, no. 4, April 1963 (1963-04), pages 391-396, XP002178234 JAPAN PUBLICATIONS TRADING CO. TOKYO., JP ISSN: 0009-2673 * Compounds II, XII and XV * --- -/--	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

C07C
C07D

INCOMPLETE SEARCH

The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.

Claims searched completely :

Claims searched incompletely :

Claims not searched :

Reason for the limitation of the search:

see sheet C

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 September 2001	Van Geyt, J

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

European Patent Office

INCOMPLETE SEARCH SHEET C

Application Number
EP 01 10 0286

Claim(s) searched incompletely:
1-9

Reason for the limitation of the search:

Present claims 1 to 9 relate to an extremely large number of possible compounds and their use. In addition to this, claim 1 contains unclear formulations: there is no upper limit for n and the values given for R and R' are not radicals. It is thus impossible to define which compounds are covered by formula (I). Because of this, a lack of clarity (and conciseness) within the meaning of Article 84 EPC arises to such an extent as to render a meaningful search of the claims impossible. Consequently, the search has been carried out for those parts of the application which do appear to be clear (and concise), namely the compounds prepared in the examples.

European Patent Office

PARTIAL EUROPEAN SEARCH REPORT

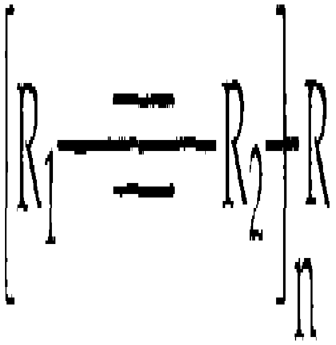
Application Number
EP 01 10 0286

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	J. LEWIS ET AL: "Synthesis and characterisation of new acetylide-functionalised oligothiophenes and their dinuclear platinum complexes" JOURNAL OF THE CHEMICAL SOCIETY, DALTON TRANSACTIONS., 1997, pages 4283-4288, XP002178235 CHEMICAL SOCIETY. LETCHWORTH., GB ISSN: 1472-7773 * Compounds IIb and IIIb * ---	1	
X	R. SKOWRONSKI ET AL: "Hydrocarbures benzéniques et anthracéniques à chaines latérales insaturées" BULLETIN DE LA SOCIETE CHIMIQUE DE FRANCE., no. 11, 1967, pages 4235-4243, XP002178236 SOCIETE FRANCAISE DE CHIMIE. PARIS., FR ISSN: 0037-8968 * table I * -----	1	TECHNICAL FIELDS SEARCHED (Int.Cl.7)

专利名称(译)	炔烃化合物，它们在真空沉积聚合中作为单体的用途，由这些聚合物形成的薄膜及其在电致发光器件中的用途		
公开(公告)号	EP1170273A1	公开(公告)日	2002-01-09
申请号	EP2001100286	申请日	2001-01-04
[标]申请(专利权)人(译)	韩国化学研究所		
申请(专利权)人(译)	韩国研究化工学院学报		
当前申请(专利权)人(译)	韩国研究化工学院学报		
[标]发明人	LEE CHANG JIN KANG YONG KU LEE SUNG KOO JUNG SANG HYUN KIM HEE JUNG		
发明人	LEE, CHANG JIN KANG, YONG KU LEE, SUNG KOO JUNG, SANG HYUN KIM, HEE JUNG		
IPC分类号	H05B33/10 C07C13/567 C07C13/70 C07C15/28 C07C15/48 C07C15/60 C07C211/54 C07D207/335 C07D209/86 C07D213/22 C07D215/04 C07D263/56 C07D271/10 C07D271/107 C07D277/64 C07D311/08 C07D333/18 C07D333/76 C07D498/04 C07D513/04 C08F2/00 C08F38/00 C23C14/12 C23C14/58 H01L51/00 H01L51/30 H01L51/40 H01L51/50 C07D271/06 C08F2/48 H05B33/02		
CPC分类号	H01L51/0041 C07C13/567 C07C15/28 C07C211/54 C07D271/107 C07D333/18 C08F38/00 H01L51/0008 H01L51/0052 H01L51/0059 H01L51/0068 H01L51/007 H01L51/0081 H01L51/5012 H01L2251/308 Y02E10/549 Y02P70/521 Y10T428/31504 Y10T428/31855		
代理机构(译)	WEBER，DIETER，DR.		
优先权	1020000037784 2000-07-03 KR		
其他公开文献	EP1170273B1		
外部链接	Espacenet		

摘要(译)

本发明涉及具有乙炔基的有机化合物，使用所述有机化合物通过真空沉积聚合形成的薄膜，用于形成所述薄膜的真空沉积聚合，以及含有所述薄膜的电致发光装置。更具体地，本发明涉及具有至少一个乙炔基的有机化合物，真空沉积聚合，其中所述有机化合物沉积在基材上并同时或通过热处理或UV照射聚合以形成聚合物薄膜。和使用至少一层所述薄膜的电致发光器件。



$$\left[R_1-\equiv-R_2\right]_n R \qquad (1)$$