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

(11) **EP 1 894 261 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
24.07.2019 Bulletin 2019/30

(21) Application number: **06726774.0**

(22) Date of filing: **13.04.2006**

(51) Int Cl.:
H01L 51/54 *(2006.01)* *H01L 27/32* *(2006.01)*
C08G 61/12 *(2006.01)*

(86) International application number:
PCT/GB2006/001376

(87) International publication number:
WO 2006/109083 (19.10.2006 Gazette 2006/42)

(54) ARYLAMINE- AND FLUORENE- POLYMERS FOR OLED DISPLAYS

ARYLAMIN- UND FLUORPOLYMERE FÜR OLED-DISPLAYS

POLYMÈRES D ARYLAMINE ET DE FLUORÈNE POUR AFFICHEURS ÉLECTROLUMINESCENTS ORGANIQUES

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR

(30) Priority: **15.04.2005 GB 0507684**

(43) Date of publication of application:
05.03.2008 Bulletin 2008/10

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Description

[0001] The present invention is concerned with displays, particularly passive matrix displays, driven by pulsed driving conditions. The present invention is further concerned with new semiconductive polymers that may be used in such displays. The present invention is still further concerned with the lifetime properties of semiconductive polymers, and in particular increasing the lifetime of a semiconductive polymer in a display driven by pulsed driving conditions.

[0002] Many displays consist of a matrix of pixels, formed at the intersection of rows and columns deposited on a substrate. Each pixel is a light-emitting diode (LED), such as a polymer LED (PLED). With reference to Figure 1, the architecture of an LED comprises a transparent glass or plastic substrate 1, an anode 2 and a cathode 4. An electroluminescent layer 3 is provided between anode 2 and cathode 4.

[0003] Coloured displays are formed by positioning matrices of red, green and blue pixels very close together. To control the pixels, and so form the image required, either 'passive' or 'active' matrix driver methods are used.

[0004] Active matrix displays incorporate a transistor (TFT) in series with each pixel which provides control over the current and hence the brightness of individual pixels. Lower currents can flow down the control wires since these have only to programme the TFT driver, and the wires can be finer as a result. Also, the transistor is able to hold the current setting, keeping the pixel at the required brightness, until it receives another control signal. DC driving conditions typically are used for an active matrix display.

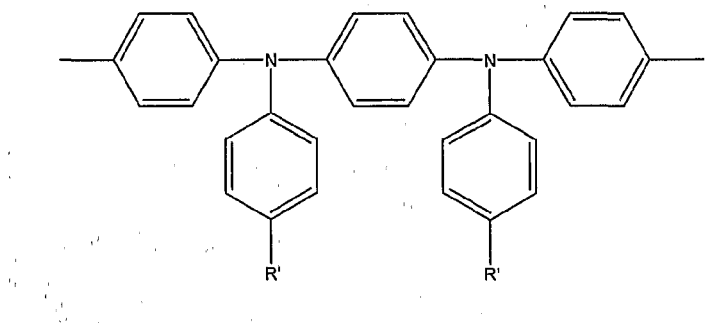
[0005] In passive matrix systems, each row and each column of the display has its own driver, and to create an image, the matrix is rapidly scanned to enable every pixel to be switched on or off as required. The controlling current has to be present whenever the pixel is required to light up.

[0006] As described in Proc. of SPIE Vol 2800 (2003) "Organic Light-Emitting Materials and Devices", the principle of passive matrix addressing is rather straightforward and uses the eye's insensitivity to the fast re-positioning of light generation. Instead of simultaneously addressing all the pixels needed to display an image frame, in the passive matrix approach, the different pixels are addressed after each other via a row to row scrolling. The intensity of the short illumination is much more intense than when all the pixels are generating light for the total frame time (the number of rows times the average overall brightness needed). If the refresh rate of the whole frame is high enough, the human eye observes the scrolled picture as a standing picture with an average brightness. The advantage of passive matrix driving is the simple substrate structure allowing for easy customization and low substrate costs. Pulsed driving conditions typically are used for a passive matrix display.

[0007] Synthetic Metals 91 (1997) 3-7 and Synthetic Metals 113 (2000) 155-159 provide information on the structure of passive matrix organic LEDs, the contents of which are hereby incorporated by reference. Reference is made in particular to Figure 11 (c) in Synthetic Metals 91 (1997) 3-7, which shows deposition of the organic emitter layer by evaporation, followed by evaporation of the cathode. Solution deposition (e.g. inkjet printing) of the emitter layer is equally applicable to this structure. The background section of the Synthetic Metals 113 (2000) 155-159 article provides detail on how the cathode is patterned into stripes using a photoresist material.

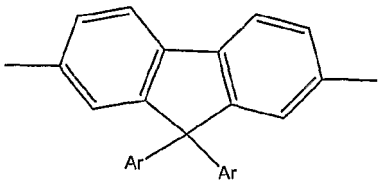
[0008] An important parameter is the lifetime of a display. Inadequate lifetimes are a particular problem for blue light-emitting polymers.

[0009] WO 02/092723 and WO 04/083277 are both concerned with blue light-emitting polymers for use in optical devices. Both disclosures refer to blue emissive repeat units comprising an optionally substituted repeat unit of formula:



wherein each R' is independently selected from hydrogen or a solubilising group. Particularly preferred solubilising groups are optionally substituted alkyl or alkoxy. Most preferably, R' is n-butyl.

[0010] Both disclosures also refer to an optionally substituted repeat unit of formula:



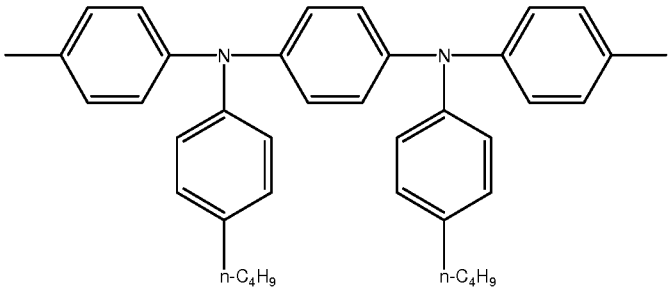
wherein preferably, each Ar is independently selected from the group comprising an optionally substituted residue of formula:

wherein n=1, 2 or 3 and R is a solubilising group or hydrogen. Particularly preferred groups R are hydrogen and optionally substituted alkyl or alkoxy. Most preferably, R is hydrogen or butyl. It is said that by "butyl" is meant n-,sec-or tert-butyl.

[0011] In the Examples in WO 02/092723 and WO 04/083277, only polymers P1 to P4 containing 9,9-diphenylfluorene repeat units were made and compared with a comparative polymer where the 9,9-diphenylfluorene repeat units were replaced with 9,9-di-n-octylfluorene repeat units.

[0012] WO 02/092723 primarily is concerned with increasing the thermal stability (Tg) of polymers. WO 04/083277 is concerned with improving device lifetime but teaches to omit TFB from the polymer to achieve this. Neither WO 02/092723 nor WO 04/083277 is concerned particularly with pulsed driven devices and neither disclosure even mentions pulsed driven devices.

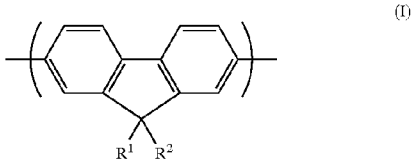
[0013] EP 1394188 is concerned with improving the lifetime of polymer compounds comprising a repeat unit:



[0014] However, EP 1394188 teaches to use a polymer compound comprising a repeating unit shown by formula (1) or (2) on page 4 of EP 1394188 in order to improve the lifetime. In these formulae, the terminal aryl groups (E_1, E_3, E_8 and E_9) each has three or more substituents.

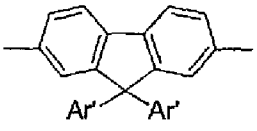
[0015] According to Proc. Of SPIE Vol 2800 (2003) "Organic Light-Emitting Materials and Devices" lifetime measurements are mostly performed at dc driving. However, it is said that the lifetime of light-emitting materials for passive matrix applications should also be tested using the pulsed driving conditions experienced in full colour displays.

[0016] US 2004/158017 discloses a polymer having a repeat unit of formula (I) where at least one of R^1 and R^2 comprises at least two substituted or unsubstituted aryl or heteroaryl groups and excluding the group having general formula (I) where one or both of R^1 and R^2 comprises a triarylamine group:

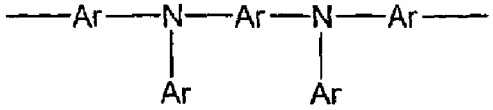


(I)

[0017] WO 03/095586 discloses a polymer for use in an optical device comprising a repeat unit of formula (I) and a repeat unit of formula (II): wherein each Ar and Ar' is the same or different and comprises an optionally substituted aryl or heteroaryl group:



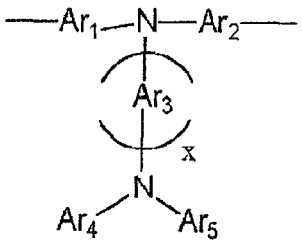
(I)



(II)

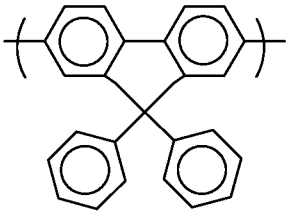
[0018] WO 2004/084260 discloses an optical device comprising an anode, a cathode comprising barium, strontium or calcium, and a layer of organic semiconducting material between the anode and the cathode wherein a layer of hole transporting and electron blocking material is located between the anode and the layer of organic semiconducting material.

[0019] EP 1310539 discloses a prepeat unit represented by formula (1) and a repeat unit represented by formula (2):



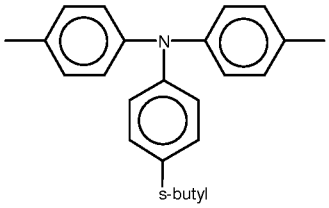
---- (1) $-Ar_6-$ (2)

[0020] Despite recent advances in the lifetimes of polymers for use in organic light-emitting diodes, there remains a need for alternative polymers for use in pulsed driven and dc driven displays comprising an organic light-emitting diode, preferably polymers with an improved lifetime. In this regard, it is the particular problem of the present invention to improve the lifetime in pulsed driven displays of semiconductive polymers comprising one of the repeat units:

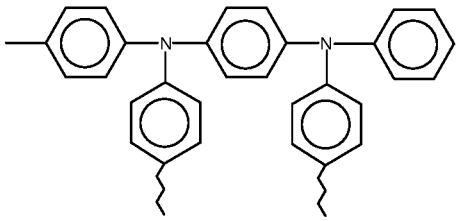


"DPF"

or



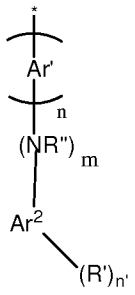
or



"PFB"

"TFB"

[0021] The present inventors have solved this problem by providing, in a first aspect of the present invention, a semiconductive polymer suitable for use in an organic light-emitting device, said polymer comprising a triarylamine repeat unit according to claim 1 comprising a triarylamine repeat unit, said triarylamine repeat unit having a group R pendent from the polymer backbone, wherein R has general formula I:



I

where Ar^1 represents phenyl or a group comprising napthyl; Ar^2 represents phenyl or a group comprising napthyl; R' represents a substituent group; R" = H or a substituent; n=0, 1, 2 or 3; m=0 or 1; and n'= 2; provided that m=0 when

m=0 and R' represents a branched C4 to C20 alkyl or alkoxy group comprising a tertiary carbon atom.

[0022] In the case where m is 1, Ar1 and Ar2 are preferably phenyl; R" is preferably a substituent, more preferably a substituent of formula:

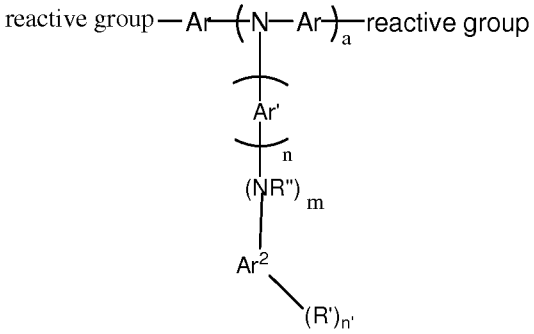
$$-Ar^2-(R')_{n'}$$

wherein Ar^2, R' and n' are as defined above. In this case, each occurrence of Ar^2, R' and n' in the group R of formula I may be the same or different.

[0023] The above defined triarylamine repeat unit in the semiconductive polymer will hereafter be referred to as T^1. A fluorene repeat unit in the semiconductive polymer having a group R pendent from the polymer backbone will hereafter be referred to as F^1.

[0024] The above defined semiconductive polymers have been found to have unexpectedly superior lifetime in pulsed driven displays as compared with the corresponding polymers containing a DPF or PFB repeat unit.

[0025] A second aspect of the present invention provides a monomer for making a semiconductive polymer having general formula II:



II

where Ar^1, Ar^2, R', R", m, n, and n' are as defined in relation to the first aspect; a = 1 or 2; Ar represents an aryl or heteroaryl group; and 'reactive group' represents a reactive group capable of participating in polymerisation.

[0026] Preferred triarylamines in the monomer according to the second aspect are as defined in relation to the first aspect for T^1.

[0027] The first aspect of the present invention is described further below.

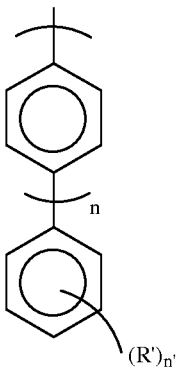
[0028] Ar^1 may represent napthyl.

[0029] Preferably Ar^1 represents phenyl.

[0030] Ar^2 may represent napthyl.

[0031] Preferably Ar^2 represents phenyl.

[0032] Preferably R has general formula III:



III

n is preferably 0 or 1 or 2.

n is preferably 1, 2 or 3.

n is preferably 1 or 2.

[0033] One or both R' may be a solubilising group.

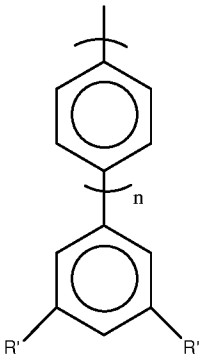
[0034] The solubilising group may be a C1 to C20 alkyl or alkoxy group. Branched C4 to C20 alkyl or alkoxy groups are preferred. Branched C4 to C20 alkyl groups are more preferred. Branched C4 to C20 alkyl or alkoxy groups comprising a tertiary carbon atom are more preferred. t-Bu is most preferred.

[0035] In one embodiment, when n=0 R' represents t-Bu.

[0036] When n is greater than 1, each Ar^1 may be the same or different.

[0037] When n is greater than 1, preferably at least one Ar^1 represents phenyl.

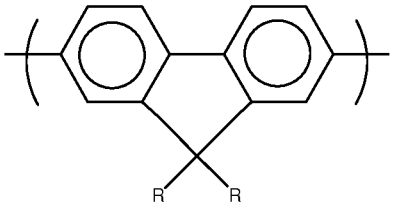
[0038] When Ar^2 represents phenyl, R' are preferably located at the meta positions. R may have general formula V:



V

[0039] Both R' are preferably t-Bu.

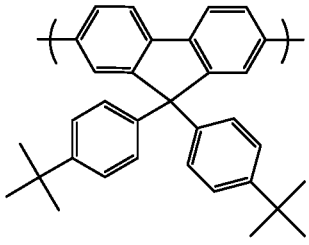
[0040] The fluorene repeat unit F^1 may have the general formula VI:



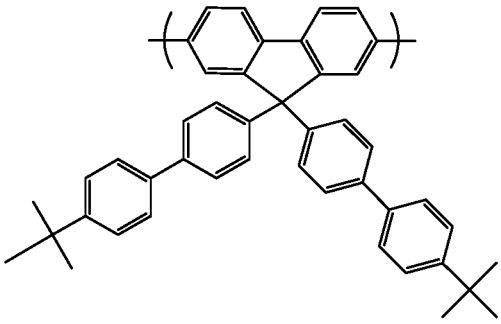
VI

where each R independently is as defined above.

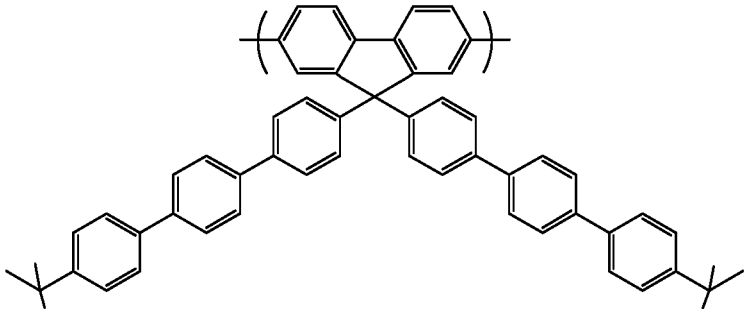
[0041] The fluorene repeat unit F^1 may have the formula VII to XII:



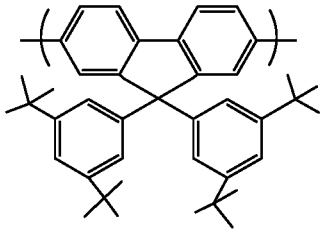
VII



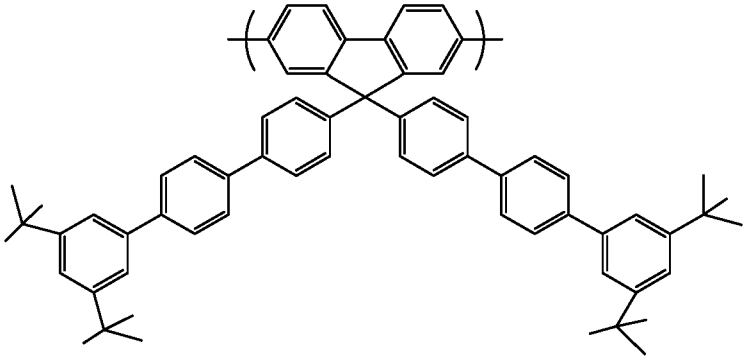
VIII



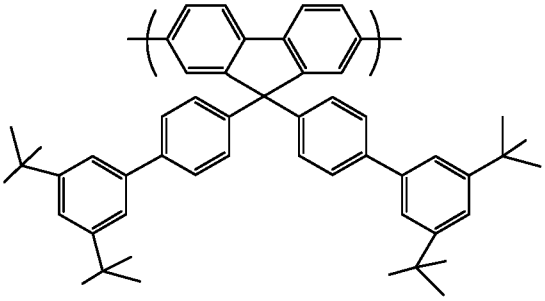
IX



X



XI



XII

[0042] The concentration of F^1 may be from 5 to 95 mol %.

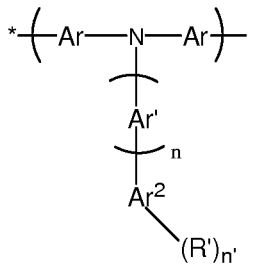
[0043] The concentration of F^1 may be from 20 to 80 mol %.

[0044] The concentration of F^1 may be from 25 to 55 mol %.

[0045] The concentration of F^1 may be from 30 to 50 mol %.

[0046] The triarylamine repeat unit T^1 may comprise a triphenylamine.

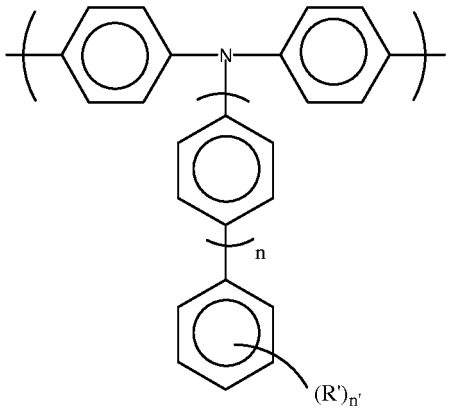
[0047] The triarylamine repeat unit T^1 may have general formula XIII:



XIII

where Ar represents an aryl or heteroaryl group; and Ar^1, Ar^2, R', n and n' are as defined anywhere in relation to the first aspect.

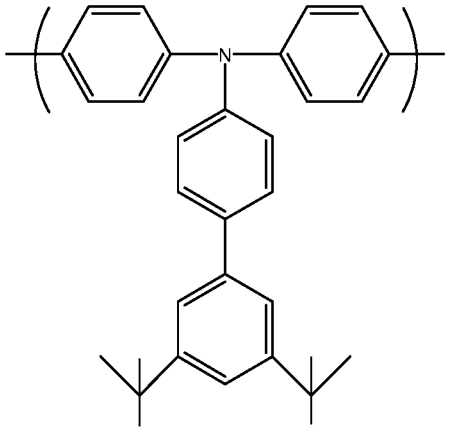
[0048] The triarylamine repeat unit T^1 may have general formula XIVa:



XIVa

where R', n and n' are as defined anywhere in relation to the first aspect.

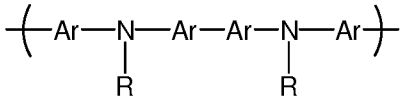
[0049] The triarylamine repeat unit T^1 may have formula XVb:



XVb

[0050] In the polymer backbone the triarylamine repeat unit T^1 may be bonded directly to two further repeat units. The further repeat units may be as defined anywhere herein.

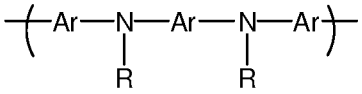
[0051] In the triarylamine repeat unit T^1, one triarylamine may be bonded directly to another triarylamine giving the formula XVI:



XVI

where each Ar and R is as defined above.

[0052] In the triarylamine repeat unit T^1, a triarylamine may be bonded directly to -N(R) (Ar), giving the formula XVII:

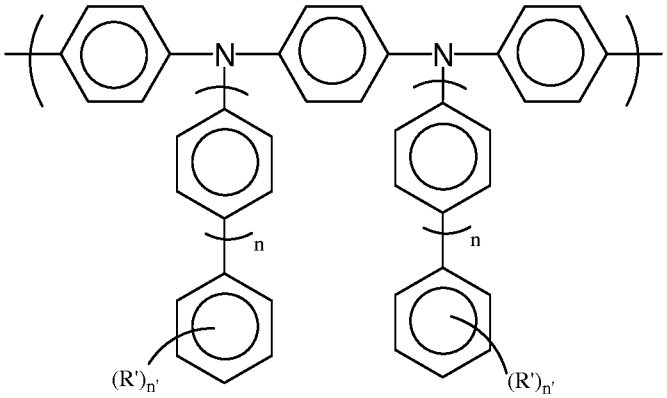


XVII

where each Ar and R is as defined above.

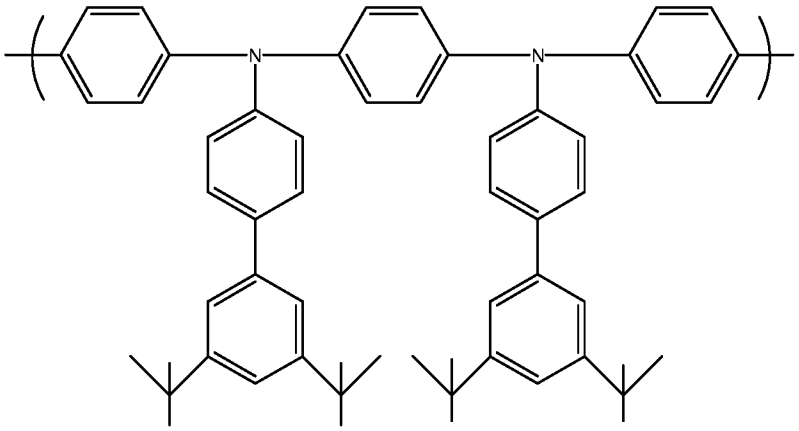
[0053] Each Ar in formulae XVI and XVII may represent phenyl.

[0054] The triarylamine repeat unit T^1 may have formula XIVb, XIX or XXI:

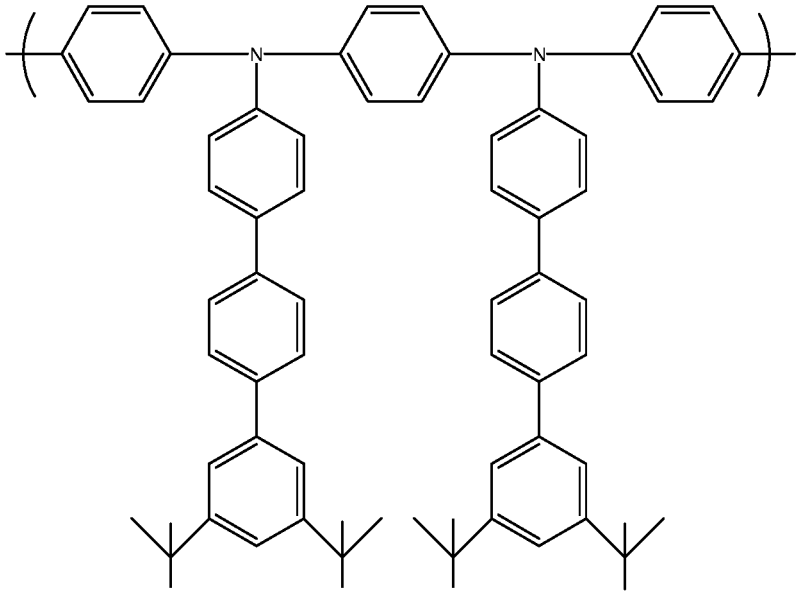


XIVb

where R', n and n' are as defined anywhere in relation to the first aspect.



XIX



XXI

[0055] The concentration of T^1 may be from 0.5 to 50 mol%.

[0056] The concentration of T^1 may be from 2 to 15 mol%.

[0057] The concentration of T^1 may be from 5 to 10 mol %.

[0058] The concentration of T^1 may be about 5 mol %.

[0059] Typically, the semiconductive polymer is conjugated.

[0060] The semiconductive polymer comprising T^1 and, optionally, F^1 may provide one or more of the functions of hole transport, electron transport and emission depending on which layer of the device it is used in and the nature of co-repeat units.

[0061] The semiconductive polymer may be blue light-emitting. By "blue light-emitting" is meant an organic material that by electroluminescence emits radiation having a wavelength in the range of 400-500 nm, more preferably 430-500 nm.

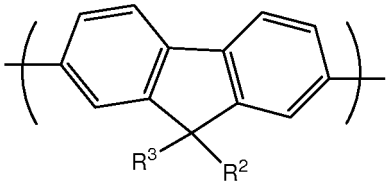
[0062] A semiconductive polymer comprising a triarylamine repeat unit T^1, may be used for emitting light, particularly emitting blue light, and/or for hole transport.

[0063] A semiconductive polymer comprising a triarylamine repeat unit T^1 and a fluorene repeat unit (F^1 or another fluorene unit) may be used for emitting light, particularly emitting blue light, and/or for hole transport.

[0064] Particularly preferred hole transporting polymers are AB copolymers of a fluorene repeat unit and a triarylamine repeat unit.

[0065] The semiconductive polymer may comprise further repeat units in addition to T^1. The further repeat units may be selected from arylene repeat units, in particular: 1,4-phenylene repeat units as disclosed in J. Appl. Phys. 1996, 79, 934; fluorene repeat units as disclosed in EP 0842208; indenofluorene repeat units as disclosed in, for example, Macromolecules 2000, 33(6), 2016-2020; and spirofluorene repeat units as disclosed in, for example EP 0707020.

[0066] Further repeat units, which may be present in a semiconductive polymer comprising T^1 and, optionally, F^1 include further fluorene repeat units, such as 2,7-linked fluorenes, most preferably repeat units of formula XXII:

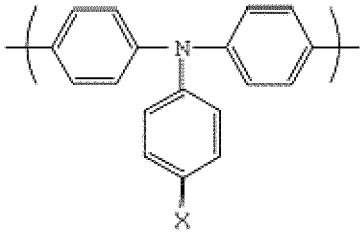


XXII

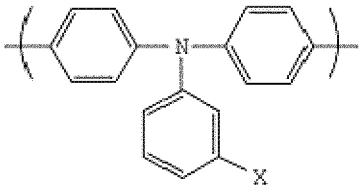
wherein R^2 and R^3 are independently selected from hydrogen or optionally substituted alkyl, alkoxy, aryl, arylalkyl, heteroaryl and heteroarylalkyl. More preferably, at least one of R^2 and R^3 comprises an optionally substituted C_4-C_{20} alkyl or aryl group.

[0067] Preferred further fluorene repeat units are selected from optionally substituted 9,9-dialkyl- or 9,9-dialkoxy-2,7-fluorenyl, more preferably 9,9-di(n-octyl)fluorene.

[0068] Further repeat units, which may be present in a semiconductive polymer comprising T^1 and, optionally, F^1 include further triarylamine repeat units, such as a repeat unit selected from formulae 1 to 6 shown below:



1



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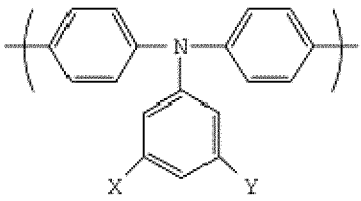

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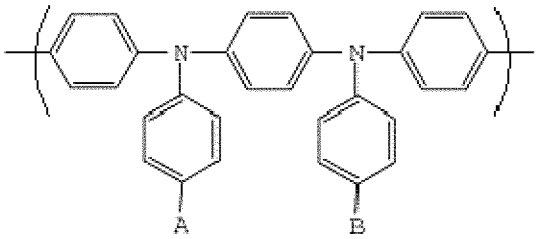

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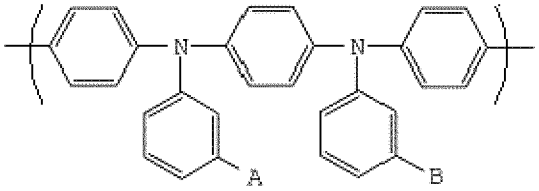

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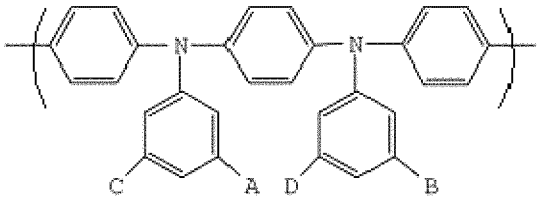
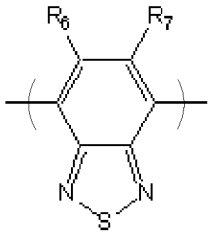


6

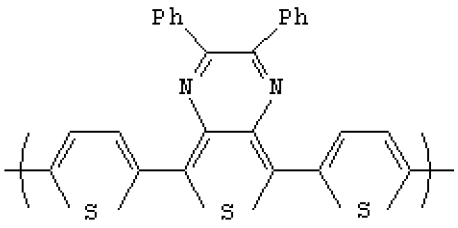
wherein X, Y, A, B, C and D are independently selected from H or a substituent group. More preferably, one or more of X, Y, A, B, C and D is independently selected from the group consisting of optionally substituted, branched or linear alkyl, aryl, perfluoroalkyl, thioalkyl, cyano, alkoxy, heteroaryl, alkylaryl and arylalkyl groups. Most preferably, X, Y, A and B are C_{1-10} alkyl.

[0069] Further repeat units, which may be present in a semiconductive polymer comprising T^1 and, optionally, F^1 include heteroarylene repeat units. Preferred heteroarylene repeat units are selected from formulae 7-21:



7

wherein R_6 and R_7 are the same or different and are each independently hydrogen or a substituent group, preferably alkyl, aryl, perfluoroalkyl, thioalkyl, cyano, alkoxy, heteroaryl, alkylaryl or arylalkyl. For ease of manufacture, R_6 and R_7 are preferably the same. More preferably, they are the same and are each a phenyl group.



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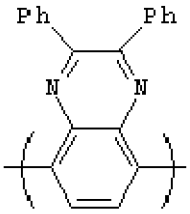

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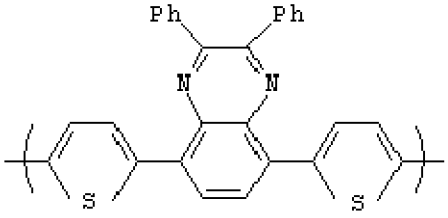

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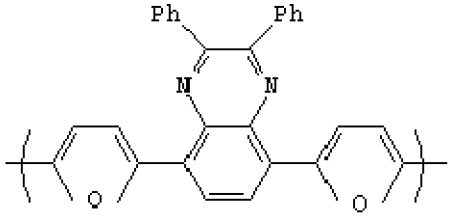

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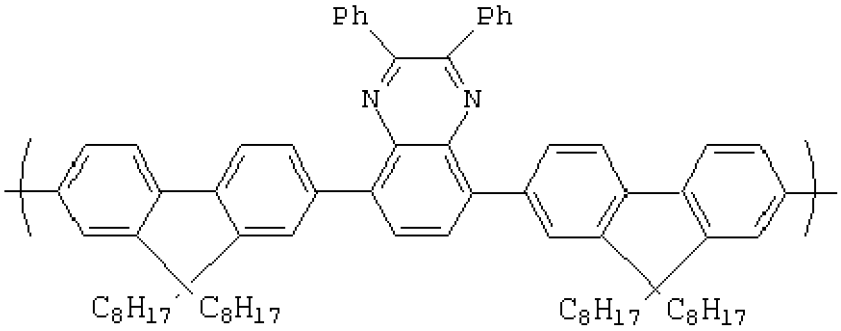
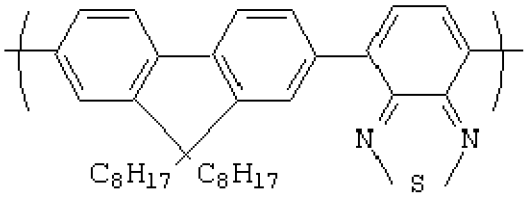


12



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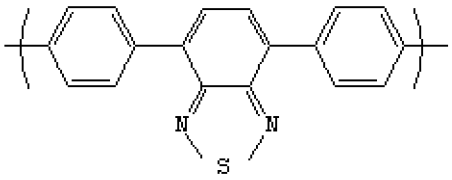

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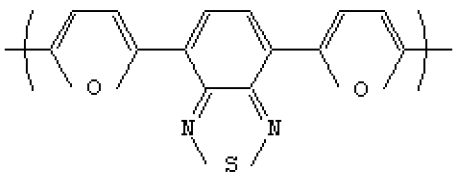

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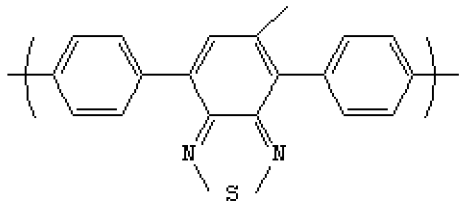

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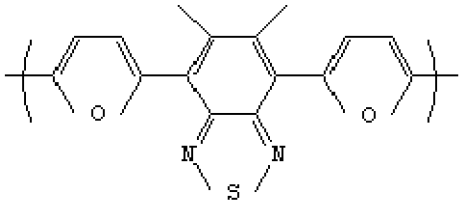

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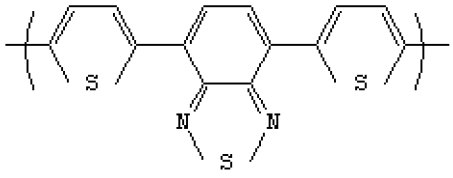
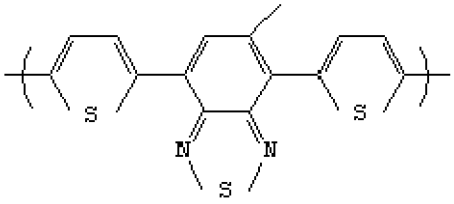


18



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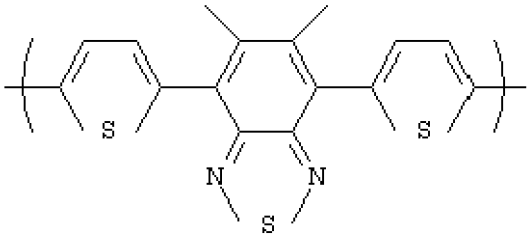

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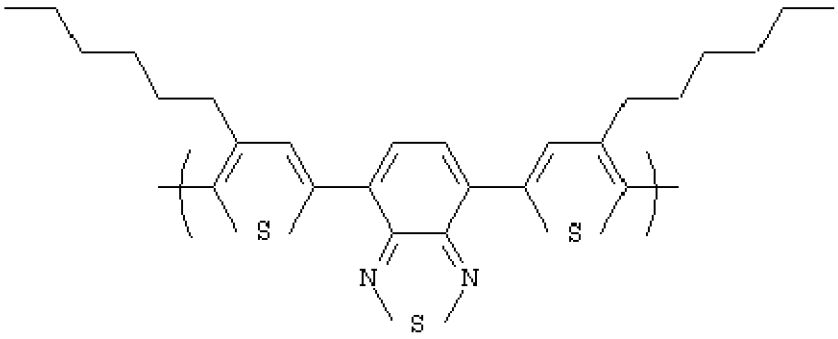


21

[0070] Each of the further repeat units is optionally substituted. Examples of substituents include solubilising groups such as C_{1-20} alkyl or alkoxy; electron withdrawing groups such as fluorine, nitro or cyano; and substituents for increasing glass transition temperature (Tg) of the polymer.

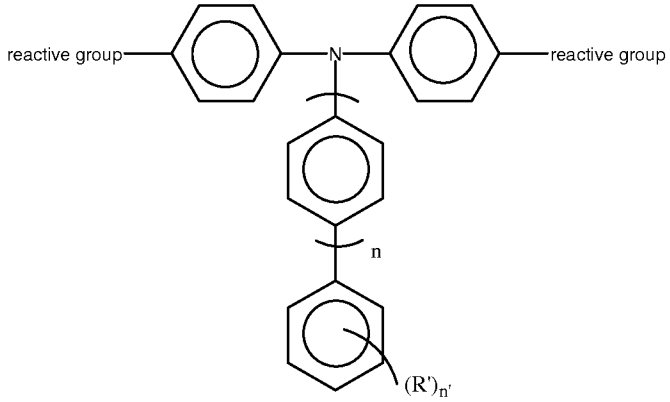
[0071] Electroluminescent copolymers may comprise an electroluminescent region and at least one of a hole transporting region and an electron transporting region as disclosed in, for example, WO 00/55927 and US 6353083. If only one of a hole transporting region and electron transporting region is provided then the electroluminescent region may also provide the other of hole transport and electron transport functionality. Suitable repeat units for a functional region are as discussed above in relation to repeat units suitable for use in a semiconductive polymer having the same function.

[0072] The different regions within such a polymer may be provided along the polymer backbone, as per US 6353083,

or as groups pendant from the polymer backbone as per WO 01/62869.

[0073] When the semiconductive polymer comprises T^1, there may be no repeat units comprising nitrogen atoms in the repeat unit backbone other than T^1.

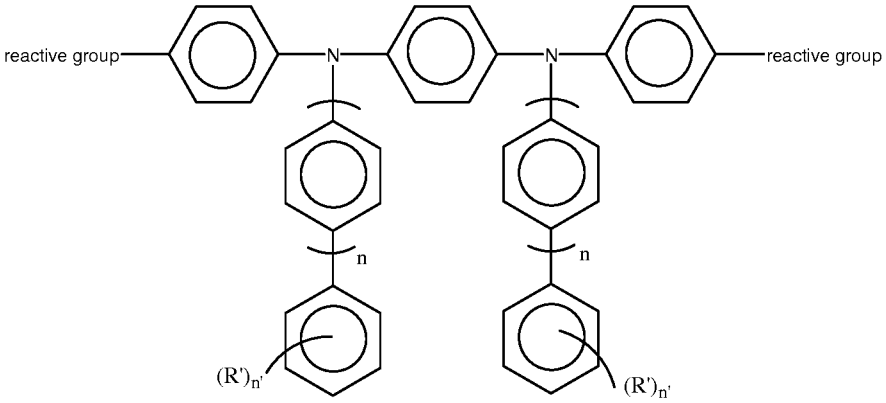
[0074] Referring to the second aspect of the present invention, the monomer may have general formula XXIII:



XXIII

where R', n and n' are as defined in relation to the first aspect.

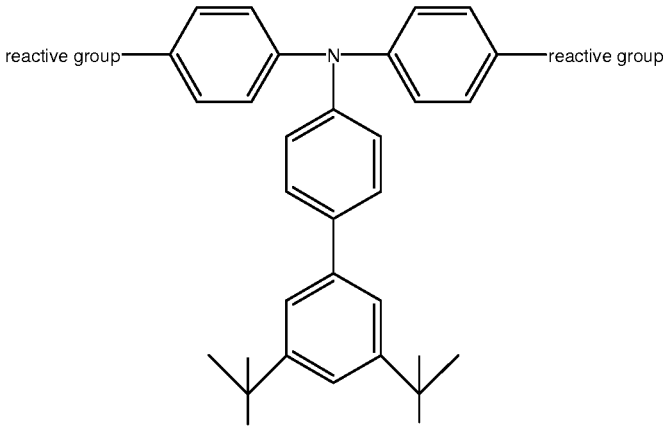
[0075] The monomer may have general formula XXIV:



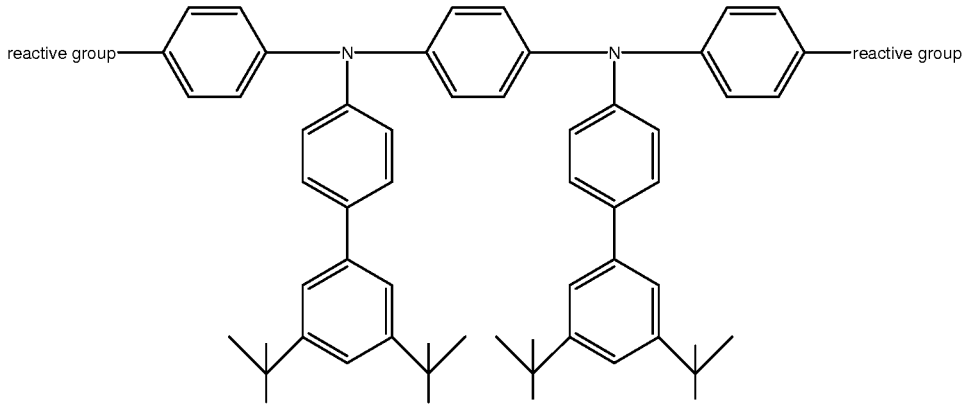
XXIV

where R', n and n' are as defined in relation to the first aspect.

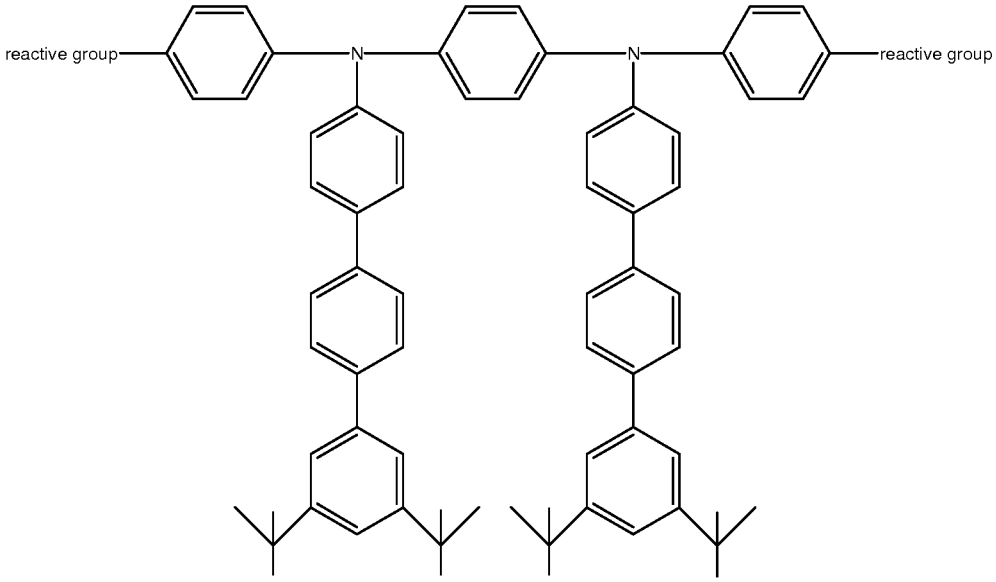
[0076] The monomer may have one of the following formulae:



XXVI



XXVIII



XXX

[0077] The reactive groups in formulae II, XXVI, XXVIII and XXX may be any reactive groups suitable for participation in polymerisation, for example reactive groups as defined anywhere below. Both reactive groups may be Br.

[0078] Preferred methods for preparation of a semiconductive polymer as defined in relation to the first aspect, optionally from a monomer according to the second aspect, are Suzuki polymerisation as described in, for example, WO 00/53656 and Yamamoto polymerisation as described in, for example, T. Yamamoto, "Electrically Conducting And Thermally Stable p - Conjugated Poly(arylene)s Prepared by Organometallic Processes", Progress in Polymer Science 1993, 17, 1153-1205. These polymerisation techniques both operate via a "metal insertion" wherein the metal atom of a metal complex catalyst is inserted between an aryl group and a leaving group of a monomer. In the case of Yamamoto polymerisation, a nickel complex catalyst is used; in the case of Suzuki polymerisation, a palladium complex catalyst is used.

[0079] For example, in the synthesis of a linear polymer by Yamamoto polymerisation, a monomer having two reactive halogen groups is used. Similarly, according to the method of Suzuki polymerisation, at least one reactive group is a boron derivative group such as a boronic acid or boronic ester and the other reactive group is a halogen. Preferred halogens are chlorine, bromine and iodine, most preferably bromine.

[0080] It will therefore be appreciated that repeat units and end groups comprising aryl groups as illustrated throughout this application may be derived from a monomer carrying a suitable reactive leaving group or groups. A repeat unit typically is derived from a monomer carrying two suitable reactive leaving groups.

[0081] Suzuki polymerisation may be used to prepare regioregular, block and random copolymers. In particular, homopolymers or random copolymers may be prepared when one reactive group is a halogen and the other reactive group is a boron derivative group. Alternatively, block or regioregular, in particular AB, copolymers may be prepared when both reactive groups of a first monomer are boron and both reactive groups of a second monomer are halogen.

[0082] As alternatives to halides, other leaving groups capable of participating in metal insertion include groups include tosylate, mesylate and triflate.

[0083] The present invention now will be described in more detail with reference to the attached Figures, in which:-

Figure 1 shows the structure of a light-emitting device.

Figure 2 shows a passive matrix device.

Figure 3 shows an active matrix device.

Figure 4 shows the structures of "PFB", "N10", "DPF", "P11", and "P15".

[0084] According to the present invention, lifetime measurements are obtained at room temperature (295ºK) by measuring the time taken for luminescence to decrease by half at a constant current.

[0085] The pulsed driven display of the first aspect may comprise a passive matrix display.

[0086] With reference to Figure 1, the LED comprised in the present pulsed driven display comprises a transparent glass or plastic substrate 1, an anode 2 of indium tin oxide and a cathode 4. An electroluminescent layer 3 is provided between anode 2 and cathode 4. Further layers may be located between anode 2 and cathode 3, such as charge transporting, charge injecting or charge blocking layers.

[0087] In particular, it is desirable to provide a conductive hole injection layer formed of a doped organic material located between the anode 2 and the electroluminescent layer 3 to assist hole injection from the anode into the layer or layers of semiconducting polymer. Examples of doped organic hole injection materials include poly(ethylene dioxythiophene) (PEDT), in particular PEDT doped with polystyrene sulfonate (PSS) as disclosed in EP 0901176 and EP 0947123, or polyaniline as disclosed in US 5723873 and US 5798170.

[0088] If present, a hole transporting layer located between anode 2 and electroluminescent layer 3 preferably has a HOMO level of less than or equal to 5.5 eV, more preferably around 4.8-5.5 eV. A semiconductive polymer comprising repeat unit T^1 and, optionally, F^1 may be used as a hole transport material in a hole transporting layer (or indeed in an electroluminescent layer 3).

[0089] Electroluminescent layer 3 may consist of an electroluminescent material alone or may comprise an electroluminescent material in combination with one or more further materials. An electroluminescent material may be blended with hole and / or electron transporting materials as disclosed in, for example, WO 99/48160. Alternatively, the electroluminescent material may be covalently bound to a charge transporting material.

[0090] Suitable electroluminescent polymers for use in layer 3 include poly(arylene vinylenes) such as poly(p-phenylene vinylenes) and polyarylenes such as: polyfluorenes, particularly 2,7-linked 9,9 dialkyl polyfluorenes or 2,7-linked 9,9 diaryl polyfluorenes; polyspirofluorenes, particularly 2,7-linked poly-9,9-spirofluorene; polyindenofluorenes, particularly 2,7-linked polyindenofluorenes; polyphenylenes, particularly alkyl or alkoxy substituted poly-1,4-phenylene. Such polymers as disclosed in, for example, Adv. Mater. 2000 12(23) 1737-1750 and references therein. A semiconductive polymer comprising repeat unit T^1 and, optionally, F^1 may be used as an electroluminescent material in layer 3.

[0091] Cathode 4 is selected from materials that have a workfunction allowing injection of electrons into the electroluminescent layer. Other factors influence the selection of the cathode such as the possibility of adverse interactions between the cathode and the electroluminescent material. The cathode may consist of a single material such as a layer of aluminium. Alternatively, it may comprise a plurality of metals, for example a bilayer of calcium and aluminium as disclosed in WO 98/10621, elemental barium disclosed in WO 98/57381, Appl. Phys. Lett. 2002, 81(4), 634 and WO 02/84759 or a thin layer of dielectric material to assist electron injection, for example lithium fluoride disclosed in WO 00/48258 or barium fluoride, disclosed in Appl. Phys. Lett. 2001, 79(5), 2001. In order to provide efficient injection of electrons into the device, the cathode preferably has a workfunction of less than 3.5 eV, more preferably less than 3.2 eV, most preferably less than 3 eV.

[0092] Light-emitting devices tend to be sensitive to moisture and oxygen. Accordingly, the substrate preferably has good barrier properties for prevention of ingress of moisture and oxygen into the device. The substrate is commonly glass, however alternative substrates may be used, in particular where flexibility of the device is desirable. For example, the substrate may comprise a plastic as in US 6268695 which discloses a substrate of alternating plastic and barrier layers or a laminate of thin glass and plastic as disclosed in EP 0949850.

[0093] The device is preferably encapsulated with an encapsulant (not shown) to prevent ingress of moisture and oxygen. Suitable encapsulants include a sheet of glass, films having suitable barrier properties such as alternating stacks of polymer and dielectric as disclosed in, for example, WO 01/81649 or an airtight container as disclosed in, for example, WO 01/19142. A getter material for absorption of any atmospheric moisture and / or oxygen that may permeate through the substrate or encapsulant may be disposed between the substrate and the encapsulant.

[0094] In a practical device, at least one of the electrodes is semi-transparent in order that light may be emitted. Where the anode is transparent, it typically comprises indium tin oxide. Examples of transparent cathodes are disclosed in, for example, GB 2348316.

[0095] The embodiment of Figure 1 illustrates a device wherein the device is formed by firstly forming an anode on a substrate followed by deposition of an electroluminescent layer and a cathode, however it will be appreciated that the

device of the invention could also be formed by firstly forming a cathode on a substrate followed by deposition of an electroluminescent layer and an anode.

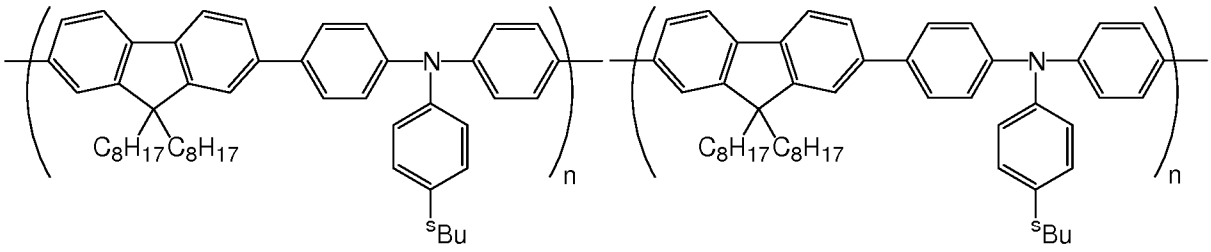
[0096] In the preparation of a display according to the first aspect, the semiconductive polymer may be deposited from solution to form a layer. Suitable solvents for polyarylenes, in particular polyfluorenes, include mono- or poly-alkylbenzenes such as toluene and xylene. Particularly preferred solution deposition techniques are spin-coating and inkjet printing.

[0097] Inkjet printing is particularly suitable for high information content displays, in particular full colour displays. Inkjet printing of OLEDs is described in, for example, EP 0880303.

[0098] If multiple layers of the device are formed by solution processing then the skilled person will be aware of techniques to prevent intermixing of adjacent layers, for example by crosslinking of one layer before deposition of a subsequent layer or selection of materials for adjacent layers such that the material from which the first of these layers is formed is not soluble in the solvent used to deposit the second layer.

EXAMPLES

[0099] Light-emitting devices were constructed as follows:
Poly(ethylene dioxythiophene) / poly(styrene sulfonate) (PEDT / PSS), available from H C Starck of Leverkusen, Germany as Baytron P ® was deposited over an indium tin oxide anode supported on a glass substrate (available from Applied Films, Colorado, USA) by spin coating. A hole transporting layer of F8-TFB (shown below) was deposited over the PEDT / PSS layer by spin coating from xylene solution to a thickness of about 10 nm and heated at 180ºC for 1 hour. Polymer 1, 2, 3, 4, 5, or 6 was deposited over the layer of F8-TFB by spin-coating from xylene solution to a thickness of around 65 nm. Then a Ba / Al cathode was formed over the polymer by evaporating a first layer of barium to a thickness of up to about 10 nm and a second layer of aluminium barium to a thickness of about 100 nm over the semiconducting polymer. Finally, the device was sealed using a metal enclosure containing a getter that is placed over the device and glued onto the substrate in order to form an airtight seal.



"F8–TFB"

[0100] The following polymers were used as emissive layers in the light-emitting devices:

1 (65% F8, 30% DPF, 5% PFB)
2 (65% F8, 30% DPF, 5% N10)
3 (50% F8, 30% DPF, 10% TFB 10% PFB)
4 (50% F8, 30% DPF, 10% TFB 10% N10)
5 (65% F8, 30% DPF, 5% PFB)
6(65% F8, 30% DPF, 5% N10)

[0101] The dc and pulsed lifetimes were obtained at room temperature (295ºK) by measuring the time taken for luminescence to decrease by half at a constant current. DC lifetimes were measured from a start luminescence of 800 cd/m^2. Pulsed lifetimes were measured from a start luminescence of 14,000 cd/m^2. For the pulsed lifetimes, the multiplex ratio (MUX) was 64 and the repeat frequency was 60Hz.

[0102] Results are shown in Tables 1 to 3.

TABLE 1

Polymer	DC LT (hrs)	Pulsed LT (hrs)	Pulsed/DC LT
1	48*	350	7.2

(continued)

Polymer	DC LT (hrs)	Pulsed LT (hrs)	Pulsed/DC LT
2	54*	601	11.1

TABLE 2

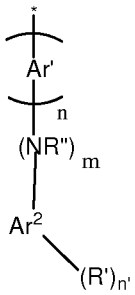
Polymer	DC LT (hrs)	Pulsed LT (hrs)	Pulsed/DC LT
3	5*	99	19.8
4	5*	339	67.8

TABLE 3

Polymer	DC LT (hrs)	Pulsed LT (hrs)	Pulsed/DC LT
5	40*	386	9.6
6	56*	575	10.3
*Extrapolated from 800 cd/m^2 (AF=2)			

Claims

1. A semiconductive polymer suitable for use in an organic light-emitting device, said polymer comprising a triarylamine repeat unit, the triarylamine repeat unit having a group R pendent from the polymer backbone, wherein R has general formula I:



I

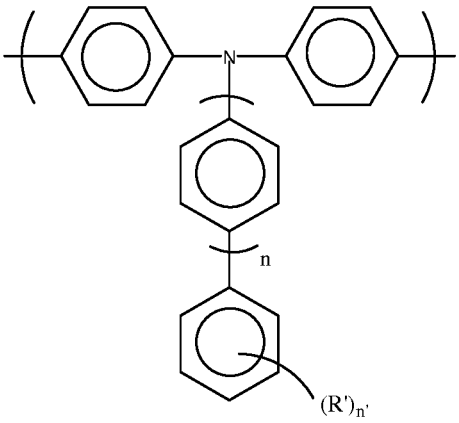
where Ar^1 represents phenyl or a group comprising napthyl; Ar^2 represents phenyl or a group comprising napthyl; R' represents a substituent group; R" represents hydrogen or a substituent group; n= 0, 1, 2 or 3; m=0 or 1; and n'= 2; provided that m=0 when n=0 and R' represents a branched C4 to C20 alkyl or alkoxy group comprising a tertiary carbon atom.

2. A polymer according to claim 1, wherein R' represents t-Bu.

3. A polymer according to any one of claims 1 to 2, wherein when Ar^2 represent phenyl, R' are located at the meta positions.

4. A polymer according to any one of the preceding claims, wherein the triarylamine repeat unit comprises a triphenylamine.

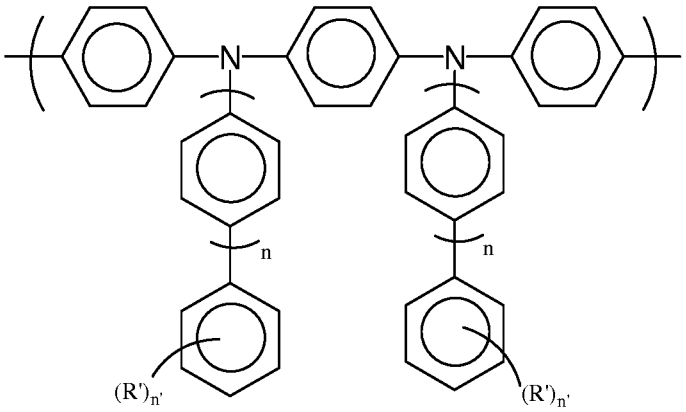
5. A polymer according to claim 4, wherein the triarylamine repeat unit has general formula XIVa:



XIVa

where R', n and n' are as defined in any one of claims 1 to 2.

6. A polymer according to claim 4, wherein the triarylamine repeat unit has general formula XIVb:



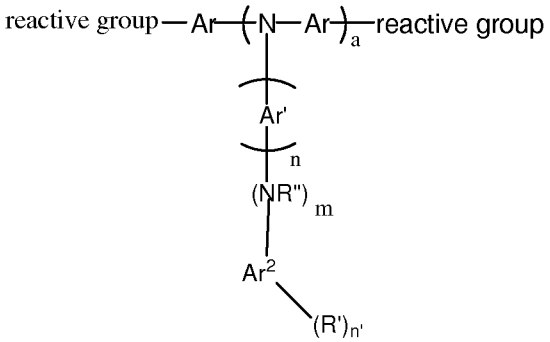
XIVb

where R', n and n' are as defined in any one of claims 1 to 4.

7. A polymer according to any one of the preceding claims, wherein the semiconductive polymer is blue light-emitting.

8. A polymer according to any preceding claim, wherein said polymer contains one or more further repeat units selected from the group consisting of 1,4-phenylene repeat units; indenofluorene repeat units; spirofluorene repeat units; 2,7-linked fluorene repeat units; triarylamine repeat units; and heteroarylene repeat units.

9. A monomer for making a semiconductive polymer according to claim 1, the monomer having general formula II:

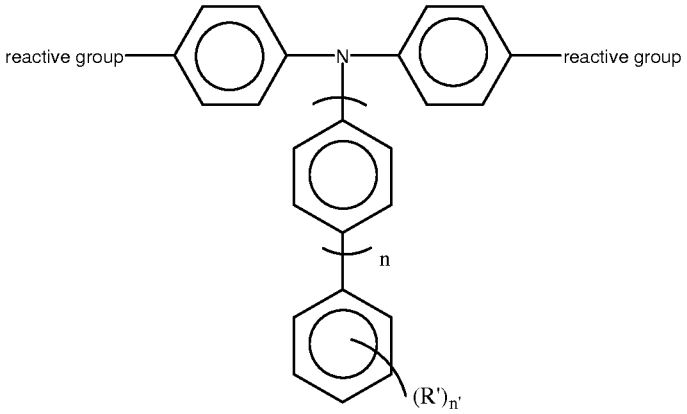


II

where Ar^1, Ar^2, R' , R", m, n, and n' are as defined in any of claims 1-3; a = 1 or 2; each Ar independently represents an aryl or heteroaryl group; and 'reactive group' represents a reactive group capable of participating in polymerisation.

10. A monomer according to claim 9, wherein Ar represents phenyl.

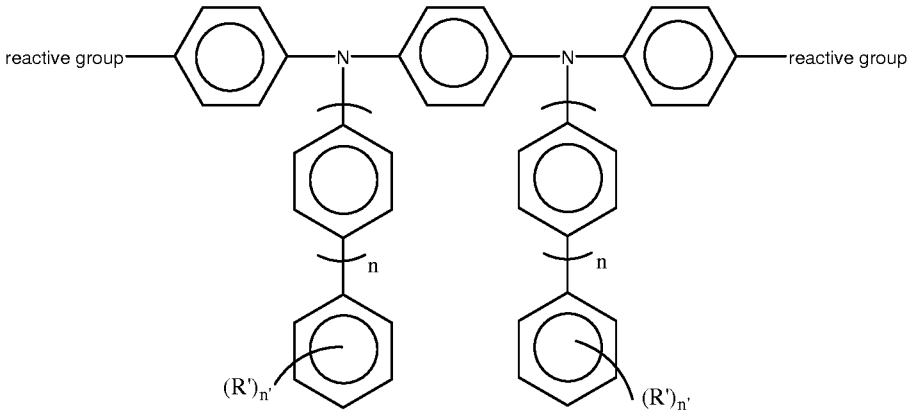
11. A monomer according to claim 10, having general formula XXIII:



XXIII

where 'reactive group' represents a reactive group capable of participating in polymerisation; R', n and n' are as defined in claim 9.

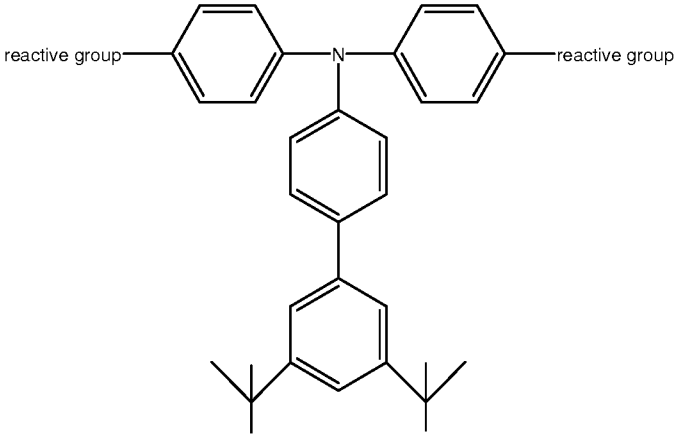
12. A monomer according to claim 11, having general formula XXIV:



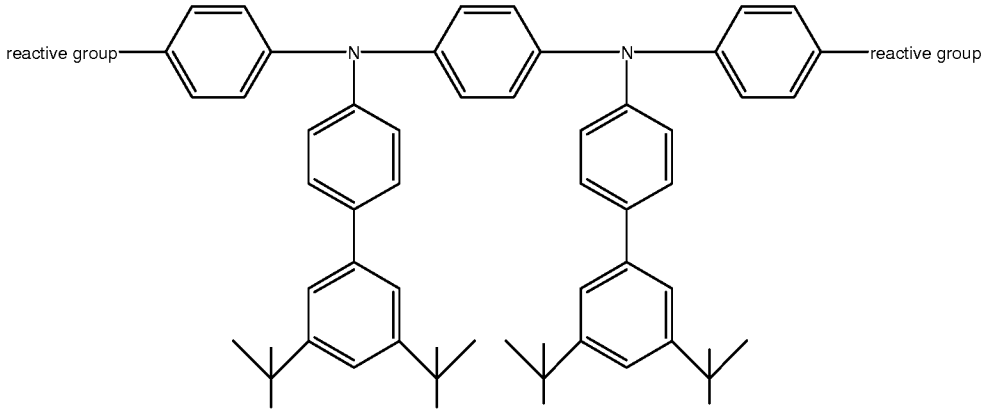
XXIV

where R', and n' are as defined in claim 9.

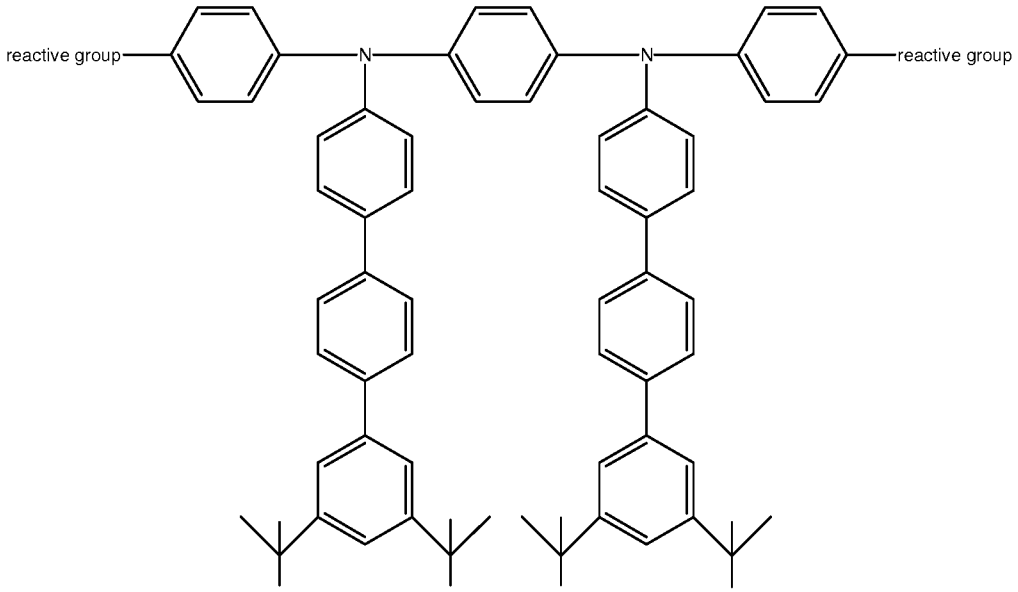
13. A monomer according to claim 10, having one of formulae XXVI, XXVIII and XXX:



XXVI



XXVIII



XXX

Where 'reactive group' represents a reactive group capable of participating in polymerisation.

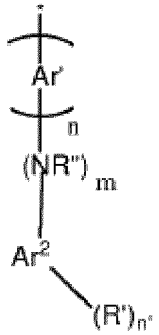
14. A method for preparing a semiconductive polymer comprising the step of polymerising monomers as defined in any one of claims 9 to 13 by Suzuki polymerisation.

15. A pulsed driven display comprising a passive matrix organic light-emitting device, said device comprising an organic layer (3) comprising a semiconductive polymer according to any of claims 1-8.

16. A method for preparing a display according to claim 15, wherein the semiconductive polymer is deposited from solution to form a layer.

Patentansprüche

1. Halbleitendes Polymer, das zur Verwendung in einer organischen lichtemittierenden Vorrichtung geeignet ist, wobei das Polymer eine Triarylamin-Wiederholungseinheit umfasst, wobei die Triarylamin-Wiederholungseinheit eine Gruppe R aufweist, die an der Polymerhauptkette anhängt, wobei R die allgemeine Formel I aufweist:



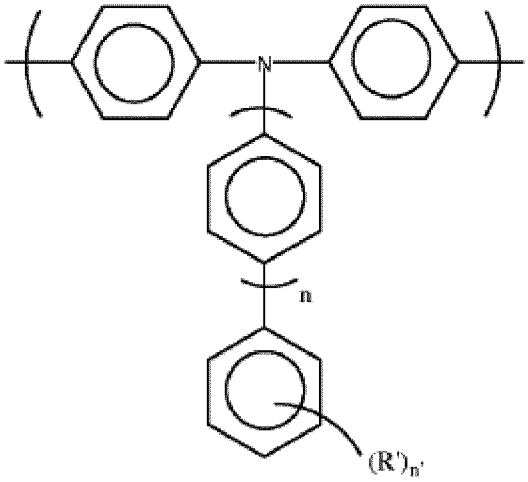
wobei Ar^1 Phenyl oder ein Gruppe umfassend Napthyl darstellt; Ar^2 Phenyl oder eine Gruppe umfassend Napthyl darstellt; R' eine Substituentengruppe darstellt; R" Wasserstoff oder eine Substituentengruppe darstellt; n=0, 1, 2 oder 3; m=0 oder 1; und n' = 2; vorausgesetzt, dass m=0 wenn n=0 und R' eine verzweigte C4- bis C20-Alkyl- oder Alkoxygruppe darstellt, die ein tertiäres Kohlenstoffatom umfasst.

2. Polymer nach Anspruch 1, wobei R' t-Bu darstellt.

3. Polymer nach einem der Ansprüche 1 bis 2, wobei wenn Ar^2 Phenyl darstellen, R' sich an den Metapositionen befinden.

4. Polymer nach einem der vorstehenden Ansprüche, wobei die Triarylamin-Wiederholungseinheit ein Triphenylamin umfasst.

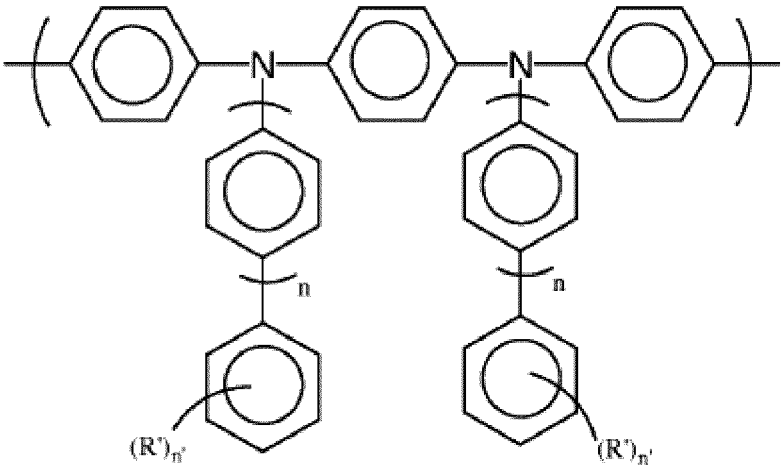
5. Polymer nach Anspruch 4, wobei die Triarylamin-Wiederholungseinheit die allgemeine Formel XIVa aufweist:



XIVa

wobei R', n und n' wie in einem der Ansprüche 1 bis 2 definiert sind.

6. Polymer nach Anspruch 4, wobei die Triarylamin-Wiederholungseinheit die allgemeine Formel XIVb aufweist:



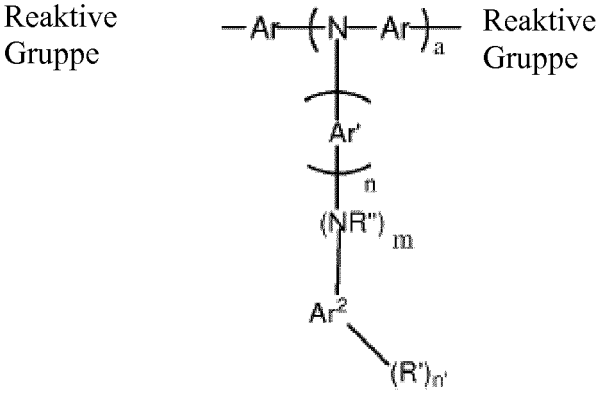
XIVb

wobei R', n und n' wie in einem der Ansprüche 1 bis 4 definiert sind.

7. Polymer nach einem der vorstehenden Ansprüche, wobei das halbleitende Polymer blaues Licht emittierend ist.

8. Polymer nach einem der vorstehenden Ansprüche, wobei das Polymer eine oder mehrere Wiederholungseinheiten enthält, die ausgewählt sind aus der Gruppe bestehend aus 1,4-phenylen-Wiederholungseinheiten; Indenofluoren-Wiederholungseinheiten; Spirofluoren-Wiederholungseinheiten; 2,7-verknüpftes Fluoren-Wiederholungseinheiten; Triarylamin-Wiederholungseinheiten; und Heteroarylen-Wiederholungsseinheiten.

9. Monomer zum Herstellen eines halbleitenden Polymers nach Anspruch 1, wobei das Monomer die allgemeine Formel II aufweist:

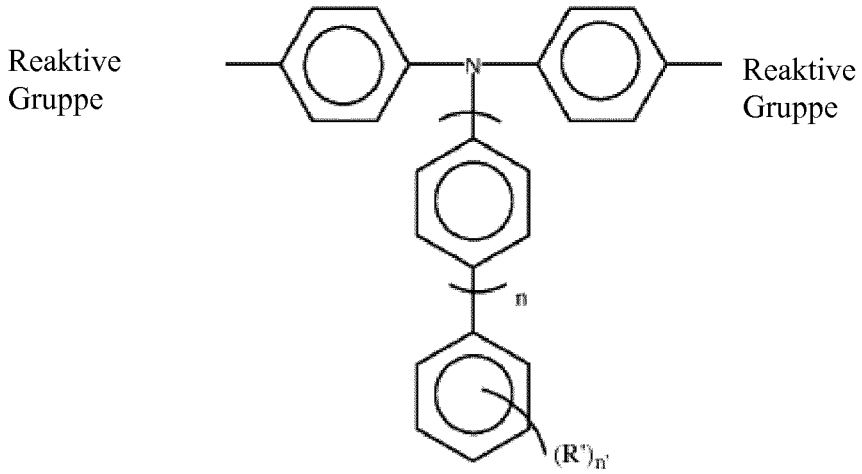


II

wobei Ar^1, Ar^2, R', R", m, n und n' wie in einem der Ansprüche 1-3 definiert sind; a = 1 oder 2; jedes Ar unabhängig eine Aryl- oder Heteroaryl-Gruppe darstellt; und ‚reaktive Gruppe' eine reaktive Gruppe darstellt, die dazu imstande ist, an einer Polymerisation teilzunehmen.

10. Monomer nach Anspruch 9, wobei Ar Phenyl darstellt.

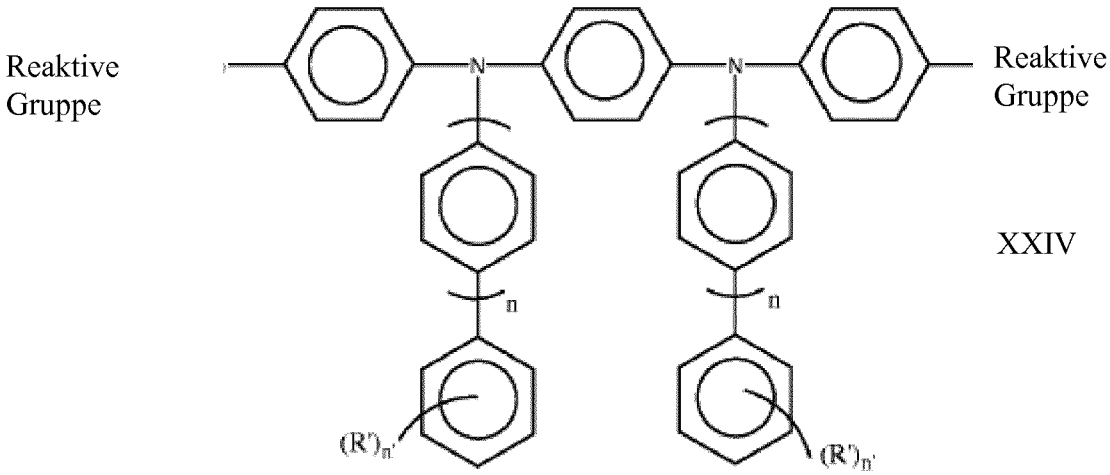
11. Monomer nach Anspruch 10, das die allgemeine Formel XXIII aufweist:



XXIII

wobei ‚reaktive Gruppe' eine reaktive Gruppe darstellt, die dazu imstande ist, an einer Polymerisation teilzunehmen; R', n und n' wie in Anspruch 9 definiert sind.

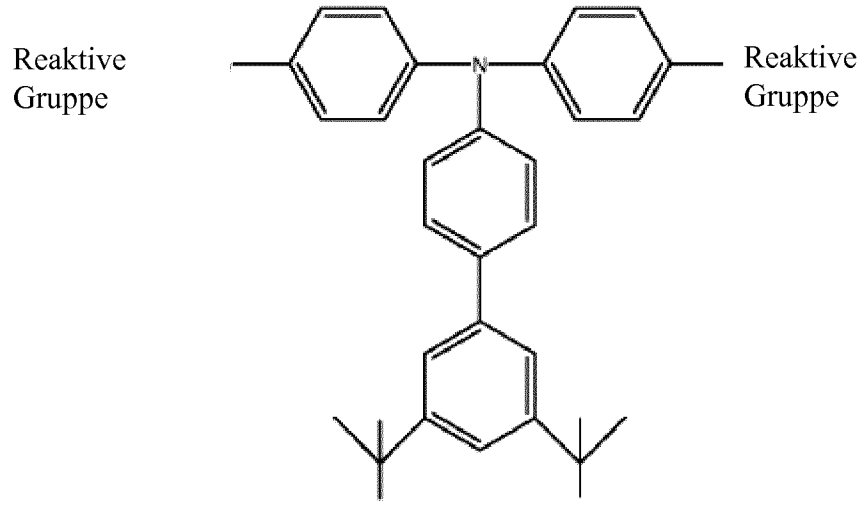
12. Monomer nach Anspruch 11, das die allgemeine Formel XXIV aufweist:



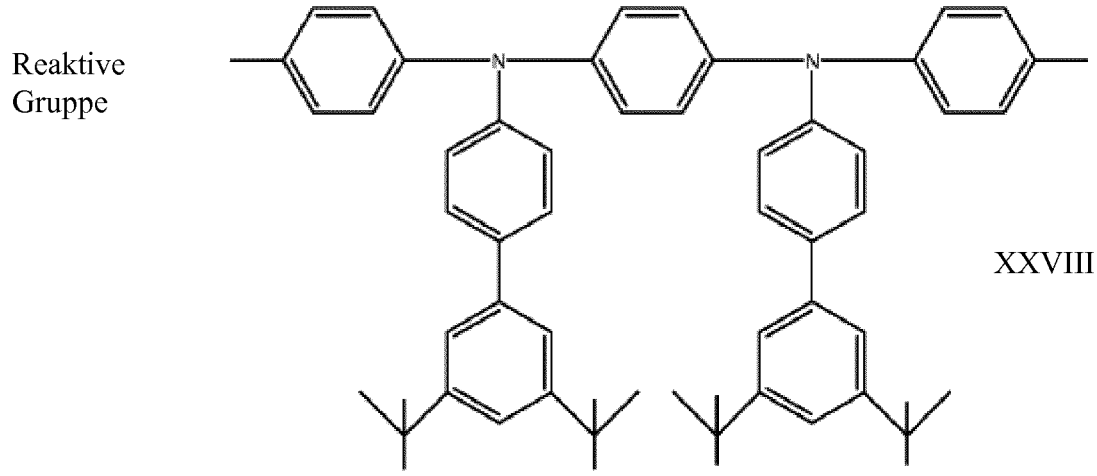
XXIV

wobei R' und n' wie in Anspruch 9 definiert sind.

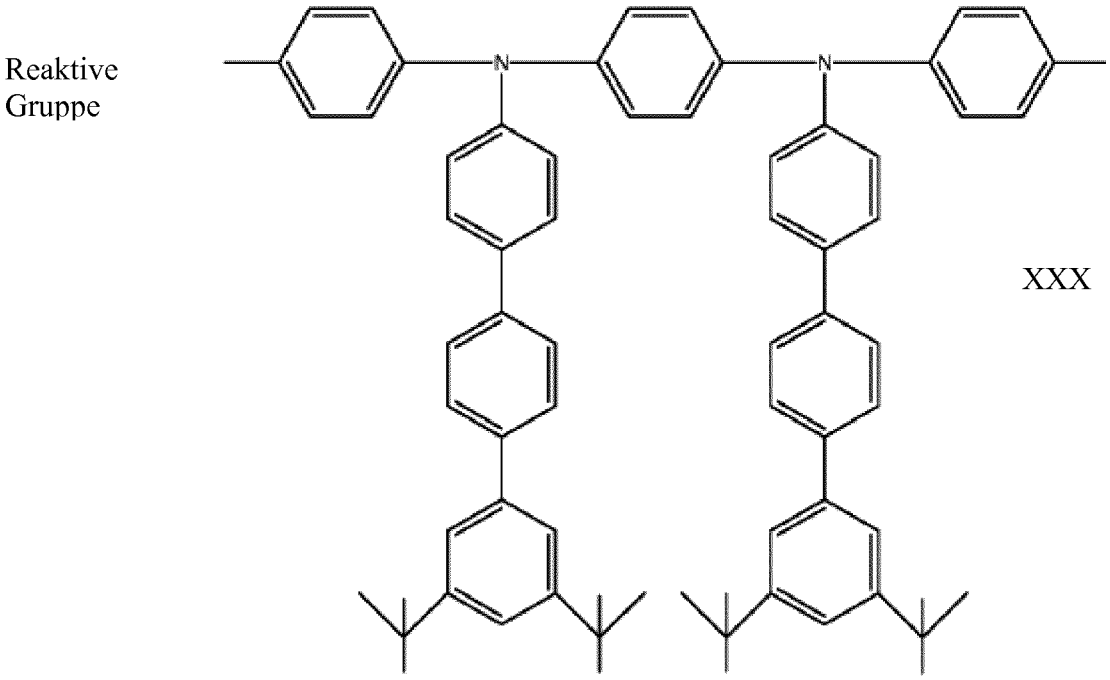
13. Monomer nach Anspruch 10, das eine der Formeln XXVI, XXVIII und XXX aufweist:



XXVI



XXVIII



XXX

Wobei ‚reaktive Gruppe' eine reaktive Gruppe darstellt, die dazu imstande ist, an einer Polymerisation teilzunehmen.

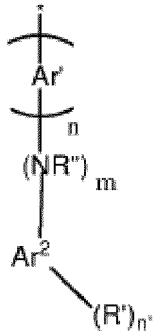
14. Verfahren zum Herstellen eines halbleitenden Polymers, das den Schritt des Polymerisierens von Monomeren wie in einem der Ansprüche 9 bis 13 definiert durch Suzuki-Polymerisation umfasst.

15. Eine gepulste angetriebene Anzeige, die ein organische lichtemittierenden Passivmatrix-Vorrichtung umfasst, wobei die Vorrichtung eine organische Schicht (3) umfasst, die ein halb leitendes Polymer nach einem der Ansprüche 1-8 umfasst.

16. Verfahren zum Herstellen einer Anzeige nach Anspruch 15, wobei das halbleitende Polymer aus einer Lösung abgeschieden wird, um eine Schicht zu bilden.

Revendications

1. Polymère semi-conducteur adapté à une utilisation dans un dispositif émetteur de lumière organique, ledit polymère comprenant un motif de répétition triarylamine, le motif de répétition triarylamine ayant un groupe R suspendu au squelette de polymère, dans lequel R a la formule générale I :



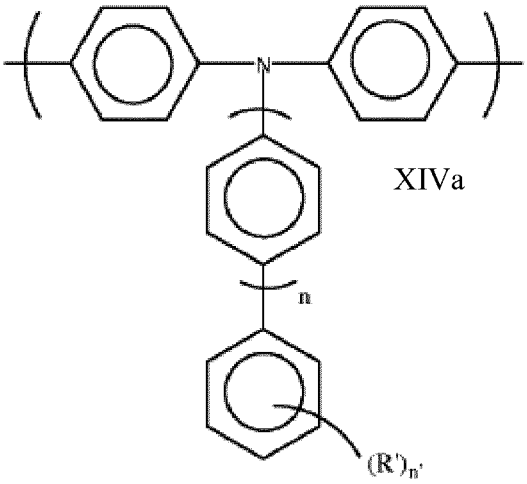
où Ar^1 représente un phényle ou un groupe comprenant un naphtyle ; Ar^2 représente un phényle ou un groupe comprenant un naphtyle ; R' représente un groupe substituant ; R" représente un hydrogène ou un groupe substituant ; n = 0, 1, 2 ou 3 ; m = 0 ou 1 ; et n' = 2 ; à condition que m = 0 quand n = 0 et R' représente un groupe alkyle ou alcoxy en C4 à C20 ramifié comprenant un atome de carbone tertiaire.

2. Polymère selon la revendication 1, dans lequel R' représente un t-Bu.

3. Polymère selon l'une quelconque des revendications 1 à 2, dans lequel quand Ar^2 représente un phényle, R' sont situés au niveau des positions méta.

4. Polymère selon l'une quelconque des revendications précédentes, dans lequel le motif de répétition triarylamine comprend une triphénylamine.

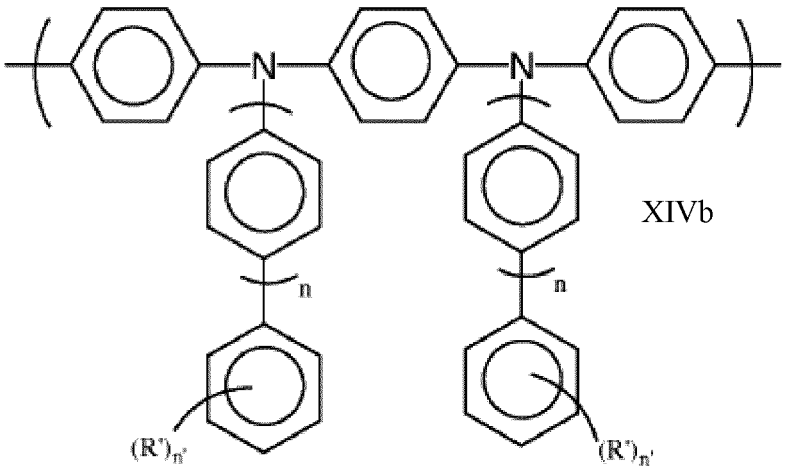
5. Polymère selon la revendication 4, dans lequel le motif de répétition triarylamine a la formule générale XIVa :



XIVa

où R', n et n' sont tels que définis dans l'une quelconque des revendications 1 à 2.

6. Polymère selon la revendication 4, dans lequel le motif de répétition triarylamine a la formule générale XIVb :



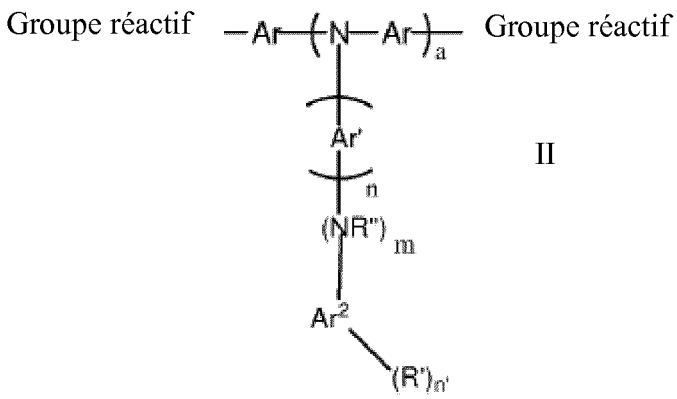
XIVb

où R', n et n' sont tels que définis dans l'une quelconque des revendications 1 à 4.

7. Polymère selon l'une quelconque des revendications précédentes, dans lequel le polymère semi-conducteur est émetteur de lumière bleue.

8. Polymère selon l'une quelconque des revendications précédentes, dans lequel ledit polymère contient un ou plusieurs motifs de répétition supplémentaires sélectionnés parmi le groupe constitué par des motifs de répétition 1,4-phénylène ; des motifs de répétition indénofluorène ; des motifs de répétition spirofluorène ; des motifs de répétition fluorène lié en 2,7 ; des motifs de répétition triarylamine ; et des motifs de répétition hétéroarylène.

9. Monomère destiné à la fabrication d'un polymère semi-conducteur selon la revendication 1, le monomère ayant la formule générale II :

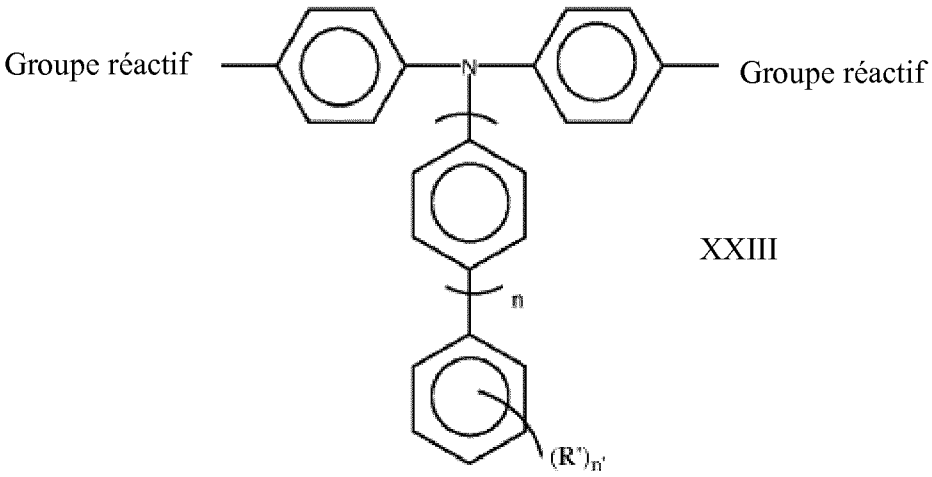


II

où Ar^1, Ar^2, R', R", m, n, et n' sont tels que définis dans l'une quelconque des revendications 1 à 3 ; a = 1 ou 2 ; chaque Ar représente indépendamment un groupe aryle ou hétéroaryle ; et « groupe réactif » représente un groupe réactif capable de participation à la polymérisation.

10. Monomère selon la revendication 9, dans lequel Ar représente un phényle.

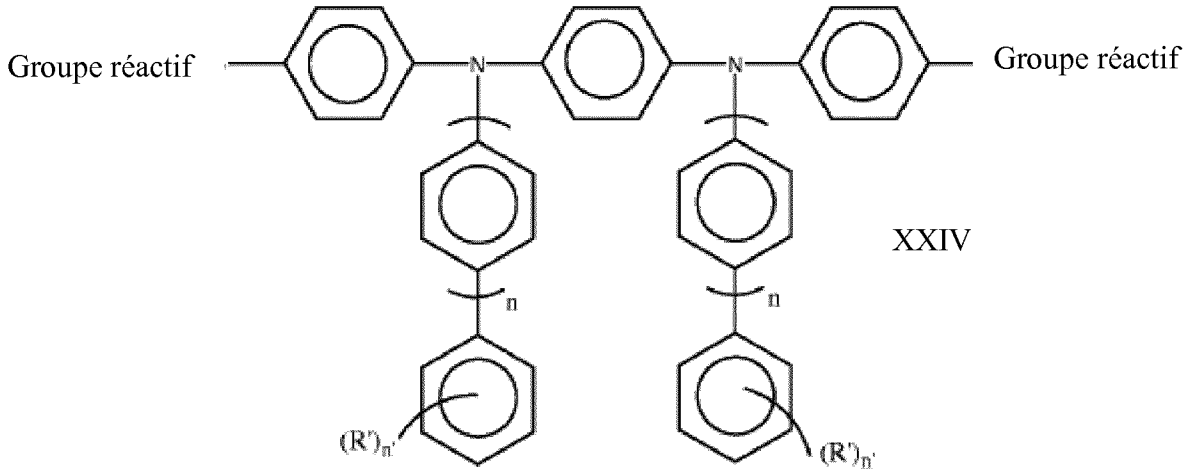
11. Monomère selon la revendication 10, ayant la formule générale XXIII :



XXIII

où « groupe réactif » représente un groupe réactif capable de participation à la polymérisation ; R' , n et n' sont tels que définis dans la revendication 9.

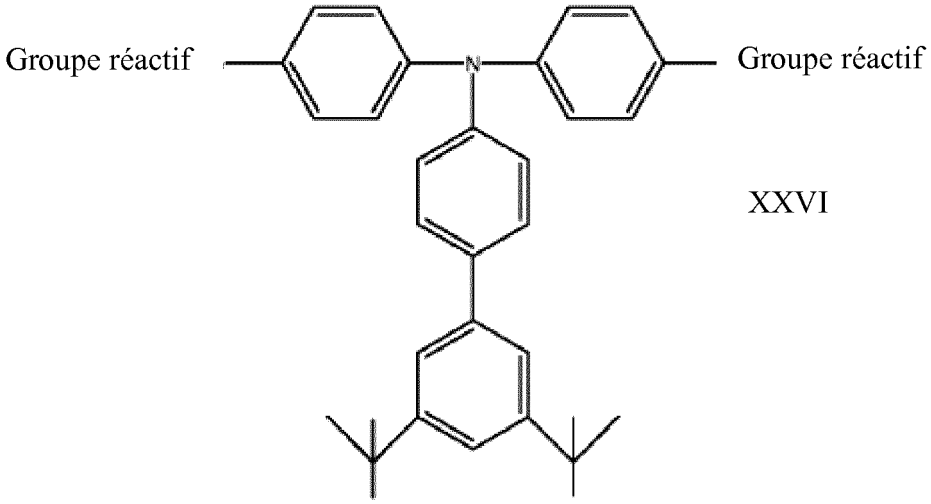
12. Monomère selon la revendication 11, ayant la formule générale XXIV :



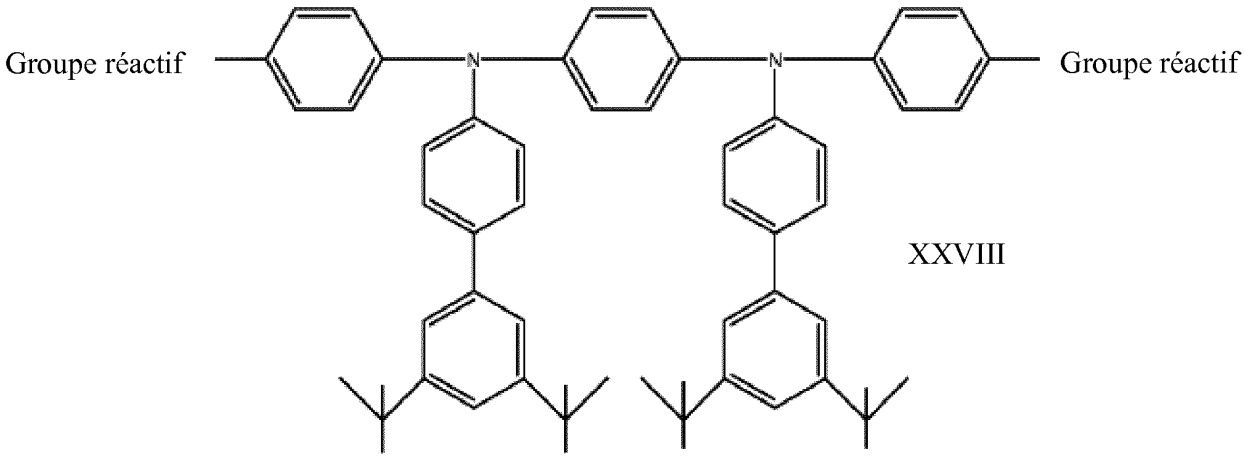
XXIV

où R', et n' sont tels que définis dans la revendication 9.

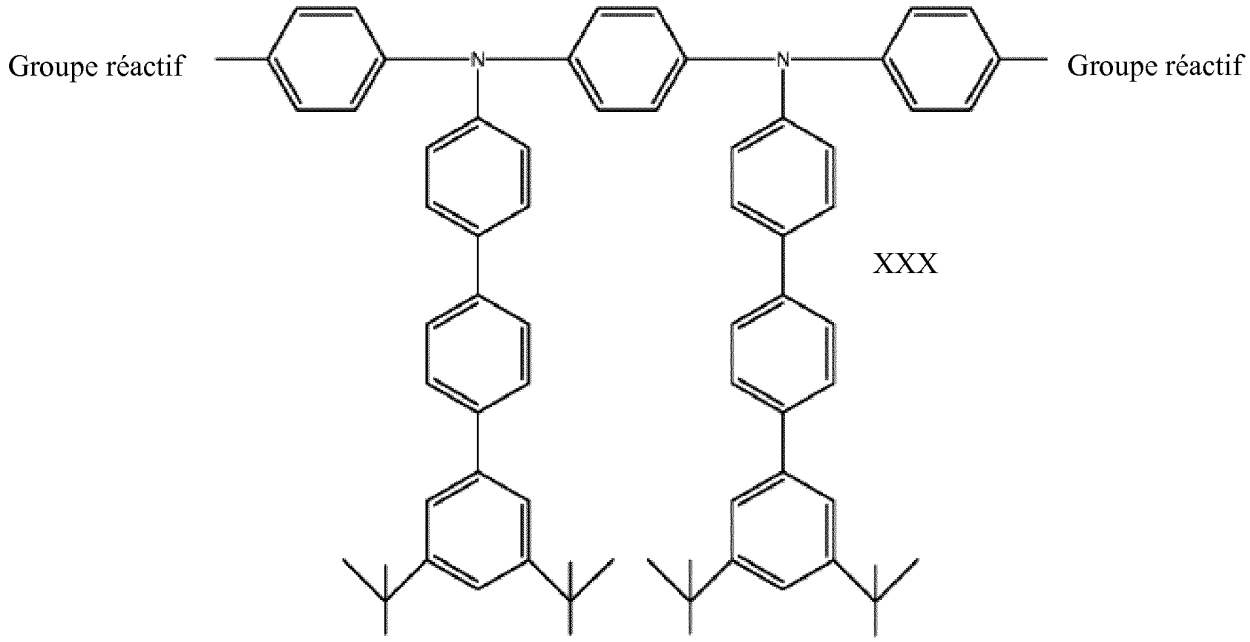
13. Monomère selon la revendication 10, ayant une des formules XXVI, XXVIII et XXX :



XXVI



XXVIII



XXX

où « groupe réactif » représente un groupe réactif capable de participation à la polymérisation.

14. Procédé de préparation d'un polymère semi-conducteur comprenant l'étape de polymérisation de monomères tels que définis dans l'une quelconque des revendications 9 à 13 par une polymérisation de Suzuki.

15. Affichage entraîné pulsé comprenant un dispositif émetteur de lumière organique à matrice passive, ledit dispositif comprenant une couche organique (3) comprenant un polymère semi-conducteur selon l'une quelconque des revendications 1 à 8.

16. Procédé de préparation d'un affichage selon la revendication 15, dans lequel le polymère semi-conducteur est déposé à partir d'une solution pour former une couche.

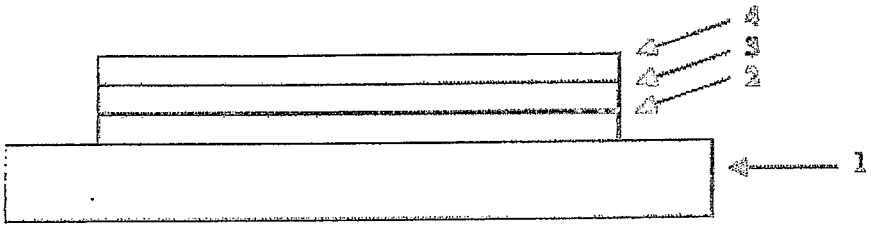


Figure 1

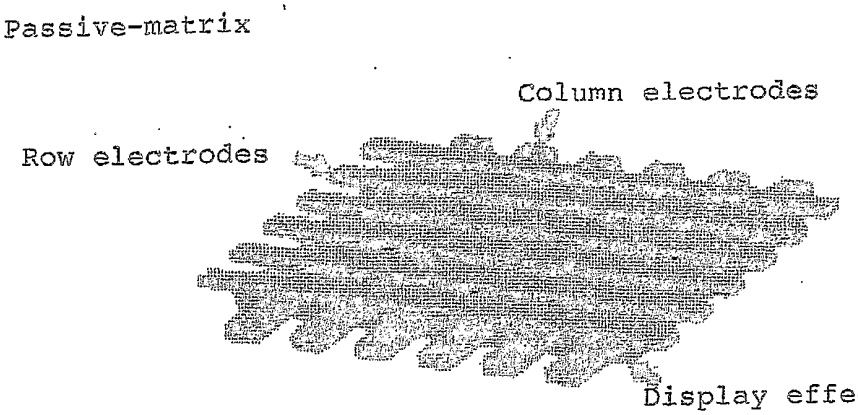


Figure 2

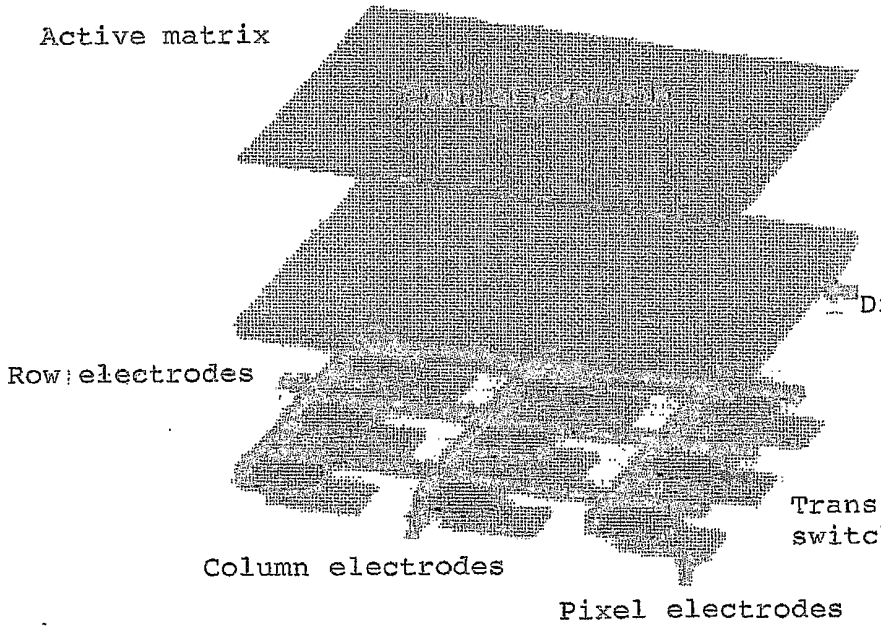
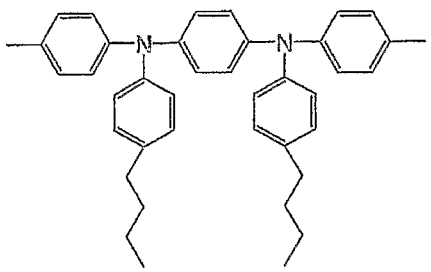
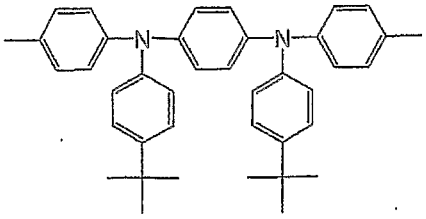


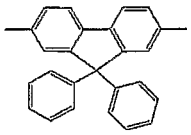
Figure 3



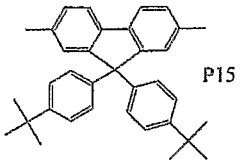
PFB



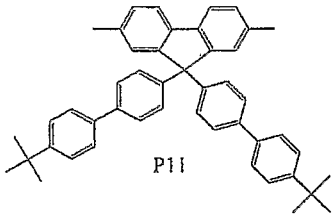
N10



DPF



P15



P11

Figure 4

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

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专利名称(译)	用于OLED显示器的芳胺和芴聚合物		
公开(公告)号	EP1894261B1	公开(公告)日	2019-07-24
申请号	EP2006726774	申请日	2006-04-13
[标]申请(专利权)人(译)	剑桥显示技术有限公司 CDT牛津有限公司		
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IPC分类号	H01L51/54 H01L27/32 C08G61/12 H01L51/30		
CPC分类号	H01L51/0043 H01L27/3281 H01L51/0035 H01L51/0039 H01L51/0059		
优先权	2005007684 2005-04-15 GB		
其他公开文献	EP1894261A1		
外部链接	Espacenet		

摘要(译)

一种脉冲驱动显示器，包括有机发光器件，所述器件包括含有半导电聚合物的有机层，所述聚合物包含芴或三芳胺重复单元，所述芴或三芳胺重复单元具有来自聚合物主链的基团R，其中R具有通式I：其中Ar1代表苯基或包含萘基的基团; Ar2表示苯基或包含萘基的基团; R'代表取代基; R“= H或取代基; n = 0,1,2或3; m = 0或1;并且n'= 1或2，条件是如果n = 0，则m = 0。