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(54) **ELECTRONIC DEVICE COMPRISING AN ORGANIC SEMICONDUCTOR, AN ORGANIC SEMICONDUCTOR, AND AN INTERMEDIATE BUFFER LAYER MADE OF A POLYMER THAT IS CATIONICALLY POLYMERIZABLE AND CONTAINS NO PHOTOACID**

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(57) **ABSTRACT**

The present invention describes a novel design principle for organic electronic elements by inserting at least one additional crosslinkable layer. The properties of the electronic devices are thereby improved. Structured construction of these devices is furthermore facilitated.

ELECTRONIC DEVICE COMPRISING AN ORGANIC SEMICONDUCTOR, AN ORGANIC SEMICONDUCTOR, AND AN INTERMEDIATE BUFFER LAYER MADE OF A POLYMER THAT IS CATIONICALLY POLYMERIZABLE AND CONTAINS NO PHOTOACID

[0001] Electronic devices which contain organic, metallorganic or polymeric semiconductors, or compounds of more than one of these three groups, are more and more frequently being used in commercial products or are shortly to be introduced onto the market. Examples of existing commercial products include organic-based charge transport materials (generally triarylamine-based hole transporters) in copiers and organic or polymeric light emitting diodes (OLEDs or PLEDs) in display devices. Organic solar cells (O-SCs), organic field effect transistors (O-FETs), organic circuit elements (O-ICs) or organic laser diodes (O-lasers) are at a highly advanced research stage and could become very important in the future.

[0002] Irrespective of the intended purpose, many of these devices have the following general layer structure which is adapted accordingly for the individual applications:

[0003] (1) substrate

[0004] (2) contacting: conductive substance, electrode; often metallic or inorganic, but also of organic or polymeric conductive materials

[0005] (3) optionally charge injection layer or interlayer to compensate for unevennesses of the electrode ("Planarization Layer"), often of a conductive doped polymer

[0006] (4) organic semiconductor

[0007] (5) optionally insulating layer

[0008] (6) second contacting: as (2); second electrode, materials as mentioned in (2)

[0009] (7) interconnection

[0010] (8) encapsulation.

[0011] One advantage which many of these organic devices have, above all those which are based on polymeric or dendritic, or oligomeric semiconductors, is that they can be produced from solution which entails less technical and cost outlay than vacuum processes, as are generally carried out for low molecular weight compounds. For example, colored electroluminescent devices can be produced comparatively simply by processing the materials by surface coating from solution (for example by spin coating, doctor blade technique, etc.). The structuring, i.e. driving of individual image points, is usually carried out here in the "leads", i.e. for example in the electrodes. This may, for example, be done using shadow masks in the manner of a template. The structuring of organic circuits and partially organic solar cell panels or laser arrays can be carried out similarly. For industrial mass production, however, this leads to significant disadvantages: after they have been used one or more times, the masks become unusable because of deposit formation, and must be elaborately regenerated. For production, it would therefore be desirable to have a process available for which shadow masks are not required.

[0012] Surface coating and structuring by shadow masks furthermore cannot be readily employed when, for example, full-color displays or organic circuits with different circuit elements are to be produced. For full-color displays, the three primary colors (red, green and, blue) in individual pixels (image points) must be applied next to one another with a high resolution. Similar considerations apply to electronic circuits with different circuit elements. While the individual image points can be produced by evaporating the individual colors using shadow masks in the case of low molecular weight evaporatable molecules (with the associated difficulties already mentioned above), this is not possible for polymeric materials and materials processed from solution, and the structuring can no longer be carried out merely by structuring the electrodes. An alternative in this case is to directly apply the active layer in a structured form (for example: the light emitting layer in OLEDs/PLEDs; similar considerations apply to lasers or charge transport layers in all applications). The fact that this presents considerable problems can be understood merely from the dimensions: it is necessary to provide structures in the range of a few tens of μm with layer thicknesses in the range of from less than 100 nm to a few μm. In particular, various printing techniques have recently been considered for this, for example inkjet printing, offset printing, etc. These printing techniques have their own problems, however, and none of them has yet been developed so that it might be usable for a mass production process. The aforementioned mask technology is furthermore used here (in the field of OLEDs) for the electrodes. Here again, this entails the aforementioned problems of deposit formation. Structurability by printing techniques must therefore still currently be regarded as an unresolved problem.

[0013] Another approach to structurability has been proposed in WO 02/10129 and *Nature* 2003, 421, 829. There, structurable materials are described which are suitable for use in structured devices such as OLEDs, PLEDs, organic lasers, organic circuit elements or organic solar cells. These are organic, in particular electroluminescent materials, which contain at least one oxetane group capable of crosslinking, the crosslinking reaction of which can be deliberately initiated and controlled. *Macromol. Rapid Commun.* 1999, 20, 225 describes N,N,N',N'-tetraphenylbenzidines functionalized with oxetane groups, which can be crosslinked in a photoinduced way. These compound classes are used as structurable hole conductors directly on the anode of the organic electronic device. At least one photoinitiator is added to the materials for crosslinking. By exposure to actinic radiation, an acid is generated which initiates a crosslinking reaction by cationic ring-opening polymerization. A pattern of regions with crosslinked material and regions with uncrosslinked material can thus be obtained by structured exposure. The regions of uncrosslinked material can then be removed by suitable operations (for example washing with suitable solvents). This leads to the desired structuring. The subsequent application of the various layers (or other materials which are to be applied in proximity to the first material) can thus be carried out after the crosslinking is completed. Exposure, as employed for the structuring, is a standard process in modern electronics and can, for example, be carried out with lasers or by surface exposure using a suitable photomask. The mask does not involve the risk of deposition here, since in this case only radiation and no material flux has to be

delimited by the mask. In *Chem Phys Chem* 2000, 207, such a crosslinked triarylamine layer is introduced as an interlayer between a conductive doped polymer and an organic luminescent semiconductor. A higher efficiency is obtained in this case. Here again, a photoacid is used for the crosslinking. This appears to be necessary for complete crosslinking of the triarylamine layer. However, the photoacid or its reaction products remain as contamination in the electronic device after the crosslinking. It is generally acknowledged that both organic and inorganic impurities can perturb the operation of organic electronic devices. For this reason, it would be desirable to be able to reduce the use of photoacids as much as possible.

[0014] EP 0637899 proposes electroluminescent arrangements having one or more layers in which at least one layer is obtained by thermal or radiation-induced crosslinking, which furthermore contain at least one emitter layer and at least one charge transport unit per layer. The crosslinking may take place radically, ionically, cationically or via a photoinduced ring closure reaction. An advantage mentioned is that a plurality of layers can thereby be formed on one another, or that the layers can also be structured in a radiation-induced way. However, no teaching is given as to which of the various crosslinking reactions can be used to produce a suitable device, and how the crosslinking reaction can best be carried out. It is merely mentioned that radically crosslinkable units or groups capable of photocycloaddition are preferred, that various types of auxiliaries, for example initiators, may be contained and that the film is preferably crosslinked by means of actinic radiation and not thermally. Suitable device configurations are also not described. It is therefore unclear how many layers the device preferably comprises, and how thick they should be, which material classes are preferably used and which of them should be crosslinked. It is therefore also not apparent to the person skilled in the art how the described invention can be successfully implemented in practice.

[0015] In devices for organic electronics, an interlayer of a conductive doped polymer is often introduced as a charge injection layer between the electrode (in particular the anode) and the function material (*Appl. Phys. Lett.* 1997, 70, 2067-2069).

[0016] Alternatively, a conductive doped polymer may also be used directly as the anode (or even as the cathode, depending on the application). The most common of these polymers are polythiophene derivatives (for example poly(ethylenedioxythiophene), PEDOT) and polyaniline (PANI), which are generally doped with polystyrene sulfonic acid or other polymer-bound Brönstedt acids and thus brought into a conductive state. Without wishing to be bound by the correctness of this special theory in the subsequent invention, we suspect that during operation of the device protons or other impurities diffuse from the acid groups into the functional layer where they are likely to perturb the functionality of the device significantly. It is thus suspected that these impurities reduce the efficiency as well as the lifetime of the devices. Protons or other cationic impurities have a negative effect in particular when the functional semiconductor layer applied onto this layer is cationically crosslinkable and, as described above, is intended to be structured. We suspect that the functional layer is already partially or fully crosslinked by the presence of protons or other cationic impurities, without providing the opportunity to control the crosslinking, for example by actinic radiation. The advantage of the controlled structurability is therefore lost. Cationically crosslinkable materials thus in principle do provide the possibility of structuring and therefore an alternative to printing techniques. However, technical implementation of these materials is not to date possible since the problem of uncontrolled crosslinking on a doped charge injection layer is not yet resolved.

[0017] Surprisingly, it has now been found that the electronic properties of the devices can be significantly improved when at least one buffer layer, which is cationically crosslinkable, is introduced between the doped interlayer and the functional organic semiconductor layer. Particularly good properties are obtained with a buffer layer whose cationic crosslinking is induced thermally, i.e. by a temperature rise to from 50 to 250° C., preferably from 80 to 200° C., and to which no photoacid is added. Another advantage of this buffer layer is that the uncontrollable crosslinking of a cationically crosslinkable semiconductor can be avoided by using the buffer layer, which for the first time permits controlled structuring of the semiconductor. Yet another advantage of crosslinking the buffer layer is that the glass transition temperature of the material and therefore the stability of the layer are increased by the crosslinking.

[0018] The invention therefore relates to electronic devices containing at least one layer of a conductive doped polymer and at least one layer of an organic semiconductor, characterized in that at least one conducting or semiconducting organic buffer layer which is cationically polymerizable, and to which less than 0.5% of a photoacid is added, is introduced between these layers.

[0019] It is preferable that no photoacid is added to the semiconducting organic buffer layer.

[0020] An organic buffer layer whose crosslinking in the corresponding device arrangement can be induced thermally, i.e. by a temperature rise to 50-250° C., preferably 80-200° C., without adding further auxiliaries, for example photoacids, is furthermore preferred.

[0021] A photoacid is a compound which releases a protic acid by a photochemical reaction when exposed to actinic radiation. Examples of photoacids are 4-(thio-phenoxyphenyl)-diphenylsulfonium hexafluoroantimonate or {4-[(2-hydroxytetradecyl)-oxyl]-phenyl}-phenyliodonium hexafluoroantimonate and the like, as described for example in EP 1308781. The photoacid may be added for the crosslinking reaction, in which case a proportion of from approximately 0.5 to approximately 3% by weight is preferably selected according to the prior art.

[0022] Electronic devices in the context of this invention are organic or polymeric light emitting diodes (OLEDs, PLEDs, for example EP 0676461, WO 98/27136), organic solar cells (O-SCs, for example WO 98/48433, WO 94/05045), organic field effect transistors (O-FETs, for example U.S. Pat. No. 5,705,826, U.S. Pat. No. 5,596,208, WO 00/42668), field quench elements (FQDs, for example US 2004/017148), organic circuit elements (O-ICs, for example WO 95/31833, WO 99/10939), organic optical amplifiers or organic laser diodes (O-lasers, WO 98/03566). Organic in the context of this invention means that at least one layer of an organic conductive doped polymer, at least one conducting or semiconducting organic buffer layer and

at least one layer containing at least one organic semiconductor are present; further organic layers (for example electrodes) may also be present in addition to these. Moreover, layers which are not based on organic materials may also be present, for example inorganic interlayers or electrodes.

[0023] In the simplest case, the electronic device is constructed from a substrate (conventionally glass or a plastic sheet), an electrode, an intermediate layer of a conductive doped polymer, a crosslinkable buffer layer according to the invention, an organic semiconductor and a back electrode. This device is accordingly (depending on the application) structured, contacted and hermetically sealed, since the lifetime of such devices is drastically shortened in the presence of water and/or air. It may also be preferred to use a conductive doped polymer as the electrode material for one or both electrodes and not to introduce an interlayer of conductive doped polymer. For applications in O-FETs, in addition to the electrode and the back electrode (source and drain), it is furthermore necessary that the structure also contains a further electrode (gate) which is separated from the organic semiconductor by an insulator layer generally having a high dielectric constant. It may furthermore be expedient to introduce yet other layers into the device.

[0024] The electrodes are selected so that their potential coincides as well as possible with the potential of the adjacent organic layer, in order to ensure maximally efficient electron or hole injection. If the cathode is to inject electrons, as is the case for example in OLEDs/PLEDs or n-type conducting O-FETs, or receive holes, as is the case for example in O-SCs, then metals with a low work function, metal alloys or multilayered structures comprising different metals, for example alkaline-earth metals, alkali metals, main group metals or lanthanides (for example Ca, Ba, Mg, Al, In, Mg, Yb, Sm, etc.) are preferred for the cathode. For multilayered structures, in addition to the aforementioned metals it is also possible to use other metals which have a relatively high work function, for example Ag, in which case combinations of the metals are generally used, for example Ca/Ag or Ba/Ag. The cathodes are conventionally between 10 and 10,000 nm, preferably between 20 and 1000 nm, thick. It may also be preferred to introduce a thin interlayer of a material having a high dielectric constant between a metal cathode and the organic semiconductor (or other functional organic layers which may optionally be present). Alkali metal or alkaline-earth metal fluorides, or alternatively the corresponding oxides, may for example be suitable for this (for example LiF, Li_2O, BaF_2, MgO, NaF, etc.). The layer thickness of this dielectric layer is preferably between 1 and 10 nm.

[0025] Materials with a high work function are preferred for the anode when holes are injected (as for example in OLEDs/PLEDs, p-type conducting O-FETs) or electrons are received (as for example O-SCs) at the anode. The anode preferably has a potential of more than 4.5 eV vs. vacuum. On the one hand, metals with a high redox potential are suitable for this, for example Ag, Pt or Au. Metal/metal oxide electrodes (for example Al/Ni/NiO_x, Al/Pt/PtO_x) may also be preferred. The anode may also consist of a conductive organic material (for example a conductive doped polymer).

[0026] For some applications, at least one of the electrodes must be transparent in order to allow either irradiation of the organic material (O-SCs) or output of light (OLEDs/PLEDs, O-lasers, organic optical amplifiers). A preferred construction uses a transparent anode. Preferred anode materials here are conductive mixed metal oxides. Indium-tin oxide (ITO) or indium-zinc oxide (IZO) are particularly preferred. Conductive doped organic materials, in particular conductive doped polymers, are furthermore preferred. A similar construction also applies to inverted structures, in which the light is output from the cathode or incident on the cathode. The cathode then preferably consists of the materials described above, with the difference that the metal is very thin and therefore transparent. The layer thickness of the cathode is preferably less than 50 nm, particularly preferably less than 30 nm, and in particular less than 10 nm. A further transparent conductive material is applied thereon, for example indium-tin oxide (ITO), indium-zinc oxide (IZO) etc.

[0027] Various organic doped conductive polymers may be suitable for the conductive doped polymer (either as an electrode or as an additional charge injection layer or "Planarization Layer", in order to compensate for unevennesses of the electrode and thus minimize short circuits). Polymers which have a conductivity of $>10^{-8}$ S/cm, depending on the application, are preferred here. In a preferred embodiment of this invention, the conductive doped polymer is applied onto the anode or functions directly as the anode. Here, the potential of the layer is preferably from 4 to 6 eV vs. vacuum. The thickness of the layer is preferably between 10 and 500 nm, particularly preferably between 20 and 250 nm. If the conductive doped polymer itself is the electrode, then the layers are generally thicker in order to ensure a good outward electrical connection and a low capacitive impedance. Derivatives of polythiophene are particularly preferably used (particularly preferably poly(ethylenedioxythiophene), PEDOT) and polyaniline (PANI). The doping is generally carried out using acids or oxidizing agents. The doping is preferably carried out using polymer-bound Brönsted acids. Generally polymer-bound sulfonic acids, in particular poly(styrene sulfonic acid), poly(vinyl sulfonic acid) and PAMPSA (poly(2-acrylamido-2-methylpropane sulfonic acid)) are particularly preferred for this. The conductive polymer is generally applied from an aqueous solution or dispersion and is insoluble in organic solvents. The subsequent layer can thereby be readily applied from organic solvents.

[0028] Low molecular weight oligomeric, dendritic or polymeric semiconducting materials are in principle suitable for the organic semiconductor. An organic material in the context of this invention is intended to mean not only purely organic materials, but also metallorganic materials and metal coordination compounds with organic ligands. The oligomeric, dendritic or polymeric materials may be conjugated, non-conjugated or partially conjugated. Conjugated polymers in the context of this invention are polymers which contain primarily sp^2-hybridized carbon atoms in the main chain, which may also be replaced by corresponding heteroatoms. In the simplest case, this means the alternate presence of double and single bonds in the main chain. Primarily means that naturally occurring defects, which lead to conjugation interruptions, do not invalidate the term "conjugated polymer". Furthermore, the term conjugated likewise applies in this application text when the main chain contains for example arylamine units and/or particular heterocycles (i.e. conjugation via N, O or S atoms) and/or

metallorganic complexes (i.e. conjugation via the metal atom). Units such as, for example, simple alkene chains, (thio)ether bridges, ester, amide or imide linkages would however be unequivocally defined as non-conjugated segments. Furthermore, the term conjugated organic material is also intended to include σ-conjugated polysilanes, -germylenes and analogues which carry organic side groups, and can therefore be applied from organic solvents, for example poly(phenylmethylsilane). Non-conjugated materials are materials in which no lengthy conjugated units occur in the main chain or in the dendrimer backbone. The term partially conjugated materials is intended to mean those materials which have lengthy conjugated sections in the main chain or in the dendrimer backbone, which are bridged by non-conjugated units, or which contain lengthy conjugated units in the side chain. Typical examples of conjugated polymers, as may for example be used in PLEDs or O-SCs, are poly-para-phenylenevinylene (PPV), polyfluorenes, polyspirobifluorenes or systems which are based in the broadest sense on poly-p-phenylene (PPP), and derivatives of the structures. Materials with a high charge carrier mobility are primarily of interest for use in O-FETs. These are for example oligo- or poly(triarylamines), oligo- or poly(thiophenes) and copolymers which contain a large proportion of these units.

[0029] The layer thickness of the organic semiconductor is preferably 10-500 nm, particularly preferably 20-250 nm, depending on the application.

[0030] Here, the term dendrimer is intended to mean a highly branched compound which is constructed from a multifunctional core to which branched monomers are bound in a regular structure, so that a tree-like structure is obtained. Both the core and the monomers may assume any branched structures which consist both of purely organic units and of organometallic compounds or coordination compounds. Here, dendrimers are to be understood as described for example in M. Fischer, F. Vögtle, *Angew. Chem., Int. Ed.* 1999, 38, 885-905.

[0031] In order to be able to apply a plurality of organic semiconductors above one another from solution, which is advantageous for many optoelectronic applications (for example PLEDs), crosslinkable organic layers have been developed (WO 02/10129). After the crosslinking reaction, these are insoluble and therefore can no longer be attacked by solvents during the application of further layers. Crosslinkable organic semiconductors also have advantages for the structuring of multicolored PLEDs. The use of crosslinkable organic semiconductors is thus furthermore preferred. Preferred crosslinking reactions are cationic polymerizations, based on electron-rich olefin derivatives, heteronuclear multiple bonds with heteroatoms or heterogroups or rings with heteroatoms (for example O, S, N, P, Si, etc.). Particularly preferred crosslinking reactions are cationic polymerizations based on rings with heteroatoms. Such crosslinking reactions are described in detail below for the buffer layer according to the invention.

[0032] Semiconducting luminescent polymers which can be chemically crosslinked are generally disclosed in WO 96/20253. Oxetane-containing semiconducting polymers, as described in WO 02/10129, have proved particularly suitable. They can be crosslinked deliberately and in a controlled way by adding a photoacid and irradiation. Crosslinkable low molecular weight compounds may furthermore be suitable, for example cationically crosslinkable triarylamines (M. S. Bayer et al., *Macromol. Rapid Commun.* 1999, 20, 224-228; D. C. Müller et al., *Chem Phys Chem* 2000, 207-211). These descriptions are incorporated into the present invention by reference.

[0033] Without wishing to be bound by a particular theory, we suspect that hydrogen atoms or other cationic impurities contained in the conductive doped polymer can already initiate a cationic polymerization when a cationically crosslinkable semiconductor is applied thereon, and therefore make the latter impossible to structure. But even layers of organic semiconductors, which are not cationically crosslinkable, on conductive doped polymers are problematic since impurities and their diffusion out of the doped polymer are likely to limit the lifetime of the electronic device. Furthermore, the hole injection out of the doped polymer into the organic semiconductor is often unsatisfactory.

[0034] According to the invention, therefore, the introduction of a buffer layer which is introduced between the conductive doped polymer and the organic semiconductor, and which carries the cationically crosslinkable units, is such that it can absorb low molecular weight cationic species and intrinsic cationic charge carriers which may diffuse out of the conductive doped polymer. Before the crosslinking, the buffer layer may be both low molecular weight and oligomeric, dendritic or polymeric. The layer thickness is preferably in the range of 5-300 nm, particularly preferably in the range of 10-200 nm. The potential of the layer preferably lies between the potential of the conductive doped polymer and that of the organic semiconductor. This can be achieved by a suitable choice of the materials for the buffer layer and suitable substitution of the materials.

[0035] Preferred materials for the buffer layer are derived from hole-conductive materials, such as those used as hole conductors in other applications. Cationically crosslinkable triarylamine-based, thiophene-based or triarylphosphine-based materials or combinations of these systems are particularly preferably preferred for this. Copolymers with other monomer units, for example fluorene, spirobifluorene, etc., with a high proportion of these hole-conductive units are also suitable. The potentials of these compounds can be adjusted by suitable substitution. By the introduction of electron-withdrawing substituents (for example F, Cl, CN, etc.) for instance, it is possible to achieve compounds with a low HOMO (=highest occupied molecular orbital), while a high HOMO can be achieved by introduction of electron-repelling substituents (for example alkoxy groups, amino groups, etc.).

[0036] The buffer layer according to the invention may comprise low molecular weight compounds which are crosslinked in the layer and thus rendered insoluble. Oligomeric, dendritic or polymeric soluble solutions, which are rendered insoluble by subsequent cationic crosslinking, may also be suitable. Mixtures of low molecular weight compounds and oligomeric, dendritic and/or polymeric compounds may furthermore be used. Without wishing to be bound by a special theory in this invention, cationic species that can diffuse out of the conductive doped polymer are firstly protons which may originally come from the dopant being used (often polymer-bound sulfonic acids) but also

ubiquitous water. Cationic species, for example metal ions, may also be present as (undesired) impurities in the conductive polymer. Another possible source of cationic species is the electrode on which the conductive polymer is applied. For example, indium ions may emerge from an ITO electrode and diffuse into the active layers of the devices. Other low molecular weight cationic species that may possibly be present are monomeric and oligomeric constituents of the conductive polymer, which are converted into a cationic state by protonation or by other doping. It is furthermore possible for charge carriers introduced by oxidative doping to diffuse into the semiconductor layer. The cationically crosslinkable buffer layer can trap diffusing cationic species so that the crosslinking reaction is subsequently initiated; on the other hand, the buffer layer is simultaneously rendered insoluble by the crosslinking, so that the subsequent application of an organic semiconductor from conventional organic solvents presents no problems. The crosslinked buffer layer represents a further barrier against diffusion.

[0037] Preferred cationically polymerizable groups of the buffer layer are the following functional groups:

[0038] 1) electron-rich olefin derivatives,

[0039] 2) heteronuclear multiple bonds with heteroatoms or heterogroups, or

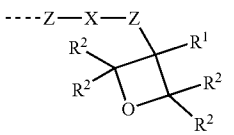
[0040] 3) rings with heteroatoms (for example O, S, N, P, Si, etc.), which react by cationic ring-opening polymerization.

[0041] Organic materials which carry at least one substituent that reacts by cationic ring-opening polymerization are preferred. A general review of cationic ring-opening polymerization is given, for example, by E. J. Goethals et al., "Cationic Ring Opening Polymerization" (*New Methods Polym. Synth.* 1992, 67-109). Non-aromatic cyclic systems, in which one or more ring atoms are identically or differently O, S, N, P, Si, etc., are generally suitable for this.

[0042] Cyclic systems having from 3 to 7 ring atoms, in which from 1 to 3 ring atoms are identically or differently O, S or N, are preferred. Examples of such systems are unsubstituted or substituted cyclic amines (for example aziridine, azeticine, tetrahydropyrrole, piperidine), cyclic ethers (for example oxiran, oxetane, tetrahydrofuran, pyran, dioxane), as well as the corresponding sulfur derivatives, cyclic acetals (for example 1,3-dioxolane, 1,3-dioxepane, trioxane), lactones, cyclic carbonates, but also cyclic structures which contain different heteroatoms in the cycle, for example oxazolines, dihydrooxazines or oxazolones. Cyclic siloxanes having from 4 to 8 ring atoms are furthermore preferred.

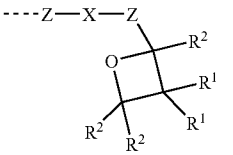
[0043] More particularly preferred are low molecular weight, oligomeric or polymeric organic materials in which at least one H atom is replaced by a group of the formula (I), (II) or (III),

Formula (I)

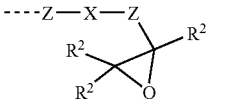


-continued

Formula (II)



Formula (III)



[0044] in which

[0045] R^1 in each occurrence is identically or differently hydrogen, a straight-chained, branched or cyclic alkyl, alkoxy or thioalkoxy group having from 1 to 20 C atoms, an aromatic or heteroaromatic ring system having from 4 to 24 aromatic ring atoms or an alkenyl group having from 2 to 10 C atoms, wherein one or more hydrogen atoms may be replaced by halogen such as Cl and F or by CN and one or more non-neighboring C atoms may be replaced by —O—, —S—, —CO—, —COO— or —O—CO—; a plurality of R^1 radicals may also form a mono- or polycyclic, aliphatic or aromatic ring system with one another or with R^2, R^3 and/or R^4;

[0046] R^2 in each occurrence is identically or differently hydrogen, a straight-chained, branched or cyclic alkyl group having from 1 to 20 C atoms, an aromatic or heteroaromatic ring system having from 4 to 24 aromatic ring atoms or an alkenyl group having from 2 to 10 C atoms, wherein one or more hydrogen atoms may be replaced by halogen such as Cl and F or by CN and one or more non-neighboring C atoms may be replaced by —O—, —S—, —CO—, —COO—or —O—CO—; a plurality of R^2 radicals may also form a mono- or polycyclic, aliphatic or aromatic ring system with one another or with R^1, R^3 and/or R^4;

[0047] X in each occurrence is identically or differently —O—, —S—, —CO—, —COO—, —O—CO— or a bivalent $—(CR^3R^4)_n—$ group;

[0048] Z in each occurrence is identically or differently a bivalent $—(CR^3R^4)_n—$ group;

[0049] R^3, R^4 in each occurrence is identically or differently hydrogen, a straight-chained, branched or cyclic alkyl, alkoxy or thioalkoxy group having from 1 to 20 C atoms, an aromatic or heteroaromatic ring system having from 4 to 24 aromatic ring atoms or an alkenyl group having from 2 to 10 C atoms, wherein one or more hydrogen atoms may be replaced by halogen such as Cl and F or by CN; two or more R^3 or R^4 radicals may also form a ring system with one another or with R^1 or R^2;

[0050] n in each occurrence is identically or differently an integer between 0 and 20, preferably between 1 and 10, in particular between 1 and 6;

with the proviso that the number of these groups according to formula (I) and/or formula (II) and/or formula (III) is limited by the maximally available, i.e. substitutable H atoms.

[0051] The crosslinking of these units is preferably carried out by thermal treatment of the device at this stage. It is not necessary, and not even desirable, to add a photoacid for the crosslinking since this would introduce impurities into the device. Without wishing to be bound by a special theory, we suspect that the crosslinking of the buffer layer is initiated by the protons emerging from the conductive doped polymer. This crosslinking preferably takes place at a temperature of from 80 to 200° C. and for a duration of from 0.1 to 120 minutes, preferably from 1 to 60 minutes, particularly preferably from 1 to 10 minutes, in an inert atmosphere. This crosslinking particularly preferably takes place at a temperature of from 100 to 180° C. and for a duration of from 20 to 40 minutes in an inert atmosphere. For the crosslinking, it may also be advantageous for further auxiliaries which are not photoacids, but which can promote the crosslinking, to be added to the buffer layer. Salts, in particular inorganic salts, for example tetrabutylammonium hexafluoroantimonate, which are added as a supporting electrolyte in order to improve the crosslinking, acids, in particular organic acids, for example acetic acid, or further addition of polystyrene sulfonic acid to the conductive polymer, or oxidizing substances, for example nitrylium or nitrosylium salts (NO^+, NO_2^+), may for example be suitable for this. After the crosslinking has been carried out, these auxiliaries can easily be washed out and therefore do not remain as contamination in the film. The auxiliaries have the advantage that the crosslinking can thereby be fully carried out more easily and that thicker buffer layers can thereby also be produced.

[0052] The following general method, which can be adapted appropriately to the particular case without any further inventive step, is in general employed for production of the devices:

[0053] A substrate (for example glass or a plastic) is coated with the anode (for example indium-tin oxide ITO, etc.). The anode is subsequently (for example photolithographically) structured and interconnected according to the intended application. In this case, the entire substrate and the corresponding interconnection may first be produced using a quite elaborate process so as to facilitate so-called active matrix control. The pre-cleaned substrate coated with the anode is treated either with ozone or with oxygen plasma or briefly exposed to an excimer lamp.

[0054] A conductive polymer, for example a doped polythiophene derivative (PEDOT) or polyaniline derivative (PANI) is subsequently applied in a thin layer, usually with a layer thickness of between 10 and 500 nm, preferably between 20 and 300 nm, onto the ITO substrate by spin coating or other coating methods.

[0055] The cationically crosslinkable buffer layer according to the invention is applied onto this layer. To this end, the corresponding compound is first dissolved in a solvent or solvent mixture and filtered. Since organic semiconductors and above all the surfaces of the layers are sometimes extremely influenced by oxygen or other air constituents, it is recommended to carry out this operation under a protective gas. Aromatic liquids, for example toluene, xylene, anisole, chlorobenzene and the like, for example cyclic ethers (for example, dioxane, methyldioxane, THF), as well as amides, for example NMP or DMF, but also solvent mixtures as described in application text WO 02/072714, are suitable as solvents for aromatic compounds. Other organic solvents, which are selected as a function of the compound class used, are also suitable for low molecular weight compounds. Using these solutions, the previously coated support can be coated or covered surface-wide, for example by spin-coating methods, flow or wave coating or doctor blade techniques. The crosslinking of the buffer layer can take place by heating the device at this stage in an inert atmosphere. Here, it is not necessary and not even desirable to add a photoacid; thermal treatment of the buffer layer on the doped polymer is sufficient in order to carry out the crosslinking reaction. Optionally, it may subsequently be flushed with a solvent, for example THF. It is then optionally dried.

[0056] A solution of an organic semiconductor is then applied. The choice of the semiconductor depends on the intended application. If a crosslinkable organic semiconductor is used, this may be structured according to the intended application by controlled crosslinking. In the case of cationically crosslinkable semiconductors, for example, this may be done by adding a photoacid, exposure through a shadow mask and subsequent thermal treatment. Since the underlying buffer layer is not acidic, the use of a photoacid should not be ruled out here. The uncrosslinked part of the semiconductor may subsequently be washed with an organic solvent in which the semiconductor is soluble. This process can be repeated for different materials, so as to successively apply a plurality of materials in a structured way. For example, electroluminescent polymers with different emission colors may be successively applied in a structured way for a full-color display, or organic field effect transistors with different functions may be successively applied for organic circuits. It is also possible to apply a plurality of crosslinkable layers above one another.

[0057] Further functional layers, for example charge injection or transport layers, further emission layers and/or hole blocking layers may optionally be applied on these polymer layers, for example from solution by methods such as those described for the buffer layer, but also by evaporation.

[0058] A cathode is subsequently applied. This is carried out according to the prior art by a vacuum process and may, for example, be done by thermal evaporation or plasma spraying (sputtering). The cathode may be applied surface-wide or using a mask so that it is structured. The contacting of the electrodes is then carried out.

[0059] Since many applications react sensitively to water, hydrogen or other constituents of the atmosphere, effective encapsulation of the device is indispensable.

[0060] The structure described above is adapted accordingly for the individual applications and can generally be used for different applications, such as organic and polymeric light emitting diodes, organic solar cells, organic field effect transistors, organic circuit elements, organic optical amplifiers or organic laser diodes.

[0061] Surprisingly, this crosslinkable buffer layer, which is introduced between the conductive doped polymer and the organic semiconductor, offers the following advantages:

[0062] 1) Introducing the crosslinkable buffer layer according to the invention improves the optoelectronic properties of the electronic device compared with a

device which does not contain such a buffer layer. For instance, a high efficiency and a longer lifetime with a reduced operating voltage are observed. It turns out that this effect is particularly pronounced when the crosslinking of the buffer layer is thermally initiated. If a photoacid is added to the buffer layer for crosslinking, as described in the literature, the lifetime remains virtually unchanged.

[0063] 2) Since the buffer layer probably traps cationic species which emerge from the conductive doped polymer, they are prevented from diffusing into the organic semiconductor. If the organic semiconductor is a cationically crosslinkable compound, then undesired crosslinking of the semiconductor is thereby avoided. This for the first time allows controlled structuring of the semiconductor, which has not previously been possible in this way.

[0064] The present invention will be explained in more detail by the following examples, which are not meant to restrict it. Only organic and polymeric light emitting diodes will be discussed in these examples. Without any inventive step, however, the person skilled in the art will be able to produce other electronic devices on the basis of the examples given, for example O-SCs, O-FETs, O-ICs, optical amplifiers and O-lasers, to mention only a few further applications.

EXAMPLES

Example 1

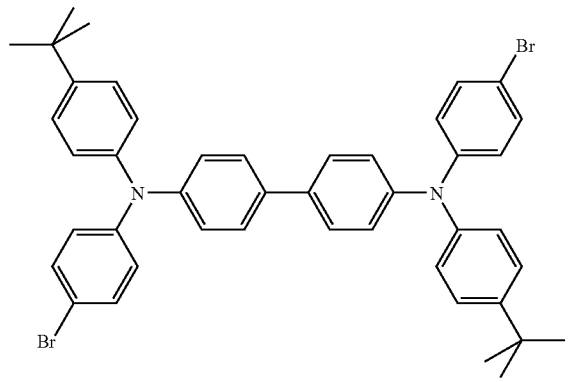
Synthesis of a Cationically Crosslinkable Compound P1 for Use as a Buffer Layer

a) Synthesis of Precursors Known from the Literature

[0065] 3-Ethyl-3-(iodomethyl)oxetane (WO 96/21657), 11-(4-bromophenoxy)-1-undecanol (M. Trollsaas et al., *Macromol. Chem. Phys.* 1996, 197, 767-779) and N,N'-diphenylbenzidine (K. Wiechert et al., *Zeitschrift Chem.* 1975, 15, 49-50) were synthesized according to the literature.

b) Synthesis of N,N'-Bis-(4-bromophenyl)-N,N'-bis-(4-tert-butylphenyl)-biphenyl-4,4'-diamine (monomer M1)

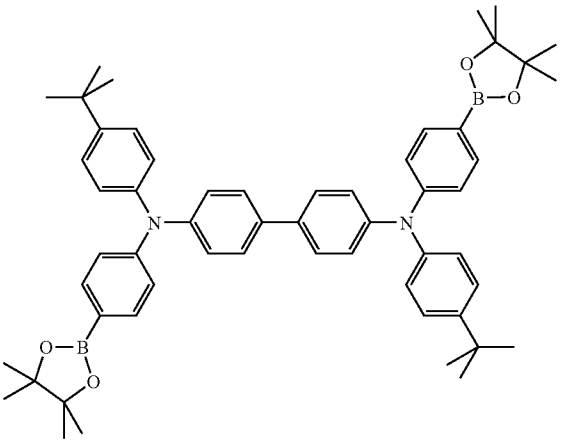
[0066]



[0067] The synthesis of monomer M1 is described in WO 02/077060.

c) Synthesis of N,N'-Bis-(4-pinacol boronate)phenyl-N,N'-bis-(4-tert-butylphenyl)-biphenyl-4,4'-diamine (monomer M2)

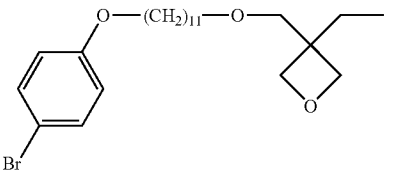
[0068]



[0069] The synthesis of monomer M2 is described in application DE 10337077.3 which has not yet been laid open.

d) Synthesis of 3-(11-(4-bromophenoxy)-undecan-1-oxy)methylene-3-ethyl-oxetane

[0070]

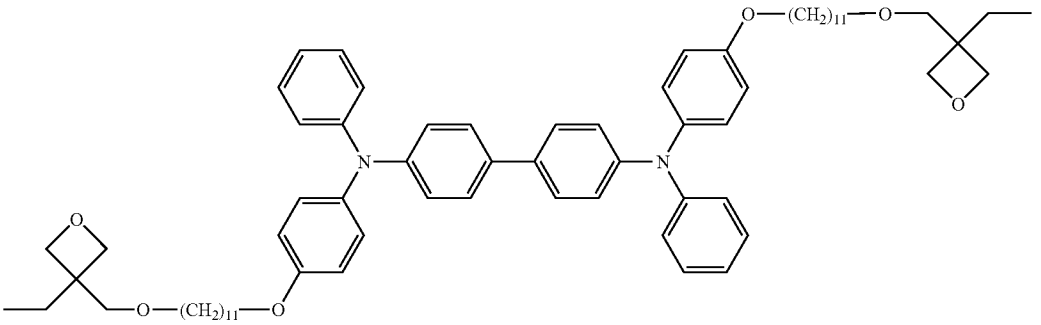


[0071] 1.6 g (30 mmol) of NaH were suspended in 70 ml of dry DMF and stirred under a protective gas. A solution of 6.8 g (20 mmol) 11-(4-Bromophenoxy)-1-undecanol in 25 ml of DMF was added thereto at 40° C. After 1 h, 2.96 g (22 mmol) of 3-ethyl-3-(iodomethyl)oxetane and 0.166 g (1.0 mmol) of KI were added and stirred for 24 h at 40° C. After cooling to room temperature, 200 ml of water and 200 ml of CH_2Cl_2 were added to the reaction mixture, the organic phase was separated, dried over Mg_2SO_4 and the solvent was removed in a vacuum. The product was purified chromatographically (silica, eluent hexane). The yield was 3.2 g (89% Th.) and the purity was 98% (according to HPLC).

[0072] ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.45 (t, J=7.3 Hz, 3H), 1.45 (m, 14H), 1.55 (m, 2H), 1.75 (m, 4H), 3.42 (t, J=6.3 Hz, 2H), 3.46 (s, 2H), 3.85 (t, J=6.3 Hz, 2H), 4.39 (d, J=5.9 Hz, 2H), 4.44 (d, J=5.9 Hz, 2H), 6.75 (d, J=9 Hz, 2H), 7.35 (d, J=9 Hz, 2H).

e) Synthesis of oxetane-substituted N,N,N',N'-tetraphenylbenzidine

[0073]

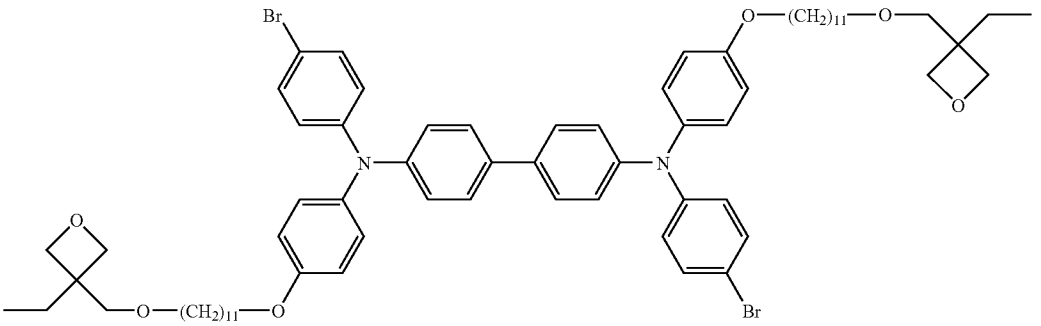


[0074] A degassed solution of 5.1 g (9.7 mmol) N,N'-diphenylbenzidine and 14 g (21.4 mmol) 3-(11-(4-bromophenoxy)-undecan-1-oxy)methylene-3-ethyl-oxetane in 250 ml of toluene was saturated for 1 h with N_2. First 0.12 g (0.39 mmol) of $P(^tBu)_3$ then 69 mg (0.19 mmol) of $Pd(OAc)_2$ were added to the solution. 3.8 g (50.4 mmol) of solid NaO^tBu were subsequently added. The reaction mixture was heated for 5 h under reflux. After cooling to room temperature, 0.85 g NaCN and 10 ml of water were added. The organic phase was washed with 4×50 ml of H_2O, dried over $MgSO_4$ and the solvent was removed in a vacuum. The pure product was obtained by recrystallization from dioxane with a purity of 99.2% (according to HPLC). The yield was 12 g (75% Th.).

[0075] ^{1}H-NMR ($CDCl_3$, 500 MHz): 0.81 (t, J=7.3 Hz, 6H), 1.17 (t, J=7.0 Hz, 12H), 1.23-1.35 (m, 28H), 3.94 (t, J=6.3 Hz, 4H), 4.03 (t, J=6.3 Hz, 8H), 4.21 (d, J=5.9 Hz, 4H), 4.29 (d, J=5.9 Hz, 4H), 6.91-7.01 (m, 14H), 7.04 (d, J=9 Hz, 4H), 7.27 (d, J=8 Hz, 4H), 7.49 (d, J=8.7 Hz, 4H).

f) Synthesis of oxetane-substituted, brominated N,N,N',N'-tetraphenylbenzidine (monomer M3)

[0076]



[0077] 45.72 g (43.7 mmol) of oxetane-substituted N,N,N',N'-tetraphenylbenzidine were prepared in 500 ml of THF. A solution of 15.15 g (84.4 mmol) NBS in 300 ml of THF was added drop-wise thereto at 0° C. while excluding light. It was allowed to reach RT and stirred for a further 4 h. 500 ml of water were added, and the mixture was extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and the solvent was removed in a vacuum. The product was hot extracted by stirring with hexane and suctioned. After repeated chromatographic purification (silica, hexane/ethyl acetate 4:1), the product was obtained with a yield of 44 g (85% Th.) as a pale brown oil which had a purity of 99.2% (according to HPLC).

[0078] ^{1}H-NMR (DMSO-d_6, 500 MHz): 0.81 (t, J=7.3 Hz, 6H), 1.17 (t, J=7.0 Hz, 12H), 1.23-1.35 (m, 28H), 3.94 (t, J=6.3 Hz, 4H), 4.03 (t, J=6.3 Hz, 8H), 4.21 (d, J=5.9 Hz, 4H), 4.29 (d, J=5.9 Hz, 4H), 6.91-7.02 (m, 12H), 7.04 (d, J=9 Hz, 4H), 7.29 (d, J=8 Hz, 4H), 7.51 (d, J=8.7 Hz, 4H).

g) Polymer synthesis: Synthesis of Polymer P1

[0079] 1.7056 g (2 mmol) of monomer M2, 0.9104 g (1.2 mmol) of monomer M1, 0.9723 g (0.8 mmol) of monomer M3 and 2.03 g (4.4 mmol) of hydrated potassium phosphate were dissolved in 12.5 ml of toluene, 12.5 ml of dioxane and 12 ml of water (all the solvents free of oxygen) and degassed at 40° C. for 30 minutes with an argon stream. 0.90 mg of

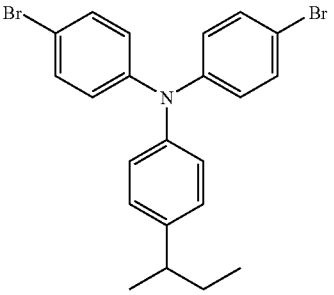
$Pd(OAc)_2$ and 6.30 mg of $P(o\text{-}tol)_3$ were added as a catalyst, and the reaction mixture was heated for 3 h under reflux. 20 ml of toluene and as an end capper 12 mg (0.04 mmol) of 3,4-bispentoxybenzeneboronic acid were added, heated for 1 h under reflux, then 20 mg (0.06 mmol) of 3,4-bispentoxybenzene bromide were added and heated for 1 h under reflux. The reaction solution was cooled to 65° C. and extracted by stirring for 4 h with 10 ml of 5% strength aqueous sodium N,N-diethyidithiocarbamate solution. The organic phase was washed with 3×80 ml of water and precipitated by adding it in two times the volume of methanol. The raw polymer was dissolved in chlorobenzene, filtered using celite and precipitated by adding two times the volume of methanol. 2.24 g (78% Th.) of the polymer P1 were obtained.

Example 2

Synthesis of a Cationically Crosslinkable Polymer P2 for use as a Buffer Layer

a) Synthesis of bis-(4-bromophenyl)-(4-^{sec}butylphenyl)-amine (monomer M4)

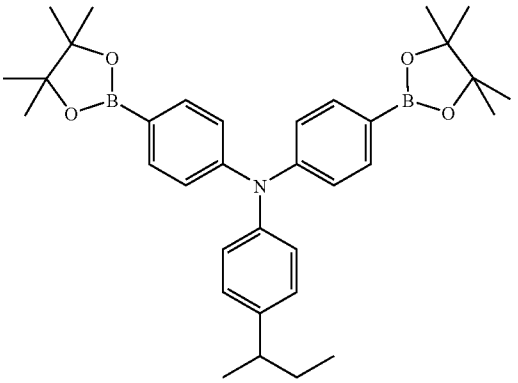
[0080]



[0081] The synthesis of M4 was carried out in analogy with the synthesis in DE 19981010.

b) Synthesis of Bis-((4-pinacole boronate)phenyl)-(4-^{sec}butylphenyl)-amine (monomer M5)

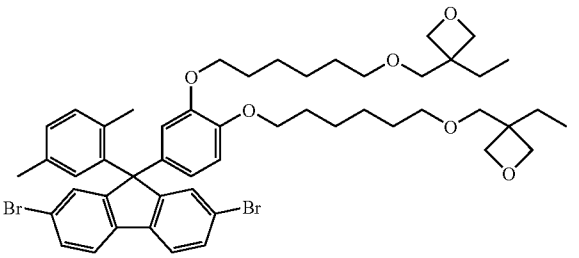
[0082]



[0083] The synthesis of monomer M5 is described in application DE 10337077.3 which has not yet been laid open.

c) Synthesis of 2,7-dibromo-(2,5-dimethylphenyl)-9-(3,4-di(3-ethyl(oxetane-3-ethyloxy)-hexyloxyphenyl))-fluorene (monomer M6)

[0084]



[0085] The synthesis of monomer M6 is described in C. D. Müller et al., *Nature* 2003, 421, 829.

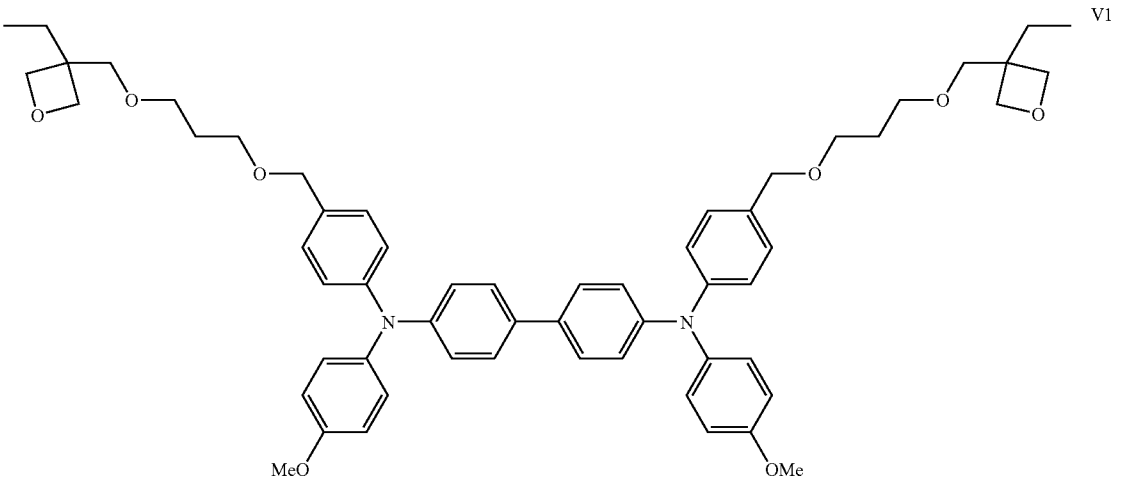
d) Polymer synthesis: Synthesis of Polymer P2

[0086] 1.4695 g (3.2 mmol) of monomer M4, 2.2134 g (4 mmol) of monomer M5, 0.7463 g (0.8 mmol) of monomer M6 and 4.05 g (8.8 mmol) of hydrated potassium phosphate were dissolved in 25 ml of toluene, 25 ml of dioxane and 25 ml of water (all solvents free of oxygen) and degassed at 40° C. for 30 minutes in an argon stream. 1.80 mg of $Pd(OAc)_2$ and 14.61 mg of $P(o\text{-}tol)_3$ were then added, and the reaction mixture was heated for 10 h under reflux. The initial amounts of $Pd(OAc)_2$ and $P(o\text{-}tol)_3$ were respectively added after 4 h, after 5.5 h and after 8.5 h. 2 ml of toluene were added after a reaction time of 8 h. 24 mg (0.08 mmol) of 3,4-bispentoxybenzolboronic acid were added as an end capper, heated for 2 h under reflux, then 40 mg (0.12 mmol) of 3,4-bispentoxybenzenebromide were added and heated for 1 h under reflux. The reaction solution was cooled to 65° C. and then extracted by stirring for 4 h with 20 ml of a 5% strength aqueous solution of sodium N,N-diethyldithiocarbamate. The phases were separated and the process was repeated once more with 40 ml of the dithiocarbamate solution. The phases were separated, the organic phase was washed with 3×150 ml of water and precipitated by adding it in two times the volume of methanol. The raw polymer was dissolved in chlorobenzene, filtered using celite and precipitated by adding two times the volume of methanol. 1.84 g (64% Th.) of the polymer P2 were obtained, which is soluble in chlorobenzene but insoluble in toluene, THF or chloroform.

Example 3

Synthesis of a Cationically Crosslinkable Molecule V1 for use as a Buffer Layer

[0087]



[0088] The synthesis of the cationically crosslinkable molecule V1 is described in M. S. Bayer et al., *Macromol. Rapid Commun.* 1999, 20, 224-228.

[0089] The device results, which were obtained when using the polymers P1 and P2 or molecule V1 as the buffer layer, are summarized in Examples 6-8.

Example 4

Production of LEDs with an Additional Buffer Layer

[0090] The LEDs were produced according to a general method which was adapted to the respective conditions (for example solution viscosity and optimal layer thickness of the functional layers in the device) in the particular case. The LEDs described below were respectively three-layer systems (three organic layers), i.e. substrate//ITO//PEDOT//buffer layer//polymer//cathode. PEDOT is a polythiophene derivative (Baytron P4083 from H. C. Stark, Goslar). Ba from Aldrich and Ag from Aldrich were used for the cathode in all cases. The way in which PLEDs can generally be produced is described in detail in WO 04/037887 and the literature cited therein.

[0091] In contrast to this, a cationically crosslinkable semiconductor was applied as a buffer layer on the PEDOT layer. Here, the crosslinkable polymers P1 and P2 or the crosslinkable low molecular weight compound V1 were used as materials for the buffer layer. A solution (with a concentration of 4-25 mg/ml in for example toluene, chlorobenzene, xylene etc.) of the crosslinkable material was taken and dissolved by stirring at room temperature. Depending on the material, it may also be advantageous to stir for some time at 50-70° C. After the complete dissolving of the compound, it was filtered through a 5 μm filter. The buffer layer was then spin coated at variable speeds (400-6000 rpm) with a spin coater in an inert atmosphere. The layer thicknesses could thus be varied in a range of from approximately 20 to 300 nm. The crosslinking was subsequently carried out by heating the device to 180° C. for 30 minutes on a hotplate in an inert atmosphere. The organic semiconductor and the cathode were then applied onto the buffer layer, as described in WO 04/037887 and the literature cited therein.

Example 5

Production of Structured LEDs with an Additional Buffer Layer

[0092] The structured LEDs were produced similarly as Example 4 up to and including the step of crosslinking the buffer layer. In contrast to this, cationically crosslinkable semiconductors were used for the organic semiconductors. These were red, green and blue emitting conjugated polymers based on poly-spirobifluorene, which were functionalized with oxetane groups. These materials and their synthesis are already described in the literature (*Nature* 2003, 421, 829). A solution (generally with a concentration of 4-25 mg/ml in for example toluene, chlorobenzene, xylene:cyclohexanone (4:1)) was taken and dissolved by stirring at room temperature. Depending on the compound, it may also be advantageous to stir for some time at 50-70° C. Approximately 0.5% by weight (expressed in terms of polymer) of the photoacid {4-[(2-hydroxytetradecyl)-oxyl]-phenyl}-phenyliodonium hexafluoroantimonate was added to the solutions of the cationically crosslinkable semiconductor. The solution of the first cationically crosslinkable semiconductor and the photoacid were then applied onto the crosslinked buffer layer by spin coating under comparable conditions as for the buffer layer. After drying the film, structured crosslinking was carried out by exposure to a UV lamp (10 W, 302 nm, 5 min.) using a mask. The film was

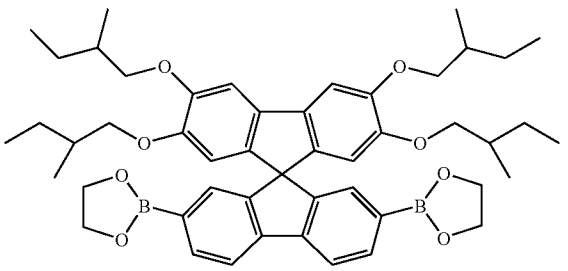
then heat-treated in an inert atmosphere for 3 minutes at 130° C., subsequently treated with a 10^{-4} molar $LiAlH_4$ solution in THF and washed with THF. The non-crosslinked positions in the film were thereby washed off. This process was repeated with the other solutions of the crosslinkable organic semiconductors, and the three primary colors were thereby successively applied in a structured way. The evaporation coating of the electrodes and the contacting were then carried out as described above.

Example 6

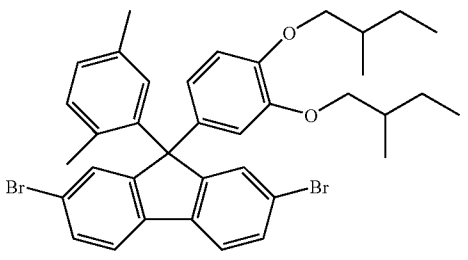
Lifetime Measurement of an LED with an Additional Buffer Layer P1

[0093] The LED was produced as described in Example 4. 20 nm of PEDOT were used. A 20 nm thick layer of polymer P1 was applied as the buffer layer, which was thermally crosslinked as described in Example 4. A blue emitting polymer was used as the semiconducting polymer (composition: 50 mol % monomer M7, 30 mol % monomer M8, 10 mol % monomer M1, 10 mol % monomer M9). The monomers are depicted below, and their synthesis is described in WO 03/020790. In electroluminescence, the polymer exhibits a lifetime (=brightness reduction to half the initial brightness) of approximately 1600 h at room temperature and an initial brightness of 300 cd/m^2. In a comparative LED without the buffer layer, under otherwise equal conditions, the polymer exhibits a lifetime of approximately 500 h. An LED was also produced whose buffer layer was photochemically crosslinked by adding 0.5% by weight of {4-[(2-hydroxytetradecyl)-oxyl]-phenyl}-phenyliodonium hexafluoroantimonate with exposure to UV radiation (3 s, 302 nm) and subsequent heating to 90° C. for 30 seconds. The buffer layer was then washed with THF and heated to 180° C. for 5 minutes. Under otherwise equal conditions, this LED had a lifetime of approximately 630 h.

M7

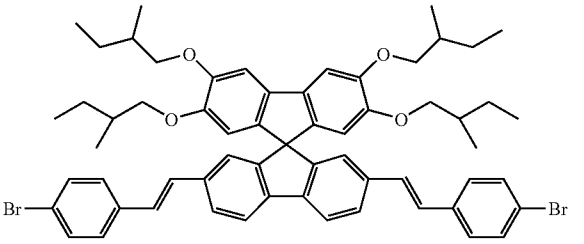


M8

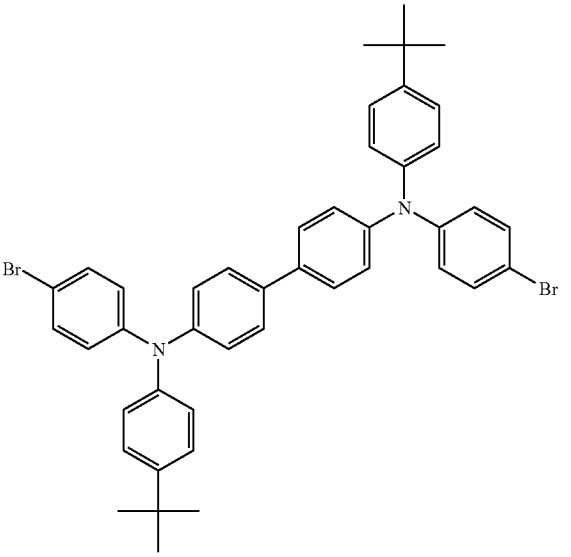


-continued

M9



M1



Example 7

Lifetime Measurement of an LED with an Additional Buffer Layer P2

[0094] The measurement was repeated with polymer P2 as the buffer layer, as described in Example 6 under otherwise identical conditions. The polymer exhibits a lifetime of approximately 1500 h without addition of photoacid to the buffer layer, and approximately 600 h with addition of photoacid.

Example 8

Lifetime Measurement of an LED with an Additional Buffer Layer V1

[0095] The measurement was repeated with compound V1 as the buffer layer, as described in Example 6 under otherwise identical conditions. The polymer exhibits a lifetime of approximately 1350 h without addition of photoacid to the buffer layer, and approximately 550 h with addition of photoacid.

1. An electronic device containing at least one layer of a conductive doped polymer and at least one layer of an organic semiconductor, characterized in that at least one conducting or semiconducting organic buffer layer which is

cationically polymerizable, and to which less than 0.5% of a photoacid is added, is introduced between these layers.

2. The electronic device as claimed in claim 1, characterized in that no photoacid is added to the buffer layer.

3. The electronic device as claimed in claim 1, characterized in that the crosslinking of the organic buffer layer is thermally initiated.

4. The electronic device as claimed in claim 1, wherein the electronic device comprises organic or polymeric light-emitting diodes (OLEDs, PLEDs), organic solar cells (O-SCs), organic field effect transistors (O-FETs), organic circuit elements (O-ICs), organic field quench devices (O-FQDs), organic optical amplifiers or organic laser diodes (O-lasers).

5. The electronic device as claimed in claim 1, wherein the electronic device contains the following elements: substrate, electrode, interlayer of a conductive doped polymer, conducting or semiconducting organic cationically crosslinkable buffer layer, organic semiconductor layer and back electrode.

6. The electronic device as claimed in claim 5, characterized in that an interlayer of a material with a high dielectric constant is introduced between a metal cathode and the organic semiconductor.

7. The electronic device as claimed in claim 1, characterized in that anode materials with a potential of more than 4.5 eV vs. vacuum are used.

8. The electronic device as claimed in claim 1, characterized in that the conductive doped polymer has a conductivity of $>10^{-8}$ S/cm and a potential of 4-6 eV vs. vacuum.

9. The electronic device as claimed in claim 8, characterized in that derivatives of polythiophene or polyaniline are used as the conductive polymer, and the doping is carried out via polymer-bound Brönsted acids.

10. The electronic device as claimed in claim 5, wherein said organic semiconductor is a low molecular weight oligomeric, dendritic or polymeric semiconducting material.

11. The electronic device as claimed in claim 10, characterized in that the organic semiconductor is a conjugated polymer.

12. The electronic device as claimed in claim 10, characterized in that the organic semiconductor is a cationically crosslinkable compound.

13. The electronic device as claimed in claim 12, characterized in that the cationic crosslinking takes place via ring-opening cationic polymerization of a heterocycle.

14. The electronic device as claimed in claim 13, characterized in that the cationic crosslinking takes place via oxetane groups which can be crosslinked via radiation by adding a photoacid.

15. The electronic device as claimed in claim 1, characterized in that the crosslinkable buffer layer is low molecular weight oligomeric, dendritic or polymeric before the crosslinking.

16. The electronic device as claimed in claim 1, characterized in that the layer thickness of the buffer layer lies in the range of 5-300 nm.

17. The electronic device as claimed in claim 1, characterized in that the potential of the buffer layer lies between the potential of the conductive doped polymer and that of the organic semiconductor.

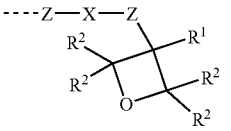
18. The electronic device as claimed in claim 1, characterized in that cationically crosslinkable hole-conductive materials are used for the buffer layer.

19. The electronic device as claimed in claim 18, characterized in that cationically crosslinkable triarylamine-based, thiophene-based or triarylphosphine-based materials are used for the buffer layer.

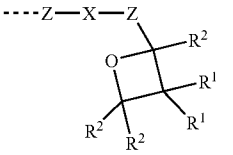
20. The electronic device as claimed in claim 1, characterized in that materials in which at least one H atom is replaced by a heterocyclic group, reacting by cationic ring-opening polymerization, are used as materials for the buffer layer.

21. The electronic device as claimed in claim 20, characterized in that the cationically polymerizable heterocycle is a group of the formula (I), (II) or (III),

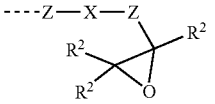
Formula (I)



Formula (II)



Formula (III)



in which

R^1 in each occurrence is identically or differently hydrogen, a straight-chained, branched or cyclic alkyl, alkoxy or thioalkoxy group having from 1 to 20 C atoms, an aromatic or heteroaromatic ring system having from 4 to 24 aromatic ring atoms or an alkenyl group having from 2 to 10 C atoms, wherein one or more hydrogen atoms may be replaced by halogen or by CN and one or more non-neighboring C atoms may be replaced by —O—, —S—, —CO—, —COO— or —O—CO—; a plurality of R^1 radicals may also form a mono- or polycyclic, aliphatic or aromatic ring system with one another or with R^2, R^3 and/or R^4;

R^2 in each occurrence is identically or differently hydrogen, a straight-chained, branched or cyclic alkyl group having from 1 to 20 C atoms, an aromatic or heteroaromatic ring system having from 4 to 24 aromatic ring atoms or an alkenyl group having from 2 to 10 C atoms, wherein one or more hydrogen atoms may be replaced by halogen or by CN and one or more non-neighboring C atoms may be replaced by —O—, —S—, —CO—, —COO— or —O—CO—; a plurality of R^2 radicals may also form a mono- or polycyclic, aliphatic or aromatic ring system with one another or with R^1, R^3 and/or R^4;

X in each occurrence is identically or differently —O—, —S—, —CO—, —COO—, —O—CO— or a bivalent $—(CR^3R^4)_n—$ group;

Z in each occurrence is identically or differently a bivalent —$(CR^3R^4)_n$— group;

R^3, R^4 in each occurrence is identically or differently hydrogen, a straight-chained, branched or cyclic alkyl, alkoxy or thioalkoxy group having from 1 to 20 C atoms, an aromatic or heteroaromatic ring system having from 4 to 24 aromatic ring atoms or an alkenyl group having from 2 to 10 C atoms, wherein one or more hydrogen atoms may be replaced by halogen or by CN; two or more R^3 or R^4 radicals may also form a ring system with one another or with R^1, R^2;

n in each occurrence is identically or differently an integer between 0 and 20;

with the proviso that the number of these groups according to formula (I) and/or formula (II) and/or formula (III) is limited by the maximally available, i.e. substitutable H atoms.

22. The electronic device as claimed in claim 21, characterized in that the crosslinking of these units is carried out by thermal treatment of the device.

23. The electronic device as claimed in claim 22, characterized in that the crosslinking takes place at a temperature of from 80 to 200° C. and for a duration of from 0.1 to 120 minutes in an inert atmosphere.

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