TRANSLATION CERTIFICATION

Date: 2025/07/31

To whom it may concern:

This is to certify that the attached translation is an accurate representation of the documents received by this office. The translation was completed from:

- German (Germany)

To:

- English (USA)

The documents are designated as:

- 'Tab 6 - WO2007054345A1.pdf'

Samuel Wu, Managing Director of this company, attests to the following:

“To the best of my knowledge, the aforementioned documents are a true, full and accurate translation of the specified documents.”

Signature of Samuel Wu, Managing Director

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
May 18, 2007 (05/18/2007)

PCT

(10) International Publication Number
WO 2007/054345 A1

(51) International Patent Classification:
H01L 51/50 (2006.01)

(21) International Application Number: PCT/EP2006/010816

(22) International Filing Date:
November 10, 2006 (11/10/2006)

(25) Language of Filing: German

(26) Language of Publication: German

(30) Priority Data:
05024515.8 November 10, 2005 (11/10/2005) EP

(71) Applicant *(for all designated States except US):* **NOVALED AG** [DE/DE]; Tatzberg 49, 01307 Dresden (DE).

(72) Inventors; and
(75) Inventors/Applicants *(for US only):* **LUX, Andrea** [DE/DE]; Beilstrasse 28, 01277 Dresden (DE). **WERNER, Ansgar** [DE/DE]; Altenberger Strasse 20, 01277 Dresden (DE). **SALBECK, Josef** [DE/DE]; Welleröderstrasse 12, 34260 Kaufungen (DE).

(74) Agents: **BITTNER, Thomas, L.** et al.; Boehmert & Boehmert, Hollerallee 32, 28209 Bremen (DE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available):* AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available):* ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For explanations of the two-letter codes and other abbreviations, see the "Guidance Notes on Codes and Abbreviations" at the beginning of each regular issue of the PCT Gazette.

WO 2007/054345 A1

(54) Title: DOPED ORGANIC SEMICONDUCTOR MATERIAL

(54) Title: DOPED ORGANIC SEMICONDUCTOR MATERIAL

(57) Abstract: The present invention relates to a doped organic semiconductor material comprising at least one organic matrix material doped with at least one dopant, the matrix material being selected from a group consisting of defined phenanthroline derivatives; and also to an organic light-emitting diode which comprises a semiconductor material of this kind.

(57) Abstract: The present invention relates to a doped organic semiconductor material comprising at least one organic matrix material doped with at least one dopant, the matrix material being selected from a group consisting of defined phenanthroline derivatives; and also to an organic light-emitting diode which comprises a semiconductor material of this kind.

Doped organic semiconductor material

The present invention relates to a doped organic semiconductor material as well as to an organic light-emitting diode (OLED) comprising this semiconductor material.

Since the demonstration of organic light-emitting diodes and solar cells in 1989 [C.W. Tang et al., Appl. Phys. Lett. 51 (12), 913 (1987)], devices made of organic thin films have been the subject of intensive research. Such layers possess advantageous properties for the mentioned applications, such as efficient electroluminescence for organic light-emitting diodes, high absorption coefficients in the visible light range for organic solar cells, low-cost material production and device fabrication for basic electronic circuits, among others. Organic light-emitting diodes have already attained commercial significance in display applications.

The performance characteristics of (opto)electronic multilayer devices are, among other things, determined by the ability of the layers to transport charge carriers. In the case of light-emitting diodes, ohmic losses in the charge transport layers during operation are related to conductivity, which directly influences the required operating voltage and also determines the thermal load on the device. Furthermore, depending on the charge carrier concentration in the organic layers, band bending occurs near a metal contact, which facilitates the injection of charge carriers and thus can reduce the contact resistance. Similar considerations lead to the conclusion that the efficiency of organic solar cells is also determined by the charge carrier transport properties.

By doping hole transport layers with a suitable acceptor material (p-doping) or electron transport layers with a donor material (n-doping), the charge carrier density in organic solids (and thus the conductivity) can be significantly increased. Furthermore, based on experience with inorganic semiconductors, applications are to be expected that rely specifically on the use of p- and n-doped layers in a single device, which would otherwise be unfeasible. US 5,093,698 describes the use of doped charge transport layers (p-doping of the hole transport layer by adding acceptor-like molecules, n-doping of the electron transport layer by adding donor-like molecules) in organic light-emitting diodes.

The following approaches are currently known for improving the conductivity of vapor-deposited organic layers:

1. Increasing charge carrier mobility by
   a) using electron transport layers consisting of organic radicals (US 5,811,833),
   b) creating highly ordered layers that allow optimal overlap of the molecules' π-orbitals.
2. Increasing the density of mobile charge carriers by
   a) purifying and gently handling materials to prevent the formation of charge carrier traps,
   b) doping organic layers using
      aa) inorganic materials (alkali metals: J. Kido et al., US 6,013,384; J. Kido et al., Appl. Phys. Lett. 73, 2866 (1998), oxidizing agents like iodine, $SbCl_5$, etc.)
      bb) organic materials (TNCQ: M. Maitrot et al., J. Appl. Phys., 60 (7), 2396–2400 (1986), F4TCNQ: M. Pfeiffer et al., Appl. Phys. Lett., 73 (22), 3202 (1998), BEDT-TTF: A. Nollau et al., J. Appl. Phys., 87 (9), 4340 (2000), naphthalene dicarboxylic acid amides: M. Thomson et al., WO 03/088271, cationic dyes: A.G. Werner, Appl. Phys. Lett. 82, 4495 (2003))
      cc) organometallic compounds (metallocenes: M. Thomson et al., WO 03/088271)
      dd) metal complexes ($Ru^0(terpy)_3$: K. Harada et al., Phys. Rev. Lett. **94,** 036601 (2005)

While sufficiently strong organic dopants already exist for p-doping (e.g., F4TCNQ), only inorganic materials, such as cesium, are available for n-doping. The use of such materials has already led to improved OLED performance parameters. For example, doping the hole transport layer with the acceptor material F4TCNQ drastically reduces the operating voltage of the light-emitting diode (X. Zhou et al., Appl. Phys. Lett., 78 (4), 410 (2001)). A similar effect is achieved by doping the electron transport layer with Cs or Li (J. Kido et al., Appl. Phys. Lett., 73 (20), 2866 (1998); J.-S. Huang et al., Appl. Phys. Lett., 80, 139 (2002)).

A major problem with n-doping has long been that only inorganic materials were available. However, the use of inorganic materials has the disadvantage that the atoms or molecules used can easily diffuse throughout the device due to their small size, making it difficult to fabricate sharply defined transitions between p-doped and n-doped regions.

In contrast, diffusion should play only a minor role when using large, space-filling organic molecules as dopants, since positional changes require overcoming higher energy barriers.

It has long been known, especially for organic polymer semiconductor materials, that effective electron transfer from a dopant (e.g., sodium) to the organic matrix (e.g., polyacetylene) is only possible if the difference between the HOMO energy level (= ionization potential) of the dopant and the LUMO energy level (= electron affinity) of the matrix is as small as possible.

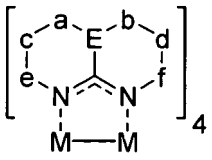
Ultraviolet photoelectron spectroscopy (UPS) is the preferred method for determining the ionization potential (e.g., R. Schlaf et al., J. Phys. Chem. B 103, 2984 (1999)). A related method, inverse photoelectron spectroscopy (IPES), is used to determine electron affinities (e.g., W. Gao et. al, Appl. Phys. Lett. 82, 4815 (2003)), but is less established. Alternatively, solid-state potentials can be estimated through electrochemical measurements of oxidation potentials (E_{ox}) and reduction potentials (E_{red}) in solution, e.g., via cyclic voltammetry (CV) (e.g., J.D. Anderson, J. Am. Chem. Soc. 120, 9646 (1998)). Several studies provide empirical formulas for converting the electrochemical voltage scale (oxidation potentials) into the physical (absolute) energy scale (ionization potentials), e.g., B.W. Andrade et al., Org. Electron. 6, 11 (2005); T.B. Tang, J. Appl. Phys. 59, 5 (1986); V.D. Parker, J. Am. Chem. Soc. 96, 5656 (1974); L.L. Miller, J. Org. Chem. 37, 916 (1972), Y. Fu et al., J. Amer. Chem. Soc. 127, 7227 (2005). There is no known correlation between reduction potential and electron affinity, as electron affinities are difficult to measure. Therefore, simplified conversions between the electrochemical and physical energy scales are made as follows: IP = 4.8 eV + e × E_{0X} (vs. ferrocene/ferrocenium) and EA = 4.8 eV + e × E_{red} (vs. ferrocene/ferrocenium), as described in B.W. Andrade, Org. Electron. 6, 11 (2005) (see also references 25–28 therein). The conversion of various standard potentials and redox pairs is, for example, described in A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, Wiley, 2nd edition, 2000.

From the above explanation, it follows that the precise determination of all energy values is currently not possible and that the values presented can only be regarded as reference points.

In n-doping, the dopant acts as an electron donor and transfers electrons to a matrix that is characterized by sufficiently high electron affinity—that is, the matrix is reduced. The transfer of electrons from the n-dopant to the matrix increases the charge carrier density in the layer. The extent to which an n-dopant is capable of donating electrons to a suitable electron-affine matrix, thereby increasing the charge carrier density and consequently the electrical conductivity, depends in turn on the relative positions of the HOMO of the n-dopant and the LUMO of the matrix. If the HOMO of the n-dopant lies above the LUMO of the electron-affine matrix, electron transfer can occur. If the HOMO of the n-dopant lies below the LUMO of the electron-affine matrix, electron transfer may also take place, provided the energy difference between the two orbitals is sufficiently small to allow for a certain thermal population of the higher-energy orbital. The smaller this energy difference, the higher the conductivity of the resulting layer should be. The highest conductivity is to be expected when the HOMO level of the n-dopant lies above the LUMO level of the electron-affine matrix. Conductivity is practically measurable and serves as an indicator of how well the electron transfer from donor to acceptor functions—assuming the charge carrier mobilities of the various matrices are comparable.

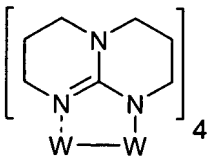
The conductivity of a thin-film sample is measured using the two-point method. In this method, contacts made from a conductive material (e.g., gold or indium tin oxide) are applied to a substrate. The thin film under investigation is then deposited over a large area on the substrate so that the contacts are covered by the thin film. After applying a voltage to the contacts, the resulting current is measured. From the geometry of the contacts and the thickness of the sample layer, the conductivity of the thin-film material is determined from the measured resistance. The two-point method is valid when the resistance of the thin film is significantly higher than the resistance of the leads or the contact resistance. Experimentally, this is ensured by a sufficiently large contact spacing, and the linearity of the current-voltage curve can be used for verification.

The inventors' investigations have shown that metal complex dopants having structure IV



Structure IV

are advantageous for use as dopants in an organic matrix material because such a dopant resolves the diffusion problem described above. For this reason, a dopant with structure IVa



Structure IVa = $W(hpp)_4$

was tested as a dopant for conventional electron transport materials, such as Alq_3 (tris(8-hydroxyquinolinato)aluminum) or BPhen (4,7-diphenyl-1,10-phenanthroline).

The gas-phase ionization potential of the dopant with structure IVa is 3.6 eV. The corresponding ionization potential in the solid state can be estimated in accordance with Y. Fu et al. (J. Am. Chem. Soc. 2005, 127, 7227–7234) and is approximately 2.5 eV.

The results are presented in the following Table 1.

Table 1: CV data, empirically determined LUMO energies, and measured conductivities of various electron transport materials ($BAlq_2$ = *bis(2-methyl-8-quinolinato)-4-(phenylphenolato)aluminum(III); BPhen = bathophenanthroline; Alq3 = tris(8-hydroxyquinoline)aluminum; Cl6-Alq = tris(5,7-dichloro-8-hydroxyquinoline)aluminum)*

Matrix material	LUMO in eV (determined by CV using Fc/Fc^+ as internal standard)	σ (conductivity) in S/cm undoped	σ (conductivity) in S/cm at a doping concentration of 5 mol%
Alq_3	2.4	< 1E-10	9.2E-8
BPhen	2.42	< 1E-10	4E-9
$BAlq_2$	2.39	< 1E-10	8e-8

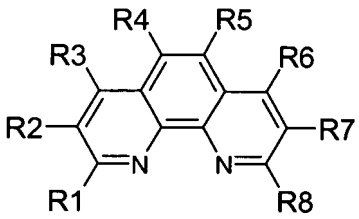
As can be seen from Table 1, the conductivities achieved with the known matrix materials are still insufficient and very low.

The object of the present invention is to provide a doped organic semiconductor material that overcomes the disadvantages of the prior art. In particular, a semiconductor material is to be provided that exhibits increased charge carrier density, effective charge carrier mobility, and improved conductivity. The semiconductor material should also demonstrate

high thermal stability, which can be evidenced by higher glass transition temperatures, higher sublimation temperatures, and higher decomposition temperatures.

Another object is to provide an organic light-emitting diode in which the semiconductor material according to the invention can be used.

This object is achieved by a doped organic semiconductor material comprising at least one organic matrix material doped with at least one dopant, wherein the matrix material is selected from the group consisting of phenanthroline derivatives having the following structures I, II, and III:



Structure I

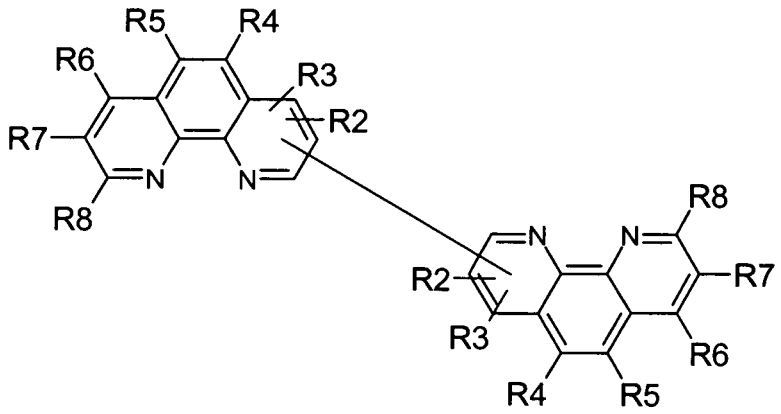
wherein:

R3 and R6 are independently selected from the group: H, C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, alkyloxy $-OR_X$, dialkylamino $-NR_xR_y$, alkylthio $-SR_X$, $-NO_2$, -CHO, $-COOR_X$, -F, -Cl, -Br, -I, -CN, -NC, -SCN, -OCN, $-SOR_X$, $-SO_2R_X$, wherein R_x and R_y = C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl;

aryl, heteroaryl, oligoaryl, oligoheteroaryl, and oligoarylheteroaryl, wherein all sp^2-hybridized carbon atoms that do not serve for ring linkage can independently be substituted with H, C_{1-20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, alkyloxy $-OR_X$, dialkylamino $-NR_xR_y$, alkylthio $-SR_X$, $-NO_2$, -CHO, $-COOR_X$, -F, -Cl, - Br, -I, -CN, -NC, -SCN, -OCN, $-SOR_X$, $-SO_2R_X$, wherein R_x and R_y = C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl; or combinations thereof;

R1, R2, R4, R5, R7, and R8 are not all simultaneously hydrogen but are otherwise independently selected from the group: H, C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, alkyloxy $-OR_X$, dialkylamino $-NR_xR_y$, alkylthio $-SR_X$, $-NO_2$, -CHO, $-COOR_X$, -F, -Cl, -Br, -I, -CN, -NC, -SCN, -OCN, $-SOR_X$, $-SO_2R_X$, wherein R_x and R_y = C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl;

aryl, heteroaryl, oligoaryl, oligoheteroaryl, and oligoarylheteroaryl, wherein all sp^2-hybridized carbon atoms that do not serve for ring linkage can independently be substituted with H, C_{1-20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, alkyloxy $-OR_X$, dialkylamino $-NR_xR_y$, alkylthio $-SR_X$, $-NO_2$, -CHO, $-COOR_X$, -F, -Cl, - Br, -I, -CN, -NC, -SCN, -OCN, $-SOR_X$, $-SO_2R_X$, wherein R_x and R_y = C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl; or combinations thereof;



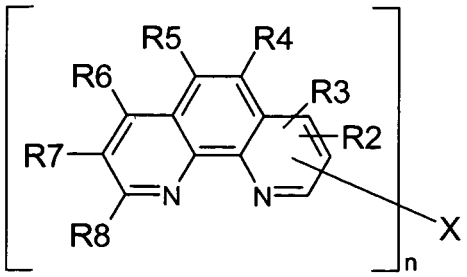
Structure II

wherein structure II is a dimer in which two phenanthroline units are linked by a single bond, which linkage may occur at the 2-, 3-, 4-, 5-, 6-, 7-, 8-, or 9-position of each phenanthroline ring, independently,

wherein

the substituents R2, R3, R4, R5, R6, R7, and R8 are not all simultaneously hydrogen but are otherwise independently selected from the group: H, C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, alkyloxy $-OR_X$, dialkylamino $-NR_xR_y$, alkylthio $-SR_X$, $-NO_2$, -CHO, $-COOR_X$, -F, -Cl, -Br, -I, -CN, -NC, -SCN, -OCN, $-SOR_X$, $-SO_2R_x$, wherein R_x and R_y = C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl,

aryl, heteroaryl, oligoaryl, oligoheteroaryl, and oligoarylheteroaryl, wherein all sp^2-hybridized carbon atoms that do not serve for ring linkage can independently be substituted with H, C_{1-20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, alkyloxy $-OR_X$, dialkylamino $-NR_xR_y$, alkylthio $-SR_X$, $-NO_2$, -CHO, $-COOR_X$, -F, -Cl, - Br, -I, -CN, -NC, -SCN, -OCN, $-SOR_X$, $-SO_2R_X$, wherein R_x and R_y = C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl; or combinations thereof;



Structure III

wherein X is connected to each phenanthroline unit via a single bond, and this bond can independently occur at the 2-, 3-, 4-, 5-, 6-,
7-, 8-, or 9-position of each phenanthroline ring,
wherein X is a central element selected from the group consisting of B, C, Si, Ge, Sn, N, O, S, P, where n is an integer from 1 to the maximum valency of the selected central element, or wherein X is a central structural unit, which may be a simple or bridged cycloalkane, an aromatic, a heteroaromatic, or a spiro-linked polycyclic system, and n is an integer from 1 to the maximum number of phenanthroline units,
wherein
the substituents R2, R3, R4, R5, R6, R7, and R8 are not all simultaneously hydrogen but are otherwise independently selected from the group: H, C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, alkyloxy $-OR_X$, dialkylamino $-NR_xR_y$, alkylthio $-SR_X$, $-NO_2$, -CHO, $-COOR_X$, -F, -Cl, -Br, -I, -CN, -NC, -SCN, -OCN, $-SOR_X$, $-SO_2R_x$, wherein R_x and R_y = C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl,
aryl, heteroaryl, oligoaryl, oligoheteroaryl, and oligoarylheteroaryl, wherein all sp^2-hybridized carbon atoms that do not serve for ring linkage can independently be substituted with H, C_{1-20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, alkyloxy $-OR_X$, dialkylamino $-NR_xR_y$, alkylthio $-SR_X$, $-NO_2$, -CHO, $-COOR_X$, -F, -Cl, - Br, -I, -CN, -NC, -SCN, -OCN, $-SOR_X$, $-SO_2R_X$, wherein R_x and R_y = C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl; or combinations thereof.

With respect to the structure shown in structure II, it is noted that the illustrated linkage is merely exemplary. The linkage of the two phenanthroline units can occur independently at any position on each phenanthroline ring, namely the 2-, 3-, 4-, 5-, 6-, 7-, 8-, or 9-position. The above-shown structure II illustrates a linkage between two phenanthroline units, each connected via an external ring element, where the R_1 substituent (1. structure I) has been removed for bonding purposes. The same applies to the structure shown in structure III, in which a linkage between X and the phenanthroline unit can occur at any suitable position, i.e., the 2-, 3-, 4-, 5-, 6-, 7-, 8-, or 9-position.

If n in structure III does not correspond to the maximum valency, one or more R_0 substituents for X may be selected from R_1-R_8 as defined above.

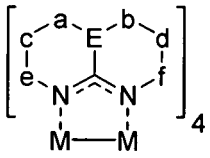
Examples of central structural units X include adamantane or spirobifluorene.

It is preferred that the matrix material is reversibly reducible.

Alternatively, it is proposed that the matrix material decomposes into stable, redox-inactive components upon reduction.

The dopant may be a metal complex.

Preferably, the metal complex has a structure IV:

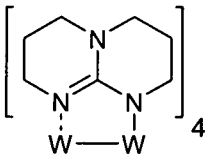


Structure IV

wherein M is a transition metal, preferably Mo or W; and wherein
- the structural elements a–f may have the following meanings: a = -CR_9R_{10}-, b = -$CR_{11}R_{12}$-, c = -$CR_{13}R_{14}$-, d = $R_{15}R_{16}$-, e = -$CR_{17}R_{18}$- and f = -$CR_{19}R_{20}$-, wherein R_9–R_{20} are independently hydrogen, C_1–C_{20} alkyl, C_1–C_{20} cycloalkyl, C_1-C_{20} alkenyl, C_1–C_{20} alkynyl, aryl, heteroaryl, -NRR or -OR, wherein R = C_1–C_{20} alkyl, C_1–C_{20} cycloalkyl, C_1-C_{20} alkenyl, C_1-C_{20} alkynyl, aryl or heteroaryl; preferably R_9, R_{11}, R_{13}, R_{15}, R_{17}, R_{19}, $^{=}$ H and R_{10}, R_{12}, R_{14}, R_{16}, R_{18}, $R_{20}{}^{=}$ = C_1-C_{20} alkyl, C_1-C_{20} cycloalkyl, C_1-C_{20} alkenyl, C_1-C_{20} alkynyl, aryl, heteroaryl, -NRR or -OR, or, in the structural elements c and/or d, C may be replaced by Si, or
- optionally, a or b or e or f is NR, where R = C_1–C_{20} alkyl, C_1–C_{20} cycloalkyl, C_1-C_{20} alkenyl, C_1–C_{20} alkynyl, aryl, heteroaryl, or
- optionally, a and f or b and e are NR, where R = C_1–C_{20} alkyl, C_1–C_{20} cycloalkyl, C_1-C_{20} alkenyl, C_1–C_{20} alkynyl, aryl, heteroaryl,

- wherein the bonds a–c, b–d, c–e, and d–f—but not simultaneously a–c and c–e, and not simultaneously b–d and d–f—can be unsaturated,
- wherein the bonds a–c, b–d, c–e, and d–f may be part of a saturated or unsaturated ring system, which may also contain heteroelements O, S, Se, N, P, Se, Ge, Sn, or
- the bonds a–c, b–d, c–e, and d–f may be part of an aromatic or fused aromatic ring system, which may also contain heteroelements O, S, Si, N,
- wherein the atom E is a main group element, preferably selected from the group C, N, P, As, Sb,
- wherein the structural element a–E–b may optionally be part of a saturated or unsaturated ring system, which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the structural element a–E–b may optionally be part of an aromatic ring system, which may also contain the heteroelements O, S, Se, N.

It is particularly preferred that the dopant has the following structure IVa:



Structure IVa = $W(hpp)_4$

Alternatively, it is also preferred that the dopant is an alkali and/or alkaline earth metal, preferably cesium.

It is further proposed that the matrix material has an energy level for the lowest unoccupied molecular orbital (LUMO) which differs from the ionization potential (HOMO) of the dopant by 0 to 0.5 V, preferably 0 to 0.3 V, and particularly preferably 0 to 0.15 V.

One embodiment is characterized in that the matrix material has an electron affinity (LUMO energy level) that lies lower than the ionization potential (HOMO) of the dopant. "Lower" in this case means that the LUMO energy level has a greater numerical value than the HOMO energy level. Since both values are given as negative with respect to the vacuum level, this means that the absolute value of the HOMO energy is greater than the absolute value of the LUMO energy.

It is also preferred that the concentration of the dopant is 0.5 to 25 percent by weight, preferably 1 to 10 percent by weight, and particularly preferably 2.5 to 5 percent by weight.

It may further be provided that the glass transition temperature (Tg) of the matrix material is higher than that of 4,7-diphenyl-1,10-phenanthroline.

Preferably, the matrix material has a sublimation temperature of at least 200°C.

The invention also relates to an organic light-emitting diode that comprises a semiconductor material according to the invention.

Surprisingly, it was found that certain phenanthroline derivatives can be used as matrix materials, which can be doped as required with metal complex dopants. By introducing suitable electron-withdrawing substituents at specific positions of the phenanthroline framework, the electronic properties of the semiconductor material can be deliberately adjusted, so that the LUMO of the phenanthroline derivative falls within a range that makes it dopable with metal complex dopants, particularly those of structure IV.

Phenanthroline derivatives have previously been used, for example, as undoped electron conductors (EP 0 564 224 A2) or hole blockers (EP 1 097 981, EP 1 097 980). The phenanthroline derivative BPhen has already been used as a cesium-doped layer in organic light-emitting diodes (US 6,013,384), albeit with the aforementioned disadvantage of metal diffusion under applied voltage, which leads to premature failure of the light-emitting diode.

The matrix materials used in accordance with the invention for the semiconductor material also exhibit improved thermal stability over the prior art, which is especially due to increased sublimation and decomposition temperatures. The performance efficiency of an OLED according to the invention is also increased.

Further features and advantages of the invention will become apparent from the following detailed description of preferred embodiments with reference to the accompanying drawings, in which

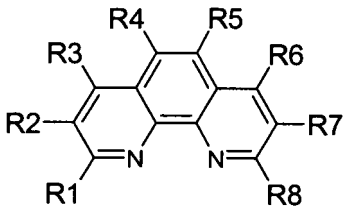
Figure 1 shows a graph illustrating the dependence of conductivity on temperature for a semiconductor material produced according to example 2;

Figure 2 shows a graph illustrating the temperature dependence of the conductivity for a semiconductor material produced according to comparative example 2; and

Figure 3 shows a graph illustrating the time dependence of the brightness of OLEDs with various semiconductor materials in accordance with the invention and the prior art.

Example 1

Selected phenanthroline derivatives shown in Table 2 below were used as matrix materials for doping with $W_2(hpp)_4$ (structure IVa), and the conductivity was measured. The results are listed in Table 2.



Structure I

Table 2:

	R	Tg (°C)	Ts (°C)	LUMO (eV)	Conductivity (S/cm)*
Ia	R2, R4, R5, R7 = H R1, R3, R6, R8 = phenyl	106	260	2.47	3E-4
Ib	R2, R4, R5, R7, R8 = H R3, R6 = phenyl R1 = 1-naphthyl	104	265	2.42	5E-6
Ic	R2, R4, R5, R7 = H R3, R6 = phenyl R1, R8 = 1-naphthyl	119	280	2.5	2E-6
Id	R2, R4, R5, R7 = H R3, R6 = phenyl R1, R8 = 1-(4,4'-biphenylyl)	140	317	2.53	6E-5
Ie	R2, R4, R5, R7 = H R3, R6 = phenyl	165	317	2.51	2E-6

	R1, R8 = 1-phenanthryl				

* Concentration of IVa ($W_2(hpp)_4$: 5 mol%

A comparison with the conductivity values for matrix materials Alq_3 and BPhen known from the prior art (Table 1) shows that the phenanthroline derivatives used according to the invention achieve significantly improved conductivity values.

Example 2

A glass substrate is provided with indium tin oxide contacts. A layer of Ie (Table 2), doped with a dopant of structure IVa, is then deposited onto the substrate. The doping concentration of dopant IVa is 4 mol%. The conductivity of the layer is 2×10^{-6} S/cm at room temperature. The sample is then subjected to a thermal cycling process consisting of individual steps. In each step, the sample is heated to a target temperature, held at that temperature for 20 minutes, and then cooled to room temperature. In successive steps, the target temperature is increased by 10°C. Conductivity of the layer is measured during the thermal cycle. The results are shown in Figure 1. It is observed that the conductivity of the mixture of Ie and IVa remains thermally stable up to 140°C. Only at 150°C does the conductivity decline significantly during the 20-minute hold time.

Comparative example 2

A comparative example 2 was conducted according to the procedure in example 2, but instead of using matrix material Ie, BPhen was used. The resulting conductivity of the layer is 4×10^{-7} S/cm. As shown in Figure 2, such a semiconductor material is only stable up to a temperature of 70°C.

A comparison of Figures 1 and 2 shows that the conductivity of a semiconductor material made from IVa:BPhen is too low for use in organic light-emitting diodes. When using the matrix material Ie, the conductivity is increased fivefold and the thermal stability is 70°C higher.

Example 3

A glass substrate is provided with indium tin oxide contacts. Sequentially deposited on it are the layers: Spiro-TTB doped with p-dopant 2-(6-dicyanomethylene-1,3,4,5,7,8-hexafluoro-6H-naphthalen-2-ylidene)-malononitrile (50 nm, 4 mol%), 2,2',7,7'-tetrakis-(N,N'-diphenylamino)-9,9'-spirobifluorene, N,N'-di(naphthalen-2-yl)-N,N'-

diphenylbenzidine doped with emitter dopant iridium(III)bis(2-methyldibenzo-[f,h]quinoxaline)(acetylacetonate) (20 nm, 10 wt%), Id (10 nm), Id doped with IVa (60 nm, 4 mol%), and Al (100 nm). The resulting organic light-emitting diode emits orange-red light.

The OLED is subjected to a stability test. The OLED is encapsulated and operated in an oven at 80°C. The time-dependent decrease in brightness at constant current density is measured.

After 10 hours, the OLED exhibits a decrease in luminance from 5000 cd/m² to 3300 cd/m², as shown by the filled symbols in Figure 3. The decrease in luminance of OLEDs with the same structure at lower initial brightness levels is represented by the three other curves with filled symbols in Figure 3. The open symbols represent the stability of the OLED from comparative example 3.

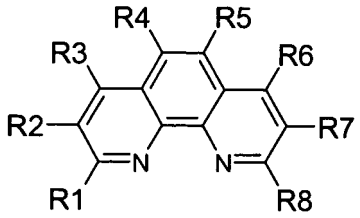
Comparative example 3

An OLED was fabricated as in example 3, but BPhen was used instead of Id. The decrease in luminance of this OLED under continuous operation is also shown in Figure 3 by open symbols. After less than one hour, the brightness decreased from 4800 cd/m² to under 1000 cd/m². Using comparable initial brightness levels for the OLEDs of comparative example 3 and example 3 allows for a direct comparison of the stability of both structures. Accordingly, the OLED using Id as the matrix material is more stable than the one doped with BPhen.

The features disclosed in the description, the claims, and the accompanying drawings may be essential to implementing the invention either individually or in any combination of embodiments.

Claims:

1. A doped organic semiconductor material comprising at least one organic matrix material doped with at least one dopant, wherein the matrix material is selected from the group consisting of phenanthroline derivatives having the following structures I, II, and III:



Structure I

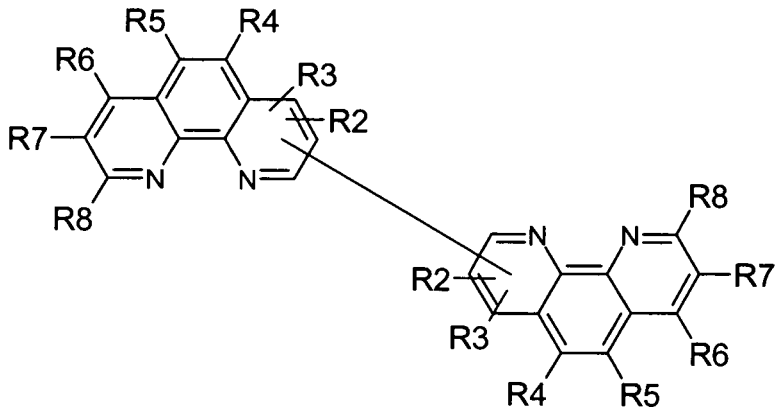
wherein:

R3 and R6 are independently selected from the group: H, C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, alkyloxy $-OR_X$, dialkylamino $-NR_xR_y$, alkylthio $-SR_X$, $-NO_2$, -CHO, $-COOR_X$, -F, -Cl, -Br, -I, -CN, -NC, -SCN, -OCN, $-SOR_X$, $-SO_2R_X$, wherein R_x and R_y = C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl;

aryl, heteroaryl, oligoaryl, oligoheteroaryl, and oligoarylheteroaryl, wherein all sp^2-hybridized carbon atoms that do not serve for ring linkage can independently be substituted with H, $C_{1\text{-}20}$ alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, alkyloxy $-OR_X$, dialkylamino $-NR_xR_y$, alkylthio $-SR_X$, $-NO_2$, -CHO, $-COOR_X$, -F, -Cl, - Br, -I, -CN, -NC, -SCN, -OCN, $-SOR_X$, $-SO_2R_X$, wherein R_x and R_y = C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl; or combinations thereof;

R1, R2, R4, R5, R7, and R8 are not all simultaneously hydrogen but are otherwise independently selected from the group: H, C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, alkyloxy $-OR_X$, dialkylamino $-NR_xR_y$, alkylthio $-SR_X$, $-NO_2$, -CHO, $-COOR_X$, -F, -Cl, -Br, -I, -CN, -NC, -SCN, -OCN, $-SOR_X$, $-SO_2R_X$, wherein R_x and R_y = C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl;

aryl, heteroaryl, oligoaryl, oligoheteroaryl, and oligoarylheteroaryl, wherein all sp^2-hybridized carbon atoms that do not serve for ring linkage can independently be substituted with H, $C_{1\text{-}20}$ alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, alkyloxy $-OR_X$, dialkylamino $-NR_xR_y$, alkylthio $-SR_X$, $-NO_2$, -CHO, $-COOR_X$, -F, -Cl, - Br, -I, -CN, -NC, -SCN, -OCN, $-SOR_X$, $-SO_2R_X$, wherein R_x and R_y = C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl; or combinations thereof;

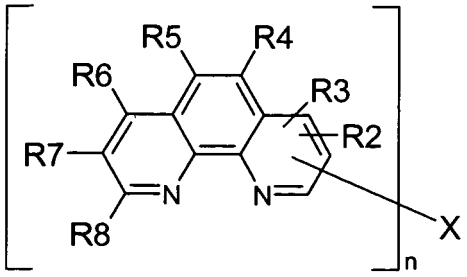


Structure II

wherein structure II is a dimer in which two phenanthroline units are linked by a single bond, which linkage may occur at the 2-, 3-, 4-, 5-, 6-, 7-, 8-, or 9-position of each phenanthroline ring, independently,

wherein the substituents R2, R3, R4, R5, R6, R7, and R8 are not all simultaneously hydrogen but are otherwise independently selected from the group: H, C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, alkyloxy $-OR_X$, dialkylamino $-NR_xR_y$, alkylthio $-SR_X$, $-NO_2$, -CHO, $-COOR_X$, -F, -Cl, -Br, -I, -CN, -NC, -SCN, -OCN, $-SOR_X$, $-SO_2R_x$, wherein R_x and R_y = C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 bis C_{20} alkynyl,

aryl, heteroaryl, oligoaryl, oligoheteroaryl, and oligoarylheteroaryl, wherein all sp^2-hybridized carbon atoms that do not serve for ring linkage can independently be substituted with H, C_{1-20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, alkyloxy $-OR_X$, dialkylamino $-NR_xR_y$, alkylthio $-SR_X$, $-NO_2$, -CHO, $-COOR_X$, -F, -Cl, - Br, -I, -CN, -NC, -SCN, -OCN, $-SOR_X$, $-SO_2R_X$, wherein R_x and R_y = C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl; or combinations thereof;



Structure III

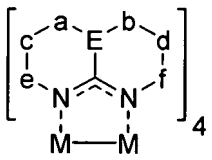
wherein X is connected to each phenanthroline unit via a single bond, and this bond can independently occur at the 2-, 3-, 4-, 5-, 6-, 7-, 8-, or 9-position of each phenanthroline ring, wherein X is a central element selected from the group consisting of B, C, Si, Ge, Sn, N, O, S, P, where n is an integer from 1 to the maximum valency of the selected central element, or wherein X is a central structural unit, which may be a simple or bridged cycloalkane, an aromatic, a heteroaromatic, or a spiro-linked polycyclic system, and n is an integer from 1 to the maximum number of phenanthroline units,
wherein
the substituents R2, R3, R4, R5, R6, R7, and R8 are not all simultaneously hydrogen but are otherwise independently selected from the group: H, C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, alkyloxy $-OR_X$, dialkylamino $-NR_xR_y$, alkylthio $-SR_X$, $-NO_2$, -CHO, $-COOR_X$, -F, -Cl, -Br, -I, -CN, -NC, -SCN, -OCN, $-SOR_X$, $-SO_2R_x$, wherein R_x and R_y = C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl,
aryl, heteroaryl, oligoaryl, oligoheteroaryl, and oligoarylheteroaryl, wherein all sp^2-hybridized carbon atoms that do not serve for ring linkage can independently be substituted with H, C_{1-20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, alkyloxy $-OR_X$, dialkylamino $-NR_xR_y$, alkylthio $-SR_X$, $-NO_2$, -CHO, $-COOR_X$, -F, -Cl, - Br, -I, -CN, -NC, -SCN, -OCN, $-SOR_X$, $-SO_2R_X$, wherein R_x and R_y = C_1 to C_{20} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl; or combinations thereof.

2. The semiconductor material according to claim 1, characterized in that the matrix material is reversibly reducible.

3. The semiconductor material according to claim 1, characterized in that the matrix material decomposes into stable, redox-inactive components upon reduction.

4. The semiconductor material according to any one of the preceding claims, characterized in that the dopant is a metal complex.

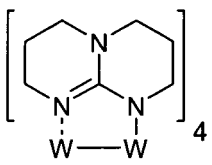
5. The semiconductor material according to claim 4, characterized in that the metal complex has a structure IV:



Structure IV

wherein M is a transition metal, preferably Mo or W; and wherein
- the structural elements a–f may have the following meanings: a = -CR_9R_{10}-, b = -$CR_{11}R_{12}$-, c = -$CR_{13}R_{14}$-, d = $R_{15}R_{16}$-, e = -$CR_{17}R_{18}$- and f = -$CR_{19}R_{20}$-, wherein R_9–R_{20} are independently hydrogen, C_1–C_{20} alkyl, C_1–C_{20} cycloalkyl, C_1-C_{20} alkenyl, C_1–C_{20} alkynyl, aryl, heteroaryl, -NRR or -OR, wherein R = C_1–C_{20} alkyl, C_1–C_{20} cycloalkyl, C_1-C_{20} alkenyl, C_1-C_{20} alkynyl, aryl or heteroaryl; preferably R_9, R_{11}, R_{13}, R_{15}, R_{17}, R_{19}, $^{=}$H and R_{10}, R_{12}, R_{14}, R_{16}, R_{18}, $R_{20}^{=}$ = C_1-C_{20} alkyl, C_1-C_{20} cycloalkyl, C_1-C_{20} alkenyl, C_1-C_{20} alkynyl, aryl, heteroaryl, -NRR or -OR, or, in the structural elements c and/or d, C may be replaced by Si, or
- optionally, a or b or e or f is NR, where R = C_1–C_{20} alkyl, C_1–C_{20} cycloalkyl, C_1-C_{20} alkenyl, C_1–C_{20} alkynyl, aryl, heteroaryl, or
- optionally, a and f or b and e are NR, where R = C_1–C_{20} alkyl, C_1–C_{20} cycloalkyl, C_1-C_{20} alkenyl, C_1–C_{20} alkynyl, aryl, heteroaryl,
- wherein the bonds a–c, b–d, c–e, and d–f—but not simultaneously a–c and c–e, and not simultaneously b–d and d–f—can be unsaturated,
- wherein the bonds a–c, b–d, c–e, and d–f may be part of a saturated or unsaturated ring system, which may also contain heteroelements O, S, Se, N, P, Se, Ge, Sn, or
- the bonds a–c, b–d, c–e, and d–f may be part of an aromatic or fused aromatic ring system, which may also contain heteroelements O, S, Si, N,
- wherein the atom E is a main group element, preferably selected from the group C, N, P, As, Sb,
- wherein the structural element a–E–b may optionally be part of a saturated or unsaturated ring system, which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the structural element a–E–b may optionally be part of an aromatic ring system, which may also contain the heteroelements O, S, Se, N.

6. The semiconductor material according to claim 5, characterized in that the dopant has the following structure IVa:



Structure IVa = $W(hpp)_4$

7. The semiconductor material according to any one of claims 1 to 3, characterized in that the dopant is an alkali metal and/or alkaline earth metal, preferably cesium.

8. The semiconductor material according to any one of the preceding claims, characterized in that the matrix material has an energy level for the lowest unoccupied molecular orbital (LUMO) which differs from the ionization potential (HOMO) of the dopant by 0 to 0.5 V, preferably 0 to 0.3 V, and particularly preferably 0 to 0.15 V.

9. The semiconductor material according to any one of the preceding claims, characterized in that the matrix material has a LUMO energy level which lies lower than the ionization potential (HOMO) of the dopant.

10. The semiconductor material according to any one of the preceding claims, characterized in that the concentration of the dopant is 0.5 to 25% by weight, preferably 1 to 10% by weight, and particularly preferably 2.5 to 5% by weight.

11. The semiconductor material according to any one of the preceding claims, characterized in that the glass transition temperature Tg of the matrix material is higher than that of 4,7-diphenyl-1,10-phenanthroline.

12. The semiconductor material according to any one of the preceding claims, characterized in that the matrix material has a sublimation temperature of at least 200°C.

13. An organic light-emitting diode comprising a semiconductor material according to any one of the preceding claims.

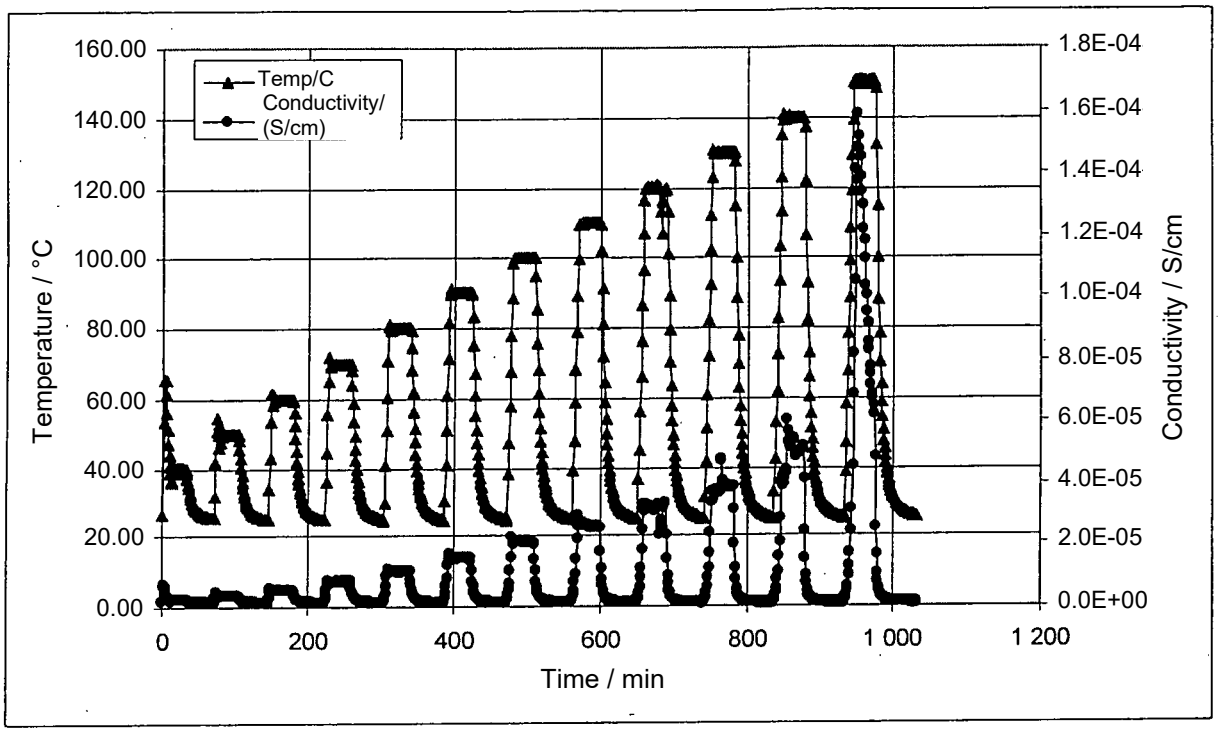

Temp/C
Conductivity/
(S/cm)
Temperature / °C
Conductivity / S/cm
Time / min
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
1.8E-04
1.6E-04
1.4E-04
1.2E-04
1.0E-04
8.0E-05
6.0E-05
4.0E-05
2.0E-05
0.0E+00
0
200
400
600
800
1 000
1 200

Fig. 1

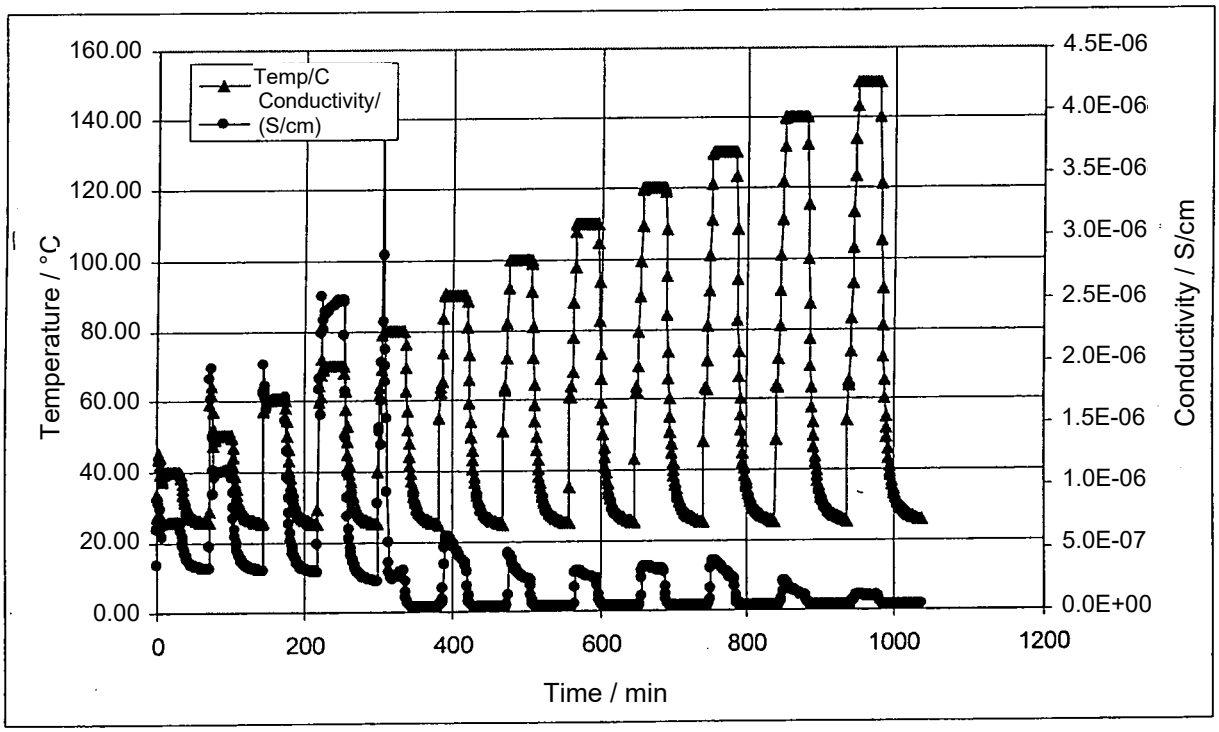

Temp/C
Conductivity/
(S/cm)
Temperature / °C
Conductivity / S/cm
Time / min
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
4.5E-06
4.0E-06
3.5E-06
3.0E-06
2.5E-06
2.0E-06
1.5E-06
1.0E-06
5.0E-07
0.0E+00
0
200
400
600
800
1000
1200

Fig. 2

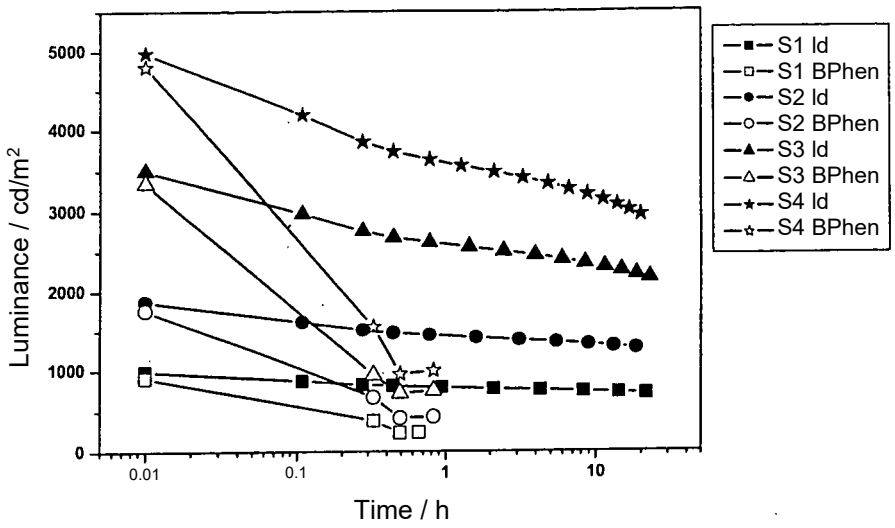

Luminance / cd/m²
5000
4000
3000
2000
1000
0
0.01
0.1
1
10
Time / h
S1 Id
S1 BPhen
S2 Id
S2 BPhen
S3 Id
S3 BPhen
S4 Id
S4 BPhen

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP 2006/010816

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L51/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2005/086251 A (NOVALED GMBH; WERNER, ANSGAR; KUEHL, OLAF; GESSLER, SIMON; HARADA, KEN) 15 September 2005 (2005-09-15) page 58 - page 60	1-6, 10-13

Y	EP 1 097 980 A (SONY CORPORATION) 9 May 2001 (2001-05-09) cited in the application compounds 28,96, 115	1-6, 10-13

	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the International filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 February 2007	09/02/2007

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	KOENIGSTEIN, C

4

Form PCT/ISA/210 (second sheet) (April 2005)

C.(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GUFENG HE ET AL: "High-efficiency and low-voltage p-i-n electrophosphorescent OLEDs with double-doping emission layers" PROCEEDINGS OF THE SPIE, SPIE, BELLINGHAM, VA, US, vol. 5464, no. 1, 2004, pages 26-31, XP002356312 ISSN: 0277-786X the whole document	1,2,7-9, 13
A	EP 1 511 094 A (NOVALED GMBH) 2 March 2005 (2005-03-02) paragraph [0028] - paragraph [0030]	1,4-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP 2006/010816

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005086251 A	15-09-2005	CA 2549309 A1	15-09-2005
		DE 102004010954 A1	06-10-2005
		EP 1721347 A2	15-11-2006
		KR 20060110269 A	24-10-2006
EP 1097980 A	09-05-2001	JP 2001131174 A	15-05-2001
		US 6972334 B1	06-12-2005
EP 1511094 A	02-03-2005	CN 1619854 A	25-05-2005
		DE 10339772 A1	14-04-2005
		JP 2005072012 A	17-03-2005
		KR 20050021919 A	07-03-2005
		US 2005110009 A1	26-05-2005

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 2006/010816

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L51/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L

Searched publications that do not belong to the minimum test material, insofar as they fall under the researched areas

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2005/086251 A (NOVALED GMBH; WERNER, ANSGAR; KUEHL, OLAF; GESSLER, SIMON; HARADA, KEN) September 15, 2005 (2005-09-15) Page 58 - Page 60	1-6, 10-13
Y	EP 1 097 980 A (SONY CORPORATION) May 9, 2001 (2001-05-09) cited in the application compounds 28,96, 115	1-6, 10-13

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
February 1, 2007	09/02/2007

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	KOENIGSTEIN, C

4

Form PCT/ISA/210 (second sheet) (April 2005)

C.(Continued) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GUFENG HE ET AL: "High-efficiency and low-voltage p-i-n electrophosphorescent OLEDs with double-doping emission layers" PROCEEDINGS OF THE SPIE, SPIE, BELLINGHAM, VA, US, vol. 5464, no. 1, 2004, pages 26-31, XP002356312 ISSN: 0277-786X the whole document	1,2,7-9, 13
A	EP 1 511 094 A (NOVALED GMBH) March 2, 2005 (2005-03-02) paragraph [0028] - paragraph [0030]	1,4-6

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No.
PCT/EP 2006/010816

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005086251 A	15-09-2005	CA 2549309 A1	15-09-2005
		DE 102004010954 A1	06-10-2005
		EP 1721347 A2	15-11-2006
		KR 20060110269 A	24-10-2006
EP 1097980 A	09-05-2001	JP 2001131174 A	15-05-2001
		US 6972334 B1	06-12-2005
EP 1511094 A	02-03-2005	CN 1619854 A	25-05-2005
		DE 10339772 A1	14-04-2005
		JP 2005072012 A	17-03-2005
		KR 20050021919 A	07-03-2005
		US 2005110009 A1	26-05-2005