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(54) Title: METHOD FOR PREPARING DEUTERATED AROMATIC COMPOUNDS

(57) Abstract: The present invention relates to a method for preparing deuterated compounds and to deuterated compounds produced by the same method.

# Method for preparing deuterated aromatic compounds

The present invention relates to a method for preparing deuterated compounds and to deuterated compounds produced by the same method.

Deuterium is one of the two stable isotope of hydrogen and has a natural abundance of approximately 0.0156% (0.312% by mass) of all the naturally occurring hydrogen in the oceans.

Deuterated compounds, in which the level of deuterium is intentionally enriched, are known, and deuterated aromatic compounds have often been used in studies of the course of chemical reactions or conversions in metabolism. Deuterated aromatic compounds are also used as starting materials for pharmaceutical compounds or markers.

Also well known is the use of deuterated organic or metallorganic compounds in electronic devices. More particularly, the use of deuterated organic or metallorganic compounds in organic electroluminescent device (OLED) can drastically improve the OLEDs performances in terms of efficiency and lifetime as disclosed, for example, in WO 2010/099534, WO 2011/050888 or J. Phys. Chem. C 2007, 111, 3490-3494. The synthesis of deuterated compounds can be quite challenging and also costly. One can obtain a deuterated compound by reacting building blocks together, where at least one of the builing block is partly or completely deuterated (like in WO 2011/050888) or by deuterating the compound once it has been synthesized (like in WO 2010/099534).

For example, undeuterated compounds can be treated with deuterated acids such as $D_2SO_4$ or $D_3PO_4$ for several hours to obtain deuterated compounds.

It is also possible to react undeuterated compound in a deuterated solvent in the presence of a Lewis acid such as aluminum trichloride to obtain deuterated compounds.

There are also some deuteration methods using high temperatures and electrical voltage or radiation.

Still other deuteration methods use $D_2$ gas, $D_2O$, or a deuterated solvent such as $C_6D_6$ as a deuterium source to perform a H-D exchange by metal catalysis like in WO 2016/073425 or KR101978651.

Method for deuteration of aromatic compounds using an acid catalyst and a deuterated aromatic solvent as deuterium source are also disclosed in the prior art, for example in WO 2011/053334.

In general, deuteration methods are costly and time-consuming. Therefore, there is always a need for deuteration methods for forming various deuterated compounds that can be used in OLEDs, but also for forming deuterated building blocks that can be used in the synthesis of deuterated compounds.

Furthermore, the known chemical H-D exchange processes generally need to be performed under harsch conditions in order to obtain a high deuteration degree, with the disadvantage that impurities might be formed at the same time. On the other side, when performed under mild conditions, only a low deuteration degree can be achieved. Therefore, there is also a need for deuteration methods that can be performed under mild conditions and still result in high deuteration degree.

The term “deuterated compound” refers here to a compound in which deuterium is present in at least 100 times the natural abundance level. A higher deuteration degree than in nature can be achieved by using building blocks which have been prealably enriched with deuterium via a deuteration method or by submitting a compound to a deuteration method.

Hereafter, the term H-D exchange method and the term deuteration method are methods which aim at replacing one or more hydrogens in a compound with deuterium atoms.

In accordance with the present invention, the deuteration degree corresponds to the number of deuterium atoms in a compound on the total number of deuterium atoms and protium atoms in the compound in %, as follows:

Deuteration degree (%) = $(N_D * 100) / (N_P + N_D)$

where:
$N_D$ is the number of deuterium atoms in the compound
$N_P$ is the number of deuterium and protium atoms in the compounds

Unless specificied otherwise, the term hydrogen in the present invention design the protium isotope of hydrogen, which accounts for more that 99.98% of the natural occurring hydrogen in the oceans.

The term “deuterated compound” correspond to a compound, in which at least one hydrogen atom is replaced by a deuterium atom and in which the abundance of deuterium at each deuterated position of the compound is higher than the natural abundance of deuterium, which is about 0.015%. To be a “deuterated compound”, a compound/precursor has to go though a deuterium enrichement or deuteration process.

The problem addressed by the present invention is that of providing methods of deuteration, which are especially suitable as methods for forming deuterated organic materials and which can be performed under mild conditions and still result in high deuteration degree.

Surprisingly, it has been found that the method described in more detail below solves this problem. In particular, the deuteration method of the present invention leads to deuterated materials having a high deuteration degree, while the synthesis conditions are mild. The deuterated compounds obtained with the method of the invention lead to OLEDs having very good performances in terms of lifetime and efficiency. The method described below as well as the compounds obtained from this method are therefore the object of the present invention.

The invention therefore provides a method for preparing a deuterated compound, said method comprising, in the following order:
(a) Performing a first deuteration reaction of the compound by an H-D exchange method to form a first deuterated compound with a deuteration degree x;
(b) Performing a second deuteration reaction of the first deuterated compound by an H-D exchange method to form a second deuterated compound with a deuteration degree y;

where the H-D exchange methods in steps (a) and (b) are selected from H-D exchange by acid catalysis and H-D exchange by metal catalysis;
where
if the H-D exchange method in step (a) is an H-D exchange by metal catalysis, then the H-D exchange method in step (b) is an H-D exchange by acid catalysis, or
if the H-D exchange method in step (a) is an H-D exchange by acid catalysis, then the H-D exchange method in step (b) is an H-D exchange by metal catalysis, and
where the following condition (eq 1) is fulfilled by the deuteration degrees x and y after step (b):

$$y \geq 1.3x \text{ (eq 1)}$$

Preferably, $y \geq 1.5x$ after step (b). More preferably, $y \geq 2x$ after step (b).

Preferably, x is ≥ 30% after step (a) and y is ≥ 50% after step (b).

More preferably, x ≥ 40% after step (a) and y is ≥ 80%, very preferably ≥ 90% after step (b).

The deuteration degree is experimentally determined by measuring the deuteration degree of a compound by quantitative $^1$H-NMR.

An H-D exchange by metal catalysis is taken to mean here a method to exchange hydrogen with deuterium in a compound either by homogeneous metal catalysis or heterogeneous metal catalysis in combination with a deuteration source. An H-D exchange by acid catalysis is taken to mean a method to exchange hydrogen with deuterium in a compound by using deuterated Brønsted acids or Lewis acids in combination with a deuterium source. Such methods are described in more details in Angew. Chem. Int Ed. 2007, 46, 7744-7765.

Preferably, the method comprises a step, where the product is isolated after step (a) and before step (b) so that the methods comprises following steps in the following order:
(a) Performing a first deuteration reaction of the compound by an H-D exchange method to form a first deuterated compound with a deuteration degree x;
(a-1) Isolating the first deuterated compound;

(b) Performing a second deuteration reaction of the first deuterated compound by an H-D exchange method to form a second deuterated compound with a deuteration degree y; where the symbols x and y have the same meaning as above.

The deuterated compound is also preferably isolated after step (b). The isolation of the compound in step (a-1) or after step (b) is performed by known techniques. This may include extraction, precipitation, filtration, distillation, chromatography or similar techniques.

In accordance with a preferred embodiment, the H-D exchange method in step (a) is an H-D exchange by metal catalysis, and the H-D exchange method in step (b) is an H-D exchange by acid catalysis.

In accordance with another preferred embodiment, the H-D exchange method in step (a) is an H-D exchange by acid catalysis and the H-D exchange method in step (b) is an H-D exchange by metal catalysis.

Preferably, the H-D exchange by metal catalysis is selected from H-D exchange by heterogeneous metal catalysis.

More preferably, the H-D exchange by metal catalysis comprises the following steps in the following order:
MC-1) Mixing a compound or a first deuterated compound; a solvent; a metal catalyst and a deuterium source;
MC-2) Heating to react.

Preferably, the step MC-2) is carried out at a temperature of 40°C to 250°C, more preferably of 80°C to 200°C, even more preferably of 100°C to 140°C.

Furthermore, the step MC-2) is preferably carried out at a pressure of 1 atm to 20 atm, preferably 1 to 10 atm, more preferably 1 to 5 atm.

It is also preferred that the the step MC-2) occurs under an inert gas, preferably selected from $N_2$, He, Argon.

The reaction can also be carried out under reflux. The solvent can then be selected accordingly so that the desired reaction temperature is achieved.

Preferably, the step MC-2) is carried out for a period of 1 to 200 hours preferably 1 to 100 hours, more preferably 1 to 50 hours depending on the reaction time. Typically, the step MC-2) is carried out for a period of 10 to 30 hours.

Still preferably, the step MC-2) is carried out in a closed vessel reactor.

The deuterium source in the H-D exchange by metal catalysis preferably comprises one of the following deuterium source: deuterium oxide ($D_2O$), deuterated benzenes, more particularly benzene-$D_6$, deuterated toluenes, more particularly toluene-$D_5$ and toluene-$D_8$, deuterated xylenes, more particularly xylene-$D_{10}$, $CDCl_3$, $CD_3OD$, and mixtures thereof. More preferably, the deuterium source in the H-D exchange by metal catalysis is $D_2O$. Deuterium oxide in the sense of the invention also refers to heavy water.

The metal catalyst in the H-D exchange by metal catalysis is preferably selected from the metal catalysts comprising platinum, palladium, rhodium, ruthenium, nickel, cobalt, oxides thereof, complexes thereof, or combinations thereof. The H-D exchange by metal catalysis can be performed by homogeneous metal catalysis or heterogeneous metal catalysis. Soluble metal catalyst complexes are used in homogeneous metal catalyses, whereas the metal catalyst is not soluble in the heterogenous metal catalysis. In the case of the heterogenous metal catalysis, the metal of the metal catalyst is preferably deposited on a solid phase which is not soluble in the composition. The solid phase can be a suitable material, for example carbon such as activated carbon or carbon black, silicates, molecular sieve or polymers. The solid phase is stable under the reaction conditions.

More preferably, the metal catalyst comprises or is a heterogeneous transition metal catalyst selected from platinum, palladium, oxides thereof, or combinations thereof. Particularly preferably, the metal catalyst is a heterogeneous transition metal catalyst selected from platinum on carbon (Pt/C), palladium on carbon (Pd/C), platin(IV)-oxid on carbon ($PtO_2$/C), palladium(II) hydroxide on carbon ($Pd(OH)_2$/C), palladium(II)-chlorideon carbon ($PdCl_2$/C) or a combination thereof. Very particularly preferably, the metal catalyst is a combination of platinum on carbon (Pt/C) and palladium on carbon (Pd/C). In the case of

a combination of Pt/C and Pd/C, a mixture of 10:1 to 1:2 of Pt/C to Pd/C, preferably 7:1 to 1:1, especially 5:1 to 1:1, measured by weight, is preferred.

The molar ratio of the metal catalyst to the compound to be deuterated is preferably from 2:1 to 100:1, especially from 2:1 to 70:1, preferably from 2:1 to 30:1. With a higher amount of catalyst, generally fewer by-products are formed.

Metal catalysts are often stored in a water-moist state. Preferably, the metal catalyst is dried before being used in the H-D exchange by metal catalysis in order to improve the activity of the catalyst.

When the heterogeneous metal catalyst is dried, the drying step is preferably carried out at a temperature of 20 °C to 200 °C, preferably 20 to 100 °C, particularly preferably at reduced pressure, in particular below 100 mbar. The drying step is preferably carried out until the water content is below 5% by weight, preferably 2% by weight as measured by the Karl-Fischer method, preferably below 1%. Very preferably, the drying step is carried out at a temperature of from 50 °C to 70 °C and at a reduced pressure of below 50 mbar, particularly preferably at a temperature of from 50 °C to 70 °C and at a reduced pressure of 30 mbar, very particularly preferably at a temperature of from 55 °C to 75 °C and at a reduced pressure of 1 to 30 mbar. The drying step is preferably carried out for a period of at least 24 hours, in particular of at least 48 hours. Preferably, the drying step is carried out between 24 and 96 hours, in particular between 48 to 96 hours.

The drying step of the metal catalyst is preferably carried out under air or inert gas such as nitrogen or argon. No activation with hydrogen or deuterium gas takes place.

Preferably, the solvent in the H-D exchange by metal catalysis comprises a solvent selected from aromatic solvents, ethers, alcohols, alkanes, cycloalkanes, acids, amides, esters and mixtures thereof. A suitable solvent is a solvent, in which the compound to be deuterated is at least partly soluble. If a deuterated aromatic solvent is used (e.g. benzene-d6), the solvent can also act as a deuterium source. In that case, an additional deuterium source (e.g. deuterium oxide) can be present, or the deuterated aromatic compound is the only deuterium source.

In accordance with a preferred embodiment, the solvent comprises an alkane, preferably a cycloalkane, very preferably a cycloalkane comprising at least one ring having 6 or more aliphatic carbon atoms. Examples of suitable cycloalkanes are cyclohexane, methylcyclohexane and also fused cycloalkanes like decalin (cis- or trans-decalin and mixture thereof).

In accordance with another preferred embodiment, the solvent comprises an ether, preferably an aliphatic ether, which might be cyclic or linear and which preferably comprises 4 to 18 carbon artoms and 1 to 4 oxygen atoms, more preferably 4 to 12 carbon artoms and 1 to 3 oxygen atoms, even more preferably 4 to 8 carbon artoms and 1 to 2 oxygen atoms. Preferably, the ether as a solvent in a cyclic aliphatic ether. Examples of suitable ethers are cyclic ethers such as 1,4-dioxane, tetrahydropyran (THP), tetrahydrofuran (THF), aliphatic monoethers such as tert-butyl methyl ether, tert-butyl ethyl ether, dibutyl ether; aliphatic diethers such as ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol dibutyl ether, diethylene glycol diethyl ether and diethylene glycol dibutyl ether. Cyclic ethers such as 1,4-dioxane, tetrahydropyran, tetrahydrofuran, in particular 1,4-dioxane or tetrahydropyran are particularly preferred.

Preferably, in the metal H-D exchange by catalysis, the solvent is used in such an amount that the organic compound dissolves at least partially; measured in volume preferably in a ratio of deuterium source:solvent of 2:1 to 1:50, preferably 1:1 to 1:30, especially 1:1.5 to 1:30, most particularly at 1:1.5 to 1:10. The ideal amount here depends on the solubility of the compound.

Further examples of suitable solvents for the H-D exchange by metal catalysis include, but are not limited to methanol, ethanol, isopropanol, acetic acid, N,N dimethylformamide, benzene, toluene, xylene, mesitylene, and mixtures thereof.

In accordance with a preferred embodiment of the invention, the solvent in the H-D exchange by metal catalysis is composed of at least two solvents selected, identically or differently from alkanes, ethers and alcohols.

The use of at least one aliphatic ether as solvent can be advantageous for organic compounds, in particular aromatic or heteroaromatic compounds, which comprise at least one NH function. The process according to the invention is therefore particularly suitable for intermediate stages of OLED production which have such free NH functions. By NH function is meant NH groups as well as $NH_2$ groups. They can be, for example, primary or secondary amines and carbazole compounds or carbazole derivatives.

In one embodiment of the invention, the mixture in step MC-1) further comprises at least one additive to improve deuteration and/or reduce by-products. Preferably, the at least one additive is selected from alkylamines, preferably alkylamines having alkyl groups with 1 to 40 C atoms, wherein non-adjacent $CH_2$ groups may be substituted by O and at least two alkyl groups may form a ring with each other, metal salts and/or metal oxides selected from salts or oxides of palladium, platinum, rhodium, ruthenium, silver, gold, copper, nickel or cobalt, wherein salts or oxides of silver or palladium, in particular of Pd(II), are preferred. In the case of the salts, they may be, for example, the chlorides, bromides, iodides, nitrates, sulfates, carboxylic acid salts such as acetates, propionates, pivalates, such as, for example, $Pd(OAc)_2$, Ag(OAc) or $Pd(OPiv)_2$. Carboxylic acid salts such as $Pd(OAc)_2$, Ag(OAc) or $Pd(OPiv)_2$ are particularly preferred.

Preferred alkylamines are alkylamines with at least two, preferably three alkyl groups, in particular with 1 to 40 C atoms, wherein non-adjacent $CH_2$ groups may be substituted by O and at least two alkyl groups may form a ring. Preferred alkyl groups are methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, 2-methyl¬butyl, n-pentyl, s-pentyl, t-pentyl, 2-pentyl, neo-pentyl, cyclopentyl, n-hexyl, s-hexyl, t-hexyl, 2-hexyl, 3-hexyl, neo-hexyl, cyclohexyl, 1-methylcyclopentyl, 2-methylpentyl, n-heptyl, 2-heptyl, 3-heptyl, 4-heptyl, cyclo¬heptyl, 1-methylcyclohexyl. Preferred are alkylamines with three alkyl groups (tertiary amines) with 1 to 5 C atoms, as well as alkylamines with three alkyl groups, where two alkyl groups form a ring, where the ring may contain an O atom.

Examples of such amines are triethylamine, dimethylethylamine, diethylmethylamine, diisopropylethylamine, triethylamine being preferred. Examples of cyclic amines are morpholine derivatives, in particular N-alkyl morpholines such as N-methylmorpholine, N-ethylmorpholine, N-propylmorpholine.

Preferably, the amine used is soluble in the composition.

More particularly, alkylamines, silver salts and/or palladium salts promote deuteration and reduce the formation of by-products. This may allow the reaction to be carried out for longer or at a higher temperature. The use of additives may depend on the compound to be deuterated.

The additives can be used in different amounts depending on the reaction procedure and the organic compound. Preferably, the at least one additive is used in a molar ratio of additive to organic compound of 1:2 to 1:100, preferably 1:2 to 1:50, in particular 1:2 to 1:30.

Preferably, the H-D exchange by acid catalysis is selected from H-D exchange by homogeneous acid catalysis.

More preferably, the the H-D exchange by acid catalysis comprises the step of:
AC-1) Mixing a compound or a first deuterated compound with a deuterated solvent;
AC-2) Treating the reaction mixture of step 1) with an acid catalyst having a pKa in water of 0 or less.

It is preferred that step AC-2) is carried out at under an inert gas, preferably selected from $N_2$, He, Argon.

It is also preferred that step AC-2) is carried out under a controlled temperature of -90°C to 120°C, preferably of from -50°C to 100°C, more preferably of from 10 bis 40°C.

The step AC-2) is generally carried out for a period of 0.5 to 200 hours, preferably 1 to 100 hours, more preferably 1 to 50 hours.

Preferably, the acid catalyst has a pKa in water of -5 or less at 20°C.

More preferably, the acid catalyst is selected from Brønsted acid, even more preferably from strong or superstrong Brønsted acids. The pKa of the acid catalyst in water is preferably of -10 or less at 20°C.

In accordance with a preferred embodiment, the acid catalyst is a deuterated acid catalyst.

In accordance with another preferred embodiment, the acid catalyst is not deuterated.

Examples of acid catalysts are $H_2SO_4$, $D_2SO_4$, $CF_3CO_2H$, $CF_3CO_2D$, $CH_3SO_3H$, $CH_3SO_3D$, $C_6H_6SO_3H$, $C_6H_6SO_3D$, $CF_3SO_3H$, $CF_3SO_3D$, $FSO_3H$, $FSO_3D$, and mixtures thereof, where more preferred acid catalysts are the superstrong Brønsted acids like $CF_3SO_3H$ and $CF_3SO_3D$.

In accordance with a preferred embodiment, the deuterated solvent in the H-D exchange by acid catalysis is a deuterated organic solvent. More preferably, the deuterated solvent in the H-D exchange by acid catalysis is a deuterated aromatic solvent.

Examples of suitable deuterated solvents for the H-D exchange by acid catalysis are deuterated benzenes, more particularly benzene-$D_6$, deuterated toluenes, more particularly toluene-$D_5$, toluene-$D_8$, deuterated xylenes, more particularly xylene-$D_{10}$, $CDCl_3$, $CD_3OD$, and mixtures thereof.

Preferably, the deuterated solvent is used as a deuteration source in the H-D exchange by acid catalysis. Therefore, the deuteration degree in the deuterated solvent decreases after the H-D exchange by acid catalysis.

In accordance with a preferred embodiment of the invention, the deuterated solvent used in the H-D exchange by acid catalysis is re-enriched in deuterium after the H-D exchange by acid catalysis by being introduced in the reaction mixture of the H-D exchange by metal catalysis. By doing so, the deuteration degree of the deuterated solvent increases and it can be re-used in the H-D exchange by acid catalysis.

Preferably, the compound to be deuterated is an organic compound.

More preferably the compound to be deuterated comprises an aromatic ring system, an heteroaromatic ring system, an aromatic amine or an organometallic compound. It is understood that the aromatic ring systems, heteroaromatic ring systems, aromatic amines

and organometallic compounds may be substituted by one or more substituents, like for example, halogens, alkyl groups, aromatic or heteroaromatic ring systems.

The following definitions of chemical groups apply for the purposes of the present application:

An aryl group in the sense of this invention contains 6 to 60 aromatic ring atoms, preferably 6 to 40 aromatic ring atoms, more preferably 6 to 20 aromatic ring atoms; a heteroaryl group in the sense of this invention contains 5 to 60 aromatic ring atoms, preferably 5 to 40 aromatic ring atoms, more preferably 5 to 20 aromatic ring atoms, at least one of which is a heteroatom. The heteroatoms are preferably selected from N, O and S. This represents the basic definition. If other preferences are indicated in the description of the present invention, for example with respect to the number of aromatic ring atoms or the heteroatoms present, these apply.

An aryl group or heteroaryl group here is taken to mean either a simple aromatic ring, i.e. benzene, or a simple heteroaromatic ring, for example pyridine, pyrimidine or thiophene, or a condensed (annellated) aromatic or heteroaromatic polycycle, for example naphthalene, phenanthrene, quinoline or carbazole. A condensed (annellated) aromatic or heteroaromatic polycycle in the sense of the present application consists of two or more simple aromatic or heteroaromatic rings condensed with one another.

An aryl or heteroaryl group, which may in each case be substituted by the above-mentioned radicals and which may be linked to the aromatic or heteroaromatic ring system via any desired positions, is taken to mean, in particular, groups derived from benzene, naphthalene, anthracene, phenanthrene, pyrene, dihydropyrene, chrysene, perylene, fluoranthene, benzanthracene, benzophenanthrene, tetracene, pentacene, benzopyrene, furan, benzofuran, isobenzofuran, dibenzofuran, thiophene, benzothiophene, isobenzothiophene, dibenzothiophene, pyrrole, indole, isoindole, carbazole, pyridine, quinoline, isoquinoline, acridine, phenanthridine, benzo-5,6-quinoline, benzo-6,7-quinoline, benzo-7,8-quinoline, phenothiazine, phenoxazine, pyrazole, indazole, imidazole, benzimidazole, naphthimidazole, phenanthrimidazole, pyridimidazole, pyrazinimidazole, quinoxalinimidazole, oxazole, benzoxazole, naphthoxazole, anthroxazole, phenanthroxazole, isoxazole, 1,2-thiazole, 1,3-thiazole, benzothiazole, pyridazine, benzopyridazine, pyrimidine, benzo-

pyrimidine, quinoxaline, pyrazine, phenazine, naphthyridine, azacarbazole, benzocarboline, phenanthroline, 1,2,3-triazole, 1,2,4-triazole, benzotriazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,3,4-thiadiazole, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, tetrazole, 1,2,4,5-tetrazine, 1,2,3,4-tetrazine, 1,2,3,5-tetrazine, purine, pteridine, indolizine and benzothiadiazole.

An aryloxy group in accordance with the definition of the present invention is taken to mean an aryl group, as defined above, which is bonded via an oxygen atom. An analogous definition applies to heteroaryloxy groups.

An aromatic ring system in the sense of this invention contains 6 to 60 C atoms in the ring system, preferably 6 to 40 C atoms, more preferably 6 to 20 C atoms. A heteroaromatic ring system in the sense of this invention contains 5 to 60 aromatic ring atoms, preferably 5 to 40 aromatic ring atoms, more preferably 5 to 20 aromatic ring atoms, at least one of which is a heteroatom. The heteroatoms are preferably selected from N, O and/or S. An aromatic or heteroaromatic ring system in the sense of this invention is intended to be taken to mean a system which does not necessarily contain only aryl or heteroaryl groups, but instead in which, in addition, a plurality of aryl or heteroaryl groups may be connected by a non-aromatic unit (preferably less than 10% of the atoms other than H), such as, for example, an $sp^3$-hybridised C, Si, N or O atom, an $sp^2$-hybridised C or N atom or an sp-hybridised C atom. Thus, for example, systems such as 9,9'-spirobifluorene, 9,9'-diarylfluorene, triarylamine, diaryl ether, stilbene, etc., are also intended to be taken to be aromatic ring systems in the sense of this invention, as are systems in which two or more aryl groups are connected, for example, by a linear or cyclic alkyl, alkenyl or alkynyl group or by a silyl group. Furthermore, systems in which two or more aryl or heteroaryl groups are linked to one another via single bonds are also taken to be aromatic or heteroaromatic ring systems in the sense of this invention, such as, for example, systems such as biphenyl, terphenyl or diphenyltriazine.

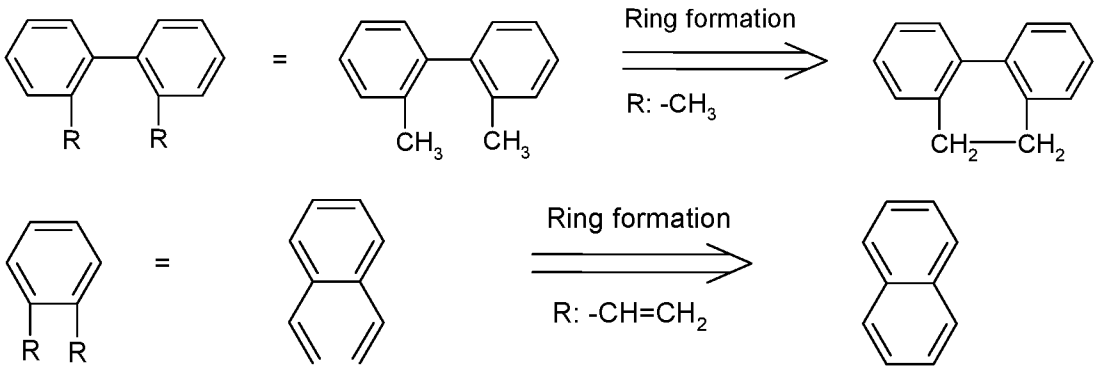
An aromatic or heteroaromatic ring system having 5 - 60 aromatic ring atoms, which may in each case also be substituted by radicals and which may be linked to the aromatic or heteroaromatic group via any desired positions, is taken to mean, in particular, groups derived from benzene, naphthalene, anthracene, benzanthracene, phenanthrene,

benzophenanthrene, pyrene, chrysene, perylene, fluoranthene, naphthacene, pentacene, benzopyrene, biphenyl, biphenylene, terphenyl, terphenylene, quaterphenyl, fluorene, spirobifluorene, dihydrophenanthrene, dihydropyrene, tetrahydropyrene, cis- or trans-indenofluorene, truxene, isotruxene, spirotruxene, spiroisotruxene, furan, benzofuran, isobenzofuran, dibenzofuran, thiophene, benzothiophene, isobenzothiophene, dibenzothiophene, pyrrole, indole, isoindole, carbazole, indolocarbazole, indenocarbazole, pyridine, quinoline, isoquinoline, acridine, phenanthridine, benzo-5,6-quinoline, benzo-6,7-quinoline, benzo-7,8-quinoline, phenothiazine, phenoxazine, pyrazole, indazole, imidazole, benzimidazole, naphthimidazole, phenanthrimidazole, pyridimidazole, pyrazinimidazole, quinoxalinimidazole, oxazole, benzoxazole, naphthoxazole, anthroxazole, phenanthroxazole, isoxazole, 1,2-thiazole, 1,3-thiazole, benzothiazole, pyridazine, benzopyridazine, pyrimidine, benzopyrimidine, quinoxaline, 1,5-diazaanthracene, 2,7-diazapyrene, 2,3-diazapyrene, 1,6-diazapyrene, 1,8-diazapyrene, 4,5-diazapyrene, 4,5,9,10-tetraazaperylene, pyrazine, phenazine, phenoxazine, phenothiazine, fluorubin, naphthyridine, azacarbazole, benzocarboline, phenanthroline, 1,2,3-triazole, 1,2,4-triazole, benzotriazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,3,4-thiadiazole, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, tetrazole, 1,2,4,5-tetrazine, 1,2,3,4-tetrazine, 1,2,3,5-tetrazine, purine, pteridine, indolizine and benzothiadiazole, or combinations of these groups.

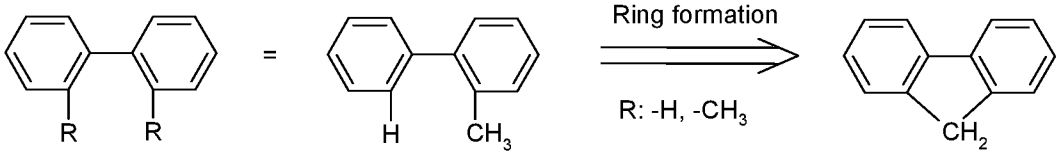
For the purposes of the present invention, a straight-chain alkyl group having 1 to 40 C atoms or a branched or cyclic alkyl group having 3 to 40 C atoms or an alkenyl or alkynyl group having 2 to 40 C atoms, in which, in addition, individual H atoms or $CH_2$ groups may be substituted by the groups mentioned above under the definition of the radicals, is preferably taken to mean the radicals methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, 2-methylbutyl, n-pentyl, s-pentyl, cyclopentyl, neopentyl, n-hexyl, cyclohexyl, neohexyl, n-heptyl, cycloheptyl, n-octyl, cyclooctyl, 2-ethylhexyl, trifluoromethyl, pentafluoroethyl, 2,2,2-trifluoroethyl, ethenyl, propenyl, butenyl, pentenyl, cyclopentenyl, hexenyl, cyclohexenyl, heptenyl, cycloheptenyl, octenyl, cyclooctenyl, ethynyl, propynyl, butynyl, pentynyl, hexynyl or octynyl. An alkoxy or thioalkyl group having 1 to 40 C atoms is preferably taken to mean methoxy, trifluoromethoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, i-butoxy, s-butoxy, t-butoxy, n-pentoxy, s-pentoxy, 2-methylbutoxy, n-hexoxy, cyclohexyloxy, n-heptoxy, cycloheptyloxy, n-octyloxy, cyclooctyloxy, 2-ethylhexyloxy, pentafluoroethoxy, 2,2,2-trifluoroethoxy, methylthio, ethylthio, n-propylthio, i-propylthio, n-

butylthio, i-butylthio, s-butylthio, t-butylthio, n-pentylthio, s-pentylthio, n-hexylthio, cyclohexylthio, n-heptylthio, cycloheptylthio, n-octylthio, cyclooctylthio, 2-ethylhexylthio, trifluoromethylthio, pentafluoroethylthio, 2,2,2-trifluoroethylthio, ethenylthio, propenylthio, butenylthio, pentenylthio, cyclopentenylthio, hexenylthio, cyclohexenylthio, heptenylthio, cycloheptenylthio, octenylthio, cyclooctenylthio, ethynylthio, propynylthio, butynylthio, pentynylthio, hexynylthio, heptynylthio or octynylthio.

The formulation that two radicals may form a ring with one another is, for the purposes of the present application, intended to be taken to mean, inter alia, that the two radicals are linked to one another by a chemical bond. This is illustrated by the following schemes:




Furthermore, however, the above-mentioned formulation is also intended to be taken to mean that, in the case where one of the two radicals represents hydrogen, the second radical is bonded at the position to which the hydrogen atom was bonded, with formation of a ring. This is illustrated by the following scheme:




When two radicals form a ring with one another, then it is preferred that the two radicals are adjacent radicals. Adjacent radicals in the sense of the present invention are radicals which are bonded to atoms which are linked directly to one another or which are bonded to the same atom.

In accordance with a preferred embodiment, the compound to be deuterated comprises an aromatic ring system. More preferably, the compounds to be deuterated is an aromatic ring system selected from aromatic ring system having 6 - 60 aromatic ring atoms, which may be substituted by one or more radicals $R^R$. Preferred aromatic ring systems are selected from benzene, naphthalene, anthracene, benzanthracene, phenanthrene, benzophenanthrene, pyrene, chrysene, perylene, fluoranthene, naphthacene, pentacene, benzopyrene, biphenyl, biphenylene, terphenyl, terphenylene, quaterphenyl, fluorene, spirobifluorene, dihydrophenanthrene, dihydropyrene, tetrahydropyrene, cis- or trans-indenofluorene, truxene, isotruxene, spirotruxene, spiroisotruxene, and combinations of these groups, which may be substituted by one or more radicals $R^R$, where

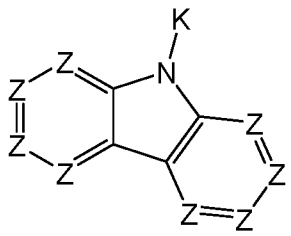
$R^R$ stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CHO, CN, C(=O)Ar, P(=O)$(Ar)_2$, S(=O)Ar, S(=O)$_2$Ar, N$(R')_2$, N$(Ar)_2$, $NO_2$, Si$(R')_3$, B$(OR')_2$, $OSO_2R'$, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or branched or a cyclic alkyl, alkoxy or thioalkyl group having 3 to 40 C atoms, each of which may be substituted by one or more radicals $R'$, where in each case one or more non-adjacent $CH_2$ groups may be replaced by $R'C{=}CR'$, C≡C, Si$(R')_2$, Ge$(R')_2$, Sn$(R')_2$, C=O, C=S, C=Se, P(=O)$(R')$, SO, $SO_2$, O, S or $CONR'$ and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or $NO_2$, an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals $R'$, or an aryloxy group having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals $R'$; where two radicals $R^R$ may form an aliphatic or aromatic ring system together, which may be substituted by one or more radicals $R'$;

Ar is, on each occurrence, identically or differently, an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case also be substituted by one or more radicals $R'$;

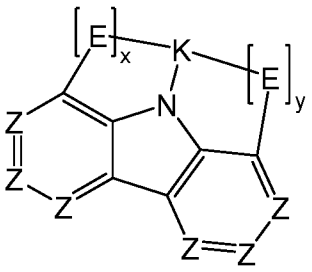
$R'$ stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CN, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 20 C atoms or branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 20 C atoms, where in each case one or more non-adjacent $CH_2$ groups may be replaced by SO, $SO_2$, O, S and where one or more H atoms may be replaced by D, F, Cl, Br or I, or an aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms.

In accordance with another preferred embodiment, the compound to be deuterated comprises an heteroaromatic ring system. More preferably, the compounds to be deuterated comprises an heteroaromatic ring system selected from substituted or unsubstituted heteroaromatic ring systems having 5 - 60 aromatic ring atoms, which may be substituted by one or more radicals $R^R$. Preferred heteroaromatic ring systems are selected from furan, benzofuran, isobenzofuran, dibenzofuran, thiophene, benzothiophene, isobenzothiophene, dibenzothiophene, pyrrole, indole, isoindole, carbazole, indolocarbazole, indenocarbazole, pyridine, quinoline, isoquinoline, acridine, phenanthridine, benzo-5,6-quinoline, benzo-6,7-quinoline, benzo-7,8-quinoline, phenothiazine, phenoxazine, pyrazole, indazole, imidazole, benzimidazole, naphthimidazole, phenanthrimidazole, pyridimidazole, pyrazinimidazole, quinoxalinimidazole, oxazole, benzoxazole, naphthoxazole, anthroxazole, phenanthroxazole, isoxazole, 1,2-thiazole, 1,3-thiazole, benzothiazole, pyridazine, benzopyridazine, pyrimidine, benzopyrimidine, quinoxaline, 1,5-diazaanthracene, 2,7-diazapyrene, 2,3-diazapyrene, 1,6-diazapyrene, 1,8-diazapyrene, 4,5-diazapyrene, 4,5,9,10-tetraazaperylene, pyrazine, phenazine, phenoxazine, phenothiazine, fluorubin, naphthyridine, azacarbazole, benzocarboline, phenanthroline, 1,2,3-triazole, 1,2,4-triazole, benzotriazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,3,4-thiadiazole, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, tetrazole, 1,2,4,5-tetrazine, 1,2,3,4-tetrazine, 1,2,3,5-tetrazine, purine, pteridine, indolizine and benzothiadiazole, or combinations of these groups, which may be substituted by one or more radicals $R^R$, where $R^R$ is as defined above.

In accordance with a preferred embodiment, the compound to be deuterated is an heteroaromatic compound selected from the compounds of the formulas (h-1) or (h-2):




Formula (h-1)




Formula (h-2)

where:

K is $Ar^{10}$ or $-L^1-N(Ar)_2$;

Z is $C-R^Z$ ; or two adjacent groups Z form a condensed ring together;

$R^Z$ is the same or different at each instance and is selected from H, D, F, Cl, Br, I, $N(Ar)_2$, $N(R)_2$, OAr, SAr, CN, $NO_2$, OR, SR, COOR, $C(=O)N(R)_2$, $Si(R)_3$, $B(OR)_2$, C(=O)R, $P(=O)(R)_2$, S(=O)R, $S(=O)_2R$, $OSO_2R$, a straight-chain alkyl group having 1 to 20 carbon atoms or an alkenyl or alkynyl group having 2 to 20 carbon atoms or a branched or cyclic alkyl group having 3 to 20 carbon atoms, where the alkyl, alkenyl or alkynyl group may in each case be substituted by one or more R radicals, where one or more nonadjacent $CH_2$ groups may be replaced by $Si(R)_2$, C=O, NR, O, S or CONR, or an aromatic or heteroaromatic ring system which has 5 to 60 aromatic ring atoms, preferably 5 to 40 aromatic ring atoms, and may be substituted in each case by one or more R radicals;

$L^1$ is a single bond or an aromatic or heteroaromatic ring system which has 5 to 30 aromatic ring atoms and may be substituted by one or more R radicals;

$Ar^{10}$ is an aromatic ring system having 6 to 40 aromatic ring atoms or a heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may be substituted by one or more R radicals;

$R^Z$ is the same or different at each instance and is H, D, F, Cl, Br, I, $N(Ar)_2$, $N(R)_2$, OAr, SAr, CN, $NO_2$, OR, SR, COOR, $C(=O)N(R)_2$, $Si(R)_3$, $B(OR)_2$, C(=O)R, $P(=O)(R)_2$, S(=O)R, $S(=O)_2R$, $OSO_2R$, a straight-chain alkyl group having 1 to 20 carbon atoms or an alkenyl or alkynyl group having 2 to 20 carbon atoms or a branched or cyclic alkyl group having 3 to 20 carbon atoms, where the alkyl, alkenyl or alkynyl group may in each case be substituted by one or more R radicals, where one or more nonadjacent $CH_2$ groups may be replaced by $Si(R)_2$, C=O, NR, O, S or CONR, or an aromatic or heteroaromatic ring system which has 5 to 60 aromatic ring atoms, preferably 5 to 40 aromatic ring atoms, and may be substituted in each case by one or more R radicals; at the same time, two $R^Z$ radicals together may also form a ring system;

E is on each occurrence, independently, a single bond or a group $C(R^0)_2$;

$R^0$ is selected on each occurrence, independently, from a straight-chain alkyl group having 1 to 10 carbon atoms or a branched or cyclic alkyl group having 3 to 10 carbon atoms, which may in each case be substituted by one or more R´ radicals;

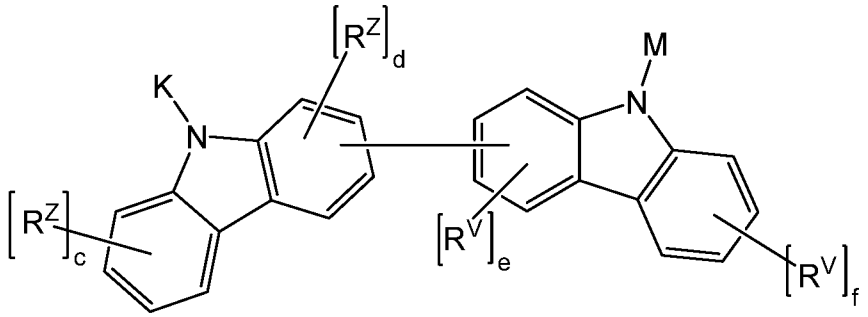
x, y are selected, independently, from 0 or 1, wherein when x or y is 0, then the corresponding group E is absent; and x + y = 1 or 2; and

R stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CHO, CN, C(=O)Ar, $P(=O)(Ar)_2$, S(=O)Ar, $S(=O)_2Ar$, $N(R´)_2$, $N(Ar)_2$, $NO_2$, $Si(R´)_3$, $B(OR´)_2$, $OSO_2R´$, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or branched or a cyclic alkyl, alkoxy or thioalkyl group having 3 to 40 C atoms, each of which may be substituted by one or more radicals R´, where in each case one or more non-adjacent $CH_2$ groups may be replaced by R´C=CR´, C≡C, $Si(R´)_2$, $Ge(R´)_2$, $Sn(R´)_2$, C=O, C=S, C=Se, P(=O)(R´), SO, $SO_2$, O, S or CONR´ and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or $NO_2$, an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R´, or an aryloxy group having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals R´; where two radicals R may form an aliphatic or aromatic ring system together, which may be substituted by one or more radicals R´;

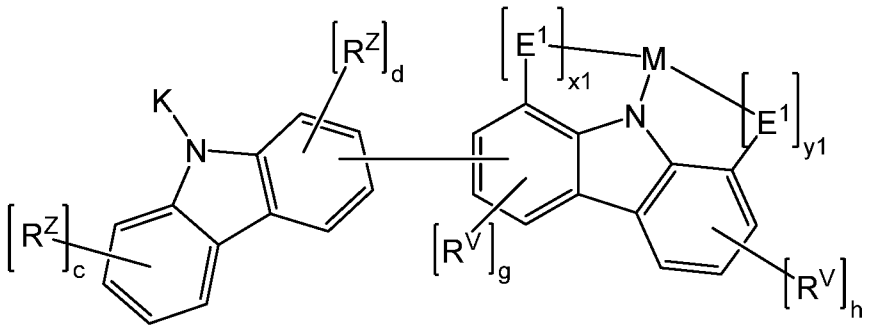
Ar is, on each occurrence, identically or differently, an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case also be substituted by one or more radicals R´;

R´ stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CN, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 20 C atoms or branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 20 C atoms, where in each case one or more non-adjacent $CH_2$ groups may be replaced by SO, $SO_2$, O, S and where one or more H atoms may be replaced by D, F, Cl, Br or I, or an aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms.

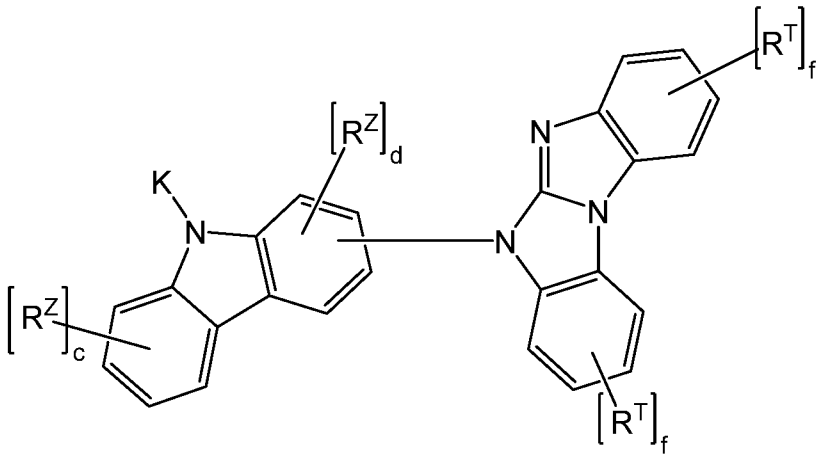
More preferably, the compound to be deuterated is an heteroaromatic compound selected from the compounds of the formulas (h-1-1) to (h-1-3), (h-2-1) to (h-2-2) and (h-3-1):



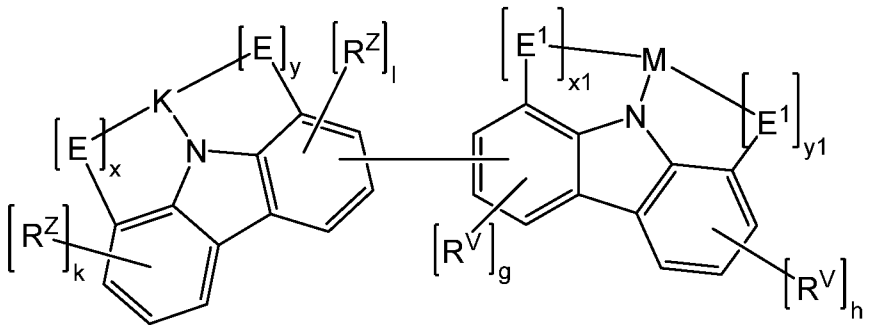
Formula (h-1-1)



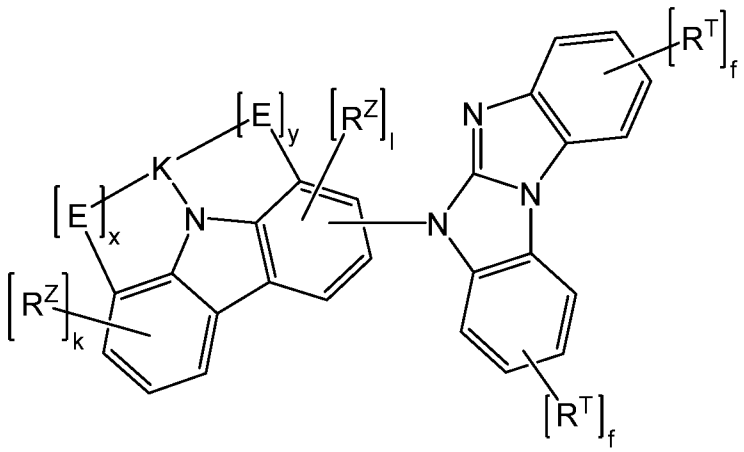
Formula (h-1-2)



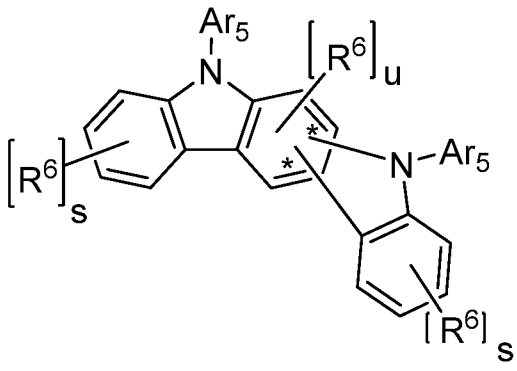
Formula (h-1-3)



Formula (h-2-1)



Formula (h-2-2)



Formula (h-3-1)

where the symbols and idices have the following meaning:

M is an aromatic ring system having 6 to 40 aromatic ring atoms or a heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may be substituted by one or more R radicals;

$E^1$ is on each occurrence, independently, a single bond or a group $C(R^0)_2$; where $R^0$ has the same meaning as in claim 28;

$Ar^5$ is on each occurrence, identically or differently, an aromatic ring system having 6 to 40 aromatic ring atoms or a heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may be substituted by one or more R radicals;

$R^T$, $R^V$, $R^6$ are the same or different at each instance and is selected from H, D, F, Cl, Br, I, $N(Ar)_2$, $N(R)_2$, OAr, SAr, CN, $NO_2$, OR, SR, COOR, $C(=O)N(R)_2$, $Si(R)_3$, $B(OR)_2$, $C(=O)R$, $P(=O)(R)_2$, $S(=O)R$, $S(=O)_2R$, $OSO_2R$, a straight-chain alkyl group having 1 to 20 carbon atoms or an alkenyl or alkynyl group having 2 to 20 carbon atoms or a branched or cyclic alkyl group having 3 to 20 carbon atoms, where the alkyl, alkenyl or alkynyl group may in each case be substituted by one or more R radicals, where one or more nonadjacent $CH_2$ groups may be replaced by $Si(R)_2$, C=O, NR, O, S or CONR, or an aromatic or heteroaromatic ring system which has 5 to 60 aromatic ring atoms, preferably 5 to 40 aromatic ring atoms, and may be substituted in each case by one or more R radicals; at the same time, two $R^T$ radicals together may form a ring system, two $R^V$ radicals together may form a ring system and/or two $R^6$ radicals together may form a ring system;

$x^1$, $y^1$ are selected, independently, from 0 or 1, wherein when $x^1$ or $y^1$ is 0, then the corresponding group $E^1$ is absent; with the proviso that $x^1 + y^1 = 1$ or 2;

c, f stands on each occurrence, identically or differently, for 0, 1, 2, 3 or 4;

d, e stands on each occurrence, identically or differently, for 0, 1, 2 or 3;

g stands for 0, 1, 2 or 3 if $x^1$=0; or for 0 ,1 or 2 if $x^1$=1;

h stands for 0, 1, 2, 3 or 4 if $y^1$=0; or for 0 ,1, 2 or 3 if $y^1$=1;

k stands for 0, 1, 2, 3 or 4 if x=0; or for 0 ,1, 2 or 3 if x=1;

l stands for 0, 1, 2 or 3 if y=0; or for 0 ,1 or 2 if y=1;

s stands on each occurrence, identically or differently, for 0, 1, 2, 3 or 4; and

u stands for 0, 1 or 2

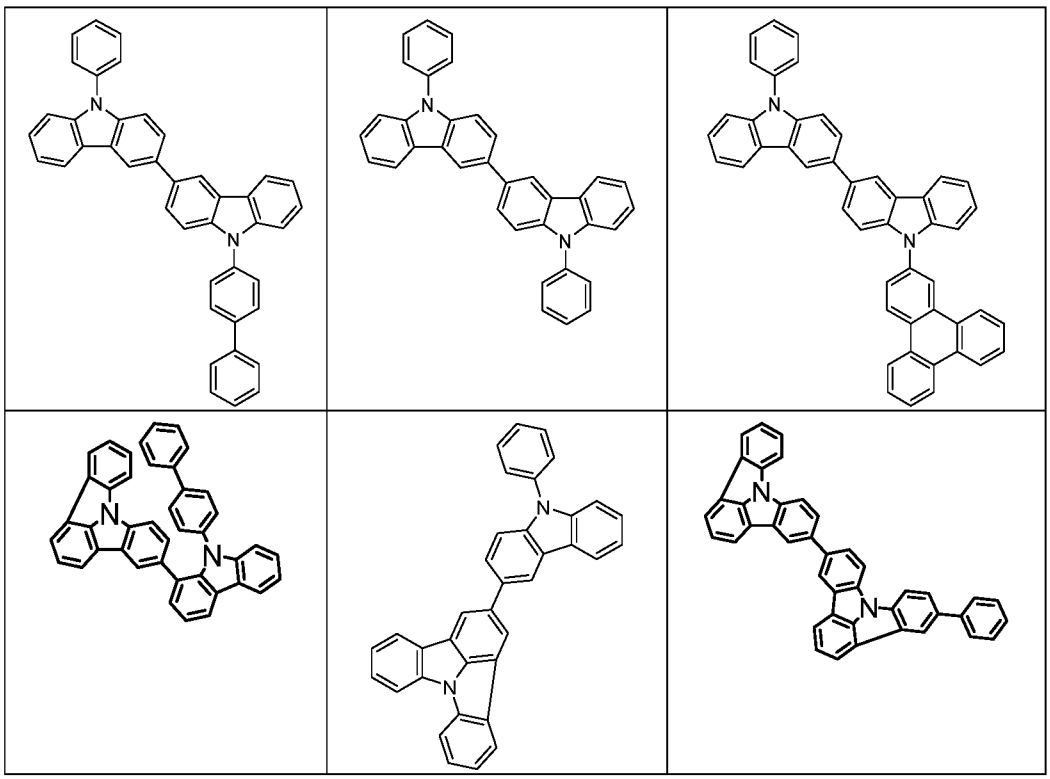
and where the symbols and indices $R^Z$, K, E, R, Ar, x and y have the same meaning as above.

Preferably, K is $Ar^{10}$ and $Ar^{10}$ is selected from aromatic ring systems having 6 to 40, preferably 6 to 30, more preferably 6 to 18 aromatic ring atoms, or an heteroaromatic ring system having 5 to 40, preferably 6 to 30, more preferably 6 to 18 aromatic ring atoms, which may be substituted by one or more R radicals.

Preferably, M is an aromatic ring system having 6 to 40 aromatic ring atoms or a heteroaromatic ring system having 5 to 40, preferably 6 to 30, more preferably 6 to 18 aromatic ring atoms, which may be substituted by one or more R radicals.

Preferably, $Ar^5$ is on each occurrence, identically or differently, an aromatic ring system having 6 to 30, preferably 6 to 18 aromatic ring atoms or a heteroaromatic ring system having 5 to 30, preferably 6 to 18 aromatic ring atoms, which may be substituted by one or more R radicals.

Examples of such heteroaromatic compounds are depicted below:



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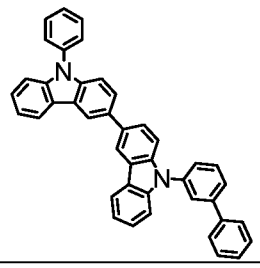
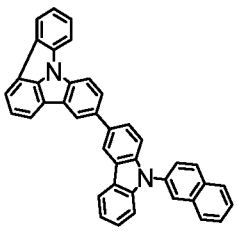
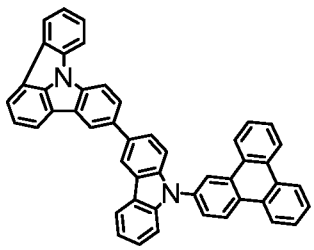
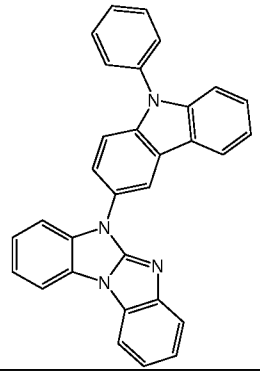
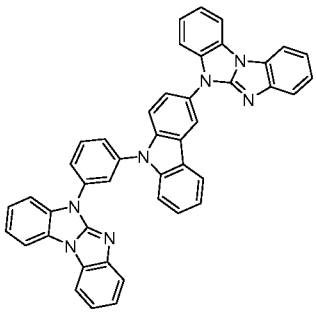
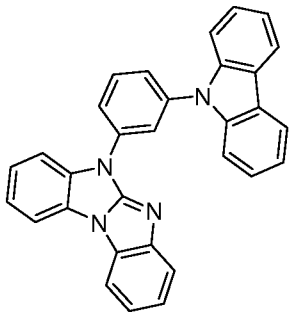
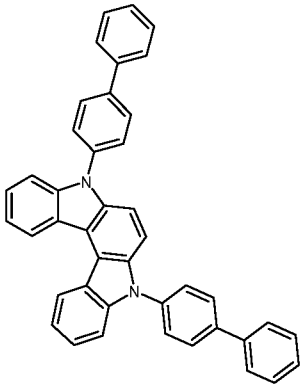
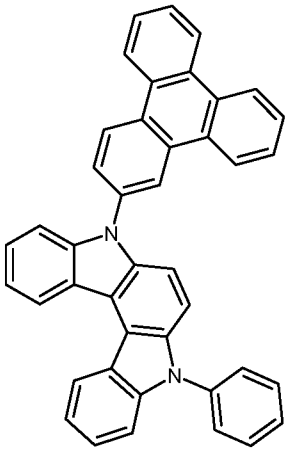
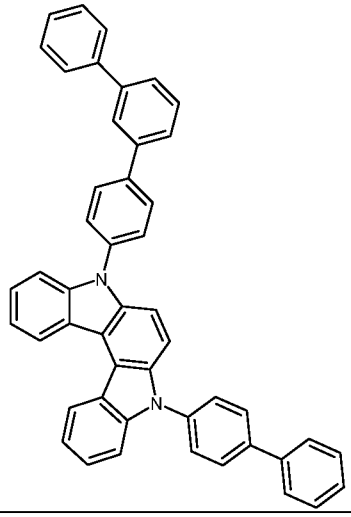
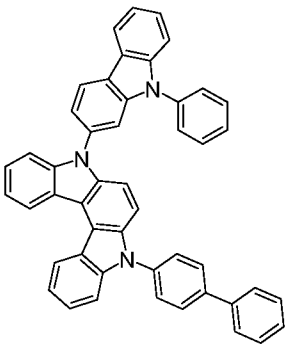
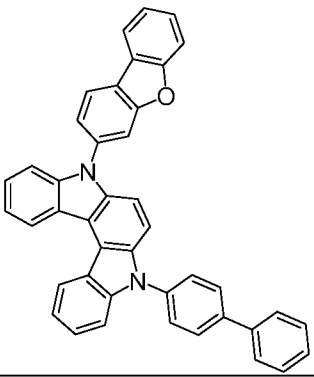
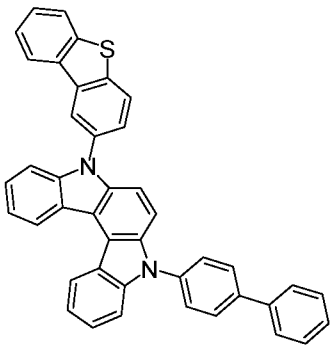
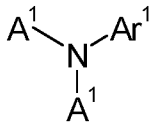
|---|---|---|
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |

In accordance with another preferred embodiment, the compound to be deuterated is an aromatic amine, where an aromatic amine comprises one, two or three groups selected

from aromatic or heteroaromatic ring systems. More preferably, the compounds to be deuterated is an aromatic amine comprising three aromatic or heteroaromatic ring systems selected from aromatic or heteroaromatic ring systems having 5 - 60 aromatic ring atoms, which may be substituted by one or more radicals $R^R$, where $R^R$ has the same definition as above.

Even more preferably, the compound to be deuterated is an aromatic amine selected from compounds of formula (A):



Formula (A)

where:

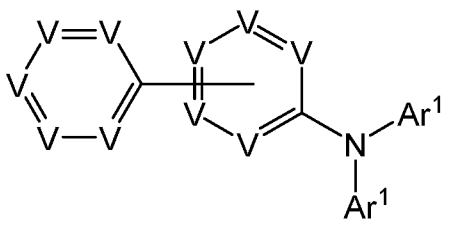
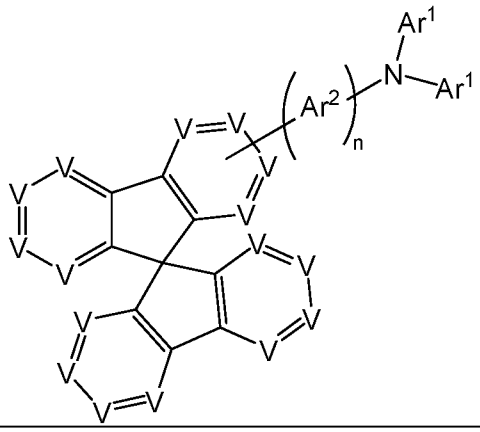
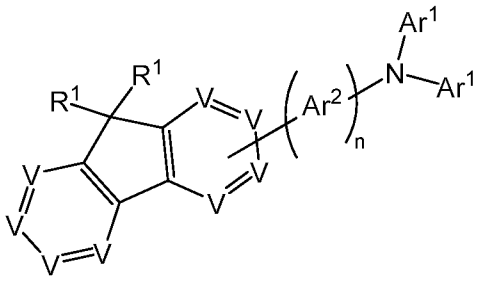
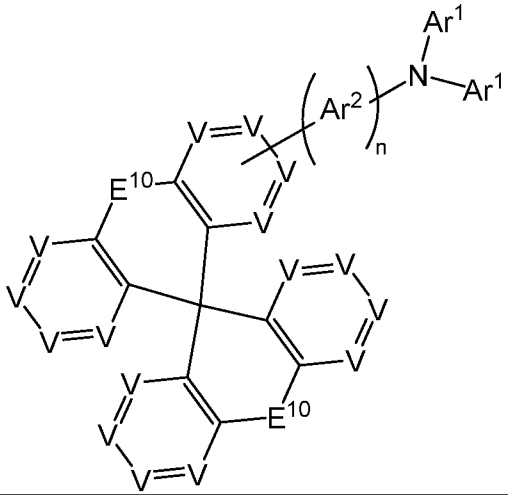
$A^1$ is the same or different at each instance and is H, an alkyl group which has 1 to 20 carbon atoms and may be substituted by one or more $R^1$ radicals, or $Ar^1$;

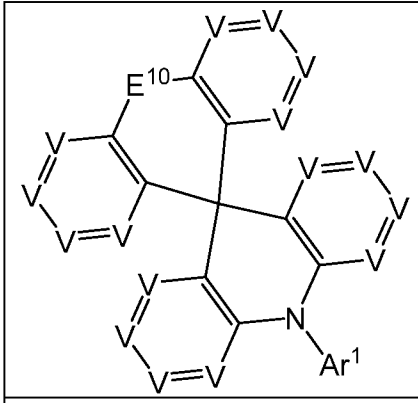
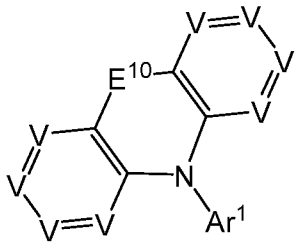
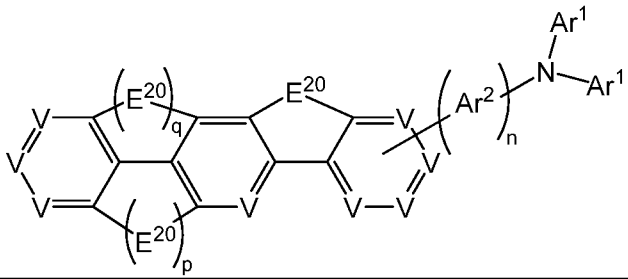
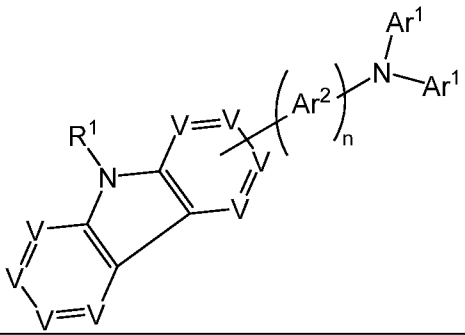
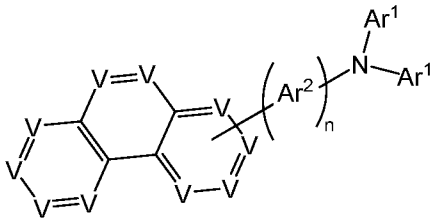
$Ar^1$ is the same or different at each instance and is an aromatic ring system which has 6 to 60 aromatic ring atoms and may be substituted by one or more $R^1$ radicals, or a heteroaromatic ring system which has 5 to 60 aromatic ring atoms and may be substituted by one or more $R^1$ radicals; $Ar^1$ and/or $A^1$ groups here may be bonded to one another via $R^1$ radicals;

$R^1$ is the same or different at each instance and is selected from H, D, F, $C(=O)R^2$, CN, $Si(R^2)_3$, $P(=O)(R^2)_2$, $OR^2$, $S(=O)R^2$, $S(=O)_2R^2$, straight-chain alkyl or alkoxy groups having 1 to 20 carbon atoms, branched or cyclic alkyl or alkoxy groups having 3 to 20 carbon atoms, alkenyl or alkynyl groups having 2 to 20 carbon atoms, aromatic ring systems having 6 to 40 aromatic ring atoms, and heteroaromatic ring systems having 5 to 40 aromatic ring atoms; where two or more $R^1$ radicals may be joined to one another and may form a ring; where the alkyl, alkoxy, alkenyl and alkynyl groups mentioned and the aromatic ring systems and heteroaromatic ring systems mentioned may each be substituted by one or more $R^2$ radicals; and where one or more $CH_2$ groups in the alkyl, alkoxy, alkenyl and alkynyl groups mentioned may be replaced by $-R^2C=CR^2-$, -C≡C-, $Si(R^2)_2$, C=O, $C=NR^2$, -C(=O)O-, $-C(=O)NR^2-$, $P(=O)(R^2)$, -O-, -S-, SO or $SO_2$;

$R^2$ is the same or different at each instance and is selected from H, D, F, CN, alkyl groups having 1 to 20 carbon atoms, aromatic ring systems having 6 to 40 aromatic ring atoms and heteroaromatic ring systems having 5 to 40 aromatic ring atoms; where two or more $R^2$ radicals may be joined to one another and may form a ring; and where the alkyl groups, aromatic ring systems and heteroaromatic ring systems mentioned may be substituted by F or CN.

Particularly preferably, the compound to be deuterated is selected from compounds of one of the formulae (A-I) to (A-IX):

| | |
|---|---|
|  |  |
| Formula (A-I) | Formula (A-II) |
|  |  |
| Formula (A-III) | Formula (A-IV) |

| | |
|---|---|
|  |  |
| Formula (A-V) | Formula (A-VI) |
|  | |
| Formula (A-VII) | |
|  |  |
| Formula (A-VIII) | Formula (A-IX) |

where one or more $R^1$ radicals may be bonded to any of the unsubstituted positions shown, and:

V is the same or different at each instance and is $CR^1$ or N;

$E^{10}$ is the same or different at each instance and is a single bond, O, S, $C(R^1)_2$, $Si(R^1)_2$, $PR^1$, $C(R^1)_2$-$C(R^1)_2$, or $CR^1$=$CR^1$, preferably O, S, $C(R^1)_2$ or $Si(R^1)_2$;

$E^{20}$ is the same or different at each instance and is O, S, $C(R^1)_2$, $Si(R^1)_2$, $PR^1$, $NR^1$, $C(R^1)_2$-$C(R^1)_2$, or $CR^1$=$CR^1$, preferably O, S, $C(R^1)_2$ or $Si(R^1)_2$;

$Ar^2$ is an aromatic ring system which has 6 to 20 aromatic ring atoms and may be substituted by one or more $R^1$ radicals, or a heteroaromatic ring system which has 5 to 20 aromatic ring atoms and may be substituted by one or more $R^1$ radicals;

n, p, q are the same or different and are each 0 or 1; and

$Ar^1$, $R^1$ are as defined above.

Preferred aromatic amine compounds are hole transport materials, which can be used in a hole transport, hole injection or electron blocker layer, such as indenofluoreneamine derivatives (for example according to WO 06/122630 or WO 06/100896), the amine derivatives disclosed in EP 1661888, hexaazatriphenylene derivatives (for example according to WO 01/049806), amine derivatives having fused aromatic systems (for example according to US 5,061,569), the amine derivatives disclosed in WO 95/09147, monobenzoindenofluoreneamines (for example according to WO 08/006449), dibenzoindenofluoreneamines (for example according to WO 07/140847), spirobifluoreneamines (for example according to WO 2012/034627 or WO2013/120577), fluoreneamines (for example according to WO 2014/015937, WO 2014/015938 and WO 2014/015935), spirodibenzopyranamines (for example according to WO 2013/083216) and dihydroacridine derivatives (for example WO 2012/150001).

Still in accordance with a preferred embodiment of the invention, the compound to be deuterated comprises an organometallic compound. Preferably, the organometallic compound comprises a metal atom selected from copper, molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold or europium. It is more preferably a compound comprising iridium or platinum, which have at least one heteroaromatic ring system. Preferred are compounds which are suitable as phosphorescent compounds (= triplet emitters). Examples of such compounds can be found in applications WO 00/70655, WO 2001/41512, WO 2002/02714, WO 2002/15645, EP 1191613, EP 1191612, EP 1191614, WO 05/033244, WO 05/019373, US 2005/0258742, WO 2009/146770, WO 2010/015307, WO 2010/031485, WO 2010/054731, WO 2010/054728, WO 2010/086089, WO 2010/099852, WO 2010/102709, WO 2011/032626, WO 2011/066898, WO 2011/157339, WO 2012/007086, WO 2014/008982,

WO 2014/023377, WO 2014/094961, WO 2014/094960, WO 2015/036074, WO 2015/104045, WO 2015/117718, WO 2016/015815, WO 2016/124304, WO 2017/032439, WO 2018/011186 and WO 2018/041769, WO 2019/020538, WO 2018/178001, WO 2019/115423 or WO 2019/158453. In general, all phosphorescent complexes as used for phosphorescent OLEDs according to the prior art and as known to those skilled in the art in the field of organic electroluminescence are suitable, and the person skilled in the art will be able to use further phosphorescent complexes without exercising inventive skill.

Preferably, the organometallic compounds are metal chelate complexes, in particular with at least one heteroaromatic ring system as chelating ligand for the metal. Preferably, at least one heteroaromatic ring system is bonded to the metal via at least one nitrogen atom and via at least one carbon atom. Preferably, these atoms are each part of an aryl group or heteroaryl group, which are linked at least via a single bond. Examples of such a compound are 2-phenylpyridine or analogous compounds in which aforementioned aryl groups or heteroaryl groups are linked via a single bond.

Preferably, in the H-D exchange either by metal catalysis or acid catalysis, the ratio of hydrogen atoms of the organic compound to deuterium of the deuterium source is at least 1:1.5, preferably 1:1.5 to 1:1000, preferably 1:2 to 1:500, particularly preferably 1:5 to 1:200. A ratio of 1:5 to 1:100 is particularly preferred.

The invention is also directed to deuterated compounds which are obtained by a deuteration method as described above.

The deuterated compounds according to the invention are suitable for use in an electronic device, in particular in an organic electroluminescent device (OLED). Depending on the substitution, the compounds can be used in different functions and layers.

An electronic device in the sense of the present invention is a device comprising at least one layer containing at least one organic compound. The component may also contain inorganic materials or layers which are composed entirely of inorganic materials.

The electronic device is preferably selected from the group consisting of organic electroluminescent devices (OLEDs), organic integrated circuits (O-ICs), organic field-effect

transistors (O-FETs), organic thin-film transistors (O-TFTs), organic light-emitting transistors (O-LETs), organic solar cells (O-SCs), dye-sensitized organic solar cells (DSSCs), organic optical detectors, organic photoreceptors, organic field quench devices (O FQDs), light-emitting electrochemical cells (LECs), organic laser diodes (O-lasers) and organic plasmon emitting devices, but preferably organic electroluminescent devices (OLEDs).

The device is particularly preferably an organic electroluminescent device comprising cathode, anode and at least one emitting layer, wherein at least one organic layer, which may be an emitting layer, hole transport layer, electron transport layer, hole blocking layer, electron blocking layer or another functional layer, comprises at least one deuterated compound according to the invention.

In addition to the cathode, anode, emitting layer, hole transport layer, electron transport layer, hole blocking layer, electron blocking layer, the organic electroluminescent device may contain further layers, selected for example from hole injection layers, hole transport layers, hole blocking layers, electron transport layers, electron injection layers, exciton blocking layers, electron blocking layers, charge generation layers and/or organic or inorganic p/n junctions. Likewise, interlayers can be inserted between two emitting layers, which, for example, have an exciton blocking function. It should be noted, however, that not all of these layers necessarily have to be present.
The organic electroluminescent device may contain one emitting layer, or it may contain several emitting layers. If several emitting layers are present, these preferably have a total of several emission maxima between 380 nm and 750 nm, so that white emission results overall, i.e. different emitting compounds that can fluoresce or phosphoresce are used in the emitting layers. In particular, systems with three emitting layers are preferred, with the three layers showing blue, green and orange or red emission (the principle structure is described, for example, in WO 2005/011013). The organic electroluminescent device according to the invention can also be a tandem OLED, in particular for white-emitting OLEDs.

In accordance with a preferred embodiment, the organic electroluminescent device contains one hole transport layer comprising at least one deuterated hole-transport material selected from deuterated aromatic amines obtained by a method according to the present invention.

In accordance with a preferred embodiment, the organic electroluminescent device contains an organic layer, preferably one emitting layer, comprising at least one host or matrix material selected from deuterated aromatic or heteroaromatic compounds obtained by a method according to the present invention.

In accordance with a preferred embodiment, the organic electroluminescent device contains one emitting layer comprising at least one phosphorescent emitter selected from deuterated organometallic compound obtained by a method according to the present invention.

In accordance with a preferred embodiment, the organic electroluminescent device contains one emitting layer comprising at least one fluorescent emitter selected from deuterated compounds comprising an aromatic ring system, heteroaromatic ring system or aromatic amine, obtained by a method according to the present invention.

Furthermore, the deuterated compound according to the invention can also be used in an electron transport layer and/or in a hole blocking layer and/or in a hole transport layer and/or in an exciton blocking layer.

The term "phosphorescent compound" typically refers to compounds in which the emission of light occurs through a spin-forbidden transition, e.g., a transition from an excited triplet state or a state with a higher spin quantum number, e.g., a quintet state.

When the deuterated compound is used as a hole transport material in a hole transport layer, a hole injection layer or an electron blocking layer, the compound may be used as a pure material, i.e. in a proportion of 100%, in the hole transport layer, or it may be used in combination with one or more other compounds. In a preferred embodiment, the organic layer containing the deuterated compound then additionally contains one or more p-dopants. P-dopants used according to the present invention are preferably those organic electron acceptor compounds capable of oxidizing one or more of the other compounds in the mixture.

The deuterated compound can also be used in an emitting layer as host (= matrix material) in combination with one or more emitting compounds, preferably phosphorescent compounds.

In this case, the proportion of the matrix material in the emitting layer is between 50.0 and 99.9 vol%, preferably between 80.0 and 99.5 vol%, particularly preferably between 92.0 and 99.5 vol%. for fluorescent emitting layers and between 85.0 and 97.0 vol% for phosphorescent emitting layers.

Accordingly, the proportion of the emitting compound is between 0.1 and 50.0 vol%, preferably between 0.5 and 20.0 vol%, particularly preferably between 0.5 and 8.0 vol% for fluorescent emitting layers and between 3.0 and 15.0 vol%. for phosphorescent emitting layers.

Examples of fluorescent emitters are aromatic anthracenamines, aromatic anthracenediamines, aromatic pyrenamines, aromatic pyrenediamines, aromatic chrysenamines or aromatic chrysenediamines. An aromatic anthracenamine is taken to mean a compound in which one diarylamino group is bonded directly to an anthracene group, preferably in the 9-position. An aromatic anthracenediamine is taken to mean a compound in which two diarylamino groups are bonded directly to an anthracene group, preferably in the 9,10-position. Aromatic pyrenamines, pyrenediamines, chrysenamines and chrysenediamines are defined analogously thereto, where the diarylamino groups are preferably bonded to the pyrene in the 1-position or in the 1,6-position. Further preferred emitters are indenofluorenamines or indenofluorenediamines, for example in accordance with WO 2006/108497 or WO 2006/122630, benzoindenofluorenamines or benzoindenofluorenediamines, for example in accordance with WO 2008/006449, and dibenzoindenofluorenamines or dibenzoindenofluorenediamines, for example in accordance with WO 2007/140847, and the indenofluorene derivatives containing condensed aryl groups which are disclosed in WO 2010/012328. Still further preferred emitters are benzanthracene derivatives as disclosed in WO 2015/158409, anthracene derivatives as disclosed in WO 2017/036573, fluorene dimers connected via heteroaryl groups like in WO 2016/150544 or phenoxazine derivatives as disclosed in WO 2017/028940 and WO 2017/028941. Preference is likewise given to the pyrenarylamines disclosed in WO 2012/048780 and WO 2013/185871. Preference is likewise given to the

benzoindenofluorenamines disclosed in WO 2014/037077, the benzofluorenamines disclosed in WO 2014/106522 and the indenofluorenes disclosed in WO 2014/111269 or WO 2017/036574, WO 2018/007421. Also preferred are the emitters comprising dibenzofuran or indenodibenzofuran moieties as disclosed in WO 2018/095888, WO 2018/095940, WO 2019/076789, WO 2019/170572. Preference is likewise given to boron derivatives as disclosed, for example, in WO 2015/102118, CN108409769, CN107266484, WO2017195669 or US2018069182.

Examples of suitable matrix materials for fluorescent compounds, include materials of various substance classes. Preferred matrix materials are selected from the classes of oligoaryls (e.g., 2,2',7,7'-tetraphenylspirobifluorene according to EP 676461 or dinaphthylanthracene), especially oligoaryls with fused aromatic groups, oligoarylenevinylenes (e.g. e.g. DPVBi or spiro-DPVBi according to EP 676461), the polypodal metal complexes (e.g. according to WO 2004/081017), the hole-conducting compounds (e.g. e.g. according to WO 2004/058911), the electron-conducting compounds, in particular ketones, phosphine oxides, sulfoxides, etc. (for example according to WO 2005/084081 and WO 2005/084082), the atropisomers (for example according to WO 2006/048268), the boronic acid derivatives (for example according to WO 2006/117052) or the benzanthracenes (for example according to WO 2008/145239). Particularly preferred matrix materials are selected from the classes of oligoarylenes with naphthalene, anthracene, benzanthracene and/or pyrene or atropisomers of these compounds, the oligoarylenevinylenes, the ketones, the phosphine oxides and the sulfoxides. Very particularly preferred matrix materials are selected from the classes of oligoarylene comprising anthracene, benzanthracene, benzophenanthrene and/or pyrene or atropisomers of these compounds. In the context of the present invention, an oligoarylene is to be understood as a compound in which at least three aryl or arylene groups are linked together. Further preferred are the anthracene derivatives disclosed in WO 2006/097208, WO 2006/131192, WO 2007/065550, WO 2007/110129, WO 2007/065678, WO 2008/145239, WO 2009/100925, WO 2011/054442 and EP 1553154, the anthracene derivatives disclosed in EP 1749809, EP 1905754 and US 2012/0187826, the pyrene compounds disclosed in WO 2015/158409, the benzanthracenylanthracene compounds disclosed in WO 2017/025165, and the phenanthrylanthracenes disclosed in WO 2017/036573.

Examples of matrix materials for phosphorescent emitters are aromatic ketones, aromatic phosphine oxides or aromatic sulfoxides or sulfones, e.g. according to WO 2004/013080, WO 2004/093207, WO 2006/005627 or WO 2010/006680, triarylamines, carbazole derivatives, e. g. e.g. CBP (N,N-biscarbazolylbiphenyl) or according to WO 2005/039246, US 2005/0069729, JP 2004/288381, EP 1205527, WO 2008/086851 or WO 2013/041176, indolo¬carbazole derivatives, e.g. e.g. according to WO 2007/063754 or WO 2008/056746, indenocarbazole derivatives, e.g. according to WO 2010/136109, WO 2011/000455, WO 2013/041176 or WO 2013/056776, azacarbazole derivatives, e.g. according to EP 1617710, EP 1617711, EP 1731584, JP 2005/347160, bipolar matrix materials, e.g. according to WO 2007/137725, silanes, e.g. according to WO 2005/111172, azaborols or boronic esters, e.g. according to WO 2006/117052, triazine derivatives, e.g. according to WO 2007/063754, WO 2008/056746, WO 2010/015306, WO 2011/057706, WO 2011/060859 or WO 2011/060877, zinc complexes, e.g. according to EP 652273 or WO 2009/062578, diazasilol or tetraazasilol derivatives, e.g. according to WO 2010/054729, diazaphosphole derivatives, e.g. according to WO 2010/054730, bridged carbazole derivatives, e.g. according to WO 2011/042107, WO 2011/060867, WO 2011/088877 and WO 2012/143080, triphenylene derivatives, e.g. according to WO 2012/048781, lactams, e.g. according to WO 2011/116865 or WO 2011/137951, or dibenzofuran derivatives, e.g. according to WO 2015/169412, WO 2016/015810, WO 2016/023608, WO 2017/148564 or WO 2017/148565. Likewise, another phos-phorescent emitter, which emits shorter wavelengths than the actual emitter, can be present in the mixture as a co-host or a compound that does not participate or does not participate to a significant extent in charge transport, as described, for example, in WO 2010/108579.

Suitable charge transport materials, such as those that can be used in the hole injection or hole transport layer or in the electron barrier layer or in the electron transport layer of the electronic device, in addition to the deuterated compounds, are for example those mentioned in Y. Shirota et al, Chem. Rev. 2007, 107(4), 953-1010, or other materials as used in these layers according to the prior art.

Preferably, the OLED comprises two or more different hole transporting layers. In this context, the deuterated compound obtained by a method of the invention may be used in one or more or in all hole transporting layers. Materials that are preferably used in hole transporting layers of the OLEDs include, in particular, indenofluorenamine derivatives

(e.g., according to WO 06/122630 or WO 06/100896), the amine derivatives disclosed in EP 1661888, hexaazatriphenylene derivatives (e.g. according to WO 01/049806), amine derivatives with fused aromatics (for example according to US 5,061,569), the amine derivatives disclosed in WO 95/09147, monobenzoindenofluorenamines (for example according to WO 08/006449), dibenzoindenofluorenamines (for example according to WO 07/140847), Spirobifluorenamines (for example according to WO 2012/034627 or WO 2013/120577), Fluorenamines (for example according to WO 2014/015937, WO 2014/015938, WO 2014/015935 and WO 2015/082056), Spirodibenzopyranamines (for example according to WO 2013/083216), Dihydroacridine derivatives (for example according to WO 2012/150001), Spirodibenzofurans and Spirodibenzothiophenes (for example according to WO 2015/022051, WO 2016/102048 and WO 2016/131521), Phenanthrendiarylamines (for example according to WO 2015/131976), Spirotribenzotropolones (for example according to WO 2016/087017), spirobifluorenes with meta-phenyldiamine groups (for example according to WO 2016/078738), spirobisacridines (for example according to WO 2015/158411), xanthenediarylamines (for example according to WO 2014/072017), and 9,10-dihydroanthracene spiro compounds with diarylamino groups according to WO 2015/086108.

Particularly preferred hole transport materials are spirobifluorenes substituted by diarylamino groups in the 4-position as hole-transporting compounds, in particular the use of those compounds claimed and disclosed in WO 2013/120577, and the use of spirobifluorenes substituted by diarylamino groups in the 2-position as hole-transporting compounds, in particular the use of those compounds claimed and disclosed in WO 2012/034627.

Suitable materials for the electron transport layer are all materials which are used as electron transport materials in the electron transport layer according to the state of the art. Particularly suitable are aluminum complexes, e.g. Alq3, zirconium complexes, e.g. Zrq4, lithium complexes, e.g. Liq, benzimidazole derivatives, triazine derivatives, pyrimidine derivatives, pyridine derivatives, pyrazine derivatives, quinoxaline derivatives, quinoline derivatives, oxadiazole derivatives, aromatic ketones, lactams, boranes, diazaphosphole derivatives and phosphine oxide derivatives. Other suitable materials include derivatives of the above compounds as disclosed in JP 2000/053957, WO 2003/060956, WO 2004/028217, WO 2004/080975, and WO 2010/072300.

All the materials mentioned above, which are all suitable as OLED materials, can be deuterated by a method according to the present invention.

The deuterated materials can be used alone in a layer or be combined with one or more deuterated or non-deuterated material(s). Therefore, another aspect of the invention is a composition comprising a deuterated compound obtained by a method as defined above and at least one further compound.

Preferred cathodes of the electronic component are metals with low work function, metal alloys or multilayer structures of different metals, e.g. alkaline earth metals, alkali metals, main group metals or lanthanides (e.g. Ca, Ba, Mg, Al, In, Mg, Yb, Sm, etc.). Additionally suitable are alloys of an alkali or alkaline earth metal and silver, e.g. an alloy of magnesium and silver. In multilayer structures, other metals with a relatively high work function can be used in addition to the metals mentioned, e.g. Ag or Al, with combinations of the metals such as Ca/Ag, Mg/Ag or Ba/Ag usually being used. It may also be advantageous to introduce a thin interlayer of a material with a high dielectric constant between a metallic cathode and the organic semiconductor. Examples of suitable materials are alkali or alkaline earth metal fluorides, but also the corresponding oxides or carbonates (e.g. LiF, Li2O, BaF2, MgO, NaF, CsF, Cs2CO3, etc.). It is also possible to use lithium quinolinate (LiQ) for this purpose. The thickness of this layer is preferably between 0.5 and 5 nm.

Preferred anodes are materials with a high work function. Preferably, the anode has a work function of more than 4.5 eV against vacuum. Firstly, metals with a high redox potential, e.g. Ag, Pt or Au, are suitable for this purpose. Secondly, metal/metal oxide electrodes (e.g. Al/Ni/NiOx, Al/PtOx) may also be preferred. For some applications, at least one of the electrodes must be transparent or partially transparent to allow irradiation of the organic material (organic solar cell) or emission of light (OLED, O-laser). Preferred anode materials here are conductive mixed metal oxides. Indium tin oxide (ITO) or indium zinc oxide (IZO) are particularly preferred. Further preferred are conductively doped organic materials, in particular conductively doped polymers. In addition, the anode can also consist of two or more layers, for example an inner layer of ITO and an outer layer of a metal oxide, preferably tungsten oxide, molybdenum oxide or vanadium oxide.

The device is structured, contacted and finally sealed to exclude harmful influences from water and air.

In the further layers of the organic electroluminescent device, all materials can be used as they are usually used according to the prior art. The skilled person can therefore use all materials known for organic electroluminescent devices in combination with the deuterated compounds without any inventive intervention. Also, the aforementioned compounds, in particular the aromatic or heteroaromatic compounds can be deuterated by the process according to the invention, in particular to improve their lifetime.

Preferably, the organic electroluminescent device comprises one or more layers, which are deposited by a sublimation process. In this process, the materials are vapor-deposited in vacuum sublimation systems at an initial pressure of less than $10^{-5}$ mbar, preferably less than $10^{-6}$ mbar. However, it is also possible for the initial pressure to be even lower, for example less than $10^{-7}$ mbar.

An organic electroluminescent device is also preferred, characterized in that one or more layers are coated using the OVPD (organic vapor phase deposition) process or with the aid of carrier gas sublimation. In this process, the materials are applied at a pressure between $10^{-5}$ mbar and 1 bar. A special case of this process is the OVJP (Organic Vapour Jet Printing) process, in which the materials are applied directly through a nozzle and thus structured.

Further preferred is an organic electroluminescent device comprising one or more layers, which are produced from solution, such as by spin coating, or by any printing process, such as screen printing, flexographic printing, offset printing, LITI (Light Induced Thermal Imaging, thermal transfer printing), ink-jet printing (inkjet printing) or nozzle printing. Soluble compounds are required for this, which can be obtained by suitable substitution, for example.

Hybrid processes are also possible, in which, for example, one or more layers of solution are applied and one or more further layers are vapor-deposited.

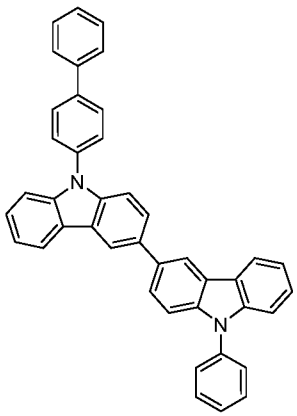
These processes are generally known to those skilled in the art and can be applied by them to organic electroluminescent devices containing the compounds of the invention without any inventive intervention.

**Examples**

Compounds were submitted to deuteration methods as described below. The deuteration degree of the compound was determined by quantitative $^1$H-NMR. The duration and temperature of each deuteration process is determined in such a way that the highest possible deuteration degree is achieved without the formation of impurities: trade-off between a high deuteration degree and a low impurity content.

Example 1:

Example 1 is a process according to the invention comprising the steps 1.1) and 1.2) as defined below.



Compound A

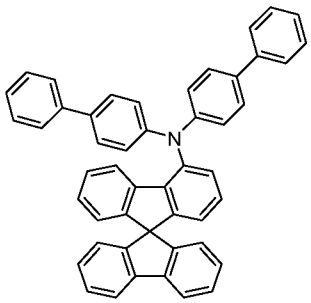
**Step 1.1)** A suspension of compound A (500 g, 0.89 mol) and cyclohexane (27.95 L) is prepared in an autoclave. A Pt-C-catalyst (200.0 g) and $D_2O$ (2.66 L) is added. The autoclave is sealed and degassed using $N_2$. The reaction mixture is stirred for 24 h at 120 °C and 4.0 bar and subsequently cooled down. After phase separation the catalyst is washed with THF. The combined organic fractions are concentrated and filtered over AlOx basic. The remaining clear solution is concentrated under vacuum and the residue

recrystallized from THF/cyclohexane (424 g, 98.9% pure by HPLC, deuteration degree of 56%).

**Step 1.2)** The product obtained by step 1.1) (9.2 g, deuteration degree of 56%) is dissolved in toluene-$d_8$ (110 mL) under inert atmosphere. At 0 °C, trifluoromethanesulfuric acid (14 mL) is added dropwise. After 5 h at 0 °C, a small amount of $D_2O$ (37 mL) is added dropwise (this step is optional – if $H_2O$ is used to quench the solution, the deuteration degree of the product obtained would be decreased slightly). This addition is strongly exothermic, the temperature is controlled to max. 15 °C. At 15 °C, aqueous NaOH (50 mL, 20% by weight) is added dropwise. The organic layer is separated, washed with brine and dist. $H_2O$. The solvent is removed under reduced pressure. The raw product is purified by short column chromatography (toluene, AlOx basic), recrystallization (toluene) and sublimation to obtain the purified product (6.6 g, 99.96% pure by HPLC, deuteration degree of 90%).

Example 2:

Example 2 is a process according to the invention comprising the steps 2.1) and 2.2) as defined below.



Compound B

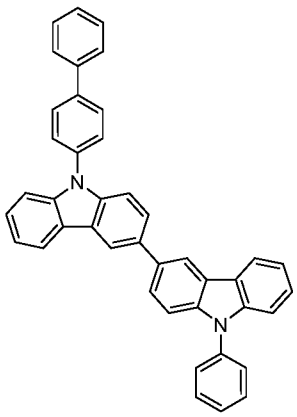
**Step 2.1)** A suspension of compound B (500 g, 0.79 mol), cyclohexane (23.3 L) and 1,4-dioxane (1.47 L) is prepared in an autoclave. A Pt/Pd-C-catalyst (375 g, 4:1) and $D_2O$ (2.75 L) is added. The autoclave is sealed and degassed using $N_2$. The reaction mixture is stirred for 20 h at 120 °C and 4.6 bar and subsequently cooled down. After phase separation the catalyst is washed with THF. The combined organic fractions are concentrated and filtered over AlOx basic. The remaining clear solution is concentrated

under vacuum and the residue recrystallized from toluene/acetonitrile and toluene/ethanol (338 g, 99.96% pure by HPLC, deuteration degree of 41%).

**Step 2.2)** The product obtained from step 2.1) (5.0 g, deuteration degree of 41%) is dissolved in toluene-$d_8$ (63 mL) under inert atmosphere. At 10 °C, trifluoromethanesulfuric acid (6.6 mL) is added dropwise. After 23 h at 20 °C, the temperature is decreased to 7 °C and a small amount of $D_2O$ (9.4 mL) is added dropwise (this step is optional – if $H_2O$ is used to quench the solution, the deuteration degree of the product obtained would be decreased slightly). This addition is strongly exothermic, the temperature is controlled to max. 15 °C. At 15 °C, aqueous NaOH (50 mL, 20% by weight) is added dropwise. The organic layer is separated, washed with brine and dist. $H_2O$, and dried with $Na_2SO_4$. After filtration, the solvent is removed under reduced pressure. The raw product is obtained as off-white solid. (5.0 g, 99.7% pure by HPLC, deuteration degree of 84%).

Comparative Example 3:

Comparative Example 3 is a comparative process comprising the steps 3.1) and 3.2) as defined below.



Compound A

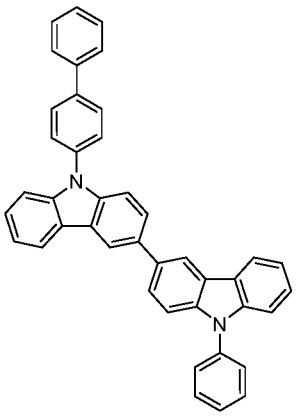
**Step 3.1)** A suspension of compound A (500 g, 0.89 mol) and cyclohexane (27.95 L) is prepared in an autoclave. A Pt-C-catalyst (200.0 g) and $D_2O$ (2.66 L) is added. The autoclave is sealed and degassed using $N_2$. The reaction mixture is stirred for 24 h at 120 °C and 4.0 bar and subsequently cooled down. After phase separation the catalyst is

washed with THF. The combined organic fractions are concentrated and filtered over AlOx basic. The remaining clear solution is concentrated under vacuum and the residue recrystallized from THF/cyclohexane (424 g, 98.9% pure by HPLC, deuteration degree of 56%).

**Step 3.2)** A suspension of the product obtained from step 3.1 (1.0 g, 1.78 mmol) and cyclohexane (43.0 g) is prepared in an autoclave. A Pt-C-catalyst (0.40 g) and $D_2O$ (6.0 g) is added. The autoclave is sealed and degassed using $N_2$. The reaction mixture is stirred for 20 h at 120 °C and 4.0 bar and subsequently cooled down. After phase separation the catalyst is washed with THF. The combined organic fractions are concentrated and filtered over AlOx basic. The remaining clear solution is concentrated under vacuum to obtain the product (deuteration degree of 67%).

Comparative Example 4:

Comparative Example 4 is a comparative process comprising the steps 4.1) and 4.2) as defined below.



Compound A

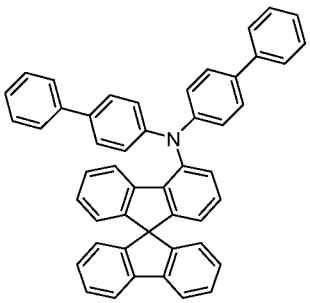
**Step 4.1)** Compound A (5.0 g) is dissolved in toluene-$d_8$ (63 mL) under inert atmosphere. At 10 °C, trifluoromethanesulfuric acid (7.8 mL) is added dropwise. After 5 h at 0 °C, a small amount of $D_2O$ (20.9 mL) is added dropwise (this step is optional – if $H_2O$ is used to quench the solution, the deuteration degree of the product obtained would be decreased slightly). This addition is strongly exothermic, the temperature is controlled to max. 15 °C. At 15 °C, aqueous NaOH (50 mL, 20% by weight) is added dropwise. The organic layer is separated, washed with brine and dist. $H_2O$, and dried with $Na_2SO_4$. After filtration, the solvent is

removed under reduced pressure. The raw product is obtained as off-white solid. (4.7 g, 99.9% pure by HPLC, deuteration degree of 52%).

**Step 4.2)** The product obtained from step 4.1) (4.7 g) is dissolved in toluene-$d_8$ (57 mL) under inert atmosphere. At 10 °C, trifluoromethanesulfuric acid (7.0 mL) is added dropwise. After 5 h at 0 °C, a small amount of $D_2O$ (18.7 mL) is added dropwise (this step is optional – if $H_2O$ is used to quench the solution, the deuteration degree of the product obtained would be decreased slightly). This addition is strongly exothermic, the temperature is controlled to max. 15 °C. At 15 °C, aqueous NaOH (50 mL, 20% by weight) is added dropwise. The organic layer is separated, washed with brine and dist. $H_2O$, and dried with $Na_2SO_4$. After filtration, the solvent is removed under reduced pressure. The raw product is obtained as off-white solid. (4.1 g, 99.9% pure by HPLC, deuteration degree of 52%).

Comparative Example 5

Comparative Example 5 is a comparative process comprising the steps 5.1) and 5.2) as defined below.



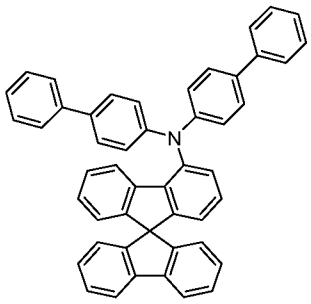
Compound B

**Step 5.1)** A suspension of compound B (500 g, 1.53 mmol), cyclohexane (23.3 L) and 1,4-dioxane (1.47 L) is prepared in an autoclave. A Pt/Pd-C-catalyst (375 g, 4:1) and $D_2O$ (2.75 L) is added. The autoclave is sealed and degassed using $N_2$. The reaction mixture is stirred for 20 h at 120 °C and 4.6 bar and subsequently cooled down. After phase separation the catalyst is washed with THF. The combined organic fractions are concentrated and filtered over AlOx basic. The remaining clear solution is concentrated under vacuum and the residue recrystallized from toluene/acetonitrile and toluene/ethanol (338 g, 99.96% pure by HPLC, deuteration degree of 41%).

**Step 5.2)** A suspension of the product obtained from process 5.1 (1 g, 0.79 mol), cyclohexane (68 mL) and 1,4-dioxane (1 mL) is prepared in an autoclave. A Pt/Pd-C-catalyst (750 mg, 4:1) and $D_2O$ (10 mL) is added. The autoclave is sealed and degassed using $N_2$. The reaction mixture is stirred for 20 h at 120 °C and 4.6 bar and subsequently cooled down. After phase separation the catalyst is washed with THF. The combined organic fractions are concentrated and filtered over AlOx basic. The remaining clear solution is concentrated under vacuum to obtain the product (deuteration degree of 62%).

Comparative Example 6

Comparative Example 6 is a comparative process comprising the steps 6.1) and 6.2) as defined below.



Compound B

**Step 6.1)** Compound B (5.0 g) is suspended in toluene-$d_8$ (67 mL) under inert atmosphere. At 10 °C, trifluoromethanesulfuric acid (6.9 mL) is added dropwise. After 20 h at 20 °C, a small amount of $D_2O$ (9.9 mL) is added dropwise (this step is optional – if $H_2O$ is used to quench the solution, the deuteration degree of the product obtained would be decreased slightly). This addition is strongly exothermic, the temperature is controlled to max. 15 °C. At 15 °C, aqueous NaOH (50 mL, 20% by weight) is added dropwise. The organic layer is separated, washed with brine and dist. $H_2O$, and dried with $Na_2SO_4$. After filtration, the solvent is removed under reduced pressure. The raw product is obtained as off-white solid. (5.2 g, 99.9% pure by HPLC, deuteration degree of 64%).

**Step 6.2)** The product obtained from process 6.1 (5.2 g) is suspended in toluene-$d_8$ (68 mL) under inert atmosphere. At 10 °C, trifluoromethanesulfuric acid (7.1 mL) is added dropwise. After 17 h at 20 °C, a small amount of $D_2O$ (10.2 mL) is added dropwise (this step is

optional – if $H_2O$ is used to quench the solution, the deuteration degree of the product obtained would be decreased slightly). This addition is strongly exothermic, the temperature is controlled to max. 15 °C. At 15 °C, aqueous NaOH (50 mL, 20% by weight) is added dropwise. The organic layer is separated, washed with brine and dist. $H_2O$, and dried with $Na_2SO_4$. After filtration, the solvent is removed under reduced pressure. The raw product is obtained as off-white solid. (4.6 g, 99.9% pure by HPLC, deuteration degree of 76%).

## Claims

1. A method for preparing a deuterated compound, said method comprising the following steps in the following order:
   (a) Performing a first deuteration reaction of the compound by an H-D exchange method to form a first deuterated compound with a deuteration degree x;
   (b) Performing a second deuteration reaction of the first deuterated compound by an H-D exchange method to form a second deuterated compound with a deuteration degree y;
   where the H-D exchange methods in step (a) and (b) are selected from H-D exchange by acid catalysis and H-D exchange by metal catalysis;
   where
   if the H-D exchange method in step (a) is an H-D exchange by metal catalysis, then the H-D exchange method in step (b) is an H-D exchange by acid catalysis, or
   if the H-D exchange method in step (a) is an H-D exchange by acid catalysis, then the H-D exchange method in step (b) is an H-D exchange by metal catalysis, and
   where the following condition (eq 1) is fulfilled by the deuteration degrees x and y after step (b):

$$y \geq 1.3x \quad \text{(eq 1)}$$

2. A method according to claim 1, characterized in that the H-D exchange method in step (a) is an H-D exchange by metal catalysis, and the H-D exchange method in step (b) is an H-D exchange by acid catalysis.

3. A method according to claim 1 or 2, characterized in that the H-D exchange method in step (a) is an H-D exchange by acid catalysis and the H-D exchange method in step (b) is an H-D exchange by metal catalysis.

4. A method according to one ore more of the preceding claims, characterized in that the H-D exchange by metal catalysis is an H-D exchange by heterogeneous metal catalysis.

5. A method according to one or more of the preceding claims, characterized in that the H-D exchange by metal catalysis comprises the following steps in the following order:

MC-1) Mixing a compound or a first deuterated compound; a solvent; a metal catalyst and a deuterium source;

MC-2) Heating to react.

6. A method according to claim 5, characterized in that the deuterium source in step MC-1) comprises one of the following deuterium source: $D_2O$, deuterated benzenes, deuterated toluenes, deuterated xylenes, $CDCl_3$, $CD_3OD$, and mixtures thereof.

7. A method according to claim 5 or 6, characterized in that the metal catalyst in step MC-1) comprises platinum, palladium, rhodium, ruthenium, nickel, cobalt, oxides thereof, complexes thereof, and combinations thereof.

8. A method according to one or more of claims 5 to 7, characterized in that the solvent in step MC-1) comprises a solvent selected from aromatic solvents, ethers, alcohols, alkanes, cycloalkanes, acids, amides, esters or a mixtures thereof.

9. A method according to one or more of claims 5 to 8, characterized in that the step MC-2) is carried out at a temperature between 40°C and 250°C.

10. A method according to one or more of claims 5 to 9, characterized in that step MC-2) occurs under an inert gas.

11. A method according to one or more of the preceding claims, characterized in that the H-D exchange by acid catalysis is selected from H-D exchange by homogeneous acid catalysis.

12. A method according to one or more of the preceding claims, characterized in that the H-D exchange by acid catalysis comprises the following steps in the following order:

AC-1) Mixing a compound or a first deuterated compound with a deuterated solvent;

AC-2) Treating the reaction mixture of step AC-1) with an acid catalyst having a pKa in water of 0 or less.

13. A method according to claim 12, characterized in that the acid catalyst has a pKa in water of - 5 or less.

14. A method according to claim 12 or 13, characterized in that the deuterated solvent is a deuterated aromatic solvent.

15. A method according to one or more of claims 12 to 14, characterized in that the deuterated solvent comprises a solvent selected from deuterated benzenes, deuterated toluenes, deuterated xylenes, $CDCl_3$, $CD_3OD$, and mixtures thereof.

16. A method according to one or more of claims 12 to 15, characterized in that the acid catalyst is $H_2SO_4$, $D_2SO_4$, $CF_3CO_2H$, $CF_3CO_2D$, $CH_3SO_3H$, $CH_3SO_3D$, $C_6H_6SO_3H$, $C_6H_6SO_3D$, $CF_3SO_3H$, $CF_3SO_3D$, $FSO_3H$, $FSO_3D$, and mixture thereof.

17. A method according to one or more of claims 12 to 16, characterized in that the deuterated solvent used in the H-D exchange by acid catalysis is re-enriched in deuterium by being introduced in a reaction mixture of a H-D exchange by metal catalysis.

18. A method according to one or more of the preceding claims, characterized in that the compound to be deuterated comprises an aromatic ring system, an heteroaromatic ring system, an aromatic amine or an organometallic compound.

19. A method according to claim 18, characterized in that the compound to be deuterated is an aromatic ring system selected from benzene, naphthalene, anthracene, benzanthracene, phenanthrene, benzophenanthrene, pyrene, chrysene, perylene, fluoranthene, naphthacene, pentacene, benzopyrene, biphenyl, biphenylene, terphenyl, terphenylene, quaterphenyl, fluorene, spirobifluorene, dihydrophenanthrene, dihydropyrene, tetrahydropyrene, cis- or trans-indenofluorene, truxene, isotruxene, spirotruxene, spiroisotruxene, and combinations of these groups, which may be substituted by one or more radicals $R^R$, where

$R^R$ stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CHO, CN, C(=O)Ar, $P(=O)(Ar)_2$, S(=O)Ar, $S(=O)_2Ar$, $N(R')_2$, $N(Ar)_2$, $NO_2$, $Si(R')_3$,

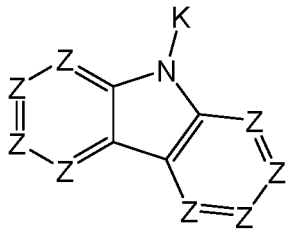
$B(OR')_2$, $OSO_2R'$, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or branched or a cyclic alkyl, alkoxy or thioalkyl group having 3 to 40 C atoms, each of which may be substituted by one or more radicals R', where in each case one or more non-adjacent $CH_2$ groups may be replaced by R'C=CR', C≡C, $Si(R')_2$, $Ge(R')_2$, $Sn(R')_2$, C=O, C=S, C=Se, P(=O)(R'), SO, $SO_2$, O, S or CONR' and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or $NO_2$, an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R', or an aryloxy group having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals R'; where two radicals $R^R$ may form an aliphatic or aromatic ring system together, which may be substituted by one or more radicals R';

Ar is, on each occurrence, identically or differently, an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case also be substituted by one or more radicals R';

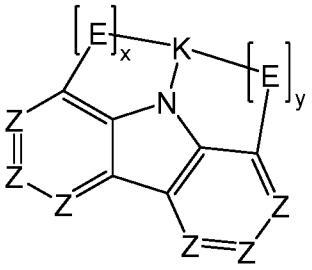
R' stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CN, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 20 C atoms or branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 20 C atoms, where in each case one or more non-adjacent $CH_2$ groups may be replaced by SO, $SO_2$, O, S and where one or more H atoms may be replaced by D, F, Cl, Br or I, or an aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms.

20. A method according to claim 18, characterized in that the compound to be deuterated is an heteroaromatic ring system selected from dibenzofuran, dibenzothiophene, carbazole, indolocarbazole, indenocarbazole, pyridine, quinoline, isoquinoline, acridine, phenanthridine, benzoquinoline, phenothiazine, phenoxazine, pyrimidine, benzopyrimidine, quinoxaline, pyrazine, phenazine, phenoxazine, phenothiazine and combinations of these groups, which may be substituted by one or more radicals $R^R$, where $R^R$ has the same definition as in claim 19.

21. A method according according to claim 18, characterized in that the compound to be deuterated is an heteroaromatic ring system selected from the compounds of the formulas (h-1) or (h-2):



Formula (h-1)



Formula (h-2)

where:

K is $Ar^{10}$ or $-L^1-N(Ar)_2$;

Z is $C-R^Z$ ; or two adjacent groups Z form a condensed ring together;

$R^Z$ is the same or different at each instance and is selected from H, D, F, Cl, Br, I, $N(Ar)_2$, $N(R)_2$, OAr, SAr, CN, $NO_2$, OR, SR, COOR, $C(=O)N(R)_2$, $Si(R)_3$, $B(OR)_2$, C(=O)R, $P(=O)(R)_2$, S(=O)R, $S(=O)_2R$, $OSO_2R$, a straight-chain alkyl group having 1 to 20 carbon atoms or an alkenyl or alkynyl group having 2 to 20 carbon atoms or a branched or cyclic alkyl group having 3 to 20 carbon atoms, where the alkyl, alkenyl or alkynyl group may in each case be substituted by one or more R radicals, where one or more nonadjacent $CH_2$ groups may be replaced by $Si(R)_2$, C=O, NR, O, S or CONR, or an aromatic or heteroaromatic ring system which has 5 to 60 aromatic ring atoms, preferably 5 to 40 aromatic ring atoms, and may be substituted in each case by one or more R radicals;

$L^1$ is a single bond or an aromatic or heteroaromatic ring system which has 5 to 30 aromatic ring atoms and may be substituted by one or more R radicals;

$Ar^{10}$ is an aromatic ring system having 6 to 40 aromatic ring atoms or a heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may be substituted by one or more R radicals;

$R^Z$ is the same or different at each instance and is H, D, F, Cl, Br, I, $N(Ar)_2$, $N(R)_2$, OAr, SAr, CN, $NO_2$, OR, SR, COOR, $C(=O)N(R)_2$, $Si(R)_3$, $B(OR)_2$, C(=O)R, $P(=O)(R)_2$, S(=O)R, $S(=O)_2R$, $OSO_2R$, a straight-chain alkyl group having 1 to 20 carbon atoms or an alkenyl or alkynyl group having 2 to 20 carbon atoms or a branched or cyclic alkyl

group having 3 to 20 carbon atoms, where the alkyl, alkenyl or alkynyl group may in each case be substituted by one or more R radicals, where one or more nonadjacent $CH_2$ groups may be replaced by $Si(R)_2$, C=O, NR, O, S or CONR, or an aromatic or heteroaromatic ring system which has 5 to 60 aromatic ring atoms, preferably 5 to 40 aromatic ring atoms, and may be substituted in each case by one or more R radicals; at the same time, two $R^z$ radicals together may also form a ring system;

E is on each occurrence, independently, a single bond or a group $C(R^0)_2$;

$R^0$ is selected on each occurrence, independently, from a straight-chain alkyl group having 1 to 10 carbon atoms or a branched or cyclic alkyl group having 3 to 10 carbon atoms, which may in each case be substituted by one or more R´ radicals;

R stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CHO, CN, C(=O)Ar, $P(=O)(Ar)_2$, S(=O)Ar, $S(=O)_2Ar$, $N(R´)_2$, $N(Ar)_2$, $NO_2$, $Si(R´)_3$, $B(OR´)_2$, $OSO_2R´$, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or branched or a cyclic alkyl, alkoxy or thioalkyl group having 3 to 40 C atoms, each of which may be substituted by one or more radicals R´, where in each case one or more non-adjacent $CH_2$ groups may be replaced by R´C=CR´, C≡C, $Si(R´)_2$, $Ge(R´)_2$, $Sn(R´)_2$, C=O, C=S, C=Se, P(=O)(R´), SO, $SO_2$, O, S or CONR´ and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or $NO_2$, an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R´, or an aryloxy group having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals R´; where two radicals R may form an aliphatic or aromatic ring system together, which may be substituted by one or more radicals R´;

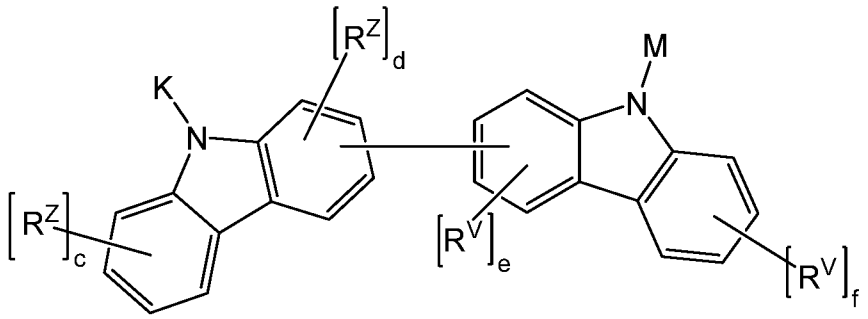
Ar is, on each occurrence, identically or differently, an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case also be substituted by one or more radicals R´;

R´ stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CN, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 20 C atoms or branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 20 C atoms, where in each case one

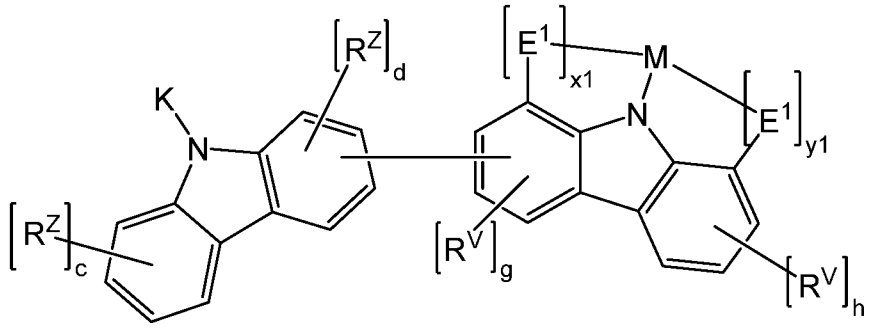
or more non-adjacent $CH_2$ groups may be replaced by SO, $SO_2$, O, S and where one or more H atoms may be replaced by D, F, Cl, Br or I, or an aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms;

x, y are selected, independently, from 0 or 1, wherein when x or y is 0, then the corresponding group E is absent; and x + y = 1 or 2.

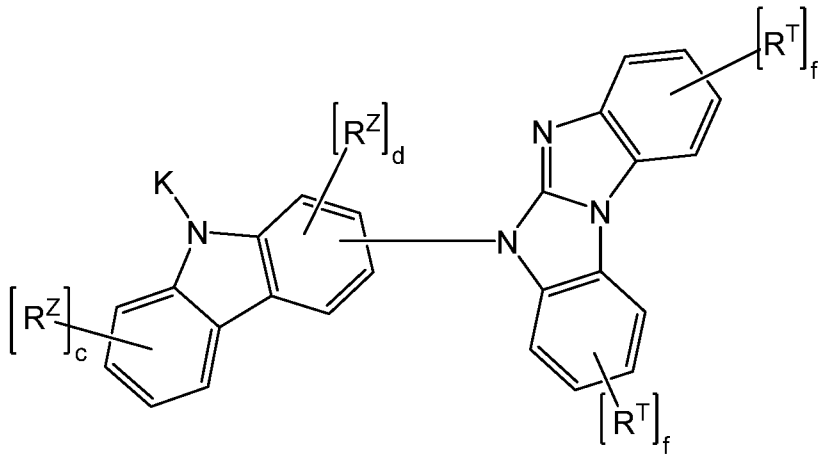
22. A method according to claim 21, characterized in that compound to be deuterated is an heteroaromatic ring system selected from the compounds of the formulas (h-1-1) to (h-1-3) and (h-2-1) to (h-2-2),



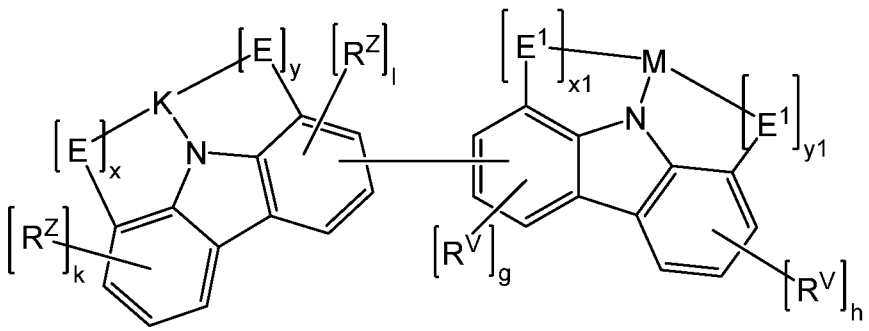
Formula (h-1-1)



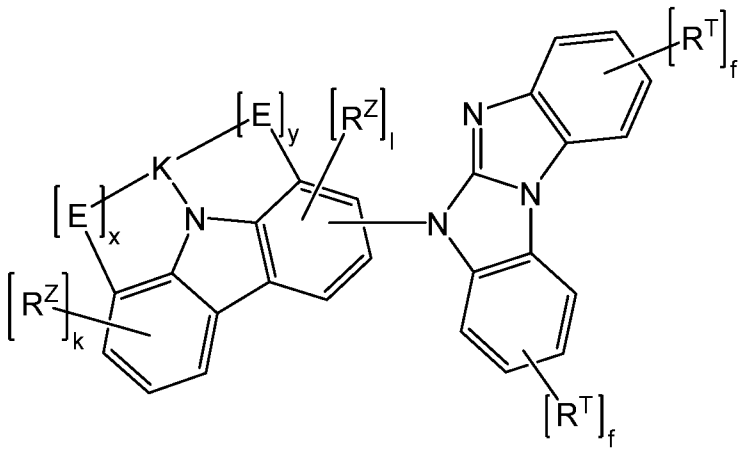
Formula (h-1-2)



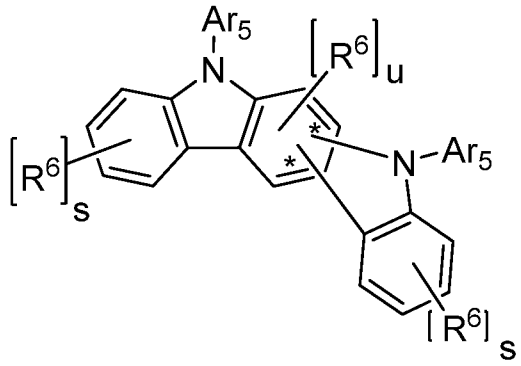
Formula (h-1-3)



Formula (h-2-1)



Formula (h-2-2)



Formula (h-3-1)

Where the symbols and idices have the following meaning:

M is an aromatic ring system having 6 to 40 aromatic ring atoms or a heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may be substituted by one or more R radicals;

$E^1$ is on each occurrence, independently, a single bond or a group $C(R^0)_2$; where $R^0$ has the same meaning as in claim 21;

$Ar^5$ is on each occurrence, identically or differently, an aromatic ring system having 6 to 40 aromatic ring atoms or a heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may be substituted by one or more R radicals;

$R^T$, $R^V$, $R^6$ are the same or different at each instance and is selected from H, D, F, Cl, Br, I, $N(Ar)_2$, $N(R)_2$, OAr, SAr, CN, $NO_2$, OR, SR, COOR, $C(=O)N(R)_2$, $Si(R)_3$, $B(OR)_2$, C(=O)R, $P(=O)(R)_2$, S(=O)R, $S(=O)_2R$, $OSO_2R$, a straight-chain alkyl group having 1 to 20 carbon atoms or an alkenyl or alkynyl group having 2 to 20 carbon atoms or a branched or cyclic alkyl group having 3 to 20 carbon atoms, where the alkyl, alkenyl or alkynyl group may in each case be substituted by one or more R radicals, where one or more nonadjacent $CH_2$ groups may be replaced by $Si(R)_2$, C=O, NR, O, S or CONR, or an aromatic or heteroaromatic ring system which has 5 to 60 aromatic ring atoms, preferably 5 to 40 aromatic ring atoms, and may be substituted in each case by one or more R radicals; at the same time, two $R^T$ radicals together may form a ring system, two $R^V$ radicals together may form a ring system and/or two $R^6$ radicals together may form a ring system;

$x^1$, $y^1$ are selected, independently, from 0 or 1, wherein when $x^1$ or $y^1$ is 0, then the corresponding group $E^1$ is absent; with the proviso that $x^1 + y^1 = 1$ or 2;

c, f stands on each occurrence, identically or differently, for 0, 1, 2, 3 or 4;

d, e stands on each occurrence, identically or differently, for 0, 1, 2 or 3;

g stands for 0, 1, 2 or 3 if $x^1$=0; or for 0 ,1 or 2 if $x^1$=1;

h stands for 0, 1, 2, 3 or 4 if $y^1$=0; or for 0 ,1, 2 or 3 if $y^1$=1;

k stands for 0, 1, 2, 3 or 4 if x=0; or for 0 ,1, 2 or 3 if x=1;

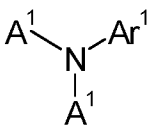
l stands for 0, 1, 2 or 3 if y=0; or for 0 ,1 or 2 if y=1;

s stands on each occurrence, identically or differently, for 0, 1, 2, 3 or 4; and

u stands for 0, 1 or 2;

and where the symbols and indices $R^Z$, K, E, R, Ar, x and y have the same meaning as in claim 21.

23. A method according to claim 18, characterized in that the compound to be deuterated is an aromatic amine selected from compounds of formula (A):



Formula (A)

where:

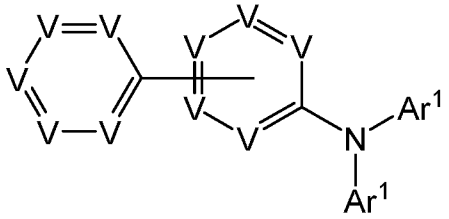
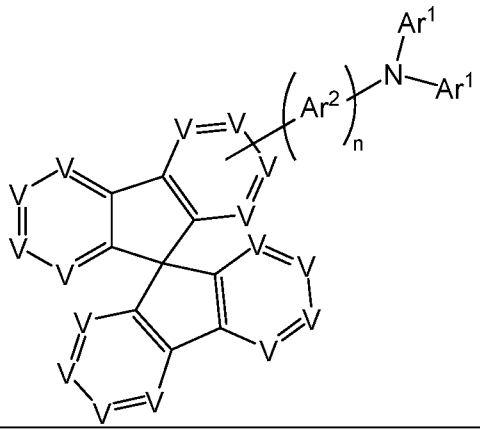
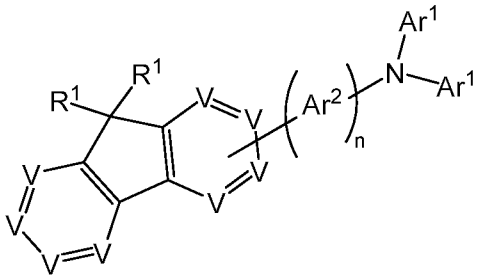
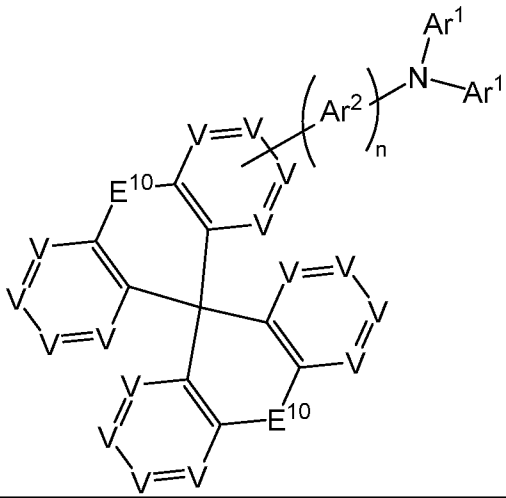
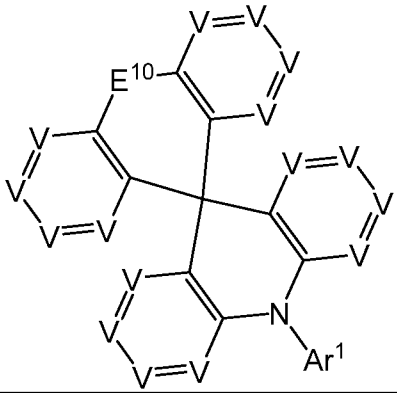
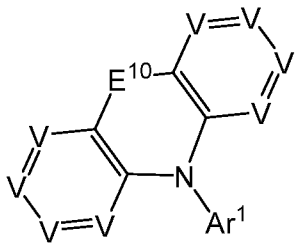
$A^1$ is the same or different at each instance and is H, an alkyl group which has 1 to 20 carbon atoms and may be substituted by one or more $R^1$ radicals, or $Ar^1$;

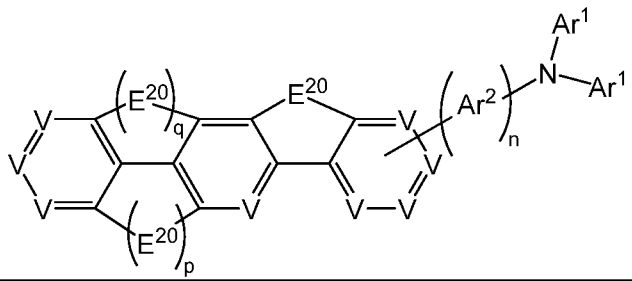
$Ar^1$ is the same or different at each instance and is an aromatic ring system which has 6 to 60 aromatic ring atoms and may be substituted by one or more $R^1$ radicals, or a heteroaromatic ring system which has 5 to 60 aromatic ring atoms and may be substituted by one or more $R^1$ radicals; $Ar^1$ and/or $A^1$ groups here may be bonded to one another via $R^1$ radicals;

$R^1$ is the same or different at each instance and is selected from H, D, F, $C(=O)R^2$, CN, $Si(R^2)_3$, $P(=O)(R^2)_2$, $OR^2$, $S(=O)R^2$, $S(=O)_2R^2$, straight-chain alkyl or alkoxy groups having 1 to 20 carbon atoms, branched or cyclic alkyl or alkoxy groups having 3 to 20 carbon atoms, alkenyl or alkynyl groups having 2 to 20 carbon atoms, aromatic ring systems having 6 to 40 aromatic ring atoms, and heteroaromatic ring systems having 5 to 40 aromatic ring atoms; where two or more $R^1$ radicals may be joined to one another and may form a ring; where the alkyl, alkoxy, alkenyl and alkynyl groups mentioned and the aromatic ring systems and heteroaromatic ring systems mentioned may each be substituted by one or more $R^2$ radicals; and where one or more $CH_2$ groups in the alkyl, alkoxy, alkenyl and alkynyl groups mentioned may be replaced by $-R^2C=CR^2-$, -C≡C-, $Si(R^2)_2$, C=O, $C=NR^2$, -C(=O)O-, $-C(=O)NR^2-$, $P(=O)(R^2)$, -O-, -S-, SO or $SO_2$;

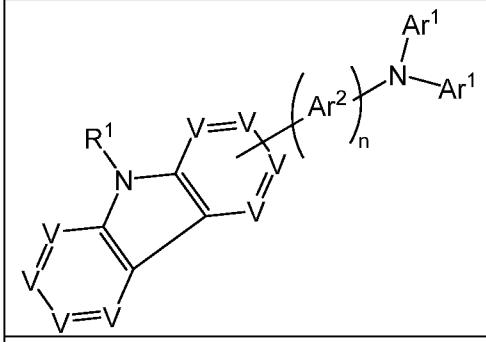
$R^2$ is the same or different at each instance and is selected from H, D, F, CN, alkyl groups having 1 to 20 carbon atoms, aromatic ring systems having 6 to 40 aromatic ring atoms and heteroaromatic ring systems having 5 to 40 aromatic ring atoms; where two or more $R^2$ radicals may be joined to one another and may form a ring; and where the alkyl groups, aromatic ring systems and heteroaromatic ring systems mentioned may be substituted by F or CN.

24. A method according to claim 23, characterized in that the aromatic amine compound is selected from compounds of one of the formulae (A-I) to (A-IX):

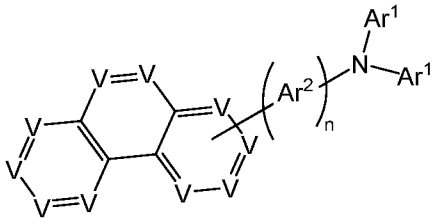
| | |
|---|---|
|  |  |
| Formula (A-I) | Formula (A-II) |
|  |  |
| Formula (A-III) | Formula (A-IV) |
|  |  |
| Formula (A-V) | Formula (A-VI) |



Formula (A-VII)



Formula (A-VIII)



Formula (A-IX)

where one or more $R^1$ radicals may be bonded to any of the unsubstituted positions shown, and:

V is the same or different at each instance and is $CR^1$ or N;

$E^{10}$ is the same or different at each instance and is a single bond, O, S, $C(R^1)_2$, $Si(R^1)_2$, $PR^1$, $C(R^1)_2$-$C(R^1)_2$, or $CR^1$=$CR^1$;

$E^{20}$ is the same or different at each instance and is O, S, $C(R^1)_2$, $Si(R^1)_2$, $PR^1$, $NR^1$, $C(R^1)_2$-$C(R^1)_2$, or $CR^1$=$CR^1$;

$Ar^2$ is an aromatic ring system which has 6 to 20 aromatic ring atoms and may be substituted by one or more $R^1$ radicals, or a heteroaromatic ring system which has 5 to 20 aromatic ring atoms and may be substituted by one or more $R^1$ radicals;

n, p, q are the same or different and are each 0 or 1; and

$Ar^1$, $R^1$ are as defined in claim 23.

25. A deuterated compound obtained by a method as defined in one or more of claims 1 to 24.

26. A composition comprising a deuterated compound obtained by a method as defined in one or more of claims 1 to 24 and a further compound.

27. An electronic device comprising a a deuterated compound obtained by a method as defined in one or more of claims 1 to 24.

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/086305

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07B59/00 C07C211/61 C07D209/82
ADD.

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)
C07B C07C C07D

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 practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | JENS ATZRODT ET AL: "The Renaissance of H/D Exchange", ANGEWANDTE CHEMIE INTERNATIONAL EDITION, vol. 46, no. 41, 15 October 2007 (2007-10-15), pages 7744-7765, XP055192405, ISSN: 1433-7851, DOI: 10.1002/anie.200700039 chapter 2.2: H/D exchange with acid-catalyzed methods; chapter 3: H/D exchange by metal catalysis<br>-----<br>-/-- | 1-27 |

[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 application or patent 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 |
|---|---|
| 27 March 2024 | 08/04/2024 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Lange, Tim |

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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. |
|---|---|---|
| X | WO 2016/073425 A2 (DU PONT [US])<br>12 May 2016 (2016-05-12) | 25,26 |
| Y | A method for deuterating an aromatic compound having aromatic hydrogens, said method comprising:<br>(a) providing a liquid composition comprising deuterium oxide having dissolved or dispersed therein the aromatic compound and a transition metal catalyst; and<br>(b) heating the liquid composition at a temperature of 120 °C or greater, and a pressure of 50 psi (345 kPa) or greater, for a period of 24 hours or less, to form a deuterated aromatic compound (see claim 1) and wherein the preferred transitions metal catalyst are Pd, Pt, Ir, Rh, Ru, or oxides thereof (see claim 6) and wherein the aromatic compounds may be aromatic hydrocarbons (see claim 3) or heteroaryl compounds such as carbazole (see claim 4).<br>----- | 1-24,27 |
| X | LIANG XUEWEI ET AL: "Efficient Brønsted-Acid-Catalyzed Deuteration of Arenes and Their Transformation to Functionalized Deuterated Products", ASIAN JOURNAL OF ORGANIC CHEMISTRY , 1(2), 160-165 CODEN: AJOCC7; ISSN: 2193-5807, vol. 6, no. 8, 1 August 2017 (2017-08-01), pages 1063-1071, XP093146372, Germany<br>ISSN: 2193-5807, DOI: 10.1002/ajoc.201700218<br>Retrieved from the Internet: URL:https://api.wiley.com/onlinelibrary/tdm/v1/articles/10.1002%2Fajoc.201700218> | 25,26 |
| Y | Brönsted-Acid catalyzed deuteration of arenes: see title and whole document; see exprimental section, general protocol, page 1068-1069<br>"Generally speaking, H/D exchange can be promoted by transition metals or under acidic/basic conditions": see page 1063, least sentence left column to first sentence right column; "As in many literature procedures deuterium is introduced using acidic conditions and/or transition metals....": see page 1063, right column, 2nd last sentence of 1st paragraph<br>-----<br>-/-- | 1-24,27 |

1

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/086305

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | TSUJI HAYATO ET AL: "The hydrogen/deuterium isotope effect of the host material on the lifetime of organic light-emitting diodes", CHEMICAL COMMUNICATIONS, vol. 50, no. 94, 1 January 2014 (2014-01-01), pages 14870-14872, XP055944140, UK ISSN: 1359-7345, DOI: 10.1039/C4CC05108D Electronic devices such as OLEDs comprising a deuterated compound: see whole document, see figures 1-3 ----- | 27 |

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2023/086305

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| WO 2016073425 A2 | 12-05-2016 | KR 20170084048 A | 19-07-2017 |
| | | US 2016130194 A1 | 12-05-2016 |
| | | WO 2016073425 A2 | 12-05-2016 |