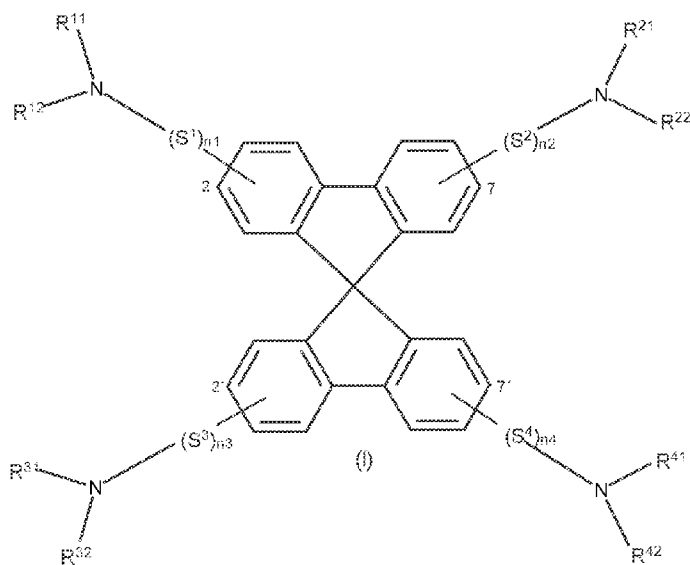




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- (72) Inventors: BRUDER, Ingmar; Neustadter Str. 30, 67112 Mutterstadt (DE). SENS, Rüdiger; Faselwiese 15, 67069 Ludwigshafen (DE). WONNEBERGER, Henrike; Richard-Wagner-Straße 15, 68165 Mannheim (DE). BERGMANN, Hermann; Kamp 68, 49074 Osnabrück (DE). SEND, Robert; Luisenstr. 25, 76137 Karlsruhe (DE). GETAUTIS, Vytautas; Gričiuo 22-10, LT-51390 Kaunas (LT). DASKEVICIENE, Maryte; Chemiku 110-9, LT-55232 Jonava (LT). MALINAUSKAS, Tadas; Ukmerges 17-27, LT-49317 Kaunas (LT).
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- (74) Common Representative: BASF SE; 67056 Ludwigshafen (DE).
- (71) Applicant: BASF SE [DE/DE]; 67056 Ludwigshafen (DE).
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- (71) Applicant (for MN only): BASF (CHINA) COMPANY LIMITED [CN/CN]; 300 Jiangxinsha Road, Shanghai, 200137 (CN).
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(54) Title: NEW SPIRO COMPOUNDS AND THEIR USE IN ORGANIC ELECTRONICS APPLICATIONS AND DEVICES



(57) Abstract: The present invention relates to 9,9'-spirobifluorene compounds of general formula I wherein the variables have the meaning R¹¹, R¹², R²¹, R²², R³¹, R³², R⁴¹ and R⁴² independently of each other aryl or heteroaryl, S¹, S², S³ and S⁴ independently of each other π -conjugated, bivalent moieties, n¹, n², n³ and n⁴ independently of each other 0, 1, 2 or 3, with the proviso that n¹ + n² + n³ + n⁴ \neq 0, in case n¹ \geq 2, n² \geq 2, n³ \geq 2 and/or n⁴ \geq 2 the moieties S¹, S², S³ and S⁴ are identical to or different from each other and in case n¹ + n² + n³ + n⁴ = 12 not all of the radicals R¹¹, R¹², R²¹, R²², R³¹, R³², R⁴¹ and R⁴² are identical, to the use of compounds of general formula I in organic electronics applications, especially in organic field effect transistors, in organic photodetectors and organic solar cells, specifically in dye-sensitized solar cells and bulk heterojunction solar cells, and to an organic field effect transistor, a dye-sensitized solar cell and a bulk heterojunction solar cell comprising compounds of general formula I.



GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

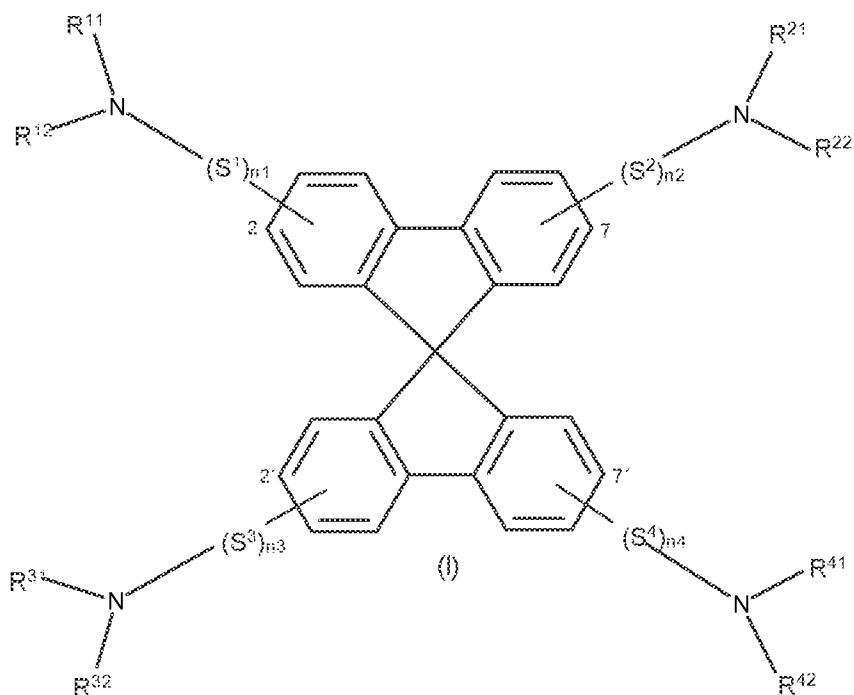
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New spiro compounds and their use in organic electronics applications and devices

Description

5 The present invention relates to 9,9'-spirobifluorene compounds of general formula I



wherein the variables have the meaning

10

R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} and R^{42} independently of each other aryl or hetaryl,

S^1 , S^2 , S^3 and S^4 independently of each other π -conjugated, bivalent moieties,

15

n^1 , n^2 , n^3 and n^4 independently of each other 0, 1, 2 or 3,

with the proviso that

$n^1 + n^2 + n^3 + n^4 \neq 0$,

20

in case $n^1 \geq 2$, $n^2 \geq 2$, $n^3 \geq 2$ and/or $n^4 \geq 2$ the moieties S^1 , S^2 , S^3 and S^4 are identical to or different from each other

and

25

in case $n^1 + n^2 + n^3 + n^4 = 12$ not all of the radicals R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} and R^{42} are identical,

to the use of compounds of general formula I in organic electronics applications, especially in organic field effect transistors, in organic photodetectors and organic solar cells, specifically in dye-sensitized solar cells and bulk heterojunction solar cells, and

- 5 to an organic field effect transistor, a dye-sensitized solar cell and a bulk heterojunction solar cell comprising compounds of general formula I.

Dye-sensitized solar cells ("DSCs") are one of the most efficient alternative solar cell technologies at present. In a liquid variant of this technology, efficiencies of up to 11% have been
10 achieved to date (e.g. Grätzel M. et al., J. Photochem. Photobiol. C, 2003, 4, 145; Chiba et al., Japanese Journal of Appl. Phys., 2006, 45, L638-L640).

The construction of a DSC is generally based on a glass substrate, which is coated with a transparent conductive layer, the working electrode. An n-conductive metal oxide is generally
15 applied to this electrode or in the vicinity thereof, for example an approx. 2-20 µm-thick nanoporous titanium dioxide layer (TiO₂). On the surface thereof, in turn, a monolayer of a light-sensitive dye, for example a ruthenium complex, is typically adsorbed, which can be converted to an excited state by light absorption. The counterelectrode may optionally have a catalytic layer of a metal, for example platinum, with a thickness of a few µm. The area between the two
20 electrodes is filled with a redox electrolyte, for example a solution of iodine (I₂) and lithium iodide (LiI).

The function of the DSC is based on the fact that light is absorbed by the dye, and electrons are transferred from the excited dye to the n-semiconductive metal oxide semiconductor and migrate thereon to the anode, whereas the electrolyte ensures that the charges are balanced via
25 the cathode. The n-semiconductive metal oxide, the dye and the (usually liquid) electrolyte are thus the most important constituents of the DSC, though cells comprising liquid electrolyte in many cases suffer from nonoptimal sealing, which leads to stability problems. Various materials have therefore been studied for their suitability as solid electrolytes/p-semiconductors.

30 Various inorganic p-semiconductors such as CuI, CuBr · 3(S(C₄H₉)₂) or CuSCN have found use to date in solid-stage DSCs. With CuI-based, solid DSCs, for example, efficiencies of more than 7% have been reported by Hitoshi Sakamoto et al. (Organic Electronics 13 (2012), 514-518).

35 Solid DSCs comprising fluorine and tin difluoride doped CsSnI₃ as hole conducting material and displaying efficiencies of around 10% were reported by In Chung et al. (Nature Vol. 485, May 24, 2012, 486-490)

Organic polymers are also used as solid p-semiconductors. Examples thereof include polypyrrole, poly(3,4-ethylenedioxythiophene), carbazole-based polymers, polyaniline, poly(4-undecyl-
40 2,2'-bithiophene), poly(3-octylthiophene), poly(triphenyldiamine) and poly(N-vinylcarbazole). In the case of poly(N-vinylcarbazole), the efficiencies reach up to 2%; with a PEDOT (poly(3,4-

ethylenedioxythiophene), polymerized in situ, an efficiency of 2.9% was even achieved (Xia et al. J. Phys. Chem. C 2008, 112, 11569), though the polymers are typically not used in pure form but usually in a mixture with additives. In addition, a concept in which polymeric p-semiconductors are bonded directly to an Ru dye is also presented (Peter, K., Appl. Phys. A 2004, 79, 65).

Recent developments in organic photovoltaics have been in the direction of the so-called "bulk heterojunction" ("BHJ") solar cells: in this case, the photoactive layer comprises the acceptor and donor compound(s) as a bicontinuous phase. As a result of photoinduced charge transfer from the excited state of the donor compound to the acceptor compound, owing to the spatial proximity of the compounds, a rapid charge separation compared to other relaxation procedures takes place, and the holes and electrons which arise are removed via the corresponding electrodes. Between the electrodes and the photoactive layer, further layers, for example hole or electron transport layers, are often applied in order to increase the efficiency of such cells.

To date, the donor materials used in such BHJ cells have usually been polymers, for example polyvinylphenylenes or polythiophenes, or dyes from the class of the phthalocyanines, e.g. zinc phthalocyanine or vanadyl phthalocyanine, and the acceptor materials used have been fullerene and fullerene derivatives and also various perylenes. Photoactive layers composed of the donor/acceptor pairs poly(3-hexyl-thiophene) ("P3HT")/ [6,6]-phenyl-C₆₁-butyric acid methyl ester ("PCBM"), poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene) ("OC₁C₁₀-PPV")/PCBM and zinc phthalocyanine/fullerene have been and are being researched intensively.

High efficiencies are also achieved with low molecular weight organic p-semiconductors. WO 98/48433 A1, for example, reports the use of the organic compound 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene ("spiro-MeOTAD") in DSCs as hole transporting material.

Spiro-MeOTAD is likewise examined by Snaith, H. J.; Moule, A. J.; Klein, C.; Meerholz, K.; Friend, R. H.; Gratzel (M. Nano Lett.; (Letter); 2007; 7(11); 3372-3376) as hole transporting material in DSCs.

Further spiro compounds as hole transporting and hole injecting materials, mainly applied in organic light emitting diodes ("OLEDs"), are described in WO 2011/116869 A1. Studies by C. Jäger et al. (Proc. SPIE 4108, 104-110 (2001)) show that spiro-MeOTAD is present in semicrystalline form, and there is a strong tendency of (re)crystallization in the processed form, i.e. in the DSC.

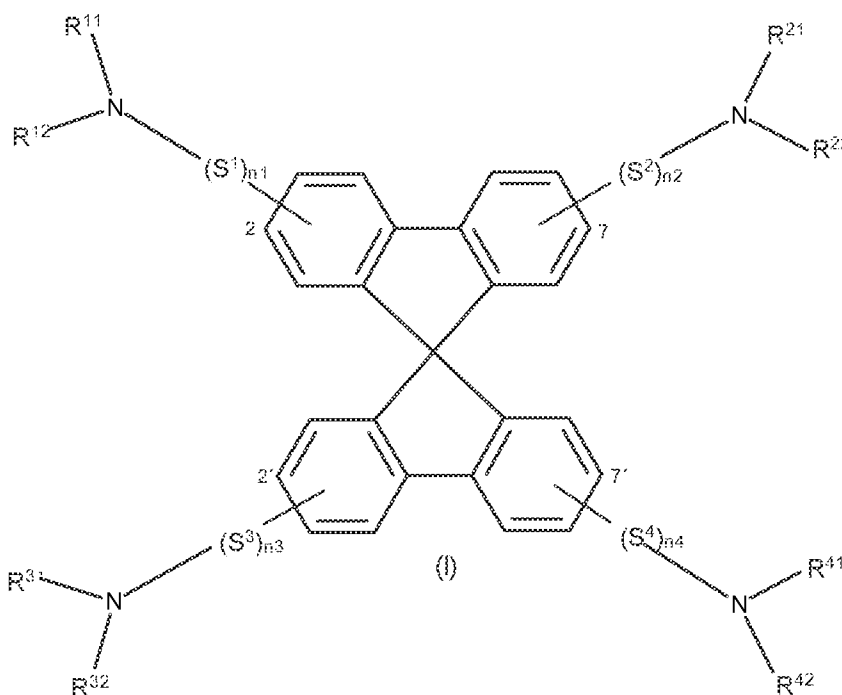
In addition, the solubility in customary process solvents is relatively low, which leads to a correspondingly low degree of pore filling.

Durrant et al., Adv. Func. Mater. 2006, 16, 1832-1838 state that, in many cases, the photocurrent is directly dependent on the yield in the hole transition from the oxidized dye to the solid p-semiconductor. This depends essentially on two factors: first on the degree of penetration of the p-semiconductor into the oxide pores, and second on the thermodynamic driving force for the charge transfer, i.e. especially on the difference in the free enthalpy ΔG between dye and p-semiconductor.

The earlier European patent application EP 12183007.9 addresses the problem of (re)crystallization by suggesting 9,9'-spirobifluorene compounds with at least one substituent R^{11} through R^{44} being different from the other substituents on the amino groups which are directly bound to the 9,9'-spirobifluorene skeleton. Thus, (re)crystallization of these spiro compounds is significantly delayed as compared with spiro-MeOTAD.

It was therefore an object of the present invention to provide further compounds which can be used advantageously as p-semiconductors in solar cells, especially in DSCs and BHJ cells. With regard to their profile of properties, these compounds should have good hole-conducting properties, have only a very low tendency, if any, to crystallize, and have good solubility in the solvents used customarily.

Accordingly, 9,9'-spirobifluorene compounds of general formula I



have been found, wherein the variables have the meaning

25

R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} and R^{42} independently of each other aryl or hetaryl,

S¹, S², S³ and S⁴ independently of each other π -conjugated, bivalent moieties,

n¹, n², n³ and n⁴ independently of each other 0, 1, 2 or 3,

5 with the proviso that

n¹ + n² + n³ + n⁴ \neq 0,

10 in case n¹ \geq 2, n² \geq 2, n³ \geq 2 and/or n⁴ \geq 2 the moieties S¹, S², S³ and S⁴ are identical to or different from each other

and

15 in case n¹ + n² + n³ + n⁴ = 12 not all of the radicals R¹¹, R¹², R²¹, R²², R³¹, R³², R⁴¹ and R⁴² are identical.

The latter proviso implies that either

20 a) all of the moieties (S¹)₃, (S²)₃, (S³)₃ and (S⁴)₃ are identical and at least one of the radicals R¹¹, R¹², R²¹, R²², R³¹, R³², R⁴¹ or R⁴² differs from the remaining radicals (combination "S-identical/R-different"), or

25 b) at least one of the moieties (S¹)₃, (S²)₃, (S³)₃ and (S⁴)₃ differs from the remaining moieties and all of the radicals R¹¹, R¹², R²¹, R²², R³¹, R³², R⁴¹ or R⁴² are identical (combination "S-different/R-identical"), or

30 c) at least one of the moieties (S¹)₃, (S²)₃, (S³)₃ and (S⁴)₃ differs from the remaining moieties and at least one of the radicals R¹¹, R¹², R²¹, R²², R³¹, R³², R⁴¹ or R⁴² differs from the remaining radicals (combination "S-different/R-different").

In preferred 9,9'-spirobifluorene compounds of general formula I the variables have the meaning

n¹, n², n³ and n⁴ independently of each other 0, 1 or 2,

35 with the proviso that

n¹ + n² + n³ + n⁴ \neq 0,

in case n¹ = 2, n² = 2, n³ = 2 and/or n⁴ = 2 the moieties S¹, S², S³ and S⁴ are identical to or different from each other

40

and

in case $n^1 + n^2 + n^3 + n^4 = 8$ not all of the radicals R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} and R^{42} are identical.

The latter proviso implies that either

5

a) all of the moieties $(S^1)_2$, $(S^2)_2$, $(S^3)_2$ and $(S^4)_2$ are identical and at least one of the radicals R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} or R^{42} differs from the remaining radicals (combination "S-identical/R-different"), or

10 b) at least one of the moieties $(S^1)_2$, $(S^2)_2$, $(S^3)_2$ and $(S^4)_2$ differs from the remaining moieties and all of the radicals R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} or R^{42} are identical (combination "S-different/R-identical"), or

15 c) at least one of the moieties $(S^1)_2$, $(S^2)_2$, $(S^3)_2$ and $(S^4)_2$ differs from the remaining moieties and at least one of the radicals R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} or R^{42} differs from the remaining radicals (combination "S-different/R-different").

In specifically preferred 9,9'-spirobifluorene compounds of general formula I the variables have the meaning

20

n^1 , n^2 , n^3 and n^4 independently of each other 0 or 1,

with the proviso that

25 $n^1 + n^2 + n^3 + n^4 \neq 0$,

and

30 in case $n^1 + n^2 + n^3 + n^4 = 4$ not all of the radicals R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} and R^{42} are identical.

The latter proviso implies that either

35 a) all of the moieties S^1 , S^2 , S^3 and S^4 are identical and at least one of the radicals R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} or R^{42} differs from the remaining radicals (combination "S-identical/R-different"), or

40 b) at least one of the moieties S^1 , S^2 , S^3 and S^4 differs from the remaining moieties and all of the radicals R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} or R^{42} are identical (combination "S-different/R-identical"), or

c) at least one of the moieties S^1 , S^2 , S^3 and S^4 differs from the remaining moieties and at least one of the radicals R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} or R^{42} differs from the remaining radicals (combination "S-different/R-different").

5 In general, not only well defined compounds of general formula I and preferred and specifically preferred aforementioned embodiments thereof shall be embraced by the instant application but also mixtures of such compounds. Such mixtures then comprise compounds with variation of the variables n^1 , n^2 , n^3 and n^4 and either identical or different moieties S^1 , S^2 , S^3 and S^4 , as well as identical or different radicals R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} and R^{42} .

10

For a given set of identical moieties S^1 , S^2 , S^3 and S^4 and identical moieties $NR^{11}R^{12}$, $NR^{21}R^{22}$, $NR^{31}R^{32}$ and $NR^{41}R^{42}$ (although within such latter moieties the radicals R^{xy} within the pairs $R^{11}R^{12}$, $R^{21}R^{22}$, $R^{31}R^{32}$ and $R^{41}R^{42}$ may be different) compounds and mixtures of compounds of general formula I of the instant application can be derived according to the following scheme:

15

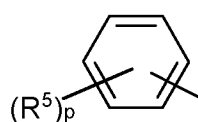
$n^1 + n^2 + n^3 + n^4 =$	limiting number for n^z	n^1	n^2	n^3	n^4
1	1	0	0	0	1
2	2	0	0	0	2
3	3	0	0	0	3
2	1	0	0	1	1
3	2	0	0	1	2
4	3	0	0	1	3
4	2	0	0	2	2
5	3	0	0	2	3
6	3	0	0	3	3
3	1	0	1	1	1
4	2	0	1	1	2
5	3	0	1	1	3
5	2	0	1	2	2
6	3	0	1	2	3
7	3	0	1	3	3
6	2	0	2	2	2
7	3	0	2	2	3
8	3	0	2	3	3
9	3	0	3	3	3
4	1	1	1	1	1
5	2	1	1	1	2
6	3	1	1	1	3
6	2	1	1	2	2
7	3	1	1	2	3
8	3	1	1	3	3
7	2	1	2	2	2
8	3	1	2	2	3
8	2	2	2	2	2
9	3	1	2	3	3
10	3	1	3	3	3
11	3	2	3	3	3
12	3	3	3	3	3

where embodiments of preferred compounds display variables $n^z \leq 2$ and of specifically preferred compounds variables $n^z \leq 1$, where z is 1, 2, 3 or 4.

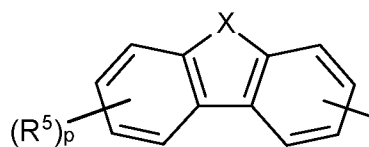
- 5 In case moieties S^1 , S^2 , S^3 and S^4 and moieties $NR^{11}R^{12}$, $NR^{21}R^{22}$, $NR^{31}R^{32}$ and $NR^{41}R^{42}$ differ from each a huge number of further compounds which derive from all possible permutations of the aforeshown scheme result.

Further variations can be imposed on the compounds of general formula I in cases where $2 \leq n^z \leq 3$ and moieties S^z within one bridge $(S^z)n^z$ differ from each other by the order of such moieties S^z .

- 5 In general, limiting numbers for n^z could even be larger than 3, e.g. 4, 5, 6 etc., thus, the moieties $(S^z)n^z$ could expand to $-S^z-S^z-S^z-S^z-$, $-S^z-S^z-S^z-S^z-S^z-$, $-S^z-S^z-S^z-S^z-S^z-S^z-$, etc. However, for synthetic and cost reasons lower limiting numbers of 3, 2 or 1 according to the aforementioned embodiments are preferred.
- 10 Preference is given to compounds of general formula I, also with respect to the aforementioned preferred and specifically preferred embodiments, wherein in general formula I the moieties $N(R^{11}R^{12})-(S^1)n^1-$, $N(R^{21}R^{22})-(S^2)n^2-$, $N(R^{31}R^{32})-(S^3)n^3-$ and $N(R^{41}R^{42})-(S^4)n^4-$ are bound to the 2, 2', 7 and 7' positions of the 9,9'-spirobifluorene skeleton.
- 15 Specifically preferred compounds, also with regard to the aforementioned preferences, are those wherein in general formula I the variables R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} and R^{42} independently of each other are moieties of formulae Ia or Ib



(Ia)



(Ib)

- 20 wherein the variables have the following meaning

R^5 hydrogen, alkyl, aryl, alkoxy, alkylthio or $-NR^6R^7$, where in case of two or more substituents (p equal or greater than 2) these may be identical or different,

- 25 p 0, 1, 2, 3, 4 or 5,

X $C(R^{53}R^{54})_2$, NR^{55} , oxygen or sulfur,

and

- 30

R^{51} to R^{55} hydrogen, alkyl, cycloalkyl, aryl or hetaryl.

- Further preference is given to compounds, also with regard to the abovementioned preferences, wherein in general formula I the variables S^1 , S^2 , S^3 and S^4 are identical to each other. As the
- 35 general proviso still holds that $n^1 + n^2 + n^3 + n^4 \neq 0$ and in case $n^1 + n^2 + n^3 + n^4 = 12$, $n^1 + n^2 + n^3 + n^4 = 8$ or $n^1 + n^2 + n^3 + n^4 = 4$, respectively, not all of the radicals R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} and R^{42} are identical, the following substitution patterns for compounds of general formula I

can be exemplified for a limiting number of n^2 equal to 1 (according to specifically preferred compounds of general formula I):

a) $n^1 + n^2 + n^3 + n^4 = 2$:

5

two of the moieties S^1 , S^2 , S^3 and S^4 are identical (two moieties are non-existent) and the corresponding two sets out of $N(R^{11}R^{12})-S^1-$, $N(R^{21}R^{22})-S^2-$, $N(R^{31}R^{32})-S^3-$ and $N(R^{41}R^{42})-S^4-$ are either identical to or different from each other. In the former case the R^{xy} radicals ($x = 1, 2, 3$ or 4 ; $y = 1, 2, 3$ or 4) within one set can be identical to or different from each.

10

b) $n^1 + n^2 + n^3 + n^4 = 3$:

three of the moieties S^1 , S^2 , S^3 and S^4 are identical (one moiety is non-existent) and either two or three of the corresponding three sets out of $N(R^{11}R^{12})-S^1-$, $N(R^{21}R^{22})-S^2-$, $N(R^{31}R^{32})-S^3-$ and $N(R^{41}R^{42})-S^4-$ are identical to each other or all of the either two or three sets are different from each other. As before the R^{xy} radicals ($x = 1, 2, 3$ or 4 ; $y = 1, 2, 3$ or 4) within one set of the two or three identical sets can be identical to or different from each other.

15

c) $n^1 + n^2 + n^3 + n^4 = 4$:

all four of the moieties S^1 , S^2 , S^3 and S^4 are identical and either two, three or four of the corresponding sets out of $N(R^{11}R^{12})-S^1-$, $N(R^{21}R^{22})-S^2-$, $N(R^{31}R^{32})-S^3-$ and $N(R^{41}R^{42})-S^4-$ are identical to each other. As before the R^{xy} radicals ($x = 1, 2, 3$ or 4 ; $y = 1, 2, 3$ or 4) within one set of the two or three identical sets can be identical to or different from each other. However, in case of all four sets out of $N(R^{11}R^{12})-S^1-$, $N(R^{21}R^{22})-S^2-$, $N(R^{31}R^{32})-S^3-$ and $N(R^{41}R^{42})-S^4-$ being identical the R^{xy} radicals ($x = 1, 2, 3$ or 4 ; $y = 1, 2, 3$ or 4) within one specific set must be different. Otherwise the proviso that not all of the radicals R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} and R^{42} be identical would fail.

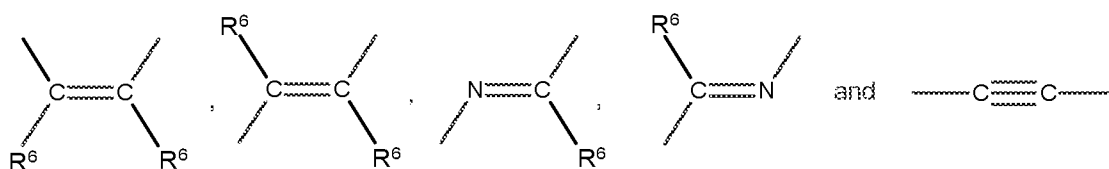
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30

Likewise such considerations can be made for larger limiting numbers of n^2 and, with this respect, reference is made to the aforementioned scheme.

Further preference, also with respect to the aforementioned preferences and the aforementioned provisos, is given to compounds, wherein in general formula I the moieties S^1 , S^2 , S^3 and S^4 are selected independently of each other from the group consisting of bivalent aryl, bivalent hetaryl and bivalent moieties

35



wherein the variables have the meaning

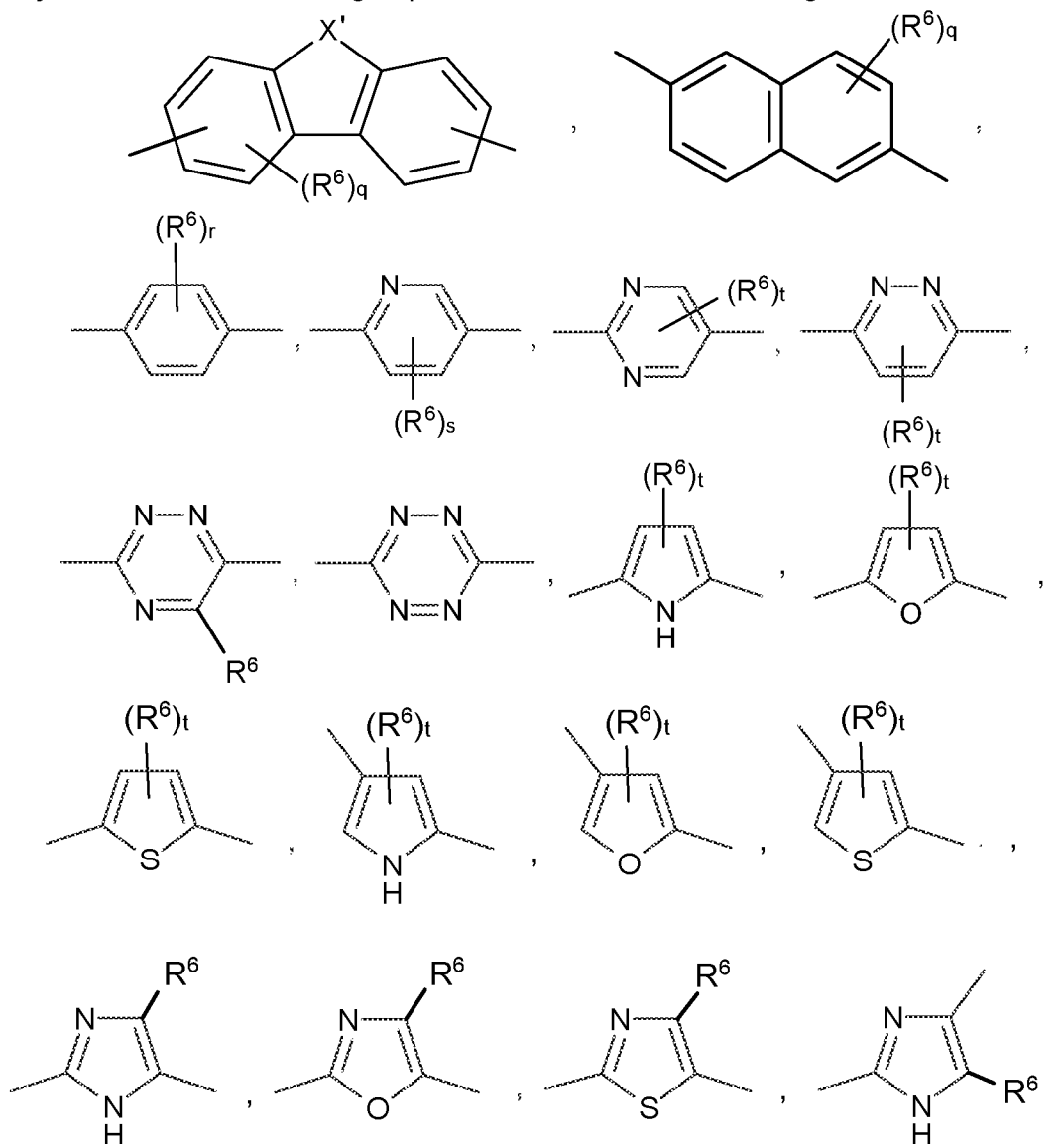
R^6 hydrogen, alkyl, aryl, alkoxy, alkylthio or $-NR^{61}R^{62}$, where in case of two substituents these may be identical or different,

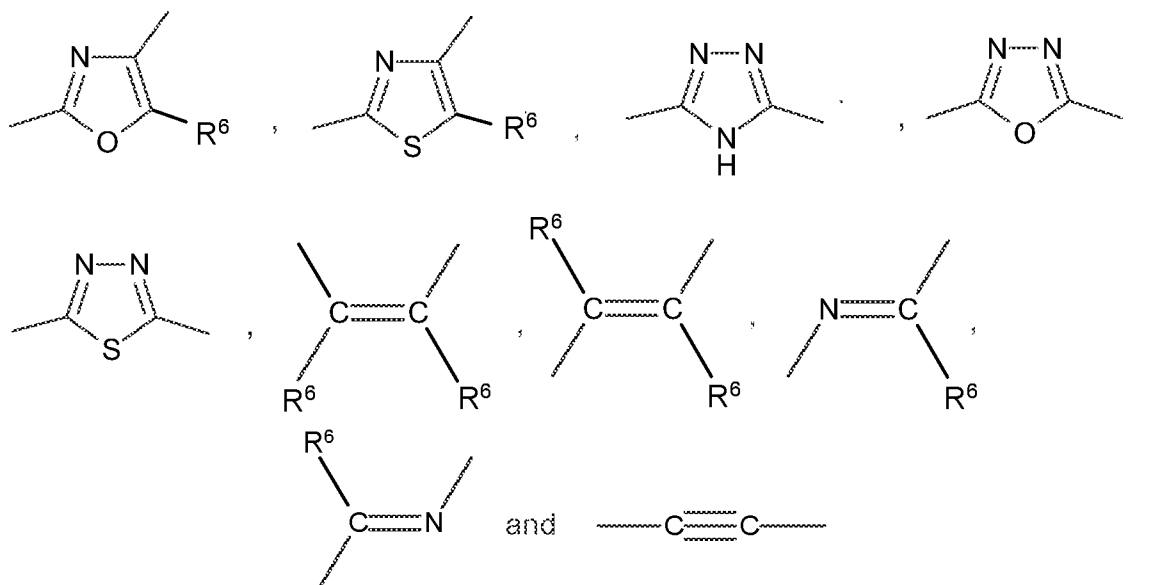
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R^{61} , R^{62} independently of each other hydrogen, alkyl, cycloalkyl, aryl or hetaryl.

Preferred compounds of general formula I, also in view of the aforementioned preferences and the aforementioned provisos, display moieties S^1 , S^2 , S^3 and S^4 which are selected inde-

10

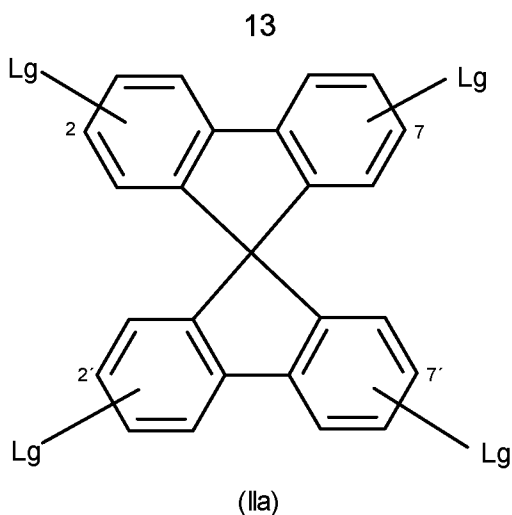




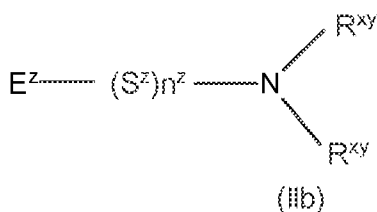
and wherein the variables have the meaning

- 5 R^6 hydrogen, alkyl, aryl, alkoxy, alkylthio or $-NR^{61}R^{62}$, where in case of two or more substituents these may be identical or different,
- q 0, 1, 2, 3, 4 or 5,
- 10 r 0, 1, 2, 3 or 4,
- s 0, 1, 2 or 3,
- t 0, 1 or 2,
- 15 X' $C(R^{63}R^{64})_2$, NR^{65} , oxygen or sulfur,
- and
- 20 R^{61} to R^{65} hydrogen, alkyl, cycloalkyl, aryl or hetaryl.

A convenient route of preparing compounds or mixtures of compounds of formula I of the instant application comprises reacting compounds of general formula IIa



with compounds of general formula IIb

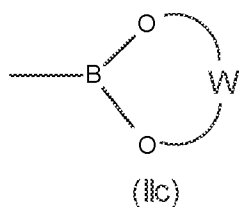


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wherein the variables have the following meaning

E^z a boron containing moiety of general formula IIc

10



z 1, 2, 3 or 4,

15 n^z independently of each other the meaning of n^1 , n^2 , n^3 and n^4 as defined in general formula I,

20 S^z independently of each other the meaning of S^1 , S^2 , S^3 and S^4 as defined in general formula I,

25 x, y independently of each other 1, 2, 3 or 4, whereby the resulting radicals correspond to the radicals R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} and R^{42} as defined in general formula I

W a bridging C_2 or C_3 moiety which may be substituted by one or more alkyl

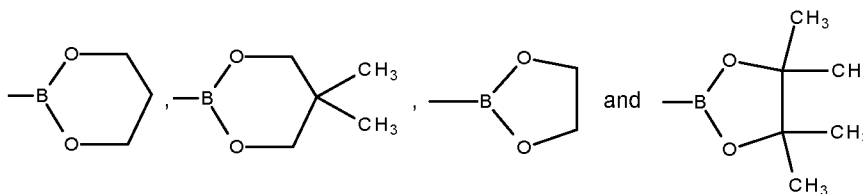
25

and

Lg leaving group,

- 5 in the presence of a palladium containing catalyst under the conditions of the Suzuki coupling reaction.

Typical examples of boron containing moieties E^z are



The preparation of the borylated compounds and the conditions of the Suzuki coupling reaction are well known to the skilled worker. Further information can be retrieved from the earlier European patent application EP 12179405.1 and the experimental part of the instant application.

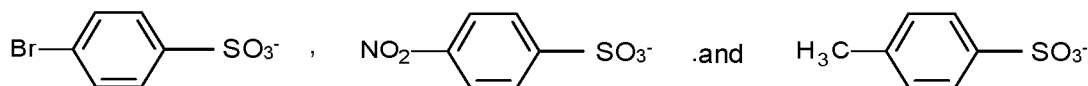
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In general, the leaving group Lg can be any group known to a person skilled in the art as being prone to easily leave the molecule. Typically, Lg consists of or comprises strongly electron-withdrawing atoms or moieties and, thus, is normally split off as anionic species.

- 20 Favorable groups Lg are chlorine, bromine, iodine, brosylate, nosylate, tosylate, mesylate and triflate which, in view of the aforesaid, leave the molecule as chloride, bromide, iodide, brosylate, nosylate, tosylate, mesylate or triflate anion.

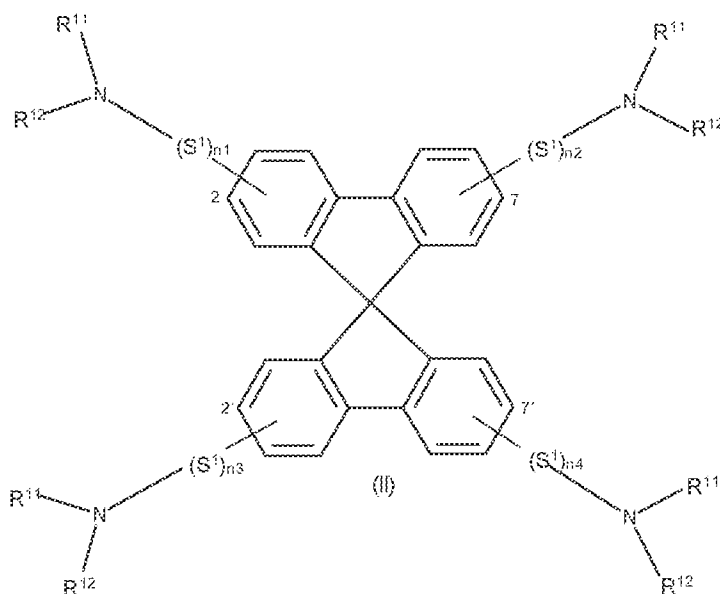
The structure of the brosylate, nosylate and tosylate are, in respective order, as follows:

25

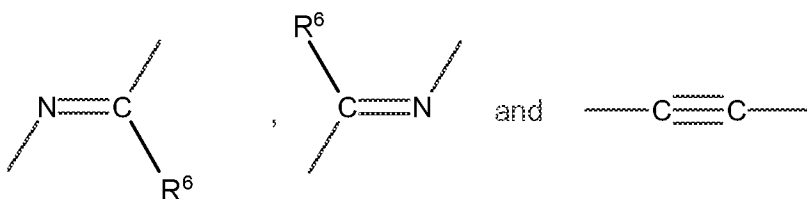


- 30 Compounds or mixtures of compounds of formula I and their preferred and specifically preferred embodiments following the abovementioned proviso that $n^1 + n^2 + n^3 + n^4 \neq 0$ and in case $n^1 + n^2 + n^3 + n^4 = 12$, $n^1 + n^2 + n^3 + n^4 = 8$ or $n^1 + n^2 + n^3 + n^4 = 4$, respectively, not all of the radicals R¹¹, R¹², R²¹, R²², R³¹, R³², R⁴¹ and R⁴² are identical and at the same time do not display randomization of the latter radicals are represented by the following formula II

15



wherein at least one of the variables n^z ($z = 1, 2, 3$ or 4) is not equal to 0, the moieties S^1 are identical and the variables R^{11} and R^{12} (accordingly $x = 1, y = 1$ and $x = 1, y = 2$, respectively, in terms of the aforementioned preparation route) differ from each other and are selected independently of each other from the group consisting of bivalent aryl, bivalent hetaryl and bivalent moieties



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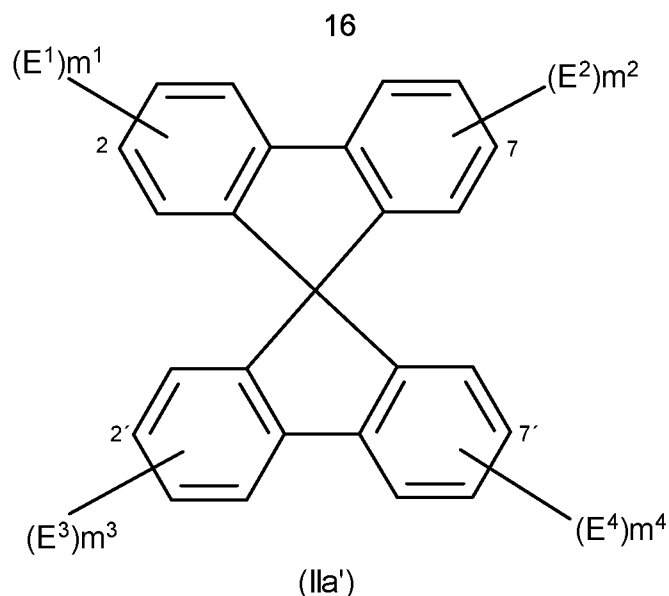
wherein the variables have the meaning

R^6 hydrogen, alkyl, aryl, alkoxy, alkylthio or $-NR^{61}R^{62}$,

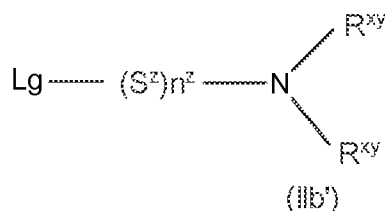
15 R^{61}, R^{62} independently of each other hydrogen, alkyl, cycloalkyl, aryl or hetaryl.

As the case may be one can also follow the reverse of the aforementioned route, i.e. compounds of general formula IIa'

20



can be reacted with compounds of general formula IIb'



5

in the presence of a palladium containing catalyst under the conditions of the Suzuki coupling reaction, wherein m^1 , m^2 , m^3 and m^4 independently of each other have the meaning of 0 or 1 and the other variables have the aforementioned meaning. In case the moiety S^z and both radicals R^{xy} of general formula IIc' refer to S^1 , R^{11} and R^{12} , respectively, one ends up with compounds of general formula II as shown before.

One route of preparing compounds or mixtures of compounds of formula I of the instant application and their preferred and specifically preferred embodiments, wherein the condition $0 < n^1 + n^2 + n^3 + n^4 < 12$, $0 < n^1 + n^2 + n^3 + n^4 < 8$ or $0 < n^1 + n^2 + n^3 + n^4 < 4$ holds, respectively, comprises reacting compounds of general formula IIa' with compounds of general formula IIb' with $n^z = 3$, $n^z = 2$ or $n^z = 1$, respectively, via Suzuki coupling in the first step and consecutive reaction of the intermediate with an appropriate amine or a mixture of appropriate amines of formulae $H-NR^{11}R^{12}$, $H-NR^{21}R^{22}$, $H-NR^{31}R^{32}$ and $H-NR^{41}R^{42}$ in the presence of a palladium containing catalyst under the conditions of the Buchwald-Hartwig amination reaction. Of course, the aforementioned reaction steps can also be conducted in reverse order.

The Buchwald-Hartwig amination reaction is a well established synthetic route and the reaction conditions can easily be determined by a person skilled in the art. Conversion of aryl bromides to arylamines is specifically addressed in the publication by Guram, A.S.; Rennels, R.A.; Buchwald, S.L., "A Simple Catalytic Method for the Conversion of Aryl Bromides to Arylamines", *Angewandte Chemie International Edition* 34 (12): 1348–1350, (1995).

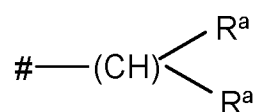
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Another preferred objective of the instant invention is the use of compounds of general formula I and II and their preferred and specifically preferred embodiments, also with respect to the limiting numbers of 2 and 1 for n^z , in dye-sensitized solar cells and bulk heterojunction solar cells.

- 5 Further objectives of the instant invention pertain to organic field effect transistor, dye-sensitized solar cells and bulk heterojunction solar cells comprising compounds of general formula I and II and their preferred and specifically preferred embodiments, also with respect to the limiting numbers of 2 and 1 for n^z .
- 10 In the context of the present invention, alkyl, aryl or heteroaryl represents unsubstituted or substituted alkyl, unsubstituted or substituted aryl or unsubstituted or substituted heteroaryl.

Alkyl comprises straight-chain or branched alkyl. Alkyl is preferably C_1 - C_{30} -alkyl, especially C_1 - C_{20} -alkyl and most preferably C_1 - C_{12} -alkyl. Examples of alkyl groups are especially methyl,
 15 ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-hexadecyl, n-octadecyl and n-eicosyl.

20 Further examples of branched alkyl groups can be represented by the following formula



in which

- 25 # denotes a bonding site, and
- R^a is selected from C_1 - to C_{28} -alkyl, where the sum of the carbon atoms of the R^a radicals is an integer from 2 to 29.
- 30 In the formula above, the R^a radicals are preferably selected from C_1 - to C_{12} -alkyl, especially C_1 - to C_8 -alkyl.

Preferred branched alkyl radicals of the above formula are, for example:

- 35 1-ethylpropyl, 1-methylpropyl, 1-propylbutyl, 1-ethylbutyl, 1-methylbutyl, 1-butylpentyl, 1-propylpentyl, 1-ethylpentyl, 1-methylpentyl, 1-pentylhexyl, 1-butylhexyl, 1-propylhexyl, 1-ethylhexyl, 1-methylhexyl, 1-hexylheptyl, 1-pentylheptyl, 1-butylheptyl, 1-propylheptyl, 1-ethylheptyl, 1-methylheptyl, 1-heptyloctyl, 1-hexyloctyl, 1-pentyloctyl, 1-butyloctyl, 1-propyloctyl,
 40 1-ethyloctyl, 1-methyloctyl, 1-octylnonyl, 1-heptylnonyl, 1-hexylnonyl, 1-pentylnonyl, 1-butylnonyl, 1-propylnonyl, 1-ethylnonyl, 1-methylnonyl, 1-nonyldecyl, 1-octyldecyl, 1-

heptyldecyl, 1-hexyldecyl, 1-pentyldecyl, 1-butyldecyl, 1-propyldecyl, 1-ethyldecyl, 1-
 methyldecyl, 1-decylundecyl, 1-nonylundecyl, 1-octylundecyl, 1-heptylundecyl, 1-hexylundecyl,
 1-pentylundecyl, 1-butylundecyl, 1-propylundecyl, 1-ethylundecyl, 1-methylundecyl,
 1-undecyldodecyl, 1-decyldodecyl, 1-nonyldodecyl, 1-octyldodecyl, 1-heptyldodecyl,
 5 1-hexyldodecyl, 1-pentyldodecyl, 1-butyl-dodecyl, 1-propyldodecyl, 1-ethyldodecyl,
 1-methyldodecyl, 1-dodecyltridecyl, 1-undecyltridecyl, 1-decyltridecyl, 1-nonyltridecyl, 1-
 octyltridecyl, 1-heptyltridecyl, 1-hexyltridecyl, 1-pentyltridecyl, 1-butyltridecyl, 1-propyltridecyl, 1-
 ethyltridecyl, 1-methyltridecyl, 1-tridecyltetradecyl, 1-undecyltetradecyl, 1-decyltetradecyl,
 10 1-nonyltetradecyl, 1-octyltetradecyl, 1-heptyltetradecyl, 1-hexyltetradecyl, 1-pentyltetradecyl, 1-
 butyltetradecyl, 1-propyltetradecyl, 1-ethyltetradecyl, 1-methyltetradecyl,
 1-pentadecylhexadecyl, 1-tetradecylhexadecyl, 1-tridecylhexadecyl, 1-dodecylhexadecyl,
 1-undecylhexadecyl, 1-decylhexadecyl, 1-nonylhexadecyl, 1-octylhexadecyl, 1-heptylhexadecyl,
 1-hexylhexadecyl, 1-pentylhexadecyl, 1-butylhexadecyl, 1-propylhexadecyl, 1-ethylhexadecyl,
 1-methylhexadecyl, 1-hexadecyloctadecyl, 1-pentadecyloctadecyl, 1-tetradecyloctadecyl,
 15 1-tridecyloctadecyl, 1-dodecyloctadecyl, 1-undecyloctadecyl, 1-decyloctadecyl,
 1-nonyloctadecyl, 1-octyloctadecyl, 1-heptyloctadecyl, 1-hexyloctadecyl, 1-pentyloctadecyl,
 1-butyl-octadecyl, 1-propyloctadecyl, 1-ethyloctadecyl, 1-methyloctadecyl, 1-nonadecyleicosanyl,
 1-octadecyleicosanyl, 1-heptadecyleicosanyl, 1-hexadecyleicosanyl, 1-pentadecyleicosanyl,
 1-tetradecyleicosanyl, 1-tridecyleicosanyl, 1-dodecyleicosanyl, 1-undecyleicosanyl,
 20 1-decyleicosanyl, 1-nonyleicosanyl, 1-octyleicosanyl, 1-heptyleicosanyl, 1-hexyleicosanyl,
 1-pentyleicosanyl, 1-butyleicosanyl, 1-propyleicosanyl, 1-ethyleicosanyl, 1-methyleicosanyl,
 1-eicosanyldocosanyl, 1-nonadecyldocosanyl, 1-octadecyldocosanyl, 1-heptadecyldocosanyl,
 1-hexadecyldocosanyl, 1-pentadecyldocosanyl, 1-tetradecyldocosanyl, 1-tridecyldocosanyl,
 1-undecyldocosanyl, 1-decyldocosanyl, 1-nonyldocosanyl, 1-octyldocosanyl, 1-heptyldocosanyl,
 25 1-hexyldocosanyl, 1-pentyldocosanyl, 1-butyl-docosanyl, 1-propyldocosanyl, 1-ethyldocosanyl,
 1-methyldocosanyl, 1-tricosanyltetracosanyl, 1-docosanyltetracosanyl, 1-nonadecyltetracosanyl,
 1-octadecyltetracosanyl, 1-heptadecyltetracosanyl, 1-hexadecyltetracosanyl,
 1-pentadecyltetracosanyl, 1-pentadecyltetracosanyl, 1-tetradecyltetracosanyl,
 1-tridecyltetracosanyl, 1-dodecyltetracosanyl, 1-undecyltetracosanyl, 1-decyltetracosanyl,
 30 1-nonyltetracosanyl, 1-octyltetracosanyl, 1-heptyltetracosanyl, 1-hexyltetracosanyl,
 1-pentyltetracosanyl, 1-butyltetracosanyl, 1-propyltetracosanyl, 1-ethyltetracosanyl,
 1-methyltetracosanyl, 1-heptacosanyloctacosanyl, 1-hexacosanyloctacosanyl,
 1-pentacosanyloctacosanyl, 1-tetracosanyloctacosanyl, 1-tricosanyloctacosanyl,
 1-docosanyloctacosanyl, 1-nonadecyloctacosanyl, 1-octadecyloctacosanyl,
 35 1-heptadecyloctacosanyl, 1-hexadecyloctacosanyl, 1-hexadecyloctacosanyl,
 1-pentadecyloctacosanyl, 1-tetradecyloctacosanyl, 1-tridecyloctacosanyl, 1-dodecyloctacosanyl,
 1-undecyloctacosanyl, 1-decyloctacosanyl, 1-nonyloctacosanyl, 1-octyloctacosanyl, 1-
 heptyloctacosanyl, 1-hexyloctacosanyl, 1-pentyloctacosanyl, 1-butyl-octacosanyl, 1-
 propyloctacosanyl, 1-ethyloctacosanyl, 1-methyloctacosanyl.

40

Alkyl also comprises alkyl radicals whose carbon chains may be interrupted by one or more nonadjacent groups selected from oxygen, sulfur, -CO-, -NR^b-, -SO- and/or -SO₂- where R^b is

preferably hydrogen, unsubstituted straight-chain or branched alkyl as described before or unsubstituted aryl as described below.

5 Substituted alkyl groups may, depending on the length of the alkyl chain, have one or more (e.g. 1, 2, 3, 4, 5 or more than 5) substituents. These are preferably each independently selected from cycloalkyl, heterocycloalkyl, aryl, hetaryl, fluorine, chlorine, bromine, cyano and nitro.

10 Aryl-substituted alkyl radicals (aralkyl) have at least one unsubstituted or substituted aryl group, as defined below. The alkyl group of the aralkyl radical may bear at least one further substituent and/or be interrupted by one or more nonadjacent groups selected from oxygen, sulfur, -CO-, -NR^b-, -SO- and/or -SO₂- where R^b is preferably hydrogen, unsubstituted straight-chain or branched alkyl as described before or unsubstituted aryl as described below. Arylalkyl is preferably phenyl-C₁-C₁₀-alkyl, more preferably phenyl-C₁-C₄-alkyl, for example benzyl, 1-phenethyl, 2-phenethyl, 1-phenprop-1-yl, 2-phenprop-1-yl, 3-phenprop-1-yl, 1-phenbut-1-yl, 2-phenbut-1-yl, 15 3-phenbut-1-yl, 4-phenbut-1-yl, 1-phenbut-2-yl, 2-phenbut-2-yl, 3-phenbut-2-yl, 4-phenbut-2-yl, 1-(phenmeth)eth-1-yl, 1-(phenmethyl)-1-(methyl)eth-1-yl or -(phenmethyl)-1-(methyl)prop-1-yl; preferably benzyl and 2-phenethyl.

20 Halogen-substituted alkyl groups (haloalkyl) comprise a straight-chain or branched alkyl group in which at least one hydrogen atom or all hydrogen atoms are replaced by halogen. The halogen atoms are preferably selected from fluorine, chlorine and bromine, especially fluorine and chlorine. Examples of haloalkyl groups are especially chloromethyl, bromomethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 1-chloroethyl, 1-bromoethyl, 1-fluoroethyl, 2-fluoroethyl, 25 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl, pentafluoroethyl, 2-fluoropropyl, 3-fluoropropyl, 2,2-difluoropropyl, 2,3-difluoropropyl, 2-chloropropyl, 3-chloropropyl, 2,3-dichloropropyl, 2-bromopropyl, 3-bromopropyl, 3,3,3-trifluoropropyl, 3,3,3-trichloropropyl, -CH₂-C₂F₅, -CF₂-C₂F₅, -CF(CF₃)₂, 1-(fluoromethyl)-2-fluoroethyl, 30 1-(chloromethyl)-2-chloroethyl, 1-(bromomethyl)-2-bromoethyl, 4-fluorobutyl, 4-chlorobutyl, 4-bromobutyl, nonafluorobutyl, 5-fluoro-1-pentyl, 5-chloro-1-pentyl, 5-bromo-1-pentyl, 5-iodo-1-pentyl, 5,5,5-trichloro-1-pentyl, undecafluoropentyl, 6-fluoro-1-hexyl, 6-chloro-1-hexyl, 6-bromo-1-hexyl, 6-iodo-1-hexyl, 6,6,6-trichloro-1-hexyl or dodecafluorohexyl.

35 The above remarks regarding unsubstituted or substituted alkyl also apply to unsubstituted or substituted alkoxy and unsubstituted or substituted dialkylamino.

40 Specific examples of unsubstituted and substituted alkyl radicals which may be interrupted by one or more nonadjacent groups selected from oxygen, sulfur, -NR^b-, -CO-, -SO- and/or -SO₂- are:

- methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-hexadecyl, n-octadecyl and n-eicosyl, 2-methoxyethyl, 2-ethoxyethyl, 2-propoxyethyl, 2-butoxyethyl, 3-methoxypropyl, 3-ethoxypropyl, 3-propoxypropyl, 3-butoxypropyl, 4-methoxybutyl, 4-ethoxybutyl, 4-propoxybutyl, 3,6-dioxaheptyl, 3,6-dioxaoctyl, 4,8-dioxanonyl, 3,7-dioxaoctyl, 3,7-dioxanonyl, 4,7-dioxaoctyl, 4,7-dioxanonyl, 2- and 4-butoxybutyl, 4,8-dioxadecyl, 3,6,9-trioxadecyl, 3,6,9-trioxaundecyl, 3,6,9-trioxadodecyl, 3,6,9,12-tetraoxatridecyl and 3,6,9,12-tetraoxatetradecyl;
- 10 2-methylthioethyl, 2-ethylthioethyl, 2-propylthioethyl, 2-butylthioethyl, 3-methylthiopropyl, 3-ethylthiopropyl, 3-propylthiopropyl, 3-butylthiopropyl, 4-methylthiobutyl, 4-ethylthiobutyl, 4-propylthiobutyl, 3,6-dithiaheptyl, 3,6-dithiaoctyl, 4,8-dithianonyl, 3,7-dithiaoctyl, 3,7-dithianonyl, 2- and 4-butylthiobutyl, 4,8-dithiadecyl, 3,6,9-trithiadecyl, 3,6,9-trithiaundecyl, 3,6,9-trithiadodecyl, 3,6,9,12-tetrathiatridecyl and 3,6,9,12-tetrathiatetradecyl;
- 15 2-monomethyl- and 2-monoethylaminoethyl, 2-dimethylaminoethyl, 2- and 3-dimethylaminopropyl, 3-monoisopropylaminopropyl, 2- and 4-monopropylaminobutyl, 2- and 4-dimethylaminobutyl, 6-methyl-3,6-diazaheptyl, 3,6-dimethyl-3,6-diazaheptyl, 3,6-diazaoctyl, 3,6-dimethyl-3,6-diazaoctyl, 9-methyl-3,6,9-triazadecyl, 3,6,9-trimethyl-3,6,9-triazadecyl, 3,6,9-triazaundecyl, 3,6,9-trimethyl-3,6,9-triazaundecyl, 12-methyl-3,6,9,12-tetraazatridecyl and 3,6,9,12-tetramethyl-3,6,9,12-tetraazatridecyl;
- 20 (1-ethylethylidene)aminoethylene, (1-ethylethylidene)aminopropylene, (1-ethylethylidene)aminobutylene, (1-ethylethylidene)aminododecylene and (1-ethylethylidene)aminododecylene;
- 25 propan-2-on-1-yl, butan-3-on-1-yl, butan-3-on-2-yl and 2-ethylpentan-3-on-1-yl;
- 30 2-methylsulfinylethyl, 2-ethylsulfinylethyl, 2-propylsulfinylethyl, 2-isopropylsulfinylethyl, 2-butylsulfinylethyl, 2- and 3-methylsulfinylpropyl, 2- and 3-ethylsulfinylpropyl, 2- and 3-propylsulfinylpropyl, 2- and 3-butylsulfinylpropyl, 2- and 4-methylsulfinylbutyl, 2- and 4-ethylsulfinylbutyl, 2- and 4-propylsulfinylbutyl and 4-butylsulfinylbutyl;
- 35 2-methylsulfonylethyl, 2-ethylsulfonylethyl, 2-propylsulfonylethyl, 2-isopropylsulfonylethyl, 2-butylsulfonylethyl, 2- and 3-methylsulfonylpropyl, 2- and 3-ethylsulfonylpropyl, 2- and 3-propylsulfonylpropyl, 2- and 3-butylsulfonylpropyl, 2- and 4-methylsulfonylbutyl, 2- and 4-ethylsulfonylbutyl, 2- and 4-propylsulfonylbutyl and 4-butylsulfonylbutyl;
- 40 carboxymethyl, 2-carboxyethyl, 3-carboxypropyl, 4-carboxybutyl, 5-carboxypentyl, 6-carboxyhexyl, 8-carboxyoctyl, 10-carboxydecyl, 12-carboxydodecyl and 14-carboxyl-tetradecyl;

sulfomethyl, 2-sulfoethyl, 3-sulfopropyl, 4-sulfobutyl, 5-sulfopentyl, 6-sulfohexyl, 8-sulfooctyl, 10-sulfodecyl, 12-sulfododecyl and 14-sulfotetradecyl;

2-hydroxyethyl, 2- and 3-hydroxypropyl, 3- and 4-hydroxybutyl and 8-hydroxyl-4-oxaocetyl;

5

2-cyanoethyl, 3-cyanopropyl, 3- and 4-cyanobutyl;

2-chloroethyl, 2- and 3-chloropropyl, 2-, 3- and 4-chlorobutyl, 2-bromoethyl, 2- and 3-bromopropyl and 2-, 3- and 4-bromobutyl;

10 2-nitroethyl, 2- and 3-nitropropyl and 2-, 3- and 4-nitrobutyl;

methoxy, ethoxy, propoxy, butoxy, pentoxy and hexoxy;

methylthio, ethylthio, propylthio, butylthio, pentylthio and hexylthio;

15

methylamino, ethylamino, propylamino, butylamino, pentylamino, hexylamino, dicyclopentylamino, dicyclohexylamino, dicycloheptylamino, diphenylamino and dibenzylamino;

formylamino, acetylamino, propionylamino and benzoylamino;

20

carbamoyl, methylaminocarbonyl, ethylaminocarbonyl, propylaminocarbonyl, butylaminocarbonyl, pentylaminocarbonyl, hexylaminocarbonyl, heptylamino-carbonyl, octylaminocarbonyl, nonylaminocarbonyl, decylaminocarbonyl and phenylamino-carbonyl;

25 aminosulfonyl, n-dodecylaminosulfonyl, N,N-diphenylaminosulfonyl, and N,N-bis(4-chlorophenyl)aminosulfonyl;

methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl hexoxycarbonyl, dodecyloxycarbonyl, octadecyloxycarbonyl, phenoxy-carbonyl, (4-tert-butylphenoxy)carbonyl and

30 (4-chlorophenoxy)carbonyl;

methoxysulfonyl, ethoxysulfonyl, propoxysulfonyl, butoxysulfonyl, hexoxysulfonyl, dodecyloxysulfonyl and octadecyloxysulfonyl.

35 In the context of the invention, cycloalkyl denotes a cycloaliphatic radical having preferably 3 to 10, more preferably 5 to 8, carbon atoms. Examples of cycloalkyl groups are especially cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl.

40 Substituted cycloalkyl groups may, depending on the ring size, have one or more (e.g. 1, 2, 3, 4, 5 or more than 5) substituents. These are preferably each independently selected from alkyl, alkoxy, alkylamino, alkylthio, cycloalkyl, heterocycloalkyl, aryl, hetaryl, fluorine, chlorine, bromine, cyano and nitro. In the case of substitution, the cycloalkyl groups preferably bear one or

more, for example one, two, three, four or five, C₁-C₆-alkyl groups. Examples of substituted cycloalkyl groups are especially 2- and 3-methylcyclopentyl, 2- and 3-ethylcyclopentyl, 2-, 3- and 4-methylcyclohexyl, 2-, 3- and 4-ethylcyclohexyl, 2-, 3- and 4-propylcyclohexyl, 2-, 3- and 4-isopropylcyclohexyl, 2-, 3- and 4-butylcyclohexyl, 2-, 3- and 4-sec.-butylcyclohexyl, 2-, 3- and 4-tert-butylcyclohexyl, 2-, 3- and 4-methylcycloheptyl, 2-, 3- and 4-ethylcycloheptyl, 2-, 3- and 4-propylcycloheptyl, 2-, 3- and 4-isopropylcycloheptyl, 2-, 3- and 4-butylcycloheptyl, 2-, 3- and 4-sec-butylcycloheptyl, 2-, 3- and 4-tert-butylcycloheptyl, 2-, 3-, 4- and 5-methylcyclooctyl, 2-, 3-, 4- and 5-ethylcyclooctyl, 2-, 3-, 4- and 5-propylcyclooctyl.

10 Specific examples of substituted and unsubstituted cycloalkyl groups are cyclopropyl, cyclobutyl, cyclopentyl, 2- and 3-methylcyclopentyl, 2- and 3-ethylcyclopentyl, cyclohexyl, 2-, 3- and 4-methylcyclohexyl, 2-, 3- and 4-ethylcyclohexyl, 3- and 4-propylcyclohexyl, 3- and 4-isopropylcyclohexyl, 3- and 4-butylcyclohexyl, 3- and 4-sec-butylcyclohexyl, 3- and 4-tert-butylcyclohexyl, cycloheptyl, 2-, 3- and 4-methylcycloheptyl, 2-, 3- and 4-ethylcycloheptyl, 3- and 4-propylcycloheptyl, 3- and 4-isopropylcycloheptyl, 3- and 4-butylcycloheptyl, 3- and 4-sec-butylcycloheptyl, 3- and 4-tert-butylcycloheptyl, cyclooctyl, 2-, 3-, 4- and 5-methylcyclooctyl, 2-, 3-, 4- and 5-ethylcyclooctyl and 3-, 4- and 5-propylcyclooctyl; 3- and 4-hydroxycyclohexyl, 3- and 4-nitrocyclohexyl and 3- and 4-chlorocyclohexyl;

20 In the context of the present invention, aryl comprises substituted or unsubstituted mono- or polycyclic aromatic hydrocarbon radicals and monocyclic aromatic hydrocarbon radicals which may be fused to one or more unfused or fused saturated or unsaturated carbocyclic or heterocyclic five or six membered rings. Aryl has preferably 6 to 14, more preferably 6 to 10, carbon atoms. Examples of aryl are especially phenyl, naphthyl, indenyl, fluorenyl, anthracenyl, phenanthrenyl, naphthacenyl, chrysenyl and pyrenyl, especially phenyl, naphthyl and fluorenyl.

Substituted aryls may, depending on the number and size of their ring systems, have one or more (e.g. 1, 2, 3, 4, 5 or more than 5) substituents. These are preferably each independently selected from alkyl, alkoxy, alkylamino, alkylthio, cycloalkyl, heterocycloalkyl, aryl, hetaryl, fluorine, chlorine, bromine, cyano and nitro. The alkyl, alkoxy, alkylamino, alkylthio, cycloalkyl, heterocycloalkyl, aryl and hetaryl substituents on the aryl may in turn be unsubstituted or substituted. Reference is made to the substituents mentioned above for these groups. The substituents on the aryl are preferably selected from alkyl, alkoxy, haloalkyl, haloalkoxy, aryl, fluorine, chlorine, bromine, cyano and nitro. Substituted aryl is more preferably substituted phenyl which generally bears 1, 2, 3, 4 or 5, preferably 1, 2 or 3, substituents.

Substituted aryl is preferably aryl substituted by at least one alkyl group ("alkaryl"). Alkaryl groups may, depending on the size of the aromatic ring system, have one or more (e.g. 1, 2, 3, 4, 5, 6, 7, 8, 9 or more than 9) alkyl substituents. The alkyl substituents may be unsubstituted or substituted. In this regard, reference is made to the above statements regarding unsubstituted and substituted alkyl. In a preferred embodiment, the alkaryl groups have exclusively unsubsti-

tuted alkyl substituents. Alkaryl is preferably phenyl which bears 1, 2, 3, 4 or 5, preferably 1, 2 or 3, more preferably 1 or 2, alkyl substituents.

5 Aryl which bears one or more radicals is, for example, 2-, 3- and 4-methylphenyl, 2,4-, 2,5-, 3,5- and 2,6-dimethylphenyl, 2,4,6-trimethylphenyl, 2-, 3- and 4-ethylphenyl, 2,4-, 2,5-, 3,5- and 2,6-diethylphenyl, 2,4,6-triethylphenyl, 2-, 3- and 4-propylphenyl, 2,4-, 2,5-, 3,5- and 2,6-di-propylphenyl, 2,4,6-tripropylphenyl, 2-, 3- and 4-isopropylphenyl, 2,4-, 2,5-, 3,5- and 2,6-diisopropylphenyl, 2,4,6-triisopropylphenyl, 2-, 3- and 4-butylphenyl, 2,4-, 2,5-, 3,5- and 2,6-dibutylphenyl, 2,4,6-tributylphenyl, 2-, 3- and 4-isobutylphenyl, 2,4-, 2,5-, 3,5- and 2,6-diisobutylphenyl, 2,4,6-triisobutylphenyl, 2-, 3- and 4-sec-butylphenyl, 2,4-, 2,5-, 3,5- and 2,6-di-sec-butylphenyl, 2,4,6-tri-sec-butylphenyl, 2-, 3- and 4-tert-butylphenyl, 2,4-, 2,5-, 3,5- and 2,6-di-tert-butylphenyl and 2,4,6-tri-tert-butylphenyl; 2-, 3- and 4-methoxyphenyl, 2,4-, 2,5-, 3,5- and 2,6-dimethoxyphenyl, 2,4,6-trimethoxyphenyl, 2-, 3- and 4-ethoxyphenyl, 2,4-, 2,5-, 3,5- and 2,6-diethoxyphenyl, 2,4,6-triethoxyphenyl, 2-, 3- and 4-propoxyphenyl, 2,4-, 2,5-, 3,5- and 2,6-dipropoxyphenyl, 2-, 3- and 4-isopropoxyphenyl, 2,4-, 2,5-, 3,5- and 2,6-diisopropoxyphenyl and 2-, 3- and 4-butoxyphenyl; 2-, 3- and 4-cyanophenyl.

The above remarks regarding unsubstituted or substituted aryl also apply to unsubstituted or substituted aryloxy and unsubstituted or substituted arylthio. Examples of aryloxy are phenoxy and naphthoxy.

In the context of the present invention, hetaryl comprises heteroaromatic, mono- or polycyclic groups and monocyclic groups which may be fused to one or more unfused or fused saturated or unsaturated carbocyclic or heterocyclic five or six membered rings. In addition to the ring carbon atoms, these have 1, 2, 3, 4 or more than 4 of the ring heteroatoms. The heteroatoms are preferably selected from oxygen, nitrogen, selenium and sulfur. The hetaryl groups have preferably 5 to 18, e.g. 5, 6, 8, 9, 10, 11, 12, 13 or 14, ring atoms.

Monocyclic hetaryl groups are preferably 5- or 6-membered hetaryl groups, such as 2-furyl (furan-2-yl), 3-furyl (furan-3-yl), 2-thienyl (thiophen-2-yl), 3-thienyl (thiophen-3-yl), selenophen-2-yl, selenophen-3-yl, 1H-pyrrol-2-yl, 1H-pyrrol-3-yl, pyrrol-1-yl, imidazol-2-yl, imidazol-1-yl, imidazol-4-yl, pyrazol-1-yl, pyrazol-3-yl, pyrazol-4-yl, pyrazol-5-yl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 1,2,4-oxadiazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,3,4-oxadiazol-2-yl, 1,2,4-thiadiazol-3-yl, 1,2,4-thiadiazol-5-yl, 1,3,4-thiadiazol-2-yl, 4H-[1,2,4]-triazol-3-yl, 1,3,4-triazol-2-yl, 1,2,3-triazol-1-yl, 1,2,4-triazol-1-yl, pyridin-2-yl, pyridin-3-yl, pyridin-4-yl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-2-yl and 1,2,4-triazin-3-yl.

Polycyclic hetaryl has 2, 3, 4 or more than 4 fused rings. The fused-on rings may be aromatic, saturated or partly unsaturated. Examples of polycyclic hetaryl groups are quinolinyl, isoquinolinyl, indolyl, isoindolyl, indoliziny, benzofuranyl, isobenzofuranyl, benzothiophenyl, benzoxazolyl, benzisoxazolyl, benzthiazolyl, benzoxadiazolyl; benzothiadiazolyl, benzoxazinyl, benzopyra-

zoyl, benzimidazolyl, benzotriazolyl, benzotriazinyl, benzoselenophenyl, thienothiophenyl, thienopyrimidyl, thiazolothiazolyl, dibenzopyrrolyl (carbazolyl), dibenzofuranyl, dibenzothiophenyl, naphtho[2,3-b]thiophenyl, naphtha[2,3-b]furyl, dihydroindolyl, dihydroindoliziny, dihydroisoindolyl, dihydroquinolinyl, dihydroisoquinolinyl.

5 Substituted heteroaryls may, depending on the number and size of their ring systems, have one or more (e.g. 1, 2, 3, 4, 5 or more than 5) substituents. These are preferably each independently selected from alkyl, alkoxy, alkylamino, alkylthio, cycloalkyl, heterocycloalkyl, aryl, hetaryl, fluo-
10 rine, chlorine, bromine, cyano and nitro. Halogen substituents are preferably fluorine, chlorine or bromine. The substituents are preferably selected from C₁-C₆-alkyl, C₁-C₆-alkoxy, hydroxyl, carboxyl, halogen and cyano.

The above remarks regarding unsubstituted or substituted heteroaryl also apply to unsubstituted or substituted heteroaryloxy and unsubstituted or substituted heteroarylthio.

15 In the context of the present invention, bivalent aryl or bivalent hetaryl as definition for moieties S¹, S², S³ and S⁴ comprises substituted or unsubstituted radicals which are derived from the aforementioned aryl and hetaryl radicals by formal abstraction of a hydrogen atom from the aromatic or heteroaromatic core of the former radicals. Examples of bivalent aryl and bivalent hetaryl
20 are especially 1,4-phenylene, 1,6-naphthylene, fluoren-diyl, dibenzopyrrol-diyl (carbazol-diyl), dibenzofuran-diyl, dibenzothiophen-diyl.

Preferred bivalent aryl and bivalent hetaryl radicals as definition for moieties S¹, S², S³ and S⁴ have already been mentioned above in the definition of said moieties.

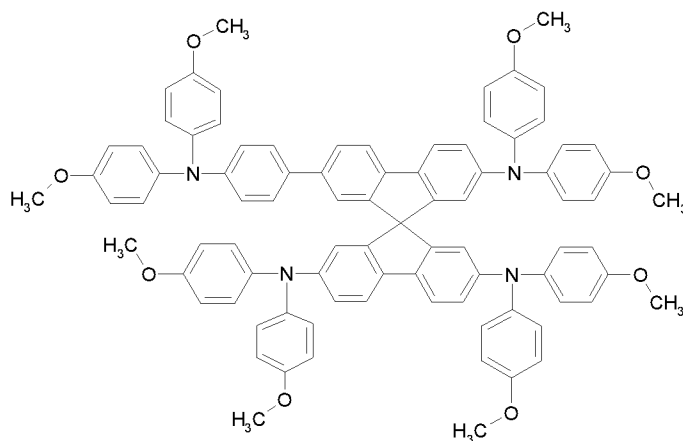
25 DSCs generally comprise the following elements: an electrically conductive layer (being part of or forming the working electrode or anode), a photosensitive layer generally comprising a semi-conductive metal oxide and a photosensitive dye, a charge transfer layer and another electrical-ly conductive layer (being part of or forming the counter electrode or cathode).

30 Regarding further details of the construction of DSCs particular reference is made to WO 2012/001628 A1, which is hereby fully incorporated by reference.

Experimental part

A. Preparation:

5 General procedure:



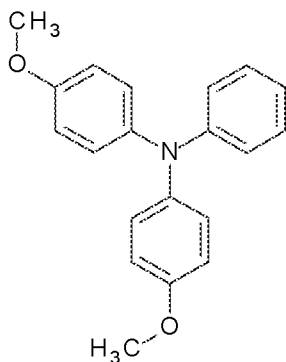
Utilizing the Buchwald–Hartwig C–N cross-coupling reaction, 4,4'-dimethoxy-triphenylamine (1) was synthesized from the respective aromatic amines and aryl halides. The resulting triphenylamine (1) was brominated and used in the reaction with trimethyl borate to isolate boronic acid (3). The palladium-catalyzed Suzuki coupling reaction was used to synthesize spiro intermediate (4). It was used in the Buchwald–Hartwig C–N cross-coupling reaction with corresponding diphenylamines to obtain the target hole transporting material ("HTM") HTM1 and HTM2.

15

Example 1: Preparation of 2,2',7-tris(4,4'-dimethoxydiphenylamino)-7'-(4-(4,4'-dimethoxydiphenylamino)phenyl)-9,9'-spirobifluorene (HTM1)

Preparation of 4,4'-dimethoxytriphenylamine (1)

20



A mixture of dioxane (50 ml) and water (0.018 g, 1 mmol) was purged with argon for 20 minutes. Pd(OAc)₂ (0.056 g, 0.25 mmol) and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl ("XPhos"; 0.358 g, 0.75 mmol) were added and the mixture was heated to 80°C for 90 sec. 4-Methoxyiodobenzene (11.7 g, 50 mmol), aniline (1.94 g, 20.8 mmol) and

25

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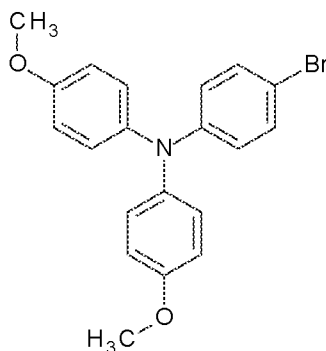
NaOt-Bu (6.73 g, 70.0 mmol) were added and the mixture was stirred at 110°C for 5 hours. After the termination of the reaction (TLC, acetone:n-hexane = 1:4, v/v) the mixture was diluted with ethyl acetate and washed with water. The organic layer was dried over anhydrous Na₂SO₄, filtered and the solvent removed. The residue was purified by column chromatography using acetone: n-hexane (0.5:24.5, v/v) as an eluent. The product was obtained as a white solid (5.2 g, 83 %).

¹H NMR (400 MHz, CDCl₃), δ, ppm: 7.16 (t, J = 7.8 Hz, 2H), 7.04 (d, J = 8.8 Hz, 4H), 6.93 (d, J = 8.0 Hz, 2H), 6.90 – 6.75 (m, 5H), 3.79 (s, 6H)

¹³C NMR (101 MHz, CDCl₃), δ, ppm: 155.79, 148.89, 141.28, 129.05, 126.52, 121.02, 120.68, 114.75, 55.61

Analysis calculated for C₂₀H₁₉NO₂: C, 78.66; H, 6.27, N, 4.59; found: C, 78.50; H, 6.12; N, 4.70.

Preparation of 4-bromo-4',4''-dimethoxytriphenylamine (2)



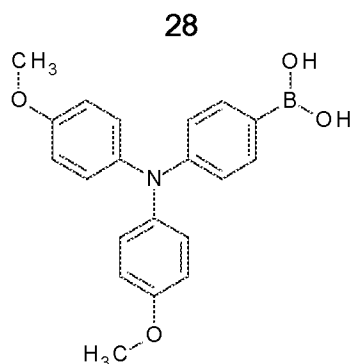
4-Bromo-4',4''-dimethoxytriphenylamine was synthesized according to the published procedure (C. Teng, X. Yang, C. Yang, S. Li, M. Cheng, A. Hagfeldt, L. Sun J. Phys. Chem. C, 114, 9101-9110; 2010.) from 4.4 g (14.4 mmol) 4,4'-dimethoxytriphenyl-amine (1). The product was obtained as a white solid (4.9 g, 89 %).

¹H NMR (400 MHz, CDCl₃), δ, ppm: 7.23 (d, J = 8.9 Hz, 2H), 7.02 (d, J = 8.9 Hz, 4H), 6.88 – 6.74 (m, 6H), 3.78 (s, 6H)

¹³C NMR (101 MHz, CDCl₃), δ, ppm: 156.13, 148.03, 140.65, 131.87, 126.68, 122.07, 114.88, 112.45, 55.60

Analysis calculated for C₂₀H₁₈BrNO₂: C, 62.51; H, 4.72, N, 3.64; found: C, 62.64; H, 4.59; N, 3.54.

Preparation of 4-(bis(4-methoxyphenyl)amino)phenylboronic acid (3)



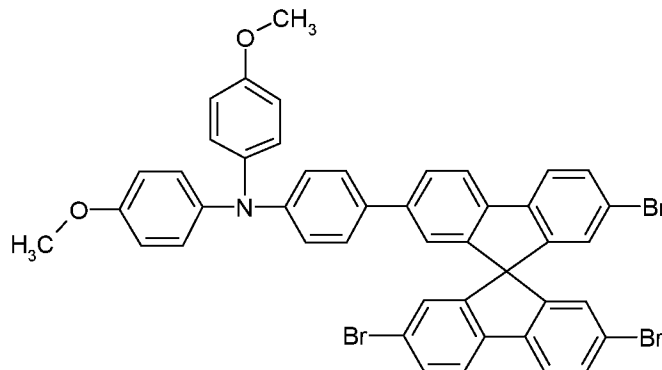
4-(Bis(4-methoxyphenyl)amino)phenylboronic acid was synthesized according to the published procedure (C. Teng, X. Yang, C. Yang, S. Li, M. Cheng, A. Hagfeldt, L. Sun J. Phys. Chem. C, 114, 9101-9110; 2010.) from 3.77 g (9.81 mmol) of 4-bromo-4',4''-dimethoxytriphenylamine (2). The product was obtained as a white solid (2.39 g, 70 %).

^1H NMR (400 MHz, CDCl_3), δ , ppm: 7.22 – 7.12 (m, 2H), 7.04 (d, $J = 8.9$ Hz, 4H), 6.93 (d, $J = 8.2$ Hz, 2H), 6.81 (d, $J = 8.8$ Hz, 4H), 3.79 (s, $J = 5.2$ Hz, 6H)

^{13}C NMR (101 MHz, CDCl_3), δ , ppm: 155.78, 148.89, 141.28, 129.05, 126.52, 121.03, 120.68, 114.75, 55.62

Analysis calculated for $\text{C}_{20}\text{H}_{20}\text{BNO}_4$: C, 68.79; H, 5.77, N, 4.01; found: C, 68.92; H, 5.88; N, 4.18.

Preparation of 2,2',7,7'-tribromo-7''-(4-(4,4'-dimethoxydiphenylamino)phenyl)-9,9'-spirobifluorene (4)



A mixture of THF (40 ml), toluene (20 ml) and a 4M solution of K_2CO_3 in water (25 ml) was purged with argon for 20 minutes. 4-(Bis(4-methoxyphenyl)amino)phenylboronic acid (3) (1.28 g, 3.7 mmol), 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (2.32 g, 3.7 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.424 g, 0.37 mmol) were added and the mixture was stirred at reflux for 8 hours. After the termination of the reaction (TLC, acetone:n-hexane = 7:18, v/v) the mixture was diluted with ethyl acetate and washed with water. The organic layer was dried over anhydrous Na_2SO_4 , filtered and the solvent removed. The residue was purified by

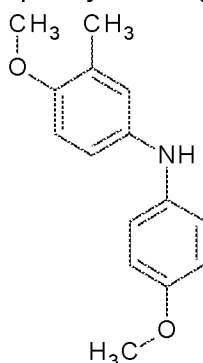
column chromatography using acetone: n-hexane (1:24, v/v) as an eluent. The product was obtained as a yellow solid (1.89 g, 60 %).

^1H NMR (400 MHz, CDCl_3), δ , ppm: 7.83 (d, $J = 8.0$ Hz, 1H), 7.74 – 7.62 (m, 3H), 7.59 (d, $J = 8.0$ Hz, 1H), 7.56 – 7.44 (m, 3H), 7.30 – 7.19 (m, 2H), 7.02 (d, $J = 8.8$ Hz, 4H), 6.92 – 6.73 (m, 10H), 3.77 (s, 6H)

^{13}C NMR (101 MHz, CDCl_3), δ , ppm: 155.99, 149.88, 149.36, 148.44, 147.64, 141.52, 140.81, 140.64, 139.72, 139.04, 132.31, 131.66, 131.57, 127.58, 127.55, 127.35, 126.96, 126.64, 122.19, 122.06, 121.69, 121.61, 121.50, 120.76, 120.72, 114.78, 65.54, 55.60

Analysis calculated for $\text{C}_{45}\text{H}_{30}\text{Br}_3\text{NO}_2$: C, 63.11; H, 3.53, N, 1.64; found: C, 63.00; H, 3.70; N, 1.85.

15 Preparation of 4,4'-Dimethoxy-3-methyldiphenylamine (5)



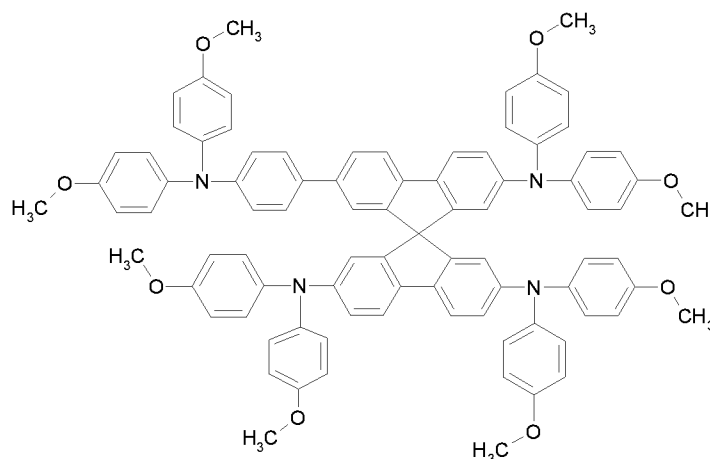
A mixture of dioxane (12 ml) and water (0.004 g, 0.22 mmol) was purged with argon for 20 minutes. $\text{Pd}(\text{OAc})_2$ (0.014 g, 0.06 mmol) and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) (0.086 g, 0.18 mmol) were added and the mixture was heated to 80°C for 90 sec. 5-bromo-2-methoxytoluene (2.44 g, 12.1 mmol), 4-methoxyaniline (1.79 g, 14.5 mmol) and NaOt-Bu (1.64 g, 17.1 mmol) were added and the mixture was stirred at 110°C for 15 minutes. After the termination of the reaction (TLC, acetone:n-hexane = 1:4, v/v) the mixture was diluted with ethyl acetate and washed with water. The organic layer was dried over anhydrous Na_2SO_4 , filtered and the solvent removed. The residue was purified by column chromatography using acetone: n-hexane (0.5:24.5, v/v) as an eluent. The product was obtained as whitish crystals (2.7 g, 92 %). M.p. = 55–56.5°C.

^1H NMR (300 MHz, CDCl_3), δ , ppm: 6.94 (d, $J = 9.0$ Hz, 2H), 6.82 (m, 4H), 6.73 (d, $J = 9.0$ Hz, 1H), 5.24 (s, 1H, NH), 3.79 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 2.18 (s, 3H, CH_3)

^{13}C NMR (75 MHz, CDCl_3), δ , ppm: 154.22, 152.67, 138.22, 137.58, 127.74, 121.59, 119.58, 116.40, 114.80, 111.19, 55.92, 55.76, 16.46

35 Analysis calculated for $\text{C}_{15}\text{H}_{17}\text{NO}_2$: C, 74.05; H, 7.04, N, 5.76; found: C, 74.16; H, 7.19; N, 5.61.

Preparation of 2,2',7-tris(4,4'-dimethoxydiphenylamino)-7'-(4-(4,4'-dimethoxydiphenylamino)phenyl)-9,9'-spirobifluorene (HTM1)



5

A mixture of 2,2',7-tribromo-7'-(4-(4,4'-dimethoxydiphenylamino)phenyl)-9,9'-spirobifluorene (4) (0.608 g, 0.71 mmol) and 4,4'-dimethoxydiphenylamine (0.733 g, 3.2 mmol) in dry toluene (10 ml) was purged with argon for 30 min. Pd(OAc)₂ (0.0087 g, 0.039 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.0233 g, 0.078 mmol) and NaO*t*-Bu (0.41 g, 4.26 mmol) were added and the mixture was refluxed for 60 hours. After the termination of the reaction (monitored by TLC, acetone:*n*-hexane = 1:4, v/v) mixture was diluted with toluene, filtered through Celite and washed with water. The organic layer was dried over anhydrous Na₂SO₄, filtered and solvent removed. The residue was purified by column chromatography using acetone: *n*-hexane (2:23 and 4:21, v/v) as an eluent and then precipitated from a 20% solution in acetone into 10-fold excess of methanol. The precipitate was filtered off and washed with methanol to give 0.52 g (57 %) of a pale yellow solid.

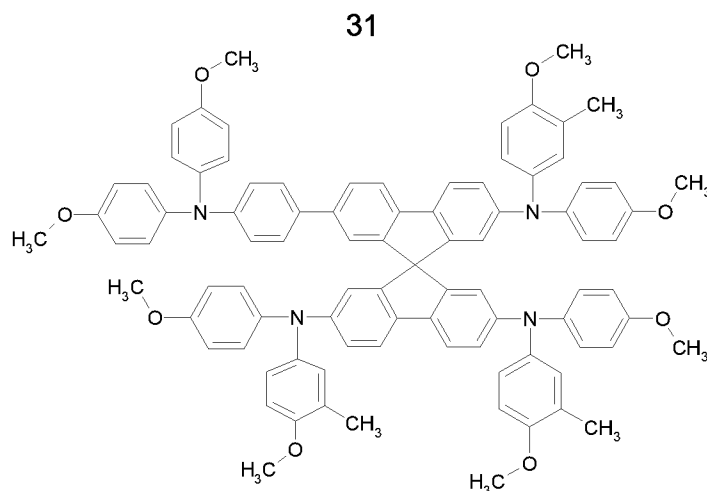
¹H NMR (400 MHz, CDCl₃), δ, ppm: 7.55 (d, J = 7.9 Hz, 2H), 7.44 (dd, J = 15.7, 8.1 Hz, 4H), 7.28 (d, J = 8.6 Hz, 6H), 7.05 (d, J = 8.9 Hz, 8H), 6.93 (d, J = 8.8 Hz, 12H), 6.80 (dd, J = 17.3, 8.9 Hz, 14H), 6.61 (s, 2H), 3.79 (s, 12H), 3.78 (s, 12H)

¹³C NMR (101 MHz, CDCl₃), δ, ppm: 155.91, 155.32, 148.10, 147.97, 141.59, 141.03, 140.00, 139.36, 133.59, 127.48, 126.57, 126.00, 125.30, 122.89, 121.77, 120.93, 119.53, 118.14, 114.79, 114.59, 55.63, 55.62, 55.56

Analysis calculated for C₈₇H₇₂N₄O₈: C, 80.29; H, 5.58, N, 4.30; found: C, 80.12; H, 5.37; N, 4.55.

Example 2: Preparation of 2,2',7-tris(3-methyl-4,4'-dimethoxydiphenylamino)-7'-(4-(4,4'-dimethoxydiphenylamino)phenyl)-9,9'-spirobifluorene (HTM2)

30



A mixture of 2,2',7,7'-tribromo-7'-(4-(4,4'-dimethoxydiphenylamino)phenyl)-9,9'-spirobifluorene (4) (0.58 g, 0.68 mmol) and 4,4'-dimethoxy-3-methyldiphenylamine (5) (0.74 g, 3.05 mmol) in dry toluene (10 ml) was purged with argon for 30 min. Pd(OAc)₂ (0.0083 g, 0.037 mmol), tri-tert-butylphosphonium tetrafluoroborate (0.0223 g, 0.074 mmol) and NaOt-Bu (0.39 g, 4.06 mmol) were added and the mixture was refluxed for 60 hours. After the termination of the reaction (TLC, acetone:n-hexane = 1:4, v/v) the mixture was diluted with toluene, filtered through Celite and washed with water. The organic layer was dried over anhydrous Na₂SO₄, filtered and solvent removed. The residue was purified by column chromatography using acetone: n-hexane (2:23 and 4:21, v/v) as an eluent and then precipitated from 20% solution in acetone into 10-fold excess of methanol. The precipitate was filtered off and washed with methanol to give 0.55 g (61 %) of a pale yellow solid.

¹H NMR (400 MHz, CDCl₃), δ, ppm: 7.53 (d, J = 7.8 Hz, 2H), 7.42 (t, J = 9.5 Hz, 4H), 7.29 (d, J = 8.5 Hz, 4H), 7.05 (d, J = 8.8 Hz, 8H), 6.93 (d, J = 8.3 Hz, 9H), 6.89 – 6.73 (m, 15H), 6.67 (d, J = 8.7 Hz, 2H), 6.63 (s, 1H), 3.78 (s, J = 3.1 Hz, 18H), 3.77 (s, 6H), 2.10 (s, 9H)

¹³C NMR (101 MHz, CDCl₃), δ, ppm: 155.86, 155.30, 153.85, 147.89, 141.06, 140.11, 139.18, 135.08, 133.68, 127.55, 127.48, 127.28, 126.50, 125.92, 125.50, 122.84, 122.06, 121.69, 121.02, 120.43, 119.41, 117.42, 114.77, 114.52, 110.63, 55.67, 55.62, 55.59, 55.46, 16.41

Analysis calculated for C₉₀H₇₈N₄O₈: C, 80.45; H, 5.85, N, 4.17; found: C, 80.27; H, 5.71; N, 3.99.

B. Preparation of the DSCs:

Preparation of the Solid-State DSCs: A TiO₂ blocking layer was prepared on a fluorine-doped tin oxide (FTO)-covered glass substrate using spray pyrolysis (cf. B. Peng, G. Jungmann, C. Jager, D. Haarer, H. W. Schmidt, M. Thelakkat, Coord. Chem. Rev. 2004, 248, 1479). Next, a TiO₂ paste (Dyesol), diluted with terpineol, was applied by screen printing, resulting in a film thickness of 1.7 μm. All films were then sintered for 45 min at 450 °C, followed by treatment in a 40 mM aqueous solution of TiCl₄ at 60 °C for 30 min, followed by another sintering step. The prepared samples with TiO₂ layers were pretreated with a 5 mM solution of the additive 2-(p-butoxyphenyl)acetohydroxamic acid sodium salt ("ADD1") in ethanol (this additive is described

on page 52 of WO 2012/001628 A1 as "Example No. 6"). The electrodes were then dyed in 0.5 mM dye solution in CH_2Cl_2 . HTM1, HTM2 and Spiro-MeOTAD (as comparative HTM) were applied by spin-coating from a solution in DCM (200 mg/mL) also containing 20 mM $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$. Fabrication of the device was completed by evaporation of 200 nm of silver as the counter electrode. The active area of the DSC was defined by the size of these contacts (0.13 cm^2), and the cells were masked by an aperture of the same area for measurements.

C. Characterization of the DSCs:

10 The Current-voltage characteristics for all cells were measured with a Keithley 2400 under 1000 W/m^2 , AM 1.5G conditions (LOT ORIEL 450 W). The incident photon to current conversion efficiency's (IPCE) were obtained with an Acton Research Monochromator using additional white background light illumination.

15 The cells were illuminated with monochromatic light from the quartz monochromator with deuterium lamp. The power of the incident light beam was $(2-5) \cdot 10^{-8} \text{ W}$. The negative voltage of -300 V was applied to the sample substrate. The counter-electrode with the $4.5 \times 15 \text{ mm}^2$ slit for illumination was placed at 8 mm distance from the sample surface. The counter-electrode was connected to the input of the BK2-16 type electrometer, working in the open input regime, for the photocurrent measurement. The $10^{-15} - 10^{-12} \text{ A}$ strong photocurrent was flowing in the circuit under illumination. The photocurrent J is strongly dependent on the incident light photon energy $h\nu$. The $J^{0.5} = f(h\nu)$ dependence was plotted. Usually the dependence of the photocurrent on incident light quanta energy is well described by a linear relationship between $J^{0.5}$ and $h\nu$ near the threshold (cf. E. Miyamoto, Y. Yamaguchi, M. Yokoyama, *Electrophotography* 1989, 28, 364 and M. Cordona, L. Ley, *Top. Appl. Phys.* 1978, 26, 1). The linear part of this dependence was extrapolated to the $h\nu$ axis and J_p value was determined as the photon energy at the interception point.

Cell results:

30

HTM	V_{oc} in mV	I_{sc} in mA	FF in %	η in %
HTM1	800	6.44	38	1.9
HTM2	800	6.44	38	1.9
Spiro-MeO-TAD	840	10.19	65	5.6

V_{oc} : Open circuit voltage; I_{sc} : Short circuit current; FF: Fill Factor; η : Efficiency

D. Longterm stability tests:

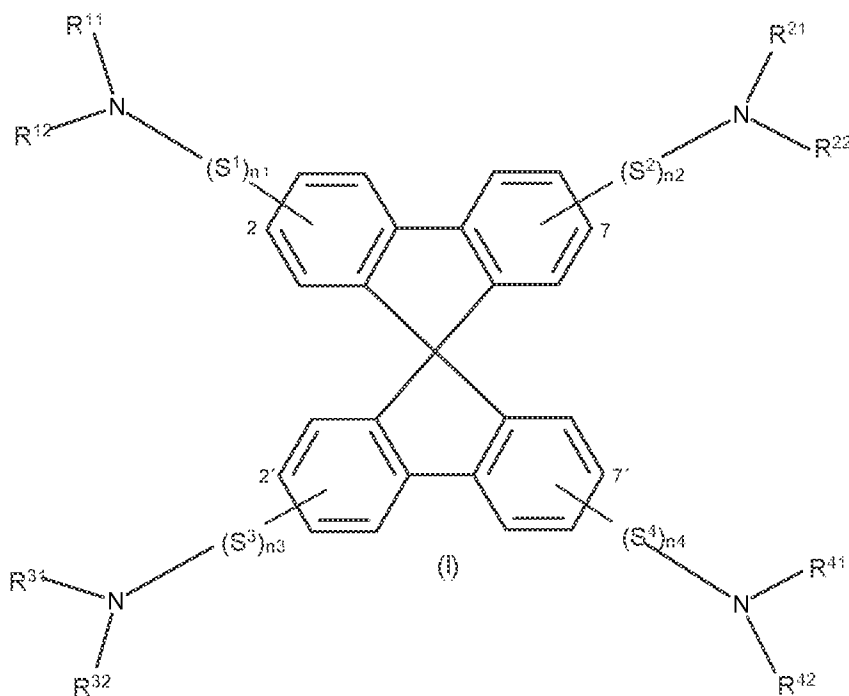
35 The lifetimes of the respective cells were demonstrated by longterm stability tests as shown in the diagram of Figure 1. After fabrication and during the longterm stability tests the sealed cells were constantly kept at 60°C and 30% humidity. The efficiency of the spiro-MeOTAD cell falls below 1% at around 750 hours, and the cell completely fails at 820 hours. By contrast, the

HTM1 and HTM2 cells still show efficiencies around 1% after 820 hours with no indication of failure.

5 Figure 1: Efficiencies and lifetimes of the cells built with spiro-MeOTAD, HTM1 and HTM2 as hole transporting material

Claims

1. 9,9'-spirobifluorene compounds of general formula I



5

wherein the variables have the meaning

10 R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} and R^{42} independently of each other aryl or hetaryl,

S^1 , S^2 , S^3 and S^4 independently of each other π -conjugated, bivalent moieties,

n^1 , n^2 , n^3 and n^4 independently of each other 0, 1, 2 or 3,

15

with the proviso that

$n^1 + n^2 + n^3 + n^4 \neq 0$,

20 in case $n^1 \geq 2$, $n^2 \geq 2$, $n^3 \geq 2$ and/or $n^4 \geq 2$ the moieties S^1 , S^2 , S^3 and S^4 are identical to or different from each other

and

25 in case $n^1 + n^2 + n^3 + n^4 = 12$ not all of the radicals R^{11} , R^{12} , R^{21} , R^{22} , R^{31} , R^{32} , R^{41} and R^{42} are identical.

2. Compounds according to claim 1, wherein in general formula I the variables have the

meaning

n^1, n^2, n^3 and n^4 independently of each other 0, 1 or 2,

5 with the proviso that

$n^1 + n^2 + n^3 + n^4 \neq 0$,

10 in case $n^1 = 2, n^2 = 2, n^3 = 2$ and/or $n^4 = 2$ the moieties S^1, S^2, S^3 and S^4 are identical to or different from each other

and

15 in case $n^1 + n^2 + n^3 + n^4 = 8$ not all of the radicals $R^{11}, R^{12}, R^{21}, R^{22}, R^{31}, R^{32}, R^{41}$ and R^{42} are identical.

3. Compounds according to claim 1, wherein in general formula I the variables have the meaning

20 n^1, n^2, n^3 and n^4 independently of each other 0 or 1,

with the proviso that

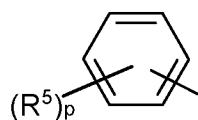
25 $n^1 + n^2 + n^3 + n^4 \neq 0$,

and

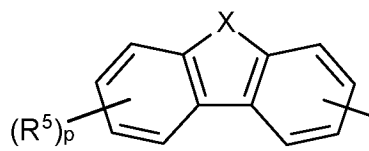
30 in case $n^1 + n^2 + n^3 + n^4 = 4$ not all of the radicals $R^{11}, R^{12}, R^{21}, R^{22}, R^{31}, R^{32}, R^{41}$ and R^{42} are identical.

4. Compounds according to claim 1, 2 or 3, wherein in general formula I the moieties $N(R^{11}R^{12})-(S^1)n^1-$, $N(R^{21}R^{22})-(S^2)n^2-$, $N(R^{31}R^{32})-(S^3)n^3-$ and $N(R^{41}R^{42})-(S^4)n^4-$ are bound to the 2, 2', 7 and 7' positions of the 9,9'-spirobifluorene skeleton.

35 5. Compounds according to claim 1, 2, 3 or 4, wherein in general formula I the variables $R^{11}, R^{12}, R^{21}, R^{22}, R^{31}, R^{32}, R^{41}$ and R^{42} independently of each other are moieties of formulae Ia or Ib



(Ia)



(Ib)

wherein the variables have the following meaning

5 R^5 hydrogen, alkyl, aryl, alkoxy, alkylthio or $-NR^{51}R^{52}$, where in case of two or more substituents (p equal or greater than 2) these may be identical or different,

p 0, 1, 2, 3, 4 or 5,

10 X $C(R^{53}R^{54})_2$, NR^{55} , oxygen or sulfur,

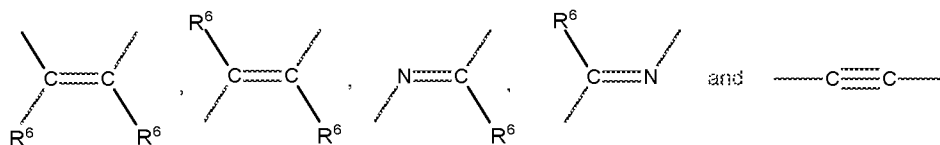
and

R^{51} to R^{55} hydrogen, alkyl, cycloalkyl, aryl or hetaryl.

15

6. Compounds according to claim 1, 2, 3, 4 or 5, wherein in general formula I the moieties S^1 , S^2 , S^3 and S^4 are identical to each other.

7. Compounds according to claim 1, 2, 3, 4, 5 or 6, wherein in general formula I the moieties S^1 , S^2 , S^3 and S^4 are selected independently of each other from the group consisting of bi-
20 valent aryl, bivalent hetaryl and bivalent moieties



25

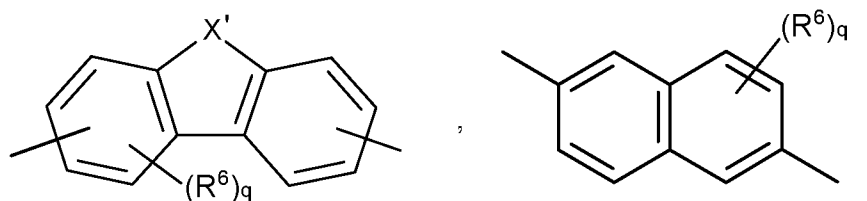
wherein the variables have the meaning

R^6 hydrogen, alkyl, aryl, alkoxy, alkylthio or $-NR^{61}R^{62}$, where in case of two substituents these may be identical or different,

30 R^{61} , R^{62} independently of each other hydrogen, alkyl, cycloalkyl, aryl or hetaryl.

8. Compounds according to claim 1, 2, 3, 4, 5 or 6, wherein in general formula I the moieties S^1 , S^2 , S^3 and S^4 are selected independently of each other from the group of bivalent moieties consisting of

35



q 0, 1, 2, 3, 4 or 5,

r 0, 1, 2, 3 or 4,

5 s 0, 1, 2 or 3,

t 0, 1 or 2,

10 X' C(R⁶³R⁶⁴)₂, NR⁶⁵, oxygen or sulfur,

and

R⁶¹ to R⁶⁵ hydrogen, alkyl, cycloalkyl, aryl or hetaryl.

15 9. Use of compounds of general formula I according to one or more of the preceding claims 1 to 8 in organic electronics applications.

20 10. Use of compounds of general formula I according to one or more of the preceding claims 1 to 8 in organic field effect transistors, organic photodetectors and organic solar cells.

11. Use of compounds of general formula I according to one or more of the preceding claims 1 to 8 in dye-sensitized solar cells and bulk heterojunction solar cells.

25 12. An organic field effect transistor, a dye-sensitized solar cell and a bulk heterojunction solar cell comprising compounds of general formula I according to one or more of the preceding claims 1 to 8.

Figure 1

