

Aromatic Compounds

The present invention relates to aromatic compounds, to the use thereof for the formation of molecular layers, in particular of self assembled
5 monolayers (SAM), to a process for the fabrication of a switching element for memristive devices comprising said molecular layers and to a memristive device comprising said switching element.

In computer technology, storage media are required which allow rapid
10 writing and reading access to information stored therein. Solid-state memories or semiconductor memories allow particularly fast and reliable storage media to be achieved, since absolutely no moving parts are necessary. At present, use is mainly made of dynamic random access memory (DRAM). DRAM allows rapid access to the stored information, but this information
15 has to be refreshed regularly, meaning that the stored information is lost when the power supply is switched off.

The prior art also discloses non-volatile semiconductor memories, such as flash memory or magnetoresistive random access memory (MRAM), in
20 which the information is retained even after the power supply has been switched off. A disadvantage of flash memory is that writing access takes place comparatively slowly and the memory cells of the flash memory cannot be erased ad infinitum. The lifetime of flash memory is typically limited to a maximum of one million read/write cycles. MRAM can be used in a
25 similar way to DRAM and has a long lifetime, but this type of memory has not been able to establish itself owing to the difficult production process.

A further alternative is memory which works on the basis of memristors. The term memristor is a contraction of the words "memory" and "resistor"
30 and denotes a component which is able to change its electrical resistance reproducibly between a high and a low electrical resistance. The respective state (high resistance or low resistance) is retained even without a supply

voltage, meaning that non-volatile memories can be achieved with memristors.

5 WO 2012/127542 A1 and US 2014/008601 A1, for example, disclose organic molecular memories which have two electrodes and an active region which is arranged between the two electrodes. The active region has a molecular layer of electrically conductive aromatic alkynes, whose conductivity can be changed under the influence of an electric field. Similar components based on redox-active bipyridinium compounds are proposed
10 in US 2005/0099209 A1.

The known memories based on a change in conductivity or resistance have the disadvantage that the free-radical intermediates formed by the flow of current through the molecules of the molecular layer are in principle
15 susceptible to degradation processes, which has an adverse effect on the lifetime of the components.

In WO 2018/007337 A2 an improved switching layer is described that makes use of a non-redox active molecular layer comprising dipolar
20 compounds linked to a substrate via an aliphatic spacer group where the compounds are reversibly switched by application of an electric field which causes re-orientation of the molecular dipole and thus enabling a low-resistive state and a high-resistive state depending on the respective orientation of the molecules.

25 In order to obtain electrically switchable tunnel junctions from organic compounds with a conformationally flexible dipole, a molecular layer enclosed as a sandwich between two conductive electrodes is required. The deposition of this molecular layer onto electrodes is achieved either by
30 spin-coating or by dip-coating from an organic solvent. The basic principle of the resulting memory device is described in WO 2016/110301 A1 and WO 2018/007337 A2. In order to limit the formation of short circuits

between top electrode and bottom electrode, the monolayer has to be as tight as possible, without pinholes allowing the permeation of top electrode material during its deposition process. There is also a strong demand for materials which form molecular layers of acceptable quality within very short deposition times.

A problem to be solved by the present invention is to provide improved materials for the fabrication of switchable molecular layers.

To solve the problem a compound of formula I shown below is provided which comprises a ring with an anchor group connected to a polar ring via a one-atomic linking group, where the compound of formula I can be bonded onto a substrate by means of the anchor group.

The present invention further relates to a process for the fabrication of a switching element comprising a molecular layer obtainable from one or more compounds of formula I. The present invention further relates to a memristive device comprising said switching element.

Preferred embodiments are subject-matter of the dependent claims and can also be taken from the description.

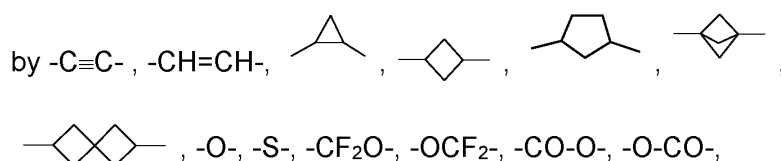
The present invention relates to a compound of formula I

$$R^1-(A^1-Z^1)_r-B^1-Z^L-A^2-(Z^3-A^3)_s-G \quad (I)$$

in which

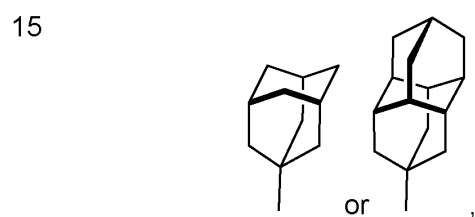
R^1 denotes straight chain or branched alkyl or alkoxy each having 1 to 20 C atoms, where one or more CH_2 groups in these radicals may each be replaced, independently of one another,

- 4 -



- 5 $-\text{SiR}^0\text{R}^{00}-$, $-\text{NH}-$, $-\text{NR}^0-$ or $-\text{SO}_2-$ in such a way that O atoms are not linked directly to one another, and in which one or more H atoms may be replaced by halogen, CN, SCN or SF_5 , or alternatively, R^1 denotes a group Dia-Z^{D} ,

- 10 **Dia** denotes a diamondoid radical, preferably derived from a lower diamantoid, very preferably selected from the group consisting of adamantyl, diamantyl, triamantyl, in which one or more H atoms can be replaced by alkyl or alkoxy having up to 12 C atoms, in particular

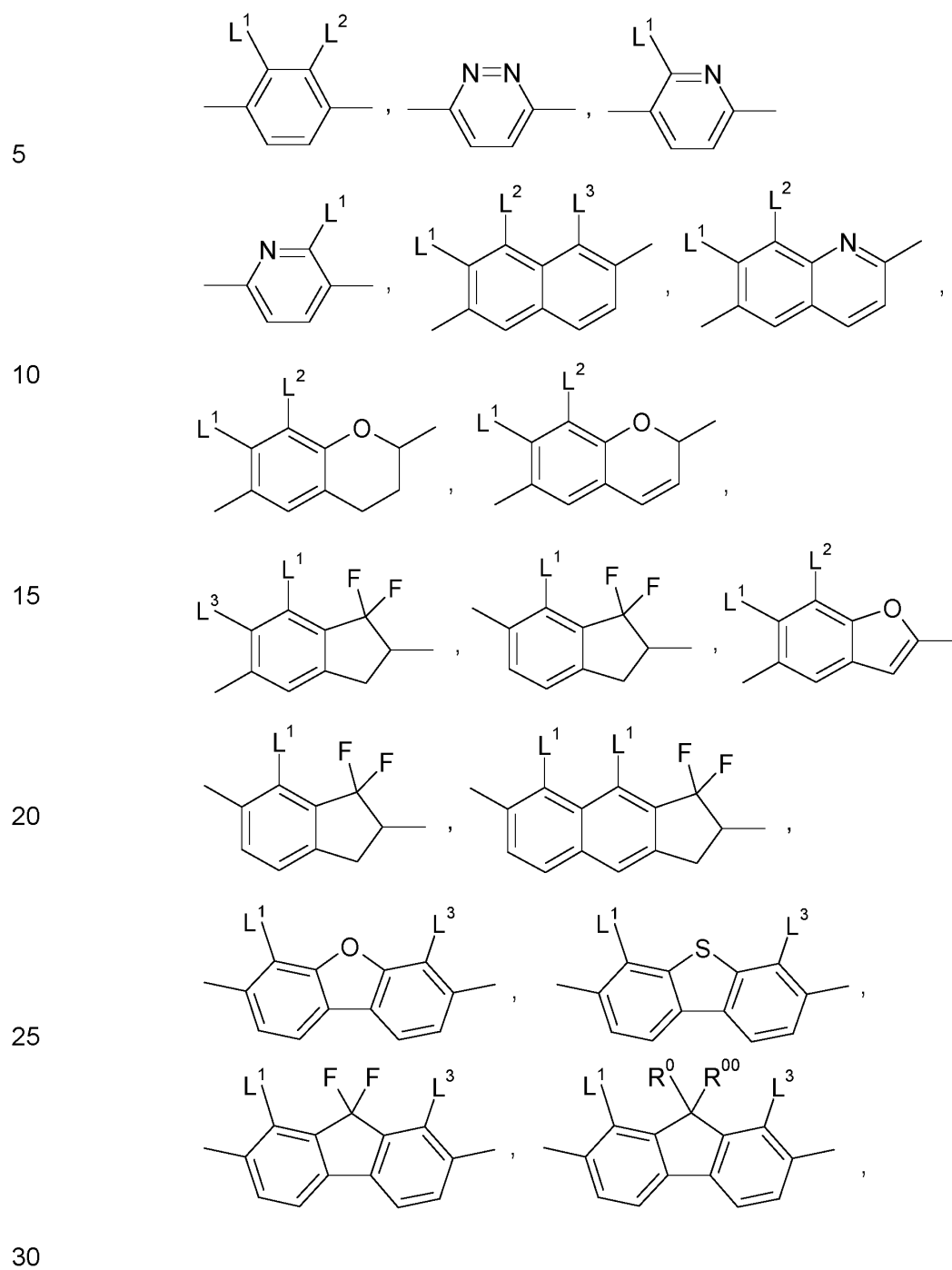


- 20 Z^{D} has one of the meanings of Z^1 and Z^3 or denotes a spacer group,

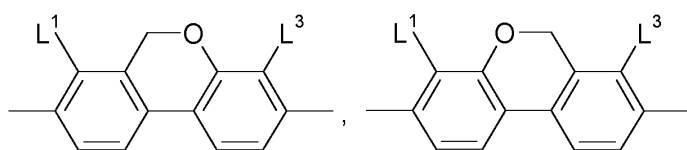
- Z^1 , Z^3 on each occurrence, identically or differently, denote a single bond, $-\text{CF}_2\text{O}-$, $-\text{OCF}_2-$, $-\text{CF}_2\text{S}-$, $-\text{SCF}_2-$, $-\text{CH}_2\text{O}-$, $-\text{OCH}_2-$,
 25 $-\text{C}(\text{O})\text{O}-$, $-\text{OC}(\text{O})-$, $-\text{C}(\text{O})\text{S}-$, $-\text{SC}(\text{O})-$, $-(\text{CH}_2)_{n1}-$, $-(\text{CF}_2)_{n2}-$,
 $-\text{CF}_2\text{CH}_2-$, $-\text{CH}_2\text{CF}_2-$, $-\text{CH}=\text{CH}-$, $-\text{CF}=\text{CF}-$, $-\text{CF}=\text{CH}-$,
 $-\text{CH}=\text{CF}-$, $-(\text{CH}_2)_{n3}\text{O}-$, $-\text{O}(\text{CH}_2)_{n4}-$, $-\text{C}\equiv\text{C}-$, $-\text{O}-$, $-\text{S}-$, $-\text{CH}=\text{N}-$,
 $-\text{N}=\text{CH}-$, $-\text{N}=\text{N}-$, $-\text{N}=\text{N}(\text{O})-$, $-\text{N}(\text{O})=\text{N}-$ or $-\text{N}=\text{C}-\text{C}=\text{N}-$,

- 30 $n1$, $n2$, $n3$, $n4$ identically or differently, are 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

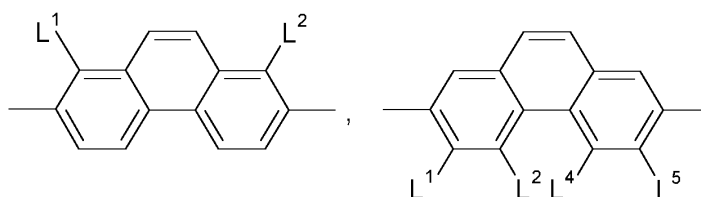
- Z^L denotes -O-, -S-, -CH₂-, -C(O)-, -CF₂-, -CHF-, -C(R^x)₂-, -S(O)-, -SO₂-,
- 5 R^0, R^{00} , identically or differently, denote an alkyl or alkoxy radical having 1 to 15 C atoms, in which, in addition, one or more H atoms may be replaced by halogen,
- R^x denotes straight-chain or branched alkyl having 1 to 6 C atoms,
- 10 A^1, A^3 on each occurrence, identically or differently, denote an aromatic, heteroaromatic, alicyclic or heteroaliphatic ring having 4 to 25 ring atoms, which may also contain condensed rings and which may be mono- or polysubstituted by Y,
- 15 A^2 denotes an aromatic or heteroaromatic ring having 5 to 25 ring atoms, which may also contain condensed rings and which may be mono- or polysubstituted by Y,
- 20 Y on each occurrence, identically or differently, denotes F, Cl, CN, SCN, SF₅ or straight-chain or branched, in each case optionally fluorinated alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy having 1 to 12 C atoms, or cycloalkyl or alkylcycloalkyl each having 3 to 12 C atoms, preferably methyl, ethyl, isopropyl, cyclopropyl, cyclobutyl,
- 25 cyclopentyl, cyclohexyl, trifluoromethyl, methoxy or trifluoromethoxy,

B¹ denotes

- 7 -



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where the groups may be oriented in both directions,

L^1 to L^5 , independently of one another, denote F, Cl, Br, I, CN, SF_5 , CF_3 or OCF_3 , preferably Cl or F, where L^3 may alternatively also denote H,

15

G denotes $-CH=CH_2$, $-OH$, $-CH(CH_2OH)_2$, $-C(CH_2OH)_3$, $-B(OH)_2$, $-SH$, $-SO_2OH$, $-OP(O)(OH)_2$, $-PO(OH)_2$, $-C(OH)(PO(OH)_2)_2$, $-COOH$, $-Si(OR^x)_3$ or $-SiCl_3$, $-SO_2OR^V$, $-OP(O)(OR^V)_2$, $-PO(OR^V)_2$, $-C(OH)(PO(OR^V)_2)_2$, $-COOR^V$, $-Si(OR^V)_3$,

20

R^V denotes alkyl having 1 to 20 C atoms, preferably secondary or tertiary alkyl having 3 to 10 C atoms,

r is 0, 1 or 2, and

25

s is 0, 1 or 2,

where $r + s \leq 4$.

30

The compounds of formula I are distinguished by excellent solubility in polar aprotic solvents, such as ethyl acetate, 1-methoxy-2-propanol acetate, acetone, ethylmethylketone, cyclohexanone and the like.

Furthermore, they enable fast formation of molecular layers, fast process times for dip-coating and high quality of monolayers deposited by spin-coating.

- 5 The molecular layers obtained from compounds of formula I are distinguished by dense packing and advantageously low water contact angles and enable the fabrication of switching elements for memristive devices that can be patterned by photolithography using standard industrial processes. Furthermore, these monolayers have a very high thermal
10 stability even at temperatures above 300°C.

Switching devices comprising a molecular layer obtained from the compounds of formula I exhibit advantageously high current densities.

- 15 Brief description of the drawings

The drawings show:

- 20 Figure 1 a schematic illustration of the layer structure of a memristive memory element,

- 25 Figure 2 an exemplary logarithmic plot of measured current density values versus applied voltages of an exemplary embodiment of a memory device having a resistive switching memory element,

- 30 Figure 3 an exemplary logarithmic plot of measured current density values versus applied voltages of a comparative resistive switching memory element.

- 30 The term "diamondoids" refers to substituted and unsubstituted cage compounds of the adamantane series including adamantane, diamantane, triamantane, tetramantanes, pentamantanes, hexamantanes,

heptamantanes, octamantanes, and the like, including all isomers and stereoisomers thereof. The compounds have a "diamondoid" topology, which means their carbon atom arrangement is superimposable on a fragment of a face centered cubic diamond lattice. Substituted diamondoids
5 from the first of the series are preferable with 1 to 4 independently-selected alkyl or alkoxy substituents.

Diamondoids include "lower diamondoids" and "higher diamondoids," as these terms are defined herein, as well as mixtures of any combination of lower and higher diamondoids. The term "lower diamondoids" refers to
10 adamantane, diamantane and triamantane and any and/or all unsubstituted and substituted derivatives of adamantane, diamantane and triamantane. These lower diamondoid components show no isomers or chirality and are readily synthesized, distinguishing them from "higher diamondoids." The term "higher diamondoids" refers to any and/or all substituted and
15 unsubstituted tetramantane components; to any and/or all substituted and unsubstituted pentamantane components; to any and/or all substituted and unsubstituted hexamantane components; to any and/or all substituted and unsubstituted heptamantane components; to any and/or all substituted and unsubstituted octamantane components; as well as mixtures of the above
20 and isomers and stereoisomers of tetramantane, pentamantane, hexamantane, heptamantane, and octamantane. Adamantane chemistry has been reviewed by Fort, Jr. et al. in "Adamantane: Consequences of the Diamondoid Structure," Chem. Rev. vol. 64, pp. 277-300 (1964).

Adamantane is the smallest member of the diamondoid series and may be
25 thought of as a single cage crystalline subunit. Diamantane contains two subunits, triamantane three, tetramantane four, and so on. While there is only one isomeric form of adamantane, diamantane, and triamantane, there are four different isomers of tetramantane, (two of which represent an enantiomeric pair), i.e., four different possible ways of arranging the four
30 adamantane subunits. The number of possible isomers increases non-linearly with each higher member of the diamondoid series, pentamantane, hexamantane, heptamantane, octamantane, etc.

As used herein, an anchor group is a functional group by means of which a compound is adsorbed onto or bonded to the surface of a substrate by physisorption, chemisorption or by chemical reaction.

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A spacer group in the sense of the present invention is a flexible chain between two rigid groups which causes a separation between these sub-structures and, owing to its flexibility, at the same time improves the mobility of at least one of these groups after bonding to a substrate.

10

If Z^D denotes a spacer group the group is preferably selected from the formula $Sp'-X'$, so that the radical $Dia-Z^D$ of formula I corresponds to the formula $Dia-Sp'-X'$, in which

15

Sp' denotes straight-chain or branched alkylene having 1 to 20, preferably 1 to 12 C atoms, which is optionally mono- or poly-substituted by F, Cl, Br, I or CN and in which, in addition, one or more non-adjacent CH_2 groups may each be replaced, independently of one another, by $-O-$, $-S-$, $-NH-$, $-NR^0$, $-SiR^{00}R^{000}$, $-CO-$, $-COO-$, $-OCO-$, $-OCO-O-$, $-S-CO-$, $-CO-S-$, $-NR^0-CO-O-$, $-O-CO-NR^0$, $-NR^0-CO-NR^0$, $-CH=CH-$ or $-C\equiv C-$ in such a way that O and/or S atoms are not linked directly to one another,

20

25

X' denotes $-O-$, $-S-$, $-CO-$, $-COO-$, $-OCO-$, $-O-COO-$, $-CO-NR^{00}$, $-NR^{00}-CO-$, $-NR^{00}-CO-NR^{00}$, $-OCH_2-$, $-CH_2O-$, $-SCH_2-$, $-CH_2S-$, $-CF_2O-$, $-OCF_2-$, $-CF_2S-$, $-SCF_2-$, $-CF_2CH_2-$, $-CH_2CF_2-$, $-CF_2CF_2-$, $-CH=N-$, $-N=CH-$, $-N=N-$, $-CH=CR^{00}$, $-CY^x=CY^x-$, $-C\equiv C-$, $-CH=CH-COO-$, $-OCO-CH=CH-$ or a single bond,

30

R^0 , R^{00}

and R^{000} each, independently of one another, denote H or alkyl having 1 to 12 C atoms, and

Y^x and $Y^{x'}$ each, independently of one another, denote H, F, Cl or CN.

5

X' is preferably -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, -CO-NR⁰-, -NR⁰-CO-, -NR⁰-CO-NR⁰- or a single bond.

10

Preferred spacer groups Sp' are $-(CH_2)_{p1}-$, $-(CF_2)_{p1}-$, $-(CH_2CH_2O)_{q1}-CH_2CH_2-$, $-(CF_2CF_2O)_{q1}-CF_2CF_2-$, $-CH_2CH_2-S-CH_2CH_2-$, $-CH_2CH_2-NH-CH_2CH_2-$ or $-(SiR^{00}R^{000}-O)_{p1}-$, in which $p1$ is an integer from 1 to 12, $q1$ is an integer from 1 to 3, and R^{00} and R^{000} have the meanings indicated above.

15

Particularly preferred groups $-X'-Sp'-$ are $-(CH_2)_{p1}-$, $-O-(CH_2)_{p1}-$, $-(CF_2)_{p1}-$, $-O(CF_2)_{p1}-$, $-OCO-(CH_2)_{p1}-$ and $-OC(O)O-(CH_2)_{p1}-$, in which $p1$ has the meaning indicated above.

20

Particularly preferred groups Sp' are, for example, in each case straight-chain ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, octadecylene, perfluoroethylene, perfluoropropylene, perfluorobutylene, perfluoropentylene, perfluorohexylene, perfluoroheptylene, perfluorooctylene, perfluorononylene, perfluorodecylene, perfluoroundecylene, perfluorododecylene, perfluorooctadecylene, ethyleneoxyethylene, methyleneoxybutylene, ethylenethioethylene, ethylene-N-methyliminoethylene, 1-methylalkylene, ethenylene, propenylene and butenylene.

25

30

Particularly preferred groups X' are -O- or a single bond.

Halogen is F, Cl, Br and I.

Herein, alkyl is straight-chain or branched and has 1 to 15 C atoms, is preferably straight-chain and has, unless indicated otherwise, 1, 2, 3, 4, 5, 6 or 7 C atoms and is accordingly preferably methyl, ethyl, propyl, butyl, pentyl, hexyl or heptyl.

5

Branched alkyl can be racemic or non-racemic (optically active).

Herein, an alkoxy radical is straight-chain or branched and contains 1 to 15 C atoms. It is preferably straight-chain and has, unless indicated otherwise, 1, 2, 3, 4, 5, 6 or 7 C atoms and is accordingly preferably methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy or heptoxy.

10

Herein, an alkenyl radical is preferably an alkenyl radical having 2 to 15 C atoms, which is straight-chain or branched and contains at least one C-C double bond. It is preferably straight-chain and has 2 to 7 C atoms. Accordingly, it is preferably vinyl, prop-1- or -2-enyl, but-1-, -2- or -3-enyl, pent-1-, -2-, -3- or -4-enyl, hex-1-, -2-, -3-, -4- or -5-enyl, hept-1-, -2-, -3-, -4-, -5- or -6-enyl. If the two C atoms of the C-C double bond are substituted, the alkenyl radical can be in the form of E and/or Z isomer (trans/cis). In general, the respective E isomers are preferred. Of the alkenyl radicals, prop-2-enyl, but-2- and -3-enyl, and pent-3- and -4-enyl are particularly preferred.

15

20

Herein, alkynyl is taken to mean an alkynyl radical having 2 to 15 C atoms, which is straight-chain or branched and contains at least one C-C triple bond. 1- and 2-propynyl and 1-, 2- and 3-butynyl are preferred.

25

In formula I, preferred aryl groups are derived, for example, from the parent structures benzene, naphthalene, tetrahydronaphthalene, 9,10-dihydro-phenanthrene, fluorene, indene and indane.

30

In formula I, preferred heteroaryl groups are, for example, five-membered rings, such as, for example, furan, thiophene, selenophene, oxazole,

isoxazole, 1,2-thiazole, 1,3-thiazole, 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 and 1,3,4-thiadiazole, six-membered rings, such as, for example, pyridine, pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, 1,2,4-
5 triazine and 1,2,3-triazine, or condensed rings, such as, for example, indole, isoindole, indolizine, indazole, benzimidazole, benzotriazole, purine, naphthimidazole, benzoxazole, naphthoxazole, benzothiazole, benzofuran, isobenzofuran, dibenzofuran, thieno[2,3b]thiophene, thieno[3,2b]thiophene, dithienothiophene, isobenzothiophene, dibenzothiophene, benzothiadiazothiophene, 2H-chromen (2H-1-benzopyran), 4H-chromene (4H-1-
10 benzopyran) and coumarin (2H-chromen-2-one), or combinations of these groups.

In formula I, preferred cyloaliphatic groups are cyclobutane, cyclopentane, 15 cyclohexane, cyclohexene, cycloheptane, decahydronaphthalene, bicyclo[1.1.1]pentane, bicyclo[2.2.2]octane, spiro[3.3]heptane and octahydro-4,7-methanoindane.

In formula I, preferred heteroaliphatic groups are tetrahydrofuran, 20 dioxolane, tetrahydrothiofuran, pyran, dioxane, dithiane, silinane, piperidine and pyrrolidine.

Preferably A¹ and A³, on each occurrence, identically or differently are selected from the following groups:

25

a) 1,4-phenylene, in which one or two CH groups may be replaced by N and in which, in addition, one or more H atoms may be replaced by Y,

30

b) the group consisting of trans-1,4-cyclohexylene and 1,4-cyclohexenylene, in which one or more non-adjacent CH₂ groups may

be replaced by -O- and/or -S- and in which, in addition, one or more H atoms may be replaced by Y, and

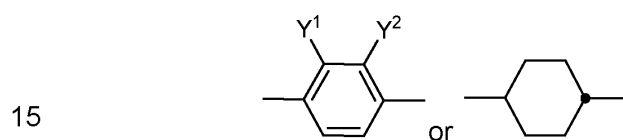
- 5 c) the group consisting of 1,3-dioxolane-2,4-diyl, tetrahydrofuran-2,5-diyl, cyclobutane-1,3-diyl, 1,4-bicyclo[2.2.2]octanediyl, piperidine-1,5-diyl and thiophene-2,5-diyl, in which one or more H atoms may be replaced by Y,

where Y has the meanings given above.

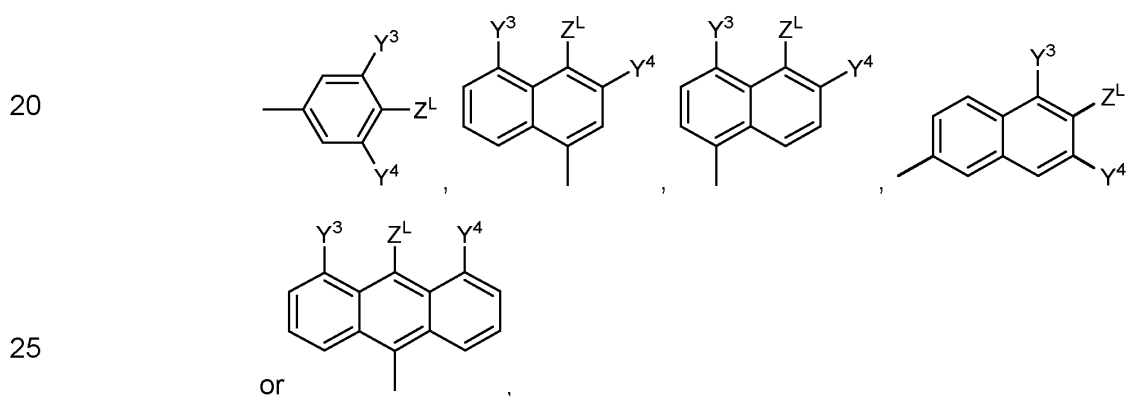
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In formula I and its subformulae, very preferably

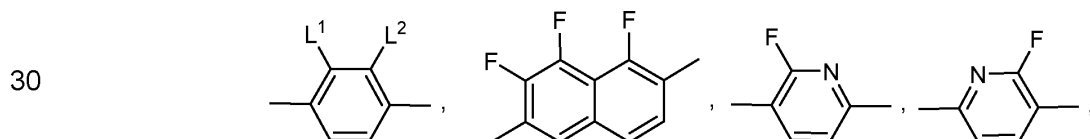
A¹ and A³ identically or differently, denote

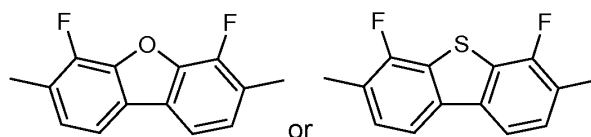


A²-Z^L denotes



B¹ denotes





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R^1 denotes H, straight chain or branched alkyl, alkenyl, alkynyl, alkoxy each having up to 12 C atoms, adamantyl or adamantylmethoxy,

10

L^1 and L^2 identically or differently, denote F or Cl,

Y^1 and Y^2 identically or differently, have one of the meanings given above for Y and preferably denote H, F or Cl,

15

Y^3 and Y^4 , identically or differently, have one of the meanings given above for Y^3 and Y^4 and preferably denote methyl, ethyl, isopropyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclopentenyl, cyclohexyl, cyclohexenyl, methoxy, trifluoromethyl, trifluoromethoxy, or trifluoromethylthio

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Z^L denotes -O-,

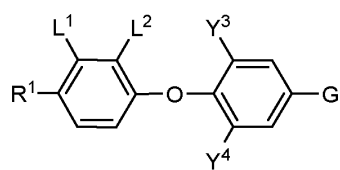
Z^1 , Z^2 , independently of one another, denote a single bond, -C(O)O-, -OC(O)-, -CF₂O-, -OCF₂-, -CH₂O-, OCH₂- or -CH₂CH₂-, in particular a single bond, and/or

25

G denotes -OP(O)(OH)₂, -PO(OH)₂, or -COH(PO(OH)₂)₂.

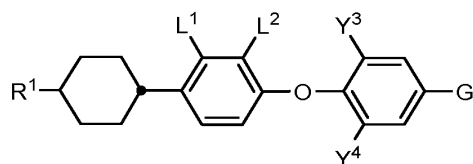
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Very preferred sub-formulae of the formula I are the sub-formulae I-1 to I-6:



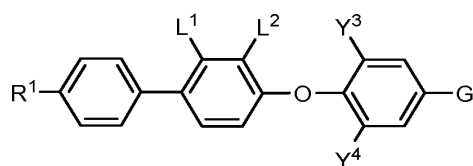
I-1

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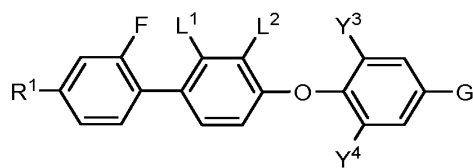
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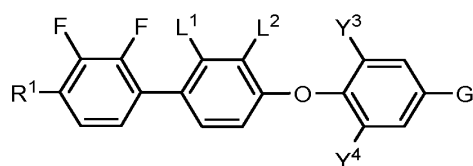
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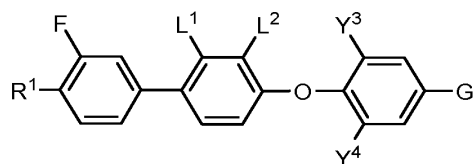
I-4

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I-5

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I-6

30 in which the occurring groups have the meanings defined above for formula I, and preferably

R¹ denotes alkyl having 1 to 7 C atom,

L¹ and L² identically or differently, denote F or Cl,

5 Y³ and Y⁴, identically or differently, have one of the meanings given above and preferably denote methyl, and

G denotes -PO(OH)₂, or -COH(PO(OH)₂)₂.

10 According to another aspect of the invention there is provided a chiral non-racemic compound of formula I.

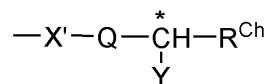
The molecular layers obtained from chiral compounds of formula I enable memristic devices with significantly reduced stochastic noise and faster
15 switching, reducing the read and write error rate, which has a positive effect on energy-efficiency. In addition, increased tunnel current are observed allowing for the integration to smaller junction sizes.

Preferably, the chiral compound has an enantiomeric excess (ee) of above
20 50%, preferably above 80%, 90%, 95%, more preferably above 97%, in particular above 98%.

Chirality is achieved by a chiral group R¹ of formula I above having one or more, preferably one or two, very preferably one, asymmetrically
25 substituted carbon atom (or: asymmetric carbon atom, C*), hereinafter referred to as R*.

In R* the asymmetric carbon atom is preferably linked to two differently substituted carbon atoms, a hydrogen atom and a substituent selected from
30 the group halogen (preferably F, Cl, or Br), alkyl or alkoxy with 1 to 5 carbon atoms in each case, and CN.

The chiral organic radical preferably has the formula

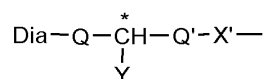


in which

- 5 X' has the meanings defined above for formula I and preferably denotes -CO-O-, -O-CO-, -O-CO-O-, -CO-, -O-, -S-, -CH=CH-, -CH=CH-COO- or a single bond, more preferably -CO-O-, -O-CO-, -O-, or a single bond, very preferably -O- or a single bond,
- 10 Q denotes a single bond or optionally fluorinated alkylene having 1 to 10 carbon atoms, in which a CH₂ group not linked with X can also be replaced by -O-, -CO-, -O-CO-, -CO-O- or -CH=CH-, preferably alkylene having 1 to 5 carbon atoms or a single bond,
- 15 particularly preferably -CH₂-, -CH₂CH₂- or a single bond,
- 20 Y denotes optionally fluorinated alkyl having 1 to 15 carbon atoms, in which one or two non-adjacent CH₂ groups can also be replaced by -O-, -CO-, -O-CO-, -CO-O- and/or -CH=CH-, further CN or halogen, preferably optionally fluorinated alkyl or alkoxy having 1 to 7 C atoms, -CN or Cl, particularly preferably -CH₃, -C₂H₅, -CF₃ or Cl,
- 25 R^{Ch} denotes an alkyl group having 1 to 15 carbon atoms that is different from Y, in which one or two non-adjacent CH₂ groups can also be replaced by -O-, -CO-, -O-CO-, -CO-O- and/or -CH=CH-, preferably denotes straight-chain alkyl having 1 to 10, in particular 1 to 7, carbon atoms, in which the CH₂ group linked to the asymmetric carbon atom can be replaced by -O-, -O-CO- or -CO-O-.
- 30 or -CO-O-.

In an embodiment in which R¹ of formula I denotes a group Dia-Z^D as defined above, the group R* has the formula Dia-Sp* in which Sp* denotes a chiral non-racemic spacer group.

5 The group Dia-Sp* preferably has the formula



in which Dia, Q, Y and X' have the meanings defined above, and

10

Q' identically or differently, has the meanings given above for Q.

The compounds of the general formula I are prepared by methods known per se, as described in the literature (for example in the standard works, such as Houben-Weyl, Methoden der organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart), to be precise under reaction conditions which are known and are suitable for the said reactions. Use can be made here of variants which are known per se, but are not mentioned here in greater detail. Chiral groups R* and Sp* are described in A. Taugerbeck, Ch. Booth, Design and Synthesis of Chiral Nematic Liquid Crystals, in: Handbook of Liquid Crystals, Volume 3, Part III, Chapter 14, Wiley VCH, Weinheim, 2014, and can preferably be synthesised according to the syntheses described therein or references cited therein.

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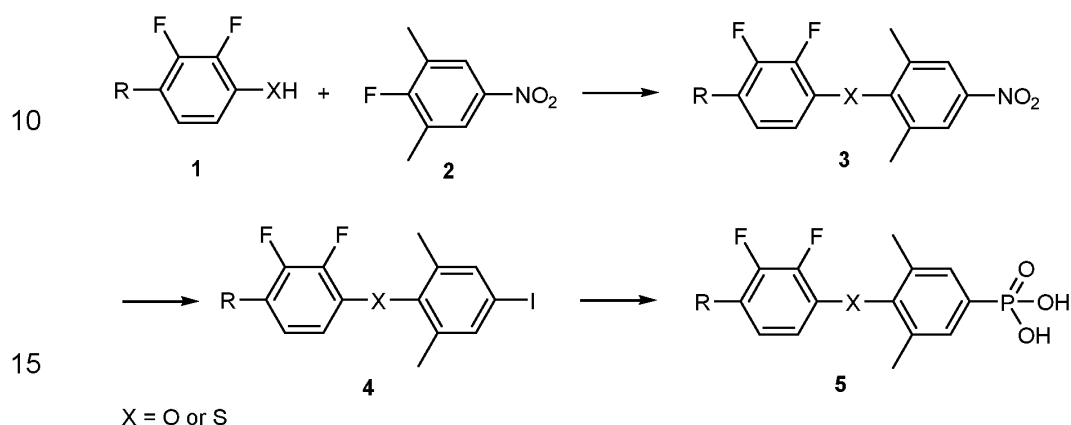
If desired, the starting materials can also be formed in situ by not isolating them from the reaction mixture, but instead immediately converting them further into the compounds of the general formula I.

30

Preferred synthetic pathways towards compounds according to the invention are shown in the scheme below and are further illustrated by means of the working examples. The syntheses can be adapted to the particular desired compounds of the general formula I by choice of suitable

starting materials. For example, as shown in scheme 1, reaction of phenolates or thiophenolates (1) with fluoronitroaromatic compounds (2) yields aryl ethers 3 by nucleophilic replacement of fluoride. The ether 3 can be converted using standard processes via iodide 4 to the phosphonic acid 5.

Scheme 1



The invention furthermore relates to a process for the production of the switching element according to the invention comprising at least the following steps:

- production of a first electrode with a surface,
- deposition of a monolayer comprising one or more compounds of the formula I onto the surface of the first electrode,
- application of a second electrode.

The deposition of the monolayer is carried out using the pure substance or from solution, preferably from solution. Suitable deposition methods and solvents are known to the person skilled in the art; examples are spin coating or dip coating.

According to another aspect of the invention the monolayer is fabricated from one or more compounds of formula I in which the anchor group G

denotes $-\text{SO}_2\text{OR}^V$, $-\text{OP}(\text{O})(\text{OR}^V)_2$, $-\text{PO}(\text{OR}^V)_2$, $-\text{C}(\text{OH})(\text{PO}(\text{OR}^V)_2)_2$,
-COOR^V or -Si(OR^V)₃ where R^V denotes alkyl having 1 to 20 C atoms,
preferably a secondary or tertiary alkyl having up to 20 C atoms. These
compounds are distinguished by a particularly high solubility and are well
5 suitable for industrial processes such as spin coating. In addition, it is
possible to process these compounds by gas phase deposition. The
compounds serve as precursors for the corresponding free acids which are
obtained in situ by thermal treatment of the compounds after deposition
onto the first electrode. The first electrode is then heated to a temperature
10 between 60°C and 300°C, preferably between 100°C and 250°C, in
particular between 140°C and 180°C.

In a preferred embodiment, the substrate is annealed after deposition of the
monolayer. The annealing is carried out at a temperature of greater than
15 20°C and less than 300°C, preferably at greater than 50°C and less than
200°C, particularly preferably at greater than 90°C and less than 150°C.
The time duration of the annealing is 1 to 48 h, preferably 4 to 24 h,
particularly preferably 8 to 16 h.

20 The molecular layer of the present invention is a layer of electrically insulat-
ing, non-conducting and non-semiconducting organic compounds.

The molecular layer preferably comprises molecules of the formula I or,
particularly preferably, consists of molecules of the formula I.

25

The thickness of the layer is preferably 10 nm or less, particularly preferably
5 nm or less, very particularly preferably 2 nm or less.

30 The molecular layer may consist of one, two, three or more molecule layers
comprising compounds of the formula I.

The molecular layer employed in accordance with the invention is preferably a molecular monolayer.

5 In an embodiment, the molecular layer is a self-assembled monolayer (SAM).

The production of self-assembled monolayers is known to the person skilled in the art; a review is given, for example, in A. Ulman, *Chem. Rev.* **1996**, 96, 1533-1554.

10 In a further embodiment, the molecular layer is bonded to the substrate by chemisorption, in particular by an addition reaction or condensation reaction.

15 In a further embodiment, the molecular layer is bonded to the substrate by physisorption.

The degree of coverage of the substrate is preferably 90% to 100%, particularly preferably 95% to 100%, very particularly preferably 98% to
20 100%.

In a further embodiment, the molecular layer is covered with 1 to 10, preferably 1 to 5, particularly preferably 1 to 3, further layers of organic or inorganic adsorbates. Suitable layers comprise, for example, dielectrics, for
25 example oxidic, fluoridic or nitridic materials, such as TiO₂, Al₂O₃, HfO₂, SiO₂, LiF and Si₃N₄, or metals, such as Pt, Pd, Pb, Au, Ag, Cu, Al and Mg, and eutectic compounds thereof, such as, for example, PdAu 20:80. Such layers can be built up in a thickness of a few nanometres by defined and high-precision deposition, for example by ALD (atomic layer deposition)
30 processes.

The molecules of the molecular layer are preferably covalently bonded to the substrate. The bonding is carried out by known methods which are familiar to the person skilled in the art, for example by the addition reaction of a compound of the formula I or by esterification with hydroxyl groups located on the surface of the substrate.

For addition reactions, a suitable substrate, preferably a silicon surface - after corresponding pre-treatment with aqueous NH_4F solution - can, for example, be treated in order to obtain a hydrogen-terminated surface. The surface treated in this way can then be treated at elevated temperature with exclusion of oxygen either directly with a suitable liquid compound of the formula I or a solution of the compound of the formula I in a suitable solvent. According to this aspect of the invention the group G in formula I preferably denotes $-\text{CH}=\text{CH}_2$.

For condensation reactions, a suitable substrate, preferably a silicon surface, can, for example, be treated with oxygen plasma in order to obtain a hydrophilic oxidic surface which is populated with hydroxyl groups. The surface treated in this way can then be reacted at elevated temperature either directly with a suitable, liquid compound of the formula I or a solution of the compound of the formula I in a suitable solvent. It is clear that an oxidic surface of this type merely serves for surface modification with the aim of possible derivatisation via condensation reactions and does not represent an insulator layer in the true sense. Sufficiently large tunnel currents through this oxidic surface are possible owing to the low thickness in the order of 1 nm.

In the switching elements according to the invention, the molecules of the molecular layer are bonded to a substrate or an interlayer located between the molecular monolayer and the substrate. The substrate according to the invention can perform various functions, depending on the structure of the

switching elements. For example, a conductive substrate can serve as first electrode. Likewise, the substrate can be a layer of a diode.

Suitable substrates are known to the person skilled in the art. Particularly
5 suitable substrates are selected from:

- element semiconductors, such as Si, Ge, C (diamond, graphite, graphene, fullerene), α -Sn, B, Se and Te;
- 10 - compound semiconductors, preferably
 - group III-V semiconductors, in particular GaAs, GaP, InP, InSb, InAs, GaSb, GaN, TaN, TiN, MoN, WN, AlN, InN, $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $\text{In}_x\text{Ga}_{1-x}\text{Ni}$,
 - group II-VI semiconductors, in particular ZnO, ZnS, ZnSe, ZnTe, 15 CdS, CdSe, CdTe, $\text{Hg}_{(1-x)}\text{Cd}_{(x)}\text{Te}$, BeSe, BeTe_x and HgS;
 - group III-VI semiconductors, in particular GaS, GaSe, GaTe, InS, InSe_x and InTe,
 - group I-III-VI semiconductors, in particular CuInSe_2 , CuInGaSe_2 , CuInS_2 and CuInGaS_2 ,
 - 20 - group IV-IV semiconductors, in particular SiC and SiGe,
 - group IV-VI semiconductors, in particular SeTe;
- organic semiconductors, in particular polythiophene, tetracene, penta- 25 cene, phthalocyanines, PTCDA, MePTCDI, quinacridone, acridone, indanthrone, flaranthrone, perinone, AlQ_3 , and mixed systems, in particular PEDOT:PSS and polyvinylcarbazole/TLNQ complexes;
- metals, in particular Ta, Ti, Co, Mo, Pt, Ru, Au, Ag, Cu, Al, W and Mg;
- 30 - conductive oxidic materials, in particular indium tin oxide (ITO), indium gallium oxide (IGO), $\text{InGa-}\alpha\text{-ZnO}$ (IGZO), aluminium-doped zinc oxide

(AZO), tin-doped zinc oxide (TZO), fluorine-doped tin oxide (FTO) and antimony tin oxide.

5 The molecular layer may optionally also be bonded to a thin (preferably 0.5 - 5 nm thick) oxidic or fluoridic interlayer, for example TiO_2 , Al_2O_3 , HfO_2 , SiO_2 or LiF , which is located on the substrate.

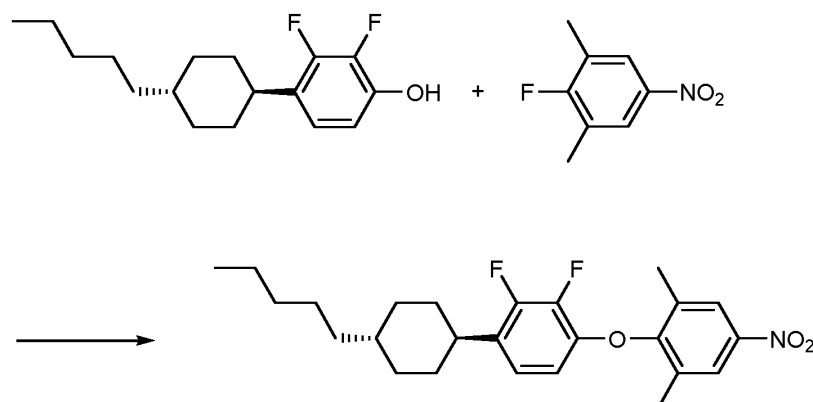
10 The counter electrode or second electrode consists of a conducting or semiconducting material or a combination (layer stack) of a plurality of these materials. Examples are the materials mentioned as substrate material. Preference is given to Hg, In, Ga, InGa, Ag, Au, Cr, Pt, PdAu, Pb, Al, Mg, W, Yb, Zn, CNT (carbon nanotubes), graphene and conductive polymers (such as PEDOT:PSS).

15 The production and structuring of the electrodes is carried out by means of processes known to the person skilled in the art. The fabrication and electrical characterisation of switching elements comprising a molecular layer obtained from one or more compounds of formula I is carried out according to procedures described in WO 2016/110301 A1 and
20 WO 2018/007337 A2.

Examples

Synthesis Example 1

25 Step 1: 1-(2,6-dimethyl-4-nitro-phenoxy)-2,3-difluoro-4-(4-pentylcyclohexyl)-benzene



5
10 A solution of 2-fluoro-1,3-dimethyl-5-nitrobenzene (24.5 g, 0.145 mol) in dimethylsulfoxide (DMSO) (245 mL) is added to a suspension of 2,3-difluoro-4-(4-pentylcyclohexyl)phenol (49.1 g, 0.174 mol) and potassium carbonate in DMSO (245 mL) and is heated at 125°C overnight under nitrogen. The mixture is cooled to 40°C, then added to water (1.5 L) and stirred for 30 min. Ethyl acetate (400 mL) and brine (50 mL) are added and the layers are separated. The aqueous layer is extracted further with ethyl acetate (2 x 300 mL). The organics are combined, dried over magnesium sulfate and the solvent is evaporated. The crude oil is dissolved in heptane (160 mL) and purified over silica gel (200 g) eluting with heptane followed by 5% ethyl acetate/heptane, followed by recrystallisation from acetonitrile to give 1-(2,6-dimethyl-4-nitro-phenoxy)-2,3-difluoro-4-(4-pentylcyclohexyl)-benzene as a beige solid.

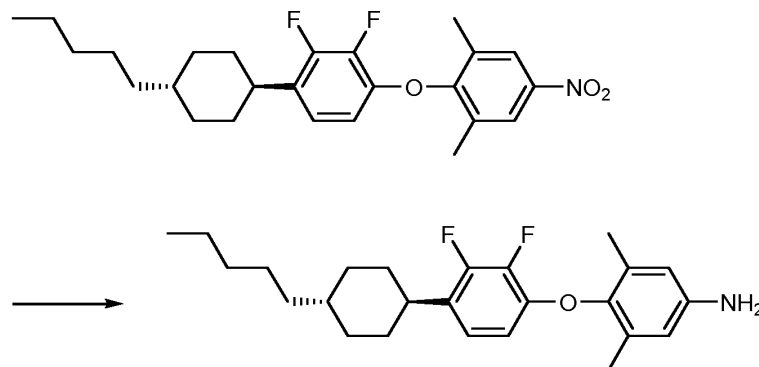
25 ¹H NMR (400 MHz, CDCl₃-d) δ ppm 0.89 (3 H, t, *J*=7.0 Hz), 1.00-1.15 (2 H, m), 1.17-1.35 (9 H, m), 1.35-1.46 (2 H, dd, *J*=12.3 Hz, 2.3 Hz), 1.86 (4 H, br. d, *J*=10.9 Hz), 2.25 (6 H, s), 2.77 (1 H, m), 6.12 (1 H, m), 6.75 (1 H, m), 8.02 (2 H, s).

30 ¹³C NMR (400 MHz, CDCl₃-d) δ ppm 14.01, 16.36, 22.64, 32.12, 32.82, 33.30, 37.00, 37.15, 37.21, 109.16 (d, *J*=2.9 Hz), 120.77 (t, *J*=5.1 Hz), 124.34, 130.12 (dd, *J*=12.5 Hz, 1.5 Hz), 132.95, 140.69 (dd, *J*=248.7 Hz,

16.1 Hz), 143.43 (dd, $J=8.8$ Hz, 2.9 Hz), 144.79, 148.37 (dd, $J=247.2$ Hz, 10.3 Hz), 155.90.

^{19}F NMR (400 MHz, $\text{CDCl}_3\text{-}d$) δ ppm -158.9 (1 F, d, $J=19.1$ Hz), -141.4 (1 F, d, $J=19.1$ Hz).

Step 2: 4-[2,3-difluoro-4-(4-pentylcyclohexyl)phenoxy]-3,5-dimethyl-aniline



Pd/C (5% loading, 50% wetted, 1.95 g) is charged to a 2L Parr pressure vessel followed by a solution of 1-(2,6-dimethyl-4-nitro-phenoxy)-2,3-difluoro-4-(4-pentylcyclohexyl)-benzene (39.0 g, 90.38 mmol) in isopropanol (585 mL) and tetrahydrofuran (THF, 117 mL). Hydrogen is charged to a pressure of 5 bar. After 90 min the pressure had dropped to ~1 bar. Hydrogen is re-charged to a pressure of 5 bar and stirred overnight. The catalyst is filtered off and washed with isopropanol (50 mL) and the filtrates concentrated to dryness to give 4-[2,3-difluoro-4-(4-pentylcyclohexyl)phenoxy]-3,5-dimethyl-aniline as an off-white solid.

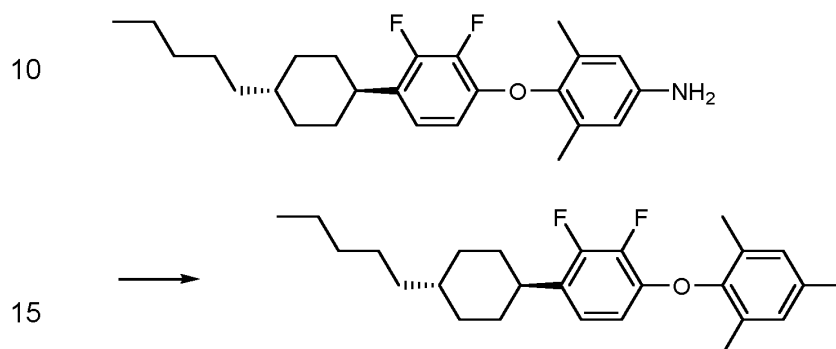
^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ ppm 0.85 (3 H, t, $J=6.9$ Hz), 0.95-1.07 (2 H, m), 1.13-1.32 (9 H, m), 1.33-1.46 (2 H, m), 1.76 (4 H, t, $J=14.3$ Hz), 1.90 (6 H, s), 2.67 (1 H, tm, $J=12.0$ Hz), 3.34 (1 H, s), 4.93 (2 H, s), 6.20 (1 H, m), 6.32 (2 H, s), 6.90 (1 H, m).

^{13}C NMR (400 MHz, $\text{DMSO-}d_6$) δ ppm 13.81, 15.70, 22.14, 26.04, 31.64, 32.36, 32.88, 36.40, 36.56, 36.78, 109.27, 114.03, 121.12 (m), 127.46 (d,

$J=11.7$ Hz), 130.19, 139.63 (dd, $J=245.4$ Hz, 15.8 Hz), 140.27, 145.1 (m), 146.13, 148.65 (dd, $J=243.6$ Hz, 10.3 Hz).

^{19}F NMR (400 MHz, DMSO- d_6) δ ppm -160.90 (1 F, d, $J=21$ Hz), -143.67 (1 F, d, $J=21$ Hz).

Step 3: 2,3-difluoro-1-(4-iodo-2,6-dimethyl-phenoxy)-4-(4-pentylcyclohexyl)benzene



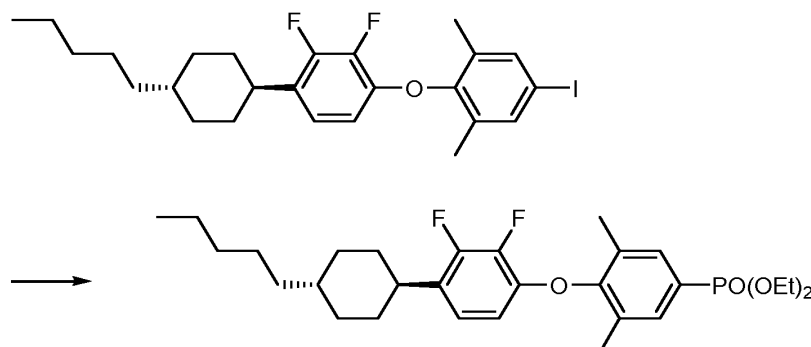
To a solution of 4-[2,3-difluoro-4-(4-pentylcyclohexyl)phenoxy]-3,5-dimethylaniline (29.8 g, 74.22 mmol) in dichloromethane (218 mL) a solution of sodium nitrite (25.6 g, 371.1 mmol) in water (218 mL) is added followed by addition of diiodomethane (39.76 g, 148.4 mmol). The mixture is stirred for 15 min, then acetic acid (89.1 g, 1.48 mol) is added dropwise. The mixture is stirred overnight at room temperature. The layers are separated and the aqueous extracted with dichloromethane. The organics are combined and washed with 20% sodium bisulfite and brine. The organics are dried over magnesium sulfate, and concentrated to dryness to give crude material as a red oil. The oil is purified on silica gel eluting with 2.5% dichloromethane/heptane and recrystallized from hot acetonitrile to give 2,3-difluoro-1-(4-iodo-2,6-dimethyl-phenoxy)-4-(4-pentylcyclohexyl)benzene as a white solid.

^1H NMR (400 MHz, CDCl_3 -*d*) δ ppm 0.91 (3 H, t, $J=7.0$ Hz), 1.04-1.12 (2 H, m), 1.18-1.47 (11 H, m), 1.87 (4 H, br. d, $J=10.8$ Hz), 2.12 (6 H, s), 2.77 (1 H, tm, $J=12.2$ Hz), 6.14 (1 H, m), 6.72 (1 H, m), 7.46 (2 H, m).

^{13}C NMR (400 MHz, CDCl_3 -*d*) δ ppm 14.11, 15.77, 22.69, 26.60, 32.17, 32.89, 33.37, 36.98, 37.20, 37.27, 89.70, 108.98 (d, $J=3.7$ Hz), 120.55 (m), 129.24 (d, $J=12.5$ Hz), 133.81, 137.84, 140.64 (dd, $J=248.0$ Hz, 16.2 Hz), 144.13 (dd, $J=8.1$ Hz, 2.9 Hz), 149.54 (dd, $J=246.5$ Hz, 10.3 Hz), 150.79.

^{19}F NMR (400 MHz, CDCl_3 -*d*) δ ppm -159.79 (1 F, d, $J=20.5$ Hz), -142.22 (1 F, d, $J=20.5$ Hz).

Step 4: 1-(4-diethoxyphosphoryl-2,6-dimethyl-phenoxy)-2,3-difluoro-4-(4-pentylcyclohexyl)benzene



To 2,3-difluoro-1-(4-iodo-2,6-dimethyl-phenoxy)-4-(4-pentylcyclohexyl)benzene (28.5 g, 55.62 mmol) in dioxane (285 mL) triethyl phosphite (23.1 g, 139.05 mmol) is added under nitrogen. $\text{Pd}(\text{OAc})_2$ (1.56 g, 6.95 mmol) is added and the reaction is heated to reflux for 75 min. The reaction is cooled to 30°C , heptane (400 mL) and water (400 mL) are added, the layers separated and the aqueous is extracted with ethyl acetate (400 mL). The organics are combined, washed with brine, dried over magnesium sulfate, filtered then concentrated to dryness. The crude material is purified on silica eluting with 10% ethyl acetate/dichloromethane to give 1-(4-diethoxyphosphoryl-2,6-dimethyl-phenoxy)-2,3-difluoro-4-(4-pentylcyclohexyl)benzene as an off-white solid.

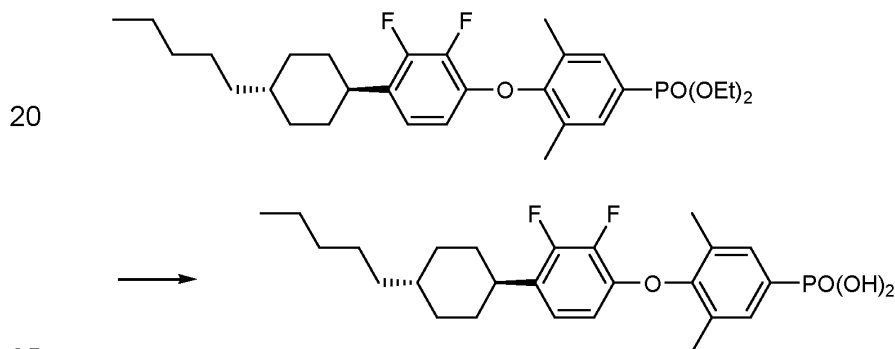
^1H NMR (400 MHz, CDCl_3 -*d*) δ ppm 0.89 (3 H, t, $J=7.0$ Hz), 1.02-1.10 (2 H, m), 1.15-1.45 (18 H, m), 1.84 (4 H, d, $J=11.0$ Hz), 2.18 (6 H, s), 2.75 (1 H, m), 4.06-4.23 (4 H, m), 6.09 (1 H, m), 6.71 (1 H, m), 7.56 (2 H, d, $J=13.3$ Hz).

5 ^{13}C NMR (400 MHz, CDCl_3 -*d*) δ ppm 13.97, 16.03, 16.25 (d, $J=6.6$ Hz), 22.58, 26.49, 32.06, 32.79, 32.26, 36.88, 37.09, 37.16, 62.07 (d, $J=5.9$ Hz), 109.08 (d, $J=2.9$ Hz), 120.51 (t, $J=5.1$ Hz), 125.15 (d, $J=189.3$ Hz), 129.36 (d, $J=11.7$ Hz), 131.82 (d, $J=16.1$ Hz), 132.64 (d, $J=10.3$ Hz), 140.58 (dd, $J=248.3$ Hz, 15.8 Hz), 143.82 (dd, $J=8.4$ Hz, 2.6 Hz), 149.47 (dd, $J=246.2$ Hz, 9.9 Hz), 154.16 (d, $J=3.7$ Hz).

10 ^{19}F NMR (400 MHz, CDCl_3 -*d*) δ ppm -159.6 (1 F, d, $J=19$ Hz), -142.1 (1 F, d, $J=19$ Hz).

^{31}P NMR (400 MHz, CDCl_3 -*d*) δ ppm 18.80.

15 Step 5: [4-[2,3-difluoro-4-(4-pentylcyclohexyl)phenoxy]-3,5-dimethyl-phenyl]phosphonic acid



To 1-(4-diethoxyphosphoryl-2,6-dimethyl-phenoxy)-2,3-difluoro-4-(4-pentylcyclohexyl)benzene (22.35 g, 42.77 mmol) in dichloromethane (325mL) trimethylsilyl bromide (65.82 g, 427.7 mmol) is added dropwise.

30 The solution is stirred overnight at room temperature. Methanol (225 mL) is added over 15 min and the solution stirred for 30 min before concentrating to dryness. The resulting solid is dissolved in tetrahydrofuran (325 mL) and

filtered through a 0.7 μ glass fibre filter. Heptane (225 mL) is added and the THF is removed slowly until solid started to precipitate out, at which point, the evaporation is stopped and the mixture allowed to cool to room temperature with stirring overnight. The resultant solid is filtered off, washed with heptane and recrystallized from ethyl acetate to give [4-[2,3-difluoro-4-(4-pentylcyclohexyl)phenoxy]-3,5-dimethyl-phenyl]phosphonic acid as a white solid.

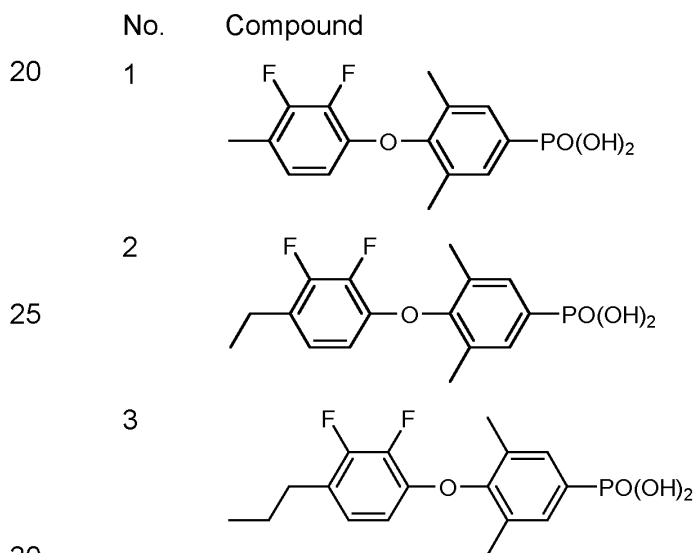
^1H NMR (400 MHz, THF-*d*) δ ppm 0.90 (3 H, t, $J=7.0$ Hz), 1.03-1.14 (2 H, m), 1.21-1.35 (9 H, m), 1.42-1.52 (2 H, m), 1.85 (4 H, t, $J=13.0$ Hz), 2.14 (6 H, s), 2.77 (1 H, tm, $J=12.1$ Hz), 6.20 (1 H, m), 6.80 (1 H, m), 7.59 (2 H, d, $J=13.4$ Hz).

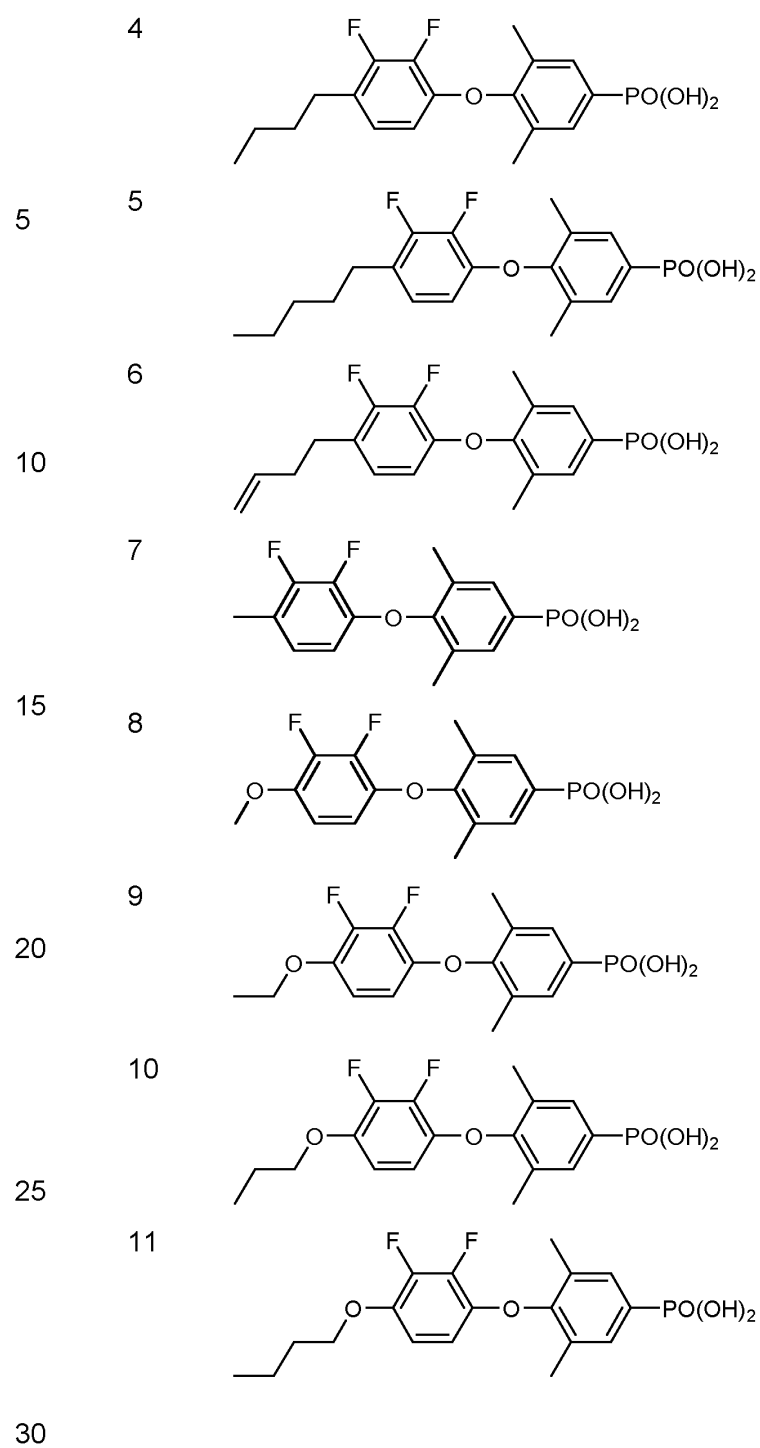
^{19}F NMR (400 MHz, THF-*d*) δ ppm -162.86 (1 F, d, $J=20.4$ Hz), -145.71 (1 F, d, $J=20.4$ Hz).

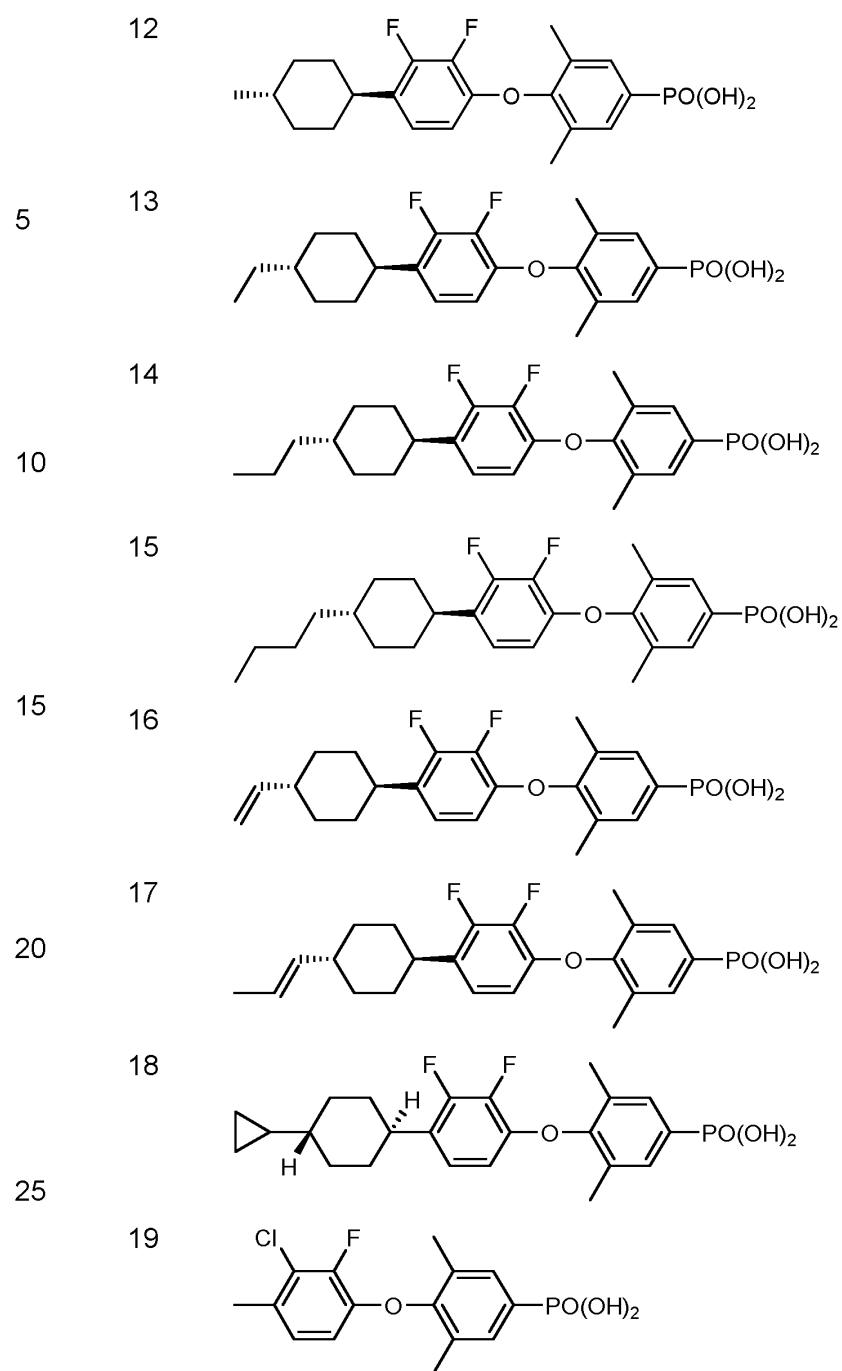
^{31}P NMR (400 MHz, THF-*d*) δ ppm 15.91.

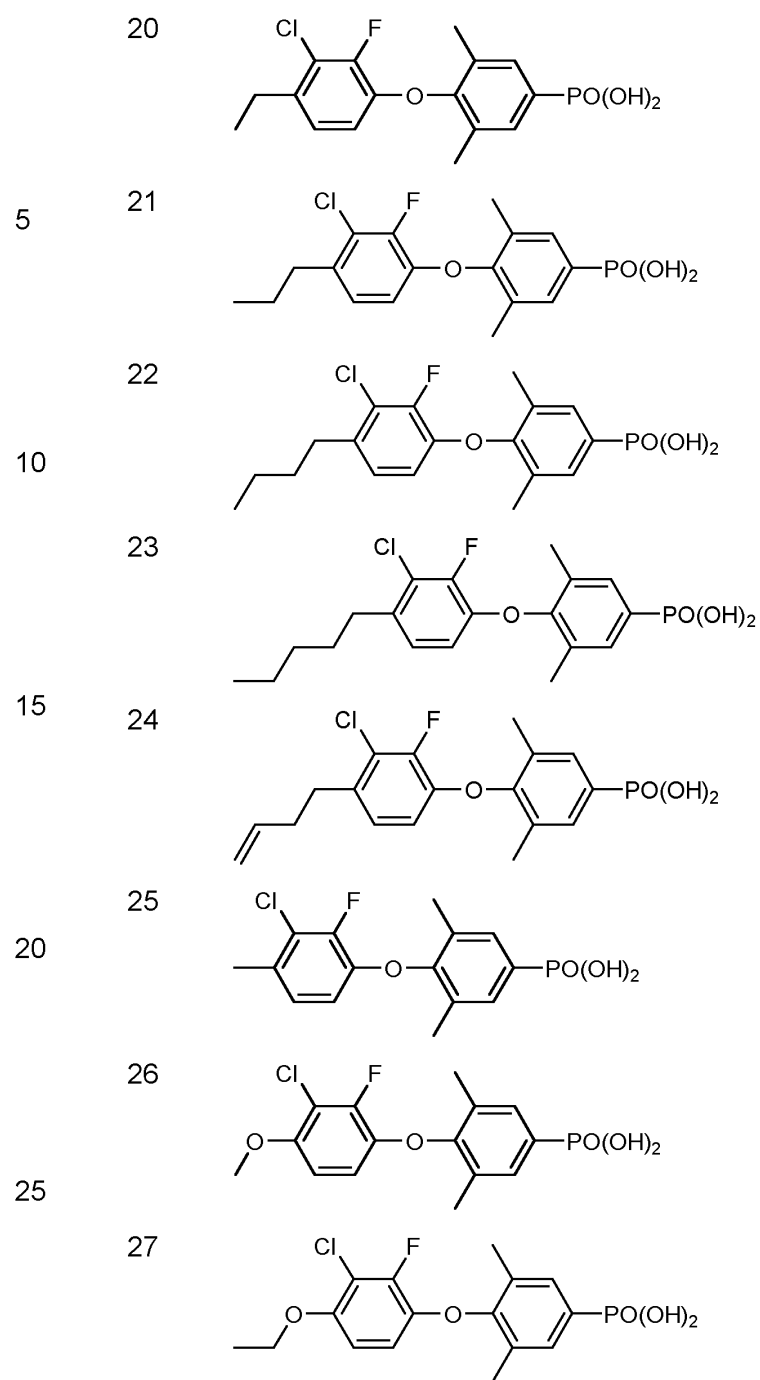
ES (-ve) MS: $m/z = 465.1998$, 100% $[\text{M}-\text{H}]^-$, $\text{C}_{25}\text{H}_{32}\text{F}_2\text{O}_4\text{P}^-$ requires 465.2006.

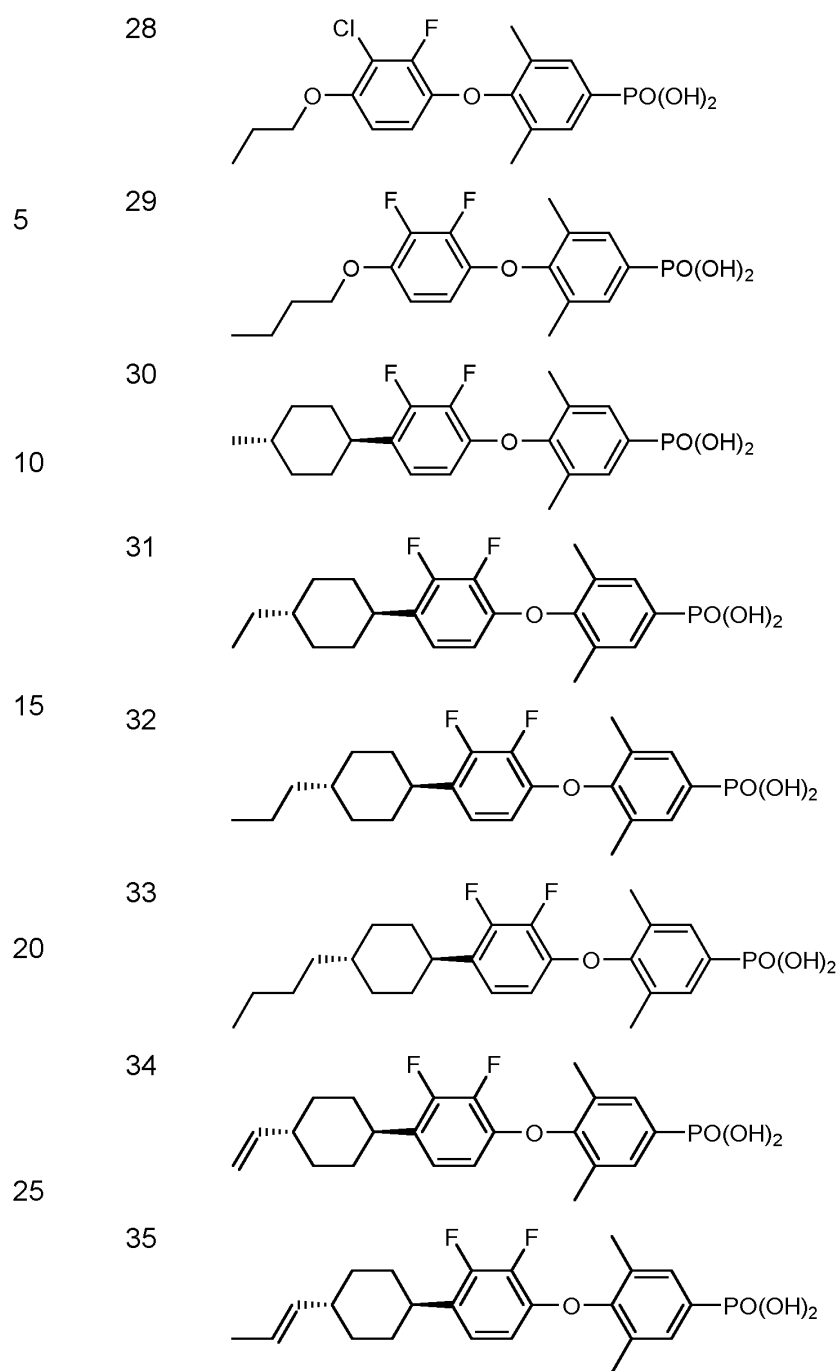
In analogy to Example 1 the following compounds are obtained:

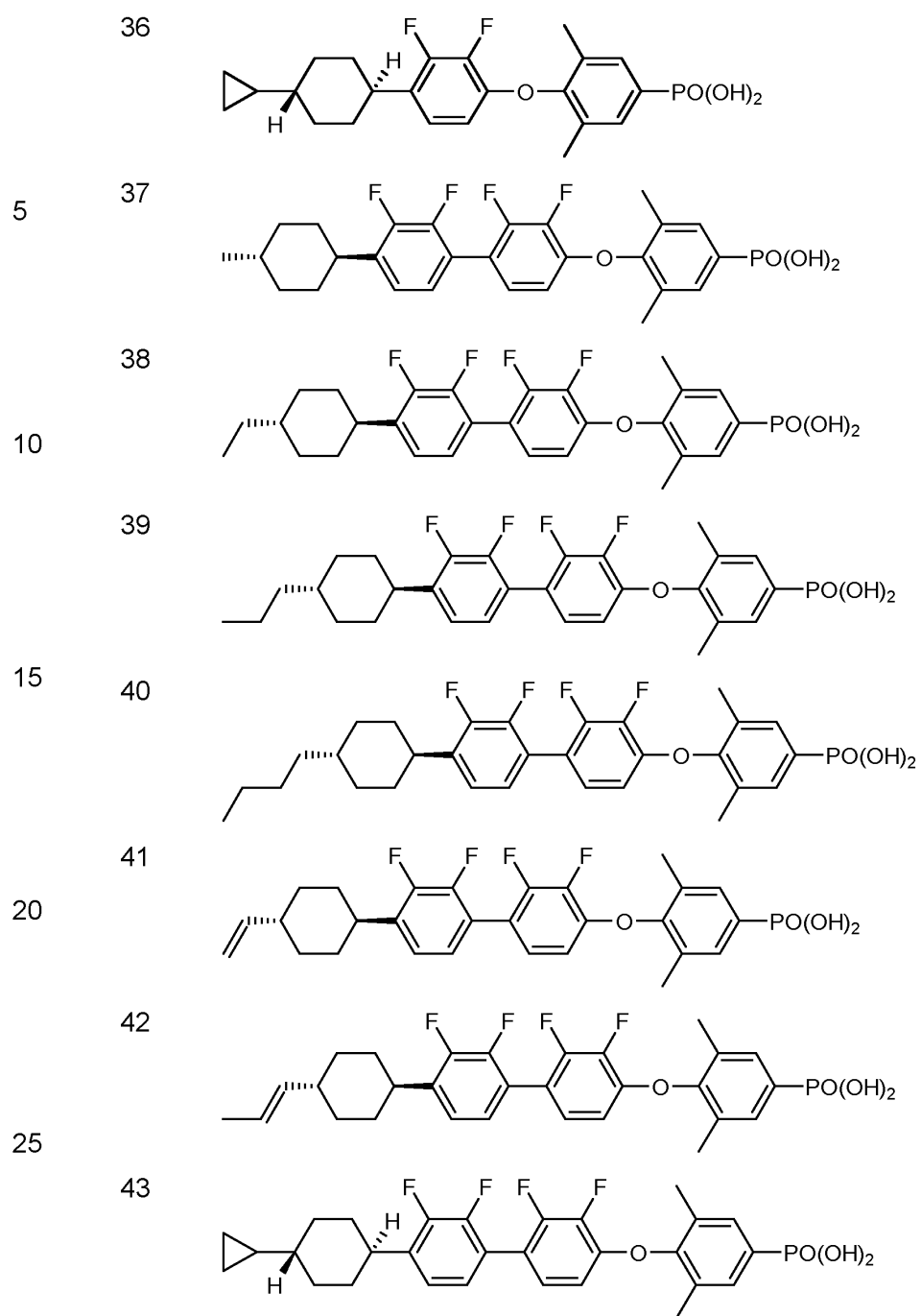


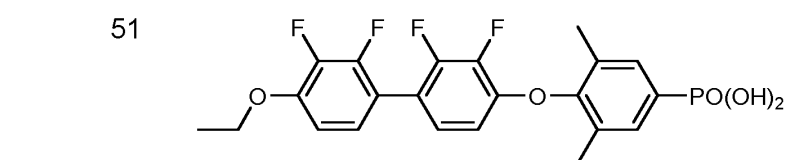
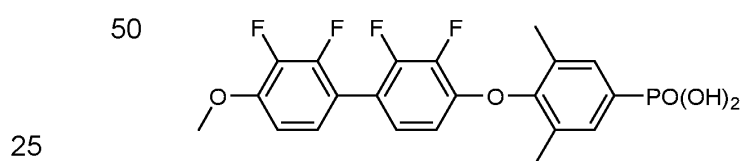
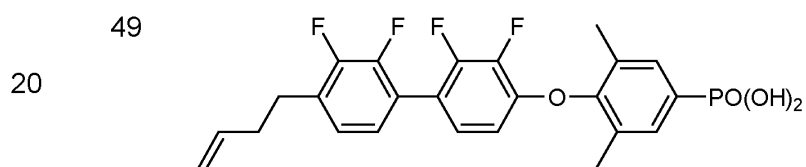
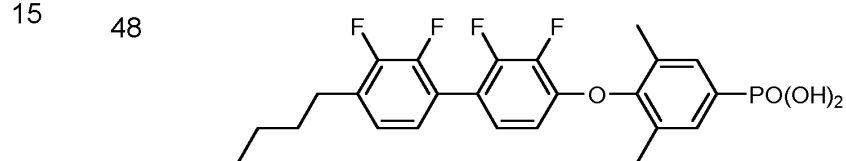
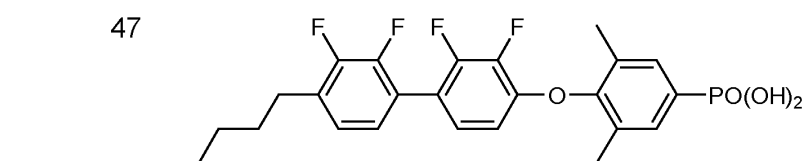
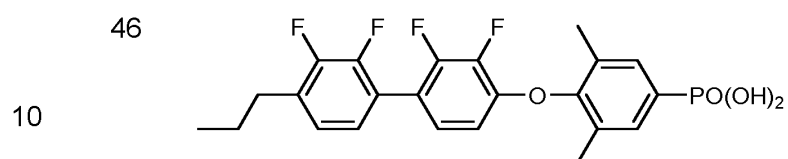
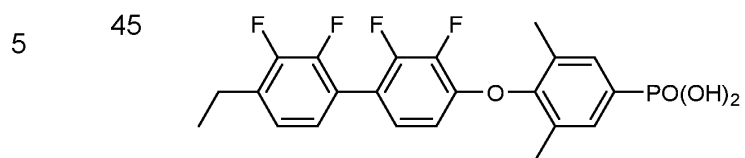
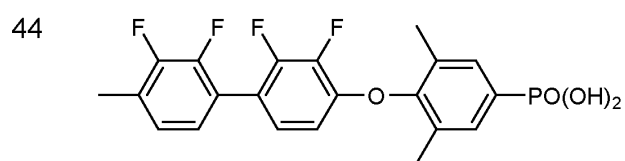


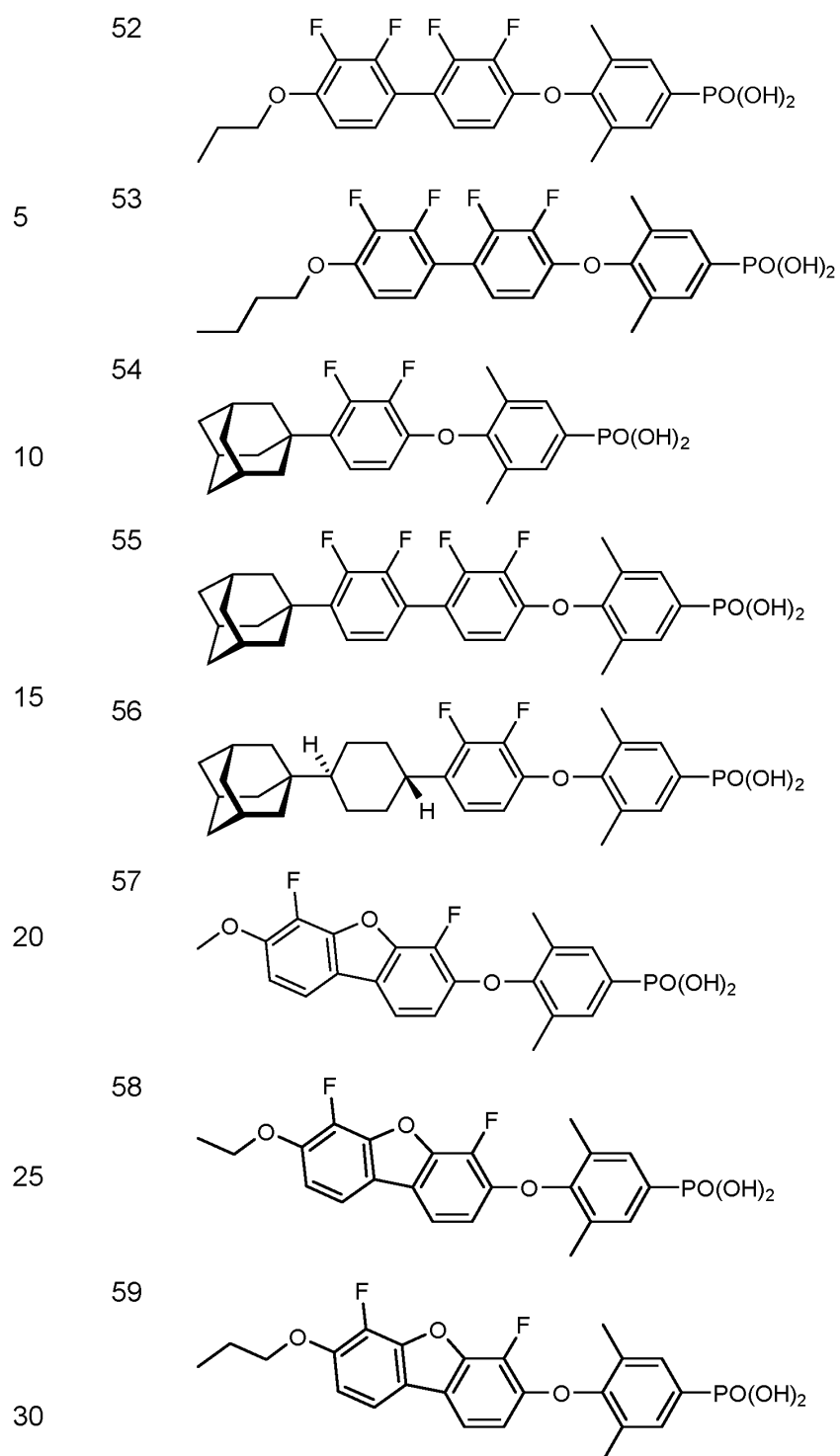


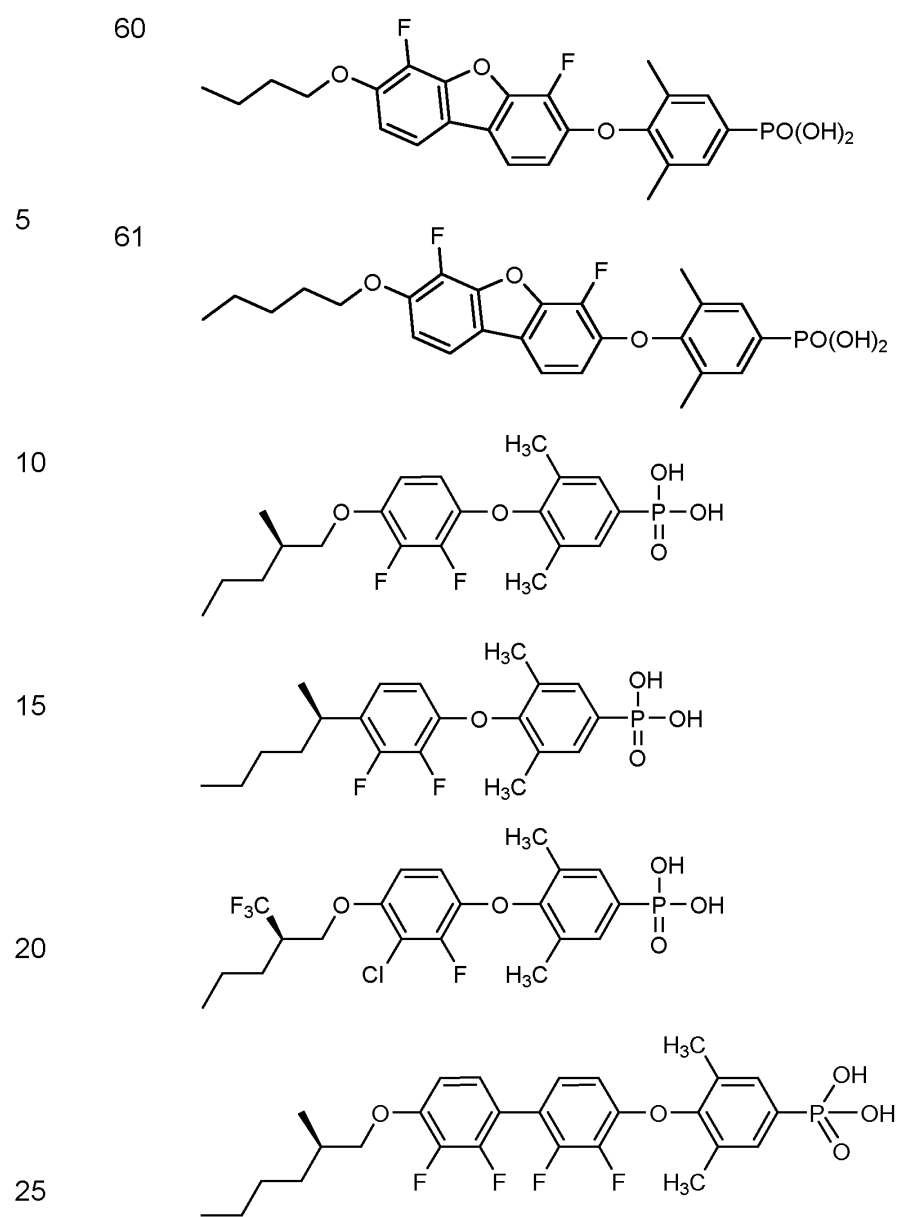




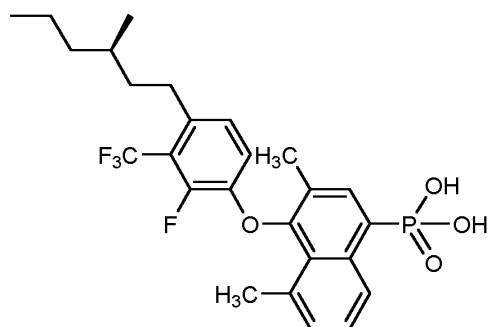








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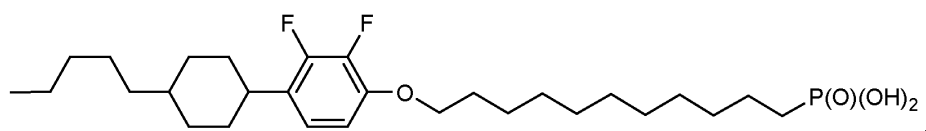


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Comparative Solubility Test

The comparative solubilities of the following Reference Compound **1** (reference from DE102017005884):

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and of Synthesis Example 1 in various solvents at 1 mM concentration at 23°C are experimentally determined. The sample is stirred for 18h at 23°C and then visually inspected. In the table below the expression “soluble” means that after 18h a clear solution is obtained. “Not soluble” means that remaining solid is observed.

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Solvent	Reference 1	Synthesis Example 1
Ethyl acetate	Not soluble	Soluble
THF	Soluble	Soluble
Toluene	Soluble	Not soluble
Chloroform	Soluble	Soluble
1-Methoxy-2-propanol acetate	Not soluble	Soluble
Cyclohexanone	Not soluble	Soluble

In contrast to Reference 1, Synthesis Example 1 is soluble in a 1 mM concentration in the industry-typical, environmentally acceptable CMOS process solvents 1-methoxy-2-propanol acetate and cyclohexanone.

5

Electrical Characterisation

The electrical characterization of a switching device 100 (Figure 1) comprising a molecular layer 140 obtained from the compound [4-[2,3-difluoro-4-(4-pentylcyclohexyl)phenoxy]-3,5-dimethyl-phenyl]phosphonic acid (Synthesis Example 1) sandwiched between a TiN first electrode 130 (thickness 50 nm) on a silicon substrate 110 with a silicon oxide layer 120, and a Ti second electrode 150 (10 nm) with gold contact 160 (80 nm) is done with a nanoprobe (Hitachi High Technologies Nano-Probe N-6000SS, probe size ca. 1 μ m) and an Agilent B1500 device analyzer under SEM control.

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For comparison, a switching device comprising a molecular layer prepared from 11-[2,3-difluoro-4-(4-pentylcyclohexyl)phenoxy]undecylphosphonic acid (PA-11O-YC-5, Reference Compound 1) is fabricated and characterized accordingly.

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The starting material is a silicon-on-insulator wafer ("SOI wafer") with a diameter of 6 inches, having a silicon layer with a thickness of 110 nm with [100] orientation on a silicon oxide layer with a thickness of 200 nm on a slightly boron-doped silicon wafer with a thickness of 525 μ m with [100] orientation and a resistivity of about 20 Ω cm.

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The upper silicon layer is highly boron-doped by ion implantation (doping concentration $c \sim 5 \times 10^{19} \text{ cm}^{-3}$, resistivity $\rho \sim 1.4 \text{ m}\Omega\text{.cm}$). After doping, the wafer is divided into square parts ("chips") measuring 8 mm $\times$ 8 mm. The chips are cleaned firstly in acetone and subsequently in isopropanol in an

30

ultrasound bath for 10 min in each case. The silicon dioxide interlayer 120 is fabricated by treatment of the wafer with oxygen plasma (200 W, 7 min).

5 The substrate is then coated with a 50 nm thick layer of TiN deposited by reactive sputtering, activated by ozone/UV treatment (110 W/300 s) and subsequently immersed into a 1 mM solution of the phosphonic acid [4-[2,3-difluoro-4-(4-pentylcyclohexyl)phenoxy]-3,5-dimethyl-phenyl]phosphonic acid (Synthesis Example 1) in tetrahydrofuran (THF) for 24 h. The chip is removed from the immersion bath, blown dry with nitrogen and annealed under
10 nitrogen at 120°C for 60 min. Then, the chip is rinsed with THF on a spin-coater and subsequently annealed again under nitrogen at 120°C for 5 min. The titanium top electrode 150 and the gold contact 160 are applied by sputtering using standard processes.

15 The result of the electrical characterisation of device 100 is shown in Fig. 2. A forward scan 210 starts at 0V and the voltage is increased to +3.5 V; a backward scan 220 then goes back to 0V, further up to -3.5 V and back to 0V. The scan speed is 300 mV/s. The resulting current is measured and the result is shown in FIG. 2. The device has an advantageously large memory
20 window.

Fig. 3 shows the current density of a device fabricated with the comparative compound Reference Compound 1. The comparison shows that the device fabricated with the compound according to the invention shows an advantageously high current density, higher by a factor of approx. 1000.

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Patent Claims

1. A compound of formula I

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$$R^1-(A^1-Z^1)_r-B^1-Z^L-A^2-(Z^3-A^3)_s-G \quad (I)$$

in which

10 R^1 denotes straight chain or branched alkyl or alkoxy radical having 1 to 20 C atoms, where one or more CH_2 groups in these radicals may each be replaced, independently of one another,

by $-C\equiv C-$, $-CH=CH-$, , , , ,

, $-O-$, $-S-$, $-CF_2O-$, $-OCF_2-$, $-CO-O-$, $-O-CO-$,

15 $-SiR^0R^{00}-$, $-NH-$, $-NR^0-$ or $-SO_2-$ in such a way that O atoms are not linked directly to one another, and in which, in addition, one or more H atoms may be replaced by halogen, CN, SCN or SF_5 , or alternatively, R^1 denotes a group $Dia-Z^D$,

20 Dia denotes a diamondoid radical,

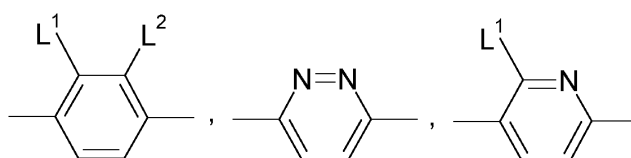
Z^D has one of the meanings of Z^1 and Z^3 or denotes a straight chain or branched spacer group,

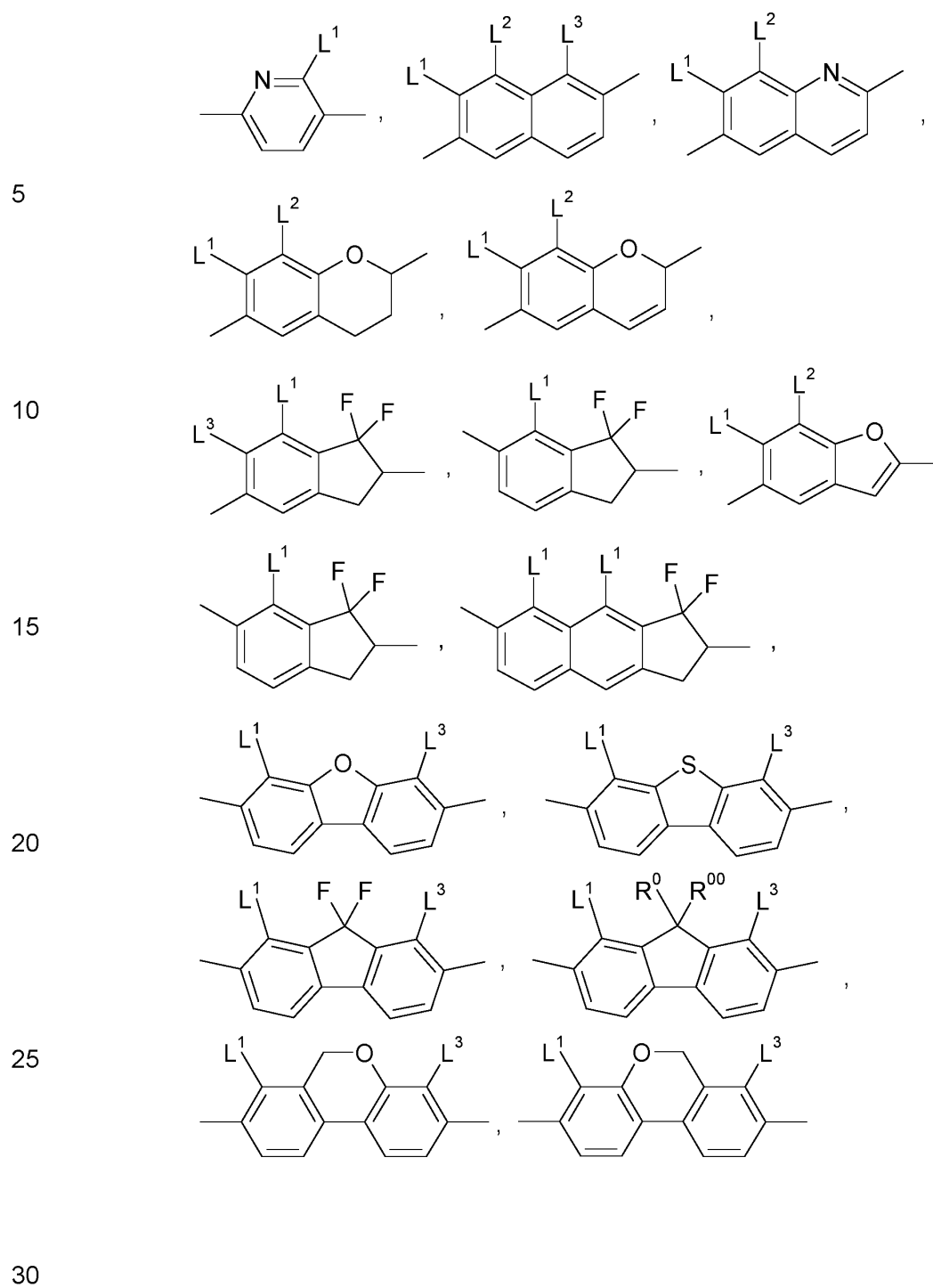
25 Z^1, Z^3 on each occurrence, identically or differently, denote a single bond, $-CF_2O-$, $-OCF_2-$, $-CF_2S-$, $-SCF_2-$, $-CH_2O-$, $-OCH_2-$, $-C(O)O-$, $-OC(O)-$, $-C(O)S-$, $-SC(O)-$, $-(CH_2)_{n1}-$, $-(CF_2)_{n2}-$, $-CF_2-CH_2-$, $-CH_2-CF_2-$, $-CH=CH-$, $-CF=CF-$, $-CF=CH-$, $-CH=CF-$, $-(CH_2)_{n3}O-$, $-O(CH_2)_{n4}-$, $-C\equiv C-$, $-O-$, $-S-$, $-CH=N-$,
30 $-N=CH-$, $-N=N-$, $-N=N(O)-$, $-N(O)=N-$ or $-N=C-C=N-$,

$n1, n2, n3, n4$ identically or differently, are 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

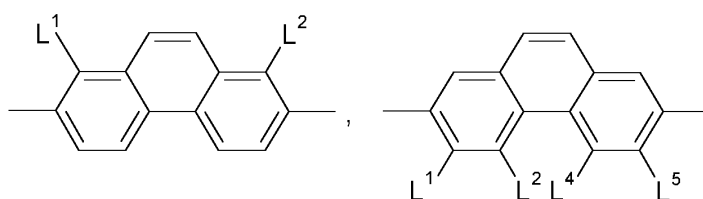
- Z^L denotes -O-, -S-, -CH₂-, -C(O)-, -CF₂-, -CHF-, -C(R^x)₂-, -S(O)- or -SO₂-,
- 5 R^0, R^{00} , identically or differently, denote an alkyl or alkoxy radical having 1 to 15 C atoms, in which one or more H atoms may be replaced by halogen,
- 10 A^1, A^3 on each occurrence, identically or differently, denote an aromatic, heteroaromatic, alicyclic or heteroaliphatic ring having 4 to 25 ring atoms, which may also contain condensed rings and which may be mono- or polysubstituted by Y,
- 15 A^2 denotes an aromatic or heteroaromatic ring having 5 to 25 ring atoms, which may also contain condensed rings and which may be mono- or polysubstituted by Y,
- 20 Y on each occurrence, identically or differently, denotes F, Cl, CN, SCN, SF₅ or straight-chain or branched, in each case optionally fluorinated alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy having 1 to 12 C atoms, or cycloalkyl or alkylcycloalkyl each having 3 to 12 C atoms, preferably methyl, ethyl, isopropyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, trifluoromethyl, methoxy or
- 25 trifluoromethoxy,

30 B^1 denotes





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where the groups may be oriented in both directions,

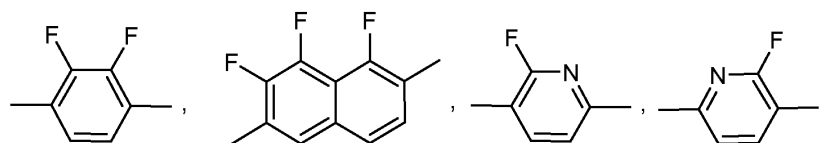
- L^1 to L^5 , independently of one another, denote F, Cl, Br, I, CN, SF_5 , CF_3 or OCF_3 , preferably Cl or F, where L^3 alternatively denotes H,
- G denotes $-CH=CH_2$, $-OH$, $-CH(CH_2OH)_2$, $-C(CH_2OH)_3$, $B(OH)_2$, $-SH$, $-SO_2OH$, $-OP(O)(OH)_2$, $-PO(OH)_2$, $-C(OH)(PO(OH)_2)_2$, $-COOH$, $-Si(OR^x)_3$ or $-SiCl_3$, $-SO_2OR^V$, $-OP(O)(OR^V)_2$, $-PO(OR^V)_2$, $-C(OH)(PO(OR^V)_2)_2$, $-COOR^V$, $-Si(OR^V)_3$,
- R^V denotes alkyl having 1 to 20 C atoms, preferably secondary or tertiary alkyl having 3 to 10 C atoms,
- R^x denotes straight-chain or branched alkyl having 1 to 6 C atoms, and
- r is 0, 1 or 2,
- s is 0, 1 or 2,

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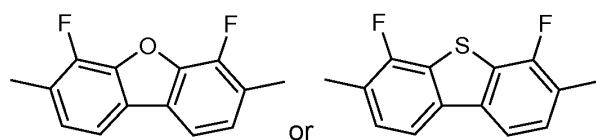
where $r + s \leq 4$.

2. The compound according to claim 1, wherein the group B^1 denotes

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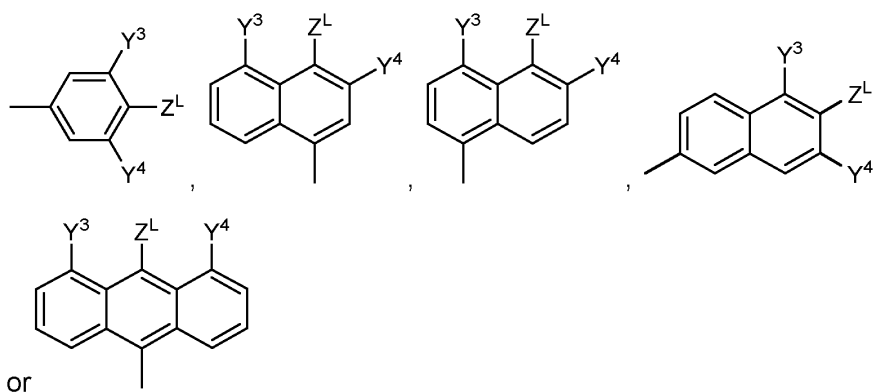


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3. The compound according to claim 1 or 2, wherein A²-Z^L denotes



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or

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in which

Y³ and Y⁴ identically or differently, have the meanings given for Y in claim 1 and

Z^L has the meanings given in claim 1.

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4. The compound according to one or more of claims 1 to 3, wherein A¹ and A³, on each occurrence, identically or differently are selected from the following groups:

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a) 1,4-phenylene, in which one or two CH groups may be replaced by N and in which, in addition, one or more H atoms may be replaced by Y,

- 5 b) the group consisting of trans-1,4-cyclohexylene and 1,4-cyclohexenylene, in which one or more non-adjacent CH₂ groups may be replaced by -O- and/or -S- and in which, in addition, one or more H atoms may be replaced by Y, and
- 10 c) the group consisting of 1,3-dioxolane-2,4-diyl, tetrahydrofuran-2,5-diyl, cyclobutane-1,3-diyl, 1,4-bicyclo[2.2.2]octanediyl, piperidine-1,5-diyl and thiophene-2,5-diyl, in which one or more H atoms may be replaced by Y,
- where Y has the meanings given in claim 1.
- 15 5. The compound according to one or more of claims 1 to 4, wherein R¹ denotes H, straight chain or branched alkyl, alkenyl, alkynyl, or alkoxy each having up to 12 C atoms, or adamantyl or adamantylmethoxy.
- 20 6. The compound according to one or more of claims 1 to 5, wherein Z¹ denotes -O-.
7. The compound according to one or more of claims 1 to 6, wherein G denotes -OP(O)(OH)₂, -PO(OH)₂, -C(OH)(PO(OH)₂)₂.
- 25 8. The compound according to one or more of claims 1 to 7, wherein s is 0.
9. The compound according to one or more of claims 1 to 8, wherein Z¹ denotes a single bond.
- 30 10. A process for the preparation of a switching element comprising at least the following steps:
 a) production of a first electrode with a surface,

- b) deposition of a molecular layer comprising one or more compounds of the formula I onto the surface of the first electrode,
- c) application of a second electrode.

- 5 11. The process according to claim 10, wherein the first electrode comprises a material selected from the element semiconductors Si, Ge, C selected from diamond, graphite, graphene, Sn having alpha modification and Se, the compound semiconductors GaAs, InAs, InP, GaSb, TaN, TiN, MoN, WN and GaN, CdSe and ZnS, the metals Au, 10 Ag, Cu, Al, W, Ta, Ti, Co, Mo, Pt, Ru and Mg and the conductive oxidic materials ITO, IGO, IGZO, AZO and FTO.
- 15 12. A switching element comprising a molecular layer sandwiched between a first electrode and a second electrode, obtainable by the process according to claim 10 or 11.
- 20 13. The switching element according to claim 12, wherein the molecular layer is a self assembled monolayer.
- 25 14. Memristive device comprising a switching element according to claim 12 or 13.
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