Electronic Switching Device

The present invention relates to an electronic switching device, in particular to tunnel junctions, comprising an organic molecular layer for use in memory, sensors, field-effect transistors or Josephson junctions. More particularly, the invention is included in the field of random access non-volatile memristive memories (RRAM). Further aspects of the invention relate to compounds for use in the molecular layer, to the use of the molecular layer and to processes for the production and operation of the electronic switching element and components based thereon.

Tunnel junctions are used for many applications in electronics industry, ranging from superconducting Josephson junctions to tunnel diodes. They require a very thin dielectric material as insulator. One of the most cost-effective ways to generate such an insulating layer with single digit nanometer thickness is by using self-assembled monolayers (SAMs).

In computer technology, storage media are required which allow rapid 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 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 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 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" 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. Crossbar arrays of memristors may be used in a variety of applications, including non-volatile solid state memory, programmable logic, signal processing, control systems, pattern recognition, and other applications. A memristive cross-bar array includes a number of row lines, a number of column lines intersecting the row lines to form a number of junctions, and a number of resistive memory devices coupled between the row lines and the column lines at the junctions.

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 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 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 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.

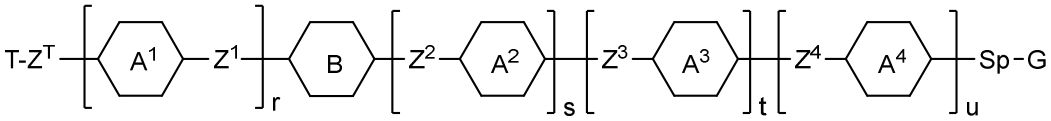
In order to obtain electrically switchable tunnel junctions from organic compounds with a conformationally flexible dipole, a molecular layer enclosed as a sandwich between two conductive electrodes is required. The deposition of this molecular layer onto electrodes is achieved either by spin-coating 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.

Information storage devices based on electrically switchable tunnel barriers made from self-assembled, dipolar monolayers are required to have long retention times of the selected states, even at elevated temperatures of for example up to 85°C. A long retention time enables a memory device that requires less refresh cycles. There is still a need in the art for devices with long retention times.

Furthermore, said information storage devices are required to have an endurance of more than 10^{15} read-write cycles. In order to achieve this extreme reliability, it is necessary to reduce the number and the mobility of ionic impurities within the molecular layer. In particular, ion migration can cause reliability problems such as reduced endurance, high cycle-to-cycle variability of electrical characteristics and low device-to-device reproducibility of electrical performance.

It is an object of the present invention to provide new compounds for the fabrication of improved electronic components comprising a molecular layer bonded to a first electrode, suitable for use in for example memristive devices, which do not have the above-mentioned disadvantages, and which bring improvements, in particular, with respect to improved endurance.

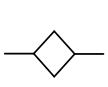
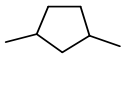
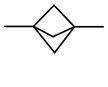
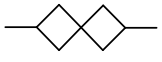
To solve the problem there is provided a compound of formula I



(I)

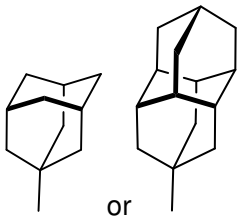
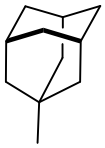
in which

T is selected from the group of radicals consisting of the following groups:

a) 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, by -C≡C- , -CH=CH-,  ,  ,  ,  ,  , -O-, -S-, -CF_2O-, -OCF_2-, -CO-O-, -O-CO- ,-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 one or more H atoms may be replaced by halogen, CN, SCN or SF_5,

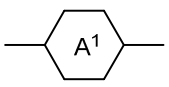
b) a three- to ten-membered saturated or partially unsaturated aliphatic ring, in which at least one $-CH_2-$ group is replaced with -O-, -S-, -S(O)-, $-SO_2-$, $-NR^x-$ or $-N(O)R^x-$, or in which at least one -CH= group is replaced with -N=,

c) a diamondoid radical, preferably derived from a lower diamondoid, very preferably selected from the group consisting of adamantyl, diamantyl, and triamantyl, in which one or more H atoms can be replaced by F, in each case optionally fluorinated alkyl, alkenyl or alkoxy having up to 12 C atoms, in particular

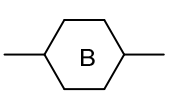
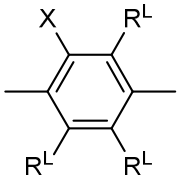
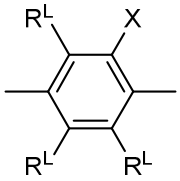
 or , very particularly ;

Z^T, Z^1, Z^2, and Z^4, 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)-, $-(CH_2)_{n1}-$, $-(CF_2)_{n2}-$, $-CF_2\ CH_2-$, $-CH_2CF_2-$, -CH=CH-,-CF=CF-, -CF=CH-, -CH=CF-, $-(CH_2)_{n3}O-$, $-O(CH_2)_{n4}-$, -C≡C-, -O-, -S-, -CH=N-, -N=CH-, -N=N-, -N=N(O)-, -N(O)=N- or -N=C-C=N-, wherein n1, n2, n3, n4, identically or differently, are 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

Z^3 denotes -O-, -S-, $-CH_2-$, -C(O)-, $-CF_2-$, -CHF-, $-C(R^x)_2-$, -S(O)- or $-SO_2-$,

,  and , 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 monosubstituted by X or which may be mono- or polysubstituted by R^L,

 denotes an aromatic or heteroaromatic ring having 5 to 25 ring atoms, which may also contain condensed rings, and which may be which may be monosubstituted by X or which may be mono- or polysubstituted by R^C,

 denotes  or ,

X denotes F, Cl, Br, I, CN, SF_5, CF_3, OCF_3, or $OCHF_2$, preferably Cl or F, very preferably F,

R^L on each occurrence, identically or differently denotes H, alkyl having 1 to 6 C atoms, alkenyl having 2 to 6 C atoms or alkoxy having 1 to 5 C atoms, preferably H or alkyl having 1 to 4 C atoms, very preferably H, methyl or ethyl,

R^C on each occurrence, identically or differently, denotes straight-chain or branched, in each case optionally fluorinated alkyl, alkoxy, alkylthio, 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, trifluoromethoxy or trifluoromethylthio,

Sp denotes a spacer group or a single bond,

R^0, R^{00}, R^x denotes straight-chain or branched alkyl having 1 to 6 C atoms,

G denotes -OH, -SH, $-SO_2OH$, $-OP(O)(OH)_2$, $-PO(OH)_2$, $-C(OH)(PO(OH)_2)_2$, -COOH, $-Si(OR^x)_3$, $-SiCl_3$, $-CH=CH_2$, $-POCl_2$, $-COH(PO(OH)_2)_2$, -CO(NHOH), $-CO(NR^0OH)$, $-Si(NMe_2)_3$; or straight chain or branched alkyl having 1 to 12 C atoms in which one, two or three not geminal H atoms are substituted by OH; or a group selected from $-O-C(O)-OR^V$, $-O-C(O)-Si(OR^x)_3$, $PO(OR^V)_2$, SO_2OR^V,

R^V denotes straight chain or branched alkyl having 1 to 12 C atoms,

r, s, t and u, identically or differently, are 0, 1 or 2, where r+s+t+u = 0, 1, 2, 3 or 4.

According to another aspect of the present invention there is provided a switching device comprising, in this sequence,

a first electrode,

a molecular layer, and

a second electrode,

where the molecular layer is essentially formed from one or more, preferably one, compounds of the formula I defined above and below.

In an embodiment, the molecular layer is bonded to the first electrode. In a preferred embodiment, an interlayer is provided between the first electrode and the molecular layer. In this case the molecular layer is bonded to the interlayer, i.e. the first electrode and the interlayer are operable as a first electrode.

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

i. production of a first electrode having a surface;

ii. deposition of a molecular layer comprising one or more compounds selected from the group of compounds of the formula I defined above onto the surface of the first electrode;
iii. application of a second electrode.

The invention furthermore relates to a method for operating the electronic component according to the invention, characterised in that a switching device of the electronic component is switched into a state of high electrical resistance by setting a corresponding first electrode to a first electrical potential and setting a corresponding second electrode to a second electrical potential, where the value of the voltage between the two electrodes is greater than a first switching voltage and the first potential is greater than the second potential, a switching device of the electronic component is switched into a state of low electrical resistance by setting a corresponding first electrode to a third electrical potential and setting a corresponding second electrode to a fourth electrical potential, where the value of the voltage between the two electrodes is greater than a second switching voltage and the fourth potential is greater than the third potential, and the state of a switching device is determined by applying a reading voltage whose value is smaller than the first and second switching voltages between corresponding electrodes and measuring the current flowing.

According to another aspect of the present invention there is provided an electronic component where the component is a memristive crossbar array comprising a multitude of switching devices according to the present invention. Said crossbar array can be integrated into a three dimensional array of cells comprising a stack of two or more crossbar arrays. Such configurations are known as 3D cross-point or 3D X-point memory devices.

The invention further relates to the use of a molecular layer obtained from one or more compounds as indicated in claim 1 in a memristive electronic component.

The resulting devices can be used in memory, sensors, field-effect transistors or Josephson junctions, preferably in resistive memory devices.

The present invention further relates to the use of the switching devices in memory, sensors, field-effect transistors or Josephson junctions.

The switching devices according to the invention are suitable for use in electronic components, in particular in memory, sensors, field-effect transistors or Josephson junctions, very particularly in memristive components such as memristive crossbar-arrays, which exhibit the advantageous properties indicated above.

The compound of formula I according to the invention enables a switching device that is distinguished by retention improved by several orders of magnitude compared to the state of the art. Tunnel junctions based on the SAM precursors of formula I above show a significantly higher current density in their current-voltage characteristics, allowing for a faster read operation and higher integration density.

The switching voltage of the switching device according to the invention is advantageously low. The switching device exhibits high reliability and endurance. Furthermore, the memory window is advantageously large and improved over the devices known from prior art.

Memory devices based on the compounds according to the invention show less noisy current-voltage (I-V) characteristics, allowing for a higher read or write speed. The reduced polarity of the compounds according to the invention compared to highly fluorinated compounds of prior art reduces intermolecular electrostatic interactions and thus increases in particular write speed. Also, the endurance is significantly improved.

The electrode materials that can be used in the device according to the invention are highly compatible with devices and fabrication processes of the semiconductor industry and are surprisingly well suitable for the formation of a stable and homogeneous molecular monolayer.

Brief description of the drawings.

Fig. 1A shows a schematic illustration of the layer structure of a first embodiment of the electronic switching device.

Fig. 1B shows a schematic illustration of the layer structure of a second embodiment of the electronic switching device according to the invention.

Fig. 2 shows a current-voltage curve of an electronic switching device according to the invention.

Fig. 3 shows a current-voltage curve of an electronic reference device without a molecular monolayer.

In claim 7, the expression “essentially formed from” is taken to mean that specific further compounds can be present in the compounds that are used for the formation of the molecular layer, namely those not materially affecting the essential characteristics of the molecular layer.

As used herein, the term “RRAM” or “resistive memory device” is taken to mean a memory device that uses a molecular switching layer whose resistance can be can be controlled by applying a voltage.

Low resistance state (LRS) or ON state of the resistive memory device is taken to mean a state in which the resistive memory device has a low electrical resistance. High resistance state (HRS) or OFF state of the resistive memory device is taken to mean a state in which the resistive memory device has a high resistance.

Memory window is taken to mean an interval of resistance values having a lower bound and an upper bound.

States having a resistance lower than the lower bound of this interval are considered as ON states.

States having a resistance higher than the upper bound of this interval are considered as OFF states.

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 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 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 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 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 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 or arranging the four adamantane subunits. The number of possible isomers increases non-linearly with each higher member of the diamondoid series, pentamantane, hexamantane, heptamantane, octamantane, etc. Adamantane, which is commercially available, has been studied extensively. The studies have been directed toward a number of areas, such as thermodynamic stability, functionalization, and the properties of adamantane-containing materials. For instance, Schreiber et al., New J. Chem., 2014, 38, 28-41 describes the synthesis and application of functionalized diamondoids to form large area SAMs on silver and gold surfaces. In K. T. Narasimha et al., Nature Nanotechnology 11, March 2016 page 267-273, monolayers of diamondoids are described to effectively confer enhanced field emission properties to metal surfaces due to a significant reduction of the work function of the metal.

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 the substrate or electrode by physisorption, chemisorption or by chemical reaction. This chemical reaction includes the transformation of a precursor of an anchor group *in situ*, for example on the surface of a substrate or electrode.

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

The spacer group can be branched or straight chain. Chiral spacers are branched and optically active and non-racemic.

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.

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.

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.

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.

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), and under reaction conditions which are known and are suitable for said reactions.

Preferred synthetic pathways are analogous to the syntheses of similar compounds described in WO 2018/007337 A2, WO 2019/238649 A2, WO 2020/225270 A2, WO 2020/225398 A2, WO 2021/078699 A2, WO 2021/078714 A2 and WO 2021/083934 A2.Use can be made here of variants which are known and described in the literature and exemplified below by the working examples.

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

In the 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-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-benzopyran) and coumarin (2H-chromen-2-one), or combinations of these groups.

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

Preferred spacer groups Sp are selected from the formula Sp'-X', so that the radical G-Sp- of formula I corresponds to the formula G-Sp'-X'-,

where

Sp' denotes straight-chain or branched alkylene having 1 to 20, preferably 1 to 12 C atoms, which is optionally mono- or polysubstituted 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,

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,

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.

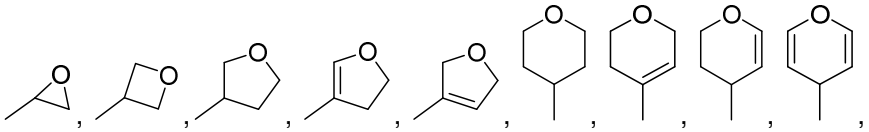
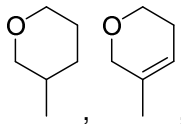
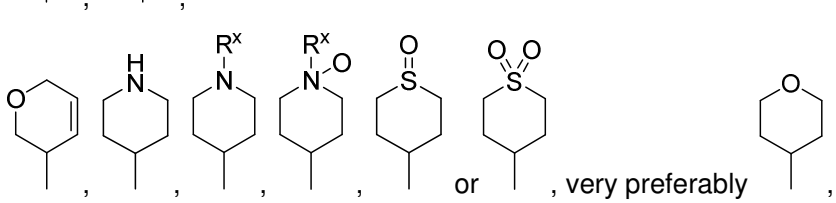
X' is preferably $-O-$, $-S-$, $-CO-$, $-COO-$, $-OCO-$, $-O-COO-$, $-CO-NR^0-$, $-NR^0-CO-$, $-NR^0-CO-NR^0-$ or a single bond.

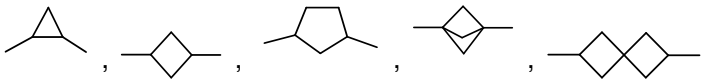
Preferred groups Sp' are $-(CH_2)_{p1}-$, $-(CF_2)_{p1}-$, $-(CH_2CH_2O)_{q1}-CH_2CH_2-$, $-(CF_2CF_2O)_{q1}-CF_2CF_2-$, $-CH_2CH_2-S-CH_2CH_2-$, $-CH_2CH_2-NH-CH_2CH_2-$ or $-(SiR^{00}R^{000}-O)_{p1}-$, in which p1 is an integer from 1 to 12, q1 is an integer from 1 to 3, and R^{00} and R^{000} have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

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.

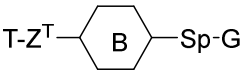
Particularly preferred groups Sp' are, for example, in each case straight-chain ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, octadecylene, perfluoroethylene, perfluoropropylene, perfluorobutylene, perfluoropentylene, perfluorohexylene,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

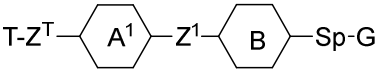
Particularly preferred groups X’ are -O- or a single bond.

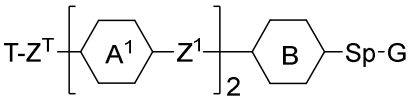
In a preferred embodiment, in formula I and its sub-formulae, the radical T preferably denotes , , , or , very preferably , in which R^x denotes alkyl having 1 to 6 C atoms, preferably methyl.

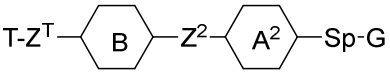
In another preferred embodiment, in formula I and its sub-formulae the radical T denotes straight chain or branched alkyl having 1 to 12 C atoms, where one or more CH_2 groups in these radicals may each be replaced, independently of one another, by -C≡C- , -CH=CH-,  or -O-, in such a way that O atoms are not linked directly to one another, and in which one or more H atoms may be replaced by halogen, preferably by F.

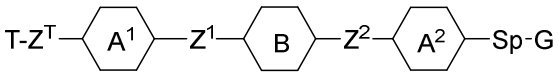
In a preferred embodiment, the compounds of the formula I are selected from the compounds of the formulae IA-1a to IA-1f

 IA-1a

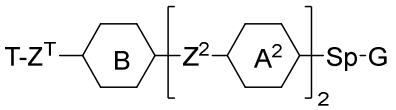
 IA-1b

 IA-1c

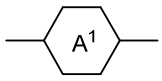
 IA-1d



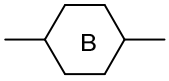
IA-1e



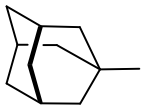
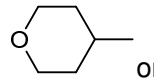
IA-1f

in which T, Z^T, 

, 

, 

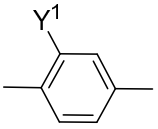
, Z^1, Z^2, Sp and G have the meanings given above for formula I, and preferably

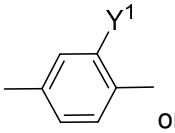
T denotes H, 
, 

or straight chain or branched alkyl or alkoxy each having 1 to 7 C atoms or straight chain or branched alkenyl having 2 to 7 C atoms, preferably straight chain alkyl or alkoxy each having 1 to 7 C atoms,

Z^T denotes CH_2O, OCH_2, CH_2CH_2, or a single bond, preferably a single bond

Z^1 and Z^2, identically or differently, denote CH_2O, OCH_2, CH_2CH_2, CF_2O, OCF_2, C(O)O, OC(O) or a single bond, preferably a single bond,

A^1 and A^2, identically or differently, denote 

, 

or 
,

Y^1 on each occurrence, identically or differently, denote H, F of Cl, preferably H or F,

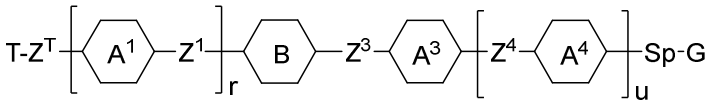
Sp denotes branched or unbranched 1,ω-alkylene having 1 to 12 C atoms, in which one or more non-adjacent CH_2-groups may be replaced by O,

G denotes $-OP(O)(OH)_2$, $-PO(OH)_2$, $-COH(PO(OH)_2)_2$ or $-PO(OR^V)_2$, preferably $-PO(OH)_2$, and

R^V denotes methyl, ethyl or secondary or tertiary alkyl having 1 to 6 C atoms.

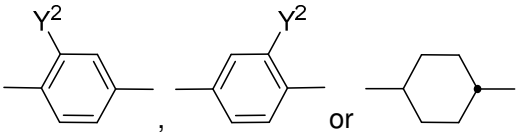
Very preferred are the compounds of the formula IA-1b and IA-1c, in particular IA-1b.

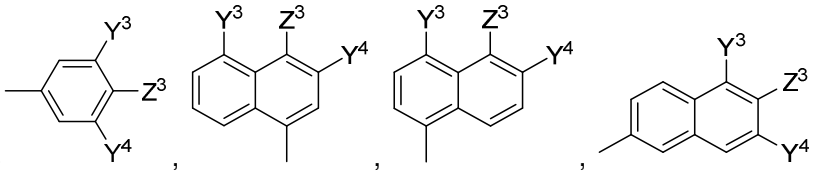
In another preferred embodiment, the compounds of the formula I are selected from the compounds of the formula IA-2



IA-2

in which the occurring groups and parameters have the meanings given above for formula I and preferably

A^1 and A^4, identically or differently, denote ;

A^3-Z^3 denotes ;

Z^T denotes a single bond, $-CH_2O-$, $-OCH_2-$ or $-CH_2CH_2-$,

L^1 and L^2 identically or differently, denote F, CF_3 or Cl,

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

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

Z^3 denotes CH_2 or O,

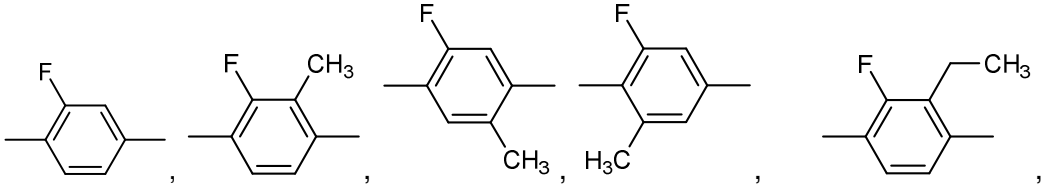
Z^1, Z^2, independently of one another, denote a single bond, $-C(O)O-$, $-OC(O)-$, $-CF_2O-$, $-OCF_2-$, $-CH_2O-$, OCH_2- or $-CH_2CH_2-$, preferably a single bond,

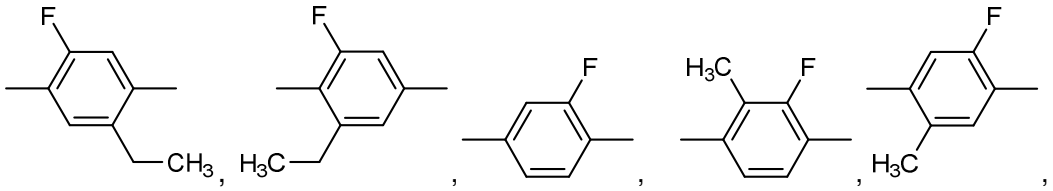
G denotes $-OP(O)(OH)_2$, $-PO(OH)_2$, $-COH(PO(OH)_2)_2$ or $-PO(OR^V)_2$,

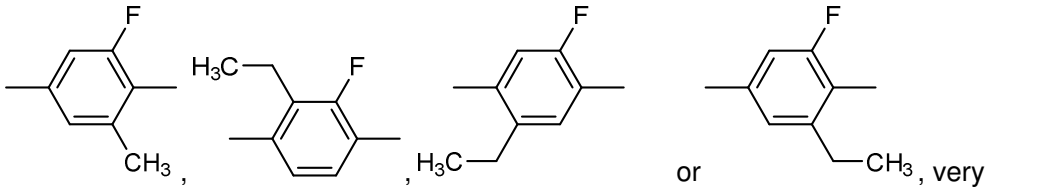
R^V denotes methyl, ethyl or secondary or tertiary alkyl having 1 to 6 C atoms and

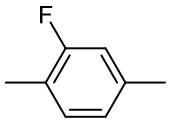
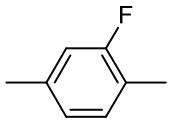
r and u independently are 0, 1 or 2, very preferably u is 0 and r is 0 or 1.

In formula I and its sub-formulae, the group  preferably denotes







preferably  or  .

According to another aspect of the invention the molecular layer comprises one or more chiral non-racemic compounds selected from the compounds of the formula I.

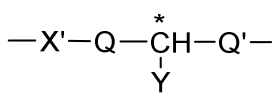
The molecular layers obtained from chiral compounds of the formula I enable memristic devices with significantly further reduced stochastic noise and faster switching, reducing the read and write error rate, which has a positive effect on energy-efficiency. In addition, increased tunnel current are observed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

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

Chirality is achieved by a branched chiral group Sp of formula I above having one or more, preferably one or two, very preferably one, asymmetrically substituted carbon atom (or: asymmetric carbon atom, C*), hereinafter referred to as Sp*. In Sp* the asymmetric carbon atom is preferably linked to two differently substituted carbon

atoms, a hydrogen atom and a substituent selected from 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 Sp* preferably has the formula



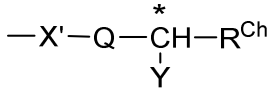
in which

X’	has the meanings defined above 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,
Q and Q’	identically or differently, denote a single bond or optionally fluorinated alkylene having 1 to 10 carbon atoms, in which a CH_2 group not linked with X can also be replaced by -O-, -CO-, -O-CO-, -CO-O- or –CH=CH-, preferably alkylene having 1 to 10 carbon atoms or a single bond, particularly preferably $–(CH_2)_{n5}$- or a single bond,
n5	is 1, 2, 3, 4, 5, or 6,
Y	denotes optionally fluorinated alkyl having 1 to 15 carbon atoms, in which one or two non-adjacent CH_2 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 $-CH_3$, $-C_2H_5$, $-CF_3$ or Cl,

In addition, chirality is achieved by a chiral group T of formula I above having one or more, preferably one or two, very preferably one, asymmetrically 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 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

	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,
	Q	denotes a single bond or optionally fluorinated alkylene having 1 to 10 carbon atoms, in which a CH_2 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, particularly preferably -CH_2-, -CH_2CH_2- or a single bond,
	Y	denotes optionally fluorinated alkyl having 1 to 15 carbon atoms, in which one or two non-adjacent CH_2 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 -CH_3, -C_2H_5, -CF_3 or Cl,
	R^{Ch}	denotes an alkyl group having 1 to 15 carbon atoms that is different from Y, in which one or two non-adjacent CH_2 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 CH_2 group linked to the asymmetric carbon atom can be replaced by -O-, -O-CO- or -CO-O-.

Preferably, the first electrodes and/or second electrodes of each cell are made from a metal, a conductive alloy, a conductive ceramic, a semiconductor, a conductive oxidic material, conductive or semi conductive organic molecules or a layered conductive 2D material. The first and/or second electrode may comprise combinations of more than one of said materials, for example in form of a multi-layer system. The material of the first and the second electrode may be chosen identically or differently.

Suitable metals include Ag, Al, Au, Co, Cr, Cu, Mo, Nb, Ni, Pt, Ru, W, Pd, Pt, wherein Al, Cr and Ti are preferred.

Suitable conductive ceramic materials include CrN, HfN, MoN, NbN, TiO_2, RuO_2, VO_2, NSTO (niobium-doped strontium titanate), TaN and TiN, WN, WCN, VN and ZrN, wherein TiN is preferred.

Suitable semiconductor materials include indium tin oxide (ITO), indium gallium oxide (IGO), InGa-α-ZnO (IGZO), aluminium-doped zinc oxide (AZO), tin-doped zinc oxide (TZO), fluorine-doped tin oxide (FTO) and antimony tin oxide.

Suitable element semiconductors include Si, Ge, C (diamond, graphite, graphene, fullerene), α-Sn, B, Se and Te. Suitable compound semiconductors include group III-V semiconductors, in particular GaAs, GaP, InP, InSb, InAs, GaSb, GaN, TaN, TiN, MoN, WN, AlN, InN, Alx Ga1−x As and Inx Ga1−x Ni, group II-VI semiconductors, in particular ZnO, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, Hg(1−x) Cd(x) Te, BeSe, BeTex and HgS; and group III-VI semiconductors, in particular GaS, GaSe, GaTe, InS, InSex and InTe, group I-III-VI semiconductors, in particular CuInSe2, CuInGaSe2, CuInS2 and CuInGaS2, group IV-IV semiconductors, in particular SiC and SiGe, group IV-VI semiconductors, in particular SeTe.

Suitable highly doped semiconductor materials include p+Si, n+Si.
An example of a suitable layered conductive 2D material is graphene.

Suitable semiconductive organic molecules include polythiophene, tetracene, pentacene, phthalocyanines, PTCDA, MePTCDI, quinacridone, acridone, indanthrone, flaranthrone, perinone, AlQ3 , and mixed systems, in particular PEDOT:PSS and polyvinylcarbazole/TLNQ complexes.

In a preferred embodiment, the first and second electrodes, identically or differently, comprise a material selected from the group consisting of Ag, Al, Au, Co, Cr, Cu, Mo, Nb, Ni, Pt, Ru, Si, W, CrN, HfN, MoN, NbN, TiN, TaN, WN, WCN, VN and ZrN.

More preferably, the first and second electrodes, identically or differently, comprise, preferably consist of a metal nitride selected from CrN, HfN, MoN, NbN, TiN, TaN, WN, tungsten carbide nitride (WCN), VN and ZrN.

In particular, the first electrode consist of a metal nitride selected from CrN, HfN, MoN, NbN, TiN, TaN, WN, WCN, VN and ZrN, and the second electrode consists of TiN.

Very particularly, the first and the second electrode both consist of TiN.

In the following description of the illustrative embodiments of the invention, identical or similar components and elements are denoted by identical or similar reference numbers, where repeated description of these components or elements is avoided in individual cases. The figures only depict the subject-matter of the invention diagrammatically.

FIG. 1A illustrates a nanoscale non-volatile solid state resistive device 100 having a molecular switching layer 103 according to an embodiment of the present invention. Device 100 is a two-terminal memory in the present embodiment. Device 100 includes a first electrode 102, a molecular switching layer 103, and a second electrode 104. Device 100 is a resistive memory device in the present embodiment, but may be other types of device in other embodiments. The molecular switching layer can be selectively set to various resistance values by applying a voltage to the electrodes and reset, using appropriate control circuitry. The resistance of the device 100 changes according to the orientation of the molecular dipoles of the molecular switching layer 103. Device 100 is formed over an outer semiconductor substrate 101. The semiconductor substrate may be a silicon substrate or a compound substrate of a III-V or II-VI type. In an embodiment, the substrate is not made of semiconductor material, e.g., made of plastic.

Particularly suitable substrates are selected from:

- element semiconductors, such as Si, Ge, C (diamond, graphite, graphene, fullerene), α-Sn, B, Se and Te;
- compound semiconductors, preferably
  - group III-V semiconductors, in particular GaAs, GaP, InP, InSb, InAs, GaSb, GaN, TaN, TiN, MoN, WN, AlN, InN, $Al_xGa_{1-x}As$ and $In_xGa_{1-x}Ni$,
  - group II-VI semiconductors, in particular ZnO, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, $Hg_{(1-x)}Cd_{(x)}Te$, 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 $CuInGaS_2$,
  - group IV-IV semiconductors, in particular SiC and SiGe,
  - group IV-VI semiconductors, in particular SeTe;
- organic semiconductors, in particular polythiophene, tetracene, pentacene, phthalocyanines, PTCDA, MePTCDI, quinacridone, acridone, indanthrone,

flavanthrone, 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;
- conductive oxidic materials, in particular indium tin oxide (ITO), indium gallium oxide (IGO), InGa-α-ZnO (IGZO), aluminium-doped zinc oxide (AZO), tin-doped zinc oxide (TZO), fluorine-doped tin oxide (FTO) and antimony tin oxide.

Preference is given to the use of crystalline silicon as substrate 101, where silicon wafers having a (100) surface are particularly preferred. Silicon wafers whose surface is oriented at (100) are employed as conventional substrate in microelectronics and are available in high quality and with a low proportion of surface defects.

In the switching devices according to the invention, the molecules of the molecular layer 103 are bonded to the first electrode 102 by means of the anchoring group G as defined above.

The molecular layer may optionally be bonded to a relatively thin (preferably 0.5 - 5 nm thick) oxidic interlayer 105, for example TiO_2, Al_2O_3, ZrO_2, HfO_2, or SiO_2, which is located on the first electrode 102, thus in this embodiment, the first electrode comprises a first layer comprising the material defined in claim 1 and a second oxidic layer to which the molecular layer 103 is bonded (Fig. 1B). Hence, first electrode 102 and interlayer 105 are operable as an alternative first electrode 102'.

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

The molecular layer is essentially formed from precursors of the formula I. Preferably, the precursors used for the formation of the molecular layer consist of compounds of the formula I.

The thickness of the molecular layer is preferably 10 nm or less, particularly preferably 5 nm or less, very particularly preferably 3 nm or less.

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.

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

Preferably, the second electrode 104 consists of TiN.

In an embodiment, first electrodes 102, which in the embodiment of Figure 1A are implemented in the form of conductor tracks which run perpendicular to the drawing plane, are arranged on the substrate 101.

A second electrode 104, which, like the first electrode 102, is in the form of a conductor track, is arranged on the side of the molecular layer 103 facing away from the substrate 101. However, the second electrode 104 is rotated by 90° relative to the first electrode 102, so that a cross-shaped arrangement arises. This arrangement is also called a crossbar array, where the 90° angle is selected here as an example and arrangements in which second electrodes 104 and first electrodes 102 cross at an angle deviating from the right angle are also conceivable. A switching device 100, which is formed from a layer system having, in this sequence, a second electrode 104, a molecular layer 103 and a first electrode 102, is arranged at each crossing point between a second electrode 104 and a first electrode 102. In an embodiment a diode is also assigned to each switching device 100.

The crossbar array enables each switching device 100 to be addressed electrically by applying a voltage between the corresponding first electrode 102 and second electrode 104.

The production and structuring of the electrodes is carried out by means of processes known to the person skilled in the art and is explained in greater detail below with reference to the working examples.

The structures of the electrodes 102,104 can be produced by means of structuring methods known to the person skilled in the art from microelectronics. For example, a lithography method can be employed for the production of the first electrodes 102. In this, a metal layer is applied to the substrate 101 by means of vapour deposition. The metal layer is subsequently coated with a photoresist, which is exposed with the structures to be produced. After development and, where necessary, baking of the resist, the parts of the metal layer that are not required are removed, for example, by wet-chemical etching. The remaining resist is subsequently removed, for example using a solvent.

A further possibility for the production of the electrodes 102, 104 is vapour deposition with the aid of a shadow mask. In this method, a mask whose openings correspond to the shape of the electrodes 102,104 to be produced is placed on the component and a metal is subsequently applied by vapour deposition. The metal vapour is only able to precipitate and form the electrode 102, 104 on the component in the areas not covered by the mask.

Suitable and preferred processes for the fabrication of the switching device according to the invention are published in EP3813132, paragraph [0113] to [0126]. The compounds according to the invention can be used as described therein.

A substrate 101 whereon a plurality of devices 100 is to be defined is provided. The substrate is silicon (p doped, resistivity <0.001 Ω cm^{-1}, prime grade) in the present embodiment. In a preferred embodiment, the silicon substrate comprises a SiO_2 layer which serves as an isolating layer and improves derivatization. In other embodiments, other semiconductor materials such as III-V and II-VI type semiconductor compounds may be used as the substrate. Device 100 may be formed as part of a front-end process or a back-end process depending on implementation. Accordingly, substrate 101 may include one or more layers of material formed and patterned thereon when the substrate is provided for the present process.

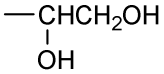
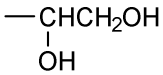
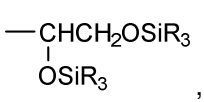
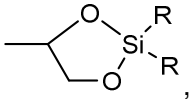
A first electrode is formed over substrate 101 using any deposition process, such as, for example, chemical vapor deposition (CVD), plasma enhanced CVD (PECVD), radio-frequency CVD (RFCVD), physical vapor deposition (PVD), atomic layer deposition (ALD), molecular beam deposition (MBD), pulsed laser deposition (PLD), and/or liquid source misted chemical deposition (LSMCD), and/or sputtering, or

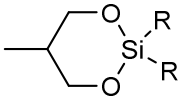
another deposition or growth process to form at least a top portion of the first electrode. The bottom electrode preferably should comprise a material having a high voltage threshold for ion migration and it can be blanket or structured by photolithography or other advanced lithography processes known to a person skilled in the art, e.g. nano-imprint lithography or dip-pen lithography.

Optionally, the first electrode is treated with oxygen, argon or nitrogen plasma or UV/ozone in order to obtain a hydrophilic oxidic surface which is populated with hydroxyl groups. 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 or interlayer 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.

A molecular layer 103 is formed over the first electrode 102.

The deposition of the molecular layer onto the first electrode is carried out with 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.

In an embodiment, the anchoring group G of the compounds forming the molecular layer, in particular of the compounds of the formula I and their sub-formulae, is selected from OH, , $-CH(CH_2OH)_2$, -COOH, and $-O-C(O)-OR^2$, in which R^2 denotes primary or secondary or tertiary alkyl having 1 to 6 C atoms, preferably tert.-butyl; preferably, the anchoring group G is selected from the group consisting of OH, , $-CH(CH_2OH)_2$ and -COOH and where the molecular layer is formed in an ALD process as described in WO2021/083934. According to another aspect of the present invention there is provided an ALD process in which the first reactant of said ALD process has fluorine atoms associated therewith and wherein the anchoring group G of the compounds forming the molecular layer, in particular of the compounds of the formula I and their sub-formulae, is selected from $-OSiR_3$, $-COOSiR_3$, $-CH(CH_2OSiR_3)_2$, , ,


, and -O-C(O)-OSiR$_3$,

in which R, on each occurrence, identically or differently, denotes alkyl having 1 to 6 C atoms, preferably methyl, ethyl or isopropyl, very preferably methyl.

The molecules of the molecular layer are preferably bonded to the first electrode by chemisorption or covalently, more preferably covalently. The bonding is carried out by known methods which are familiar to the person skilled in the art, for example by condensation with hydroxyl groups located on the surface of the substrate.
In an alternative embodiment, the molecular layer 103 can also be linked to a first electrode not directly but via a thin oxidic adhesion layer 105 derived from a metal different from that of the first electrode (e.g. Al_2O_3, ZrO_2) and which is deposited onto the first electrode using the deposition techniques mentioned above for the first electrode, preferably CVD.

Preferred is grafting of a molecular layer directly onto a titanium nitride first electrode 102 by means of molecules of formula I in which the anchor group G is a phosphonic acid group.

In a preferred embodiment, the device is annealed after deposition of the monolayer. The annealing is carried out at a temperature of greater than 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.
According to another aspect of the invention the monolayer is fabricated from one or more compounds of formulae I in which the anchor group G denotes -SO_2OR^V, -$OP(O)(OR^V)_2$, -$PO(OR^V)_2$, -$C(OH)(PO(OR^V)_2)_2$, -$COOR^V$ 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 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 between 60°C and 300°C, preferably between 100°C and 250°C, in particular between 140°C and 180°C.

The first electrode 102 is patterned to obtain an electrode extending along a direction (e.g., horizontal direction). A plurality of first electrodes extending along the first direction in parallel is formed at this step.
Patterned second electrodes are formed on the molecular layer 103 by a lift-off process using a known processing sequence including a lift-off photoresist, patterning step, electrode deposition, and lift off, or using a photoresist.

The second electrode 104 can be deposited, e.g., by sputtering or atomic layer deposition, preferably by sputtering.

According to another aspect of the present invention, a plurality of cells is arranged in a three dimensional array of cells. Accordingly, the array extends in two directions of a plane, which may be defined by a substrate onto which the electronic element is formed, and may also extend in a vertical direction perpendicular to this plane. A number of cells arranged in the each of the two directions or dimensions of the plane may be very high, ranging from at least two to several thousands, millions or even billions of cells. For example, in a configuration of 1024 cells in an x-direction and 1024 cells in a y-direction, a single two dimensional layer of cells comprises 1048576 cells. Such a two-dimensional arrangement of cells, wherein each of the cells is located at a crossing of two orthogonal electrode lines is known as crossbar array.

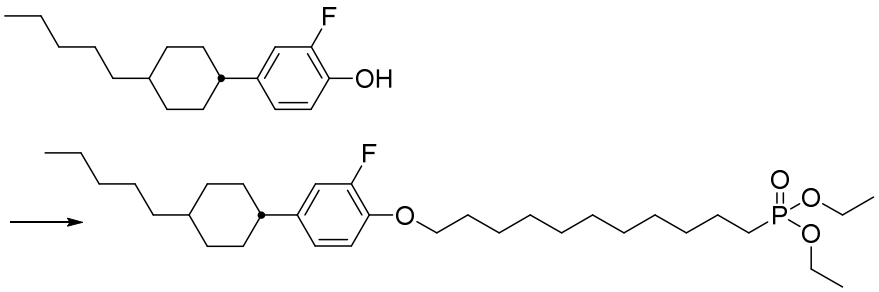
The number of levels or layers of cells arranged in the vertical direction or dimension is typically lower and ranges from 2 to at least 64, preferably up to at least 1024 or even higher. Preferably, the array comprises at least 16 levels of cells, more preferably at least 32 levels of cells and most preferred at least 64 levels of cells. Such a three-dimensional arrangement of cells is known as a 3D crossbar array or 3D cross point device.

Examples

Synthesis Examples

Example 1: (11-{2-fluoro-4-[4-pentylcyclohexyl]phenoxy}undecyl)phosphonic acid

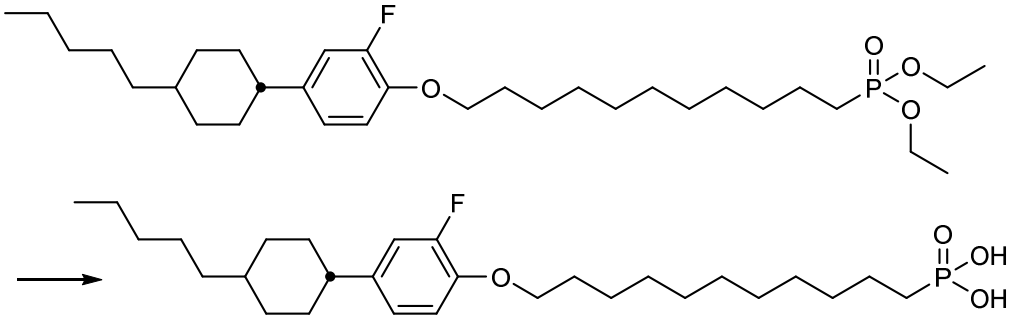
Step 1: Diethyl (11-{2-fluoro-4-[4-pentylcyclohexyl]phenoxy}undecyl)phosphonate



2-Fluoro-4-(4-pentylcyclohexyl)phenol (5.0 g, 18.9 mmol), diethyl (11-bromoundecyl)-phosphonate (9.1 g, 24.6 mmol), potassium carbonate (10.5 g, 75.7 mmol), sodium iodide (0.14 g, 0.95 mmol) and butanone (65 ml) are heated to reflux under nitrogen for 20 hours. The reaction mixture is filtered, and the filtrates are evaporated to dryness to give an orange oil. The oil is purified by column chromatography on silica with ethyl acetate/dichloromethane to give diethyl (11-{2-fluoro-4-[4-pentylcyclohexyl]-phenoxy}undecyl)phosphonate as a colorless oil.

^{1}H NMR (400 MHz, chloroform-*d*) δ ppm 0.90 (3 H, t, *J*=7.0 Hz), 0.96 - 1.09 (2 H, m), 1.15 - 1.51 (31 H, m), 1.52 - 1.66 (2 H, m), 1.67 - 1.92 (8 H, m), 2.39 (1 H, tt, *J*=12.2, 2.8 Hz), 3.99 (2 H, t, *J*=6.6 Hz), 4.03 - 4.17 (4 H, m), 6.83 - 6.90 (2 H, m), 6.92 (1 H, d, *J*=13.4 Hz).

Step 2: (11-{2-fluoro-4-[(4-pentylcyclohexyl]phenoxy}undecyl)phosphonic acid



Diethyl (11-{2-fluoro-4-[4-pentylcyclohexyl]phenoxy}undecyl)phosphonate (7.1 g, 12.8 mmol) is dissolved in dichloromethane (107 ml) under nitrogen. Bromotrimethylsilane (19.7 g, 128.0 mmol) is added dropwise and stirred overnight. The reaction mixture is evaporated to dryness *in vacuo* and the resultant yellow oil is dissolved in methanol (85 ml), then evaporated again to yield a yellow solid. The solid is re-dissolved by in dichloromethane (67 ml), then methanol (67 ml) is added. The solution is slowly concentrated in vacuo at 40°C until crystallization begins, at which point the distillation is stopped and the flask is transferred to an ice-acetone bath at -5°C and stirred for 45 min. The resultant solid is collected by filtration and washed with cold methanol (3 x 10

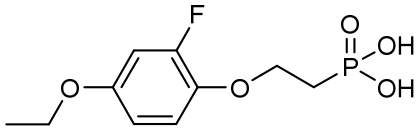
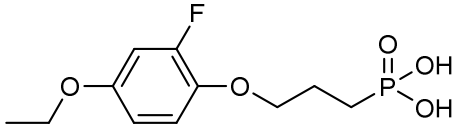
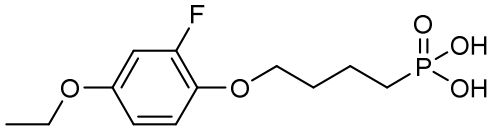
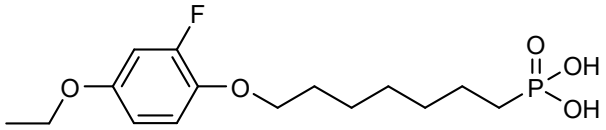
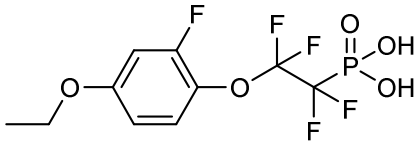
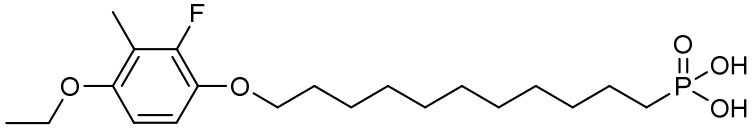
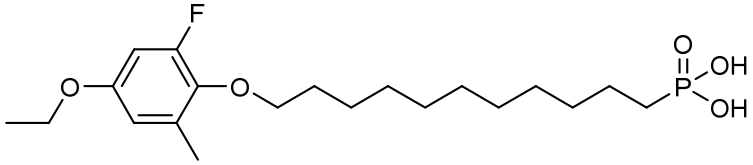
ml) on the filter and dried to give (11-{2-fluoro-4-[(4-pentylcyclohexyl]phenoxy}-undecyl)phosphonic acid as a colorless solid.

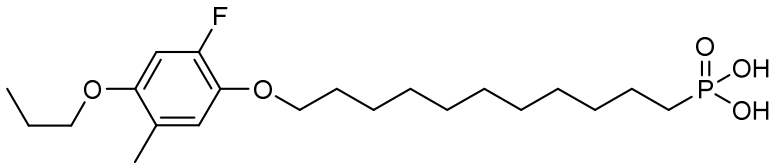
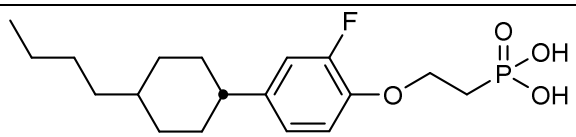
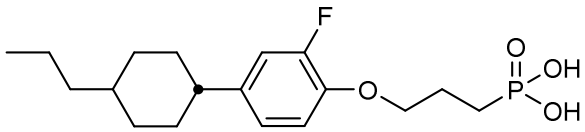
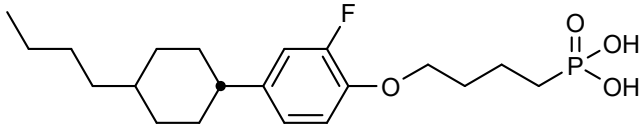
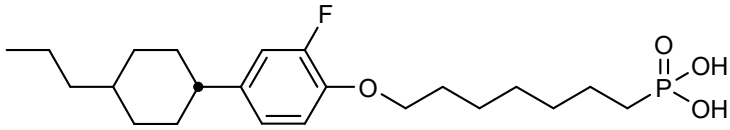
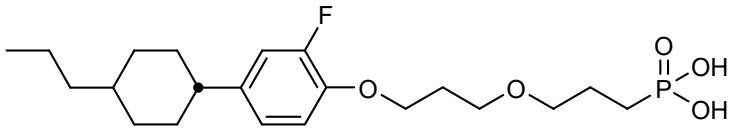
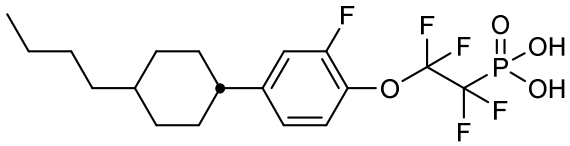
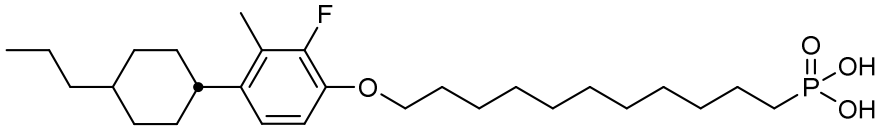
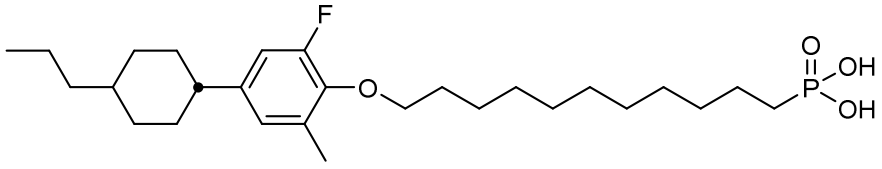
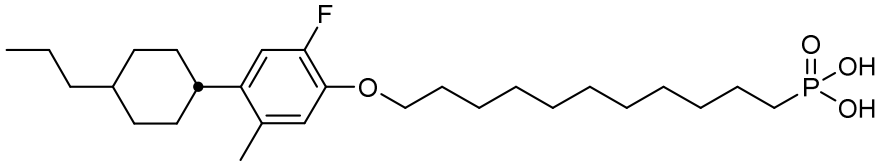
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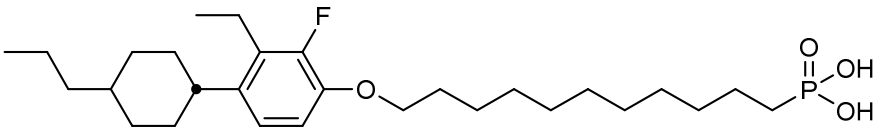
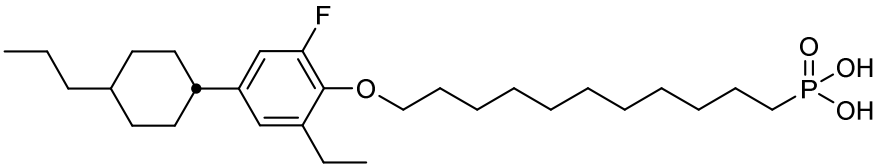
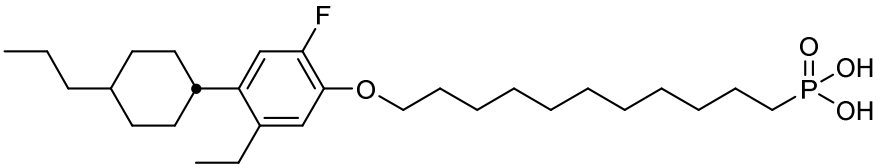
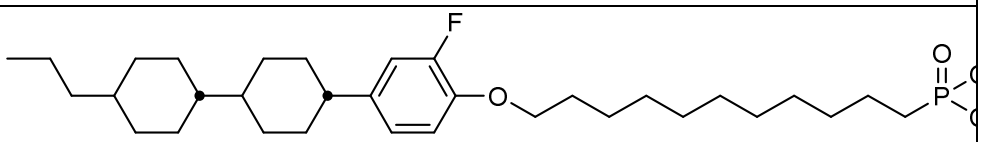
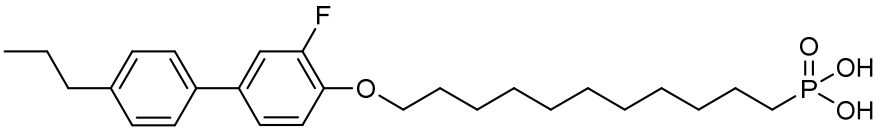
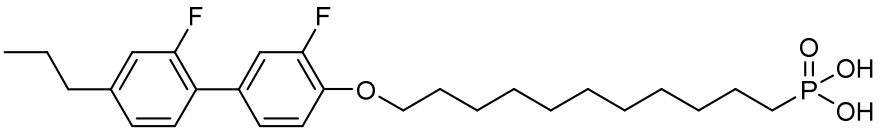
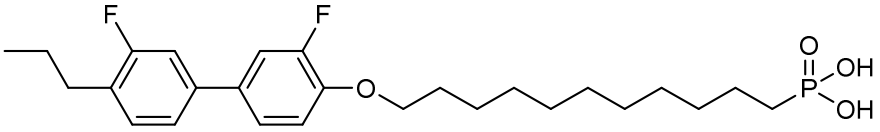
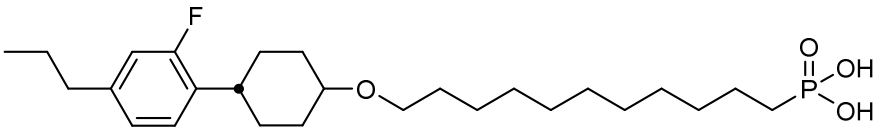
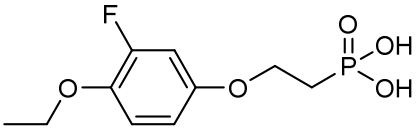
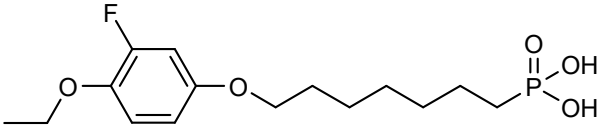
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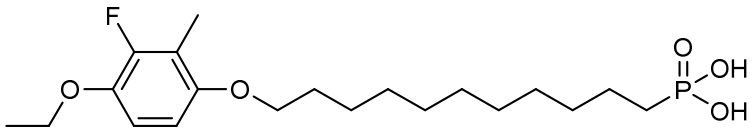
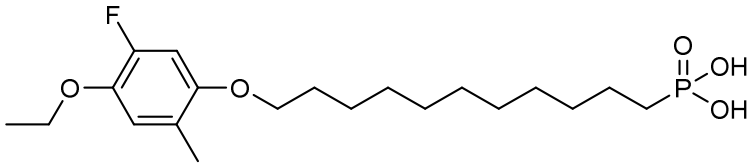
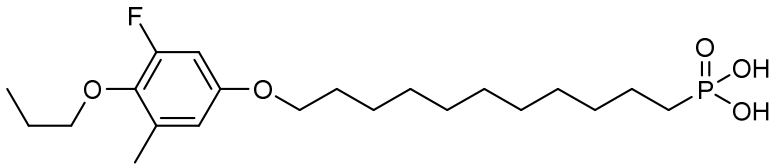
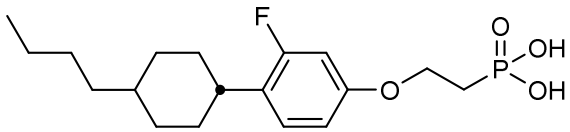
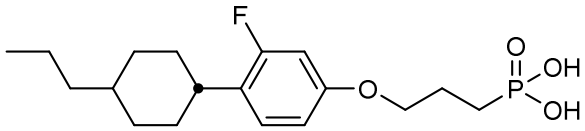
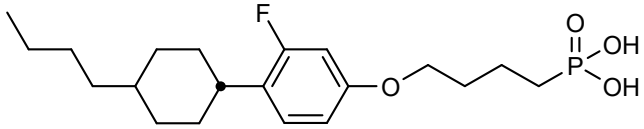
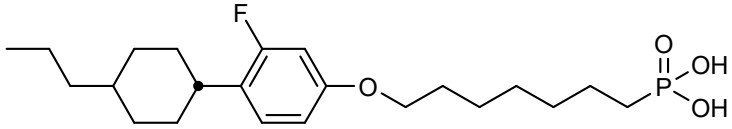
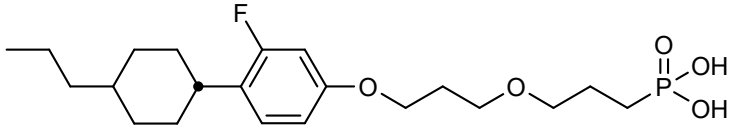
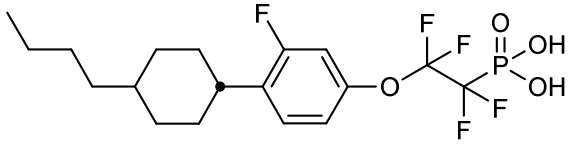
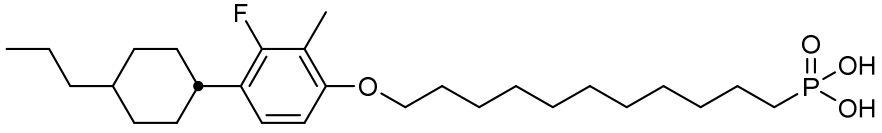
^{31}P NMR (162 MHz, THF-d_8) δ ppm 30.62.

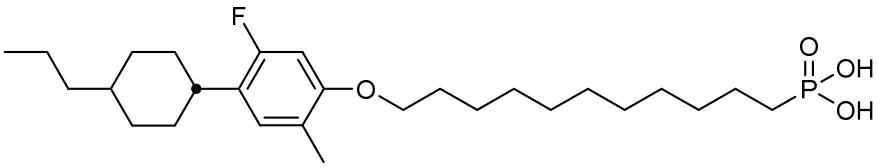
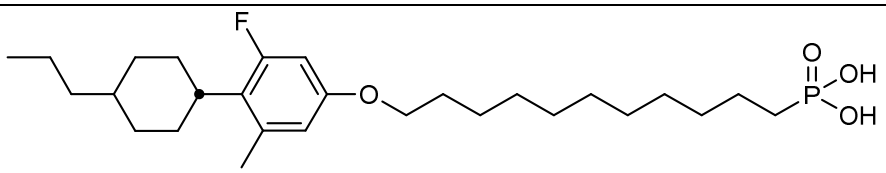
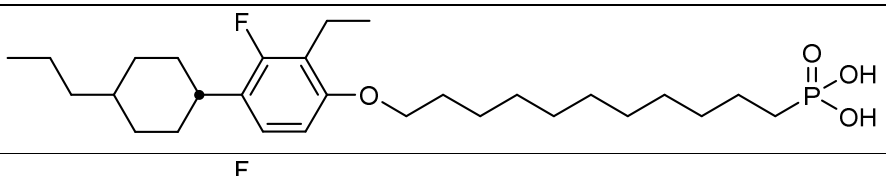
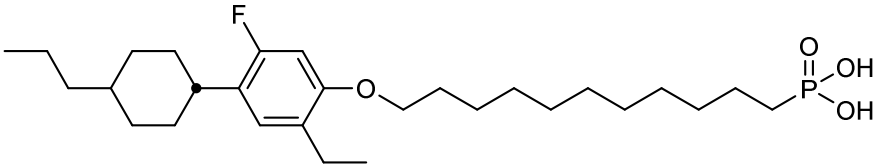
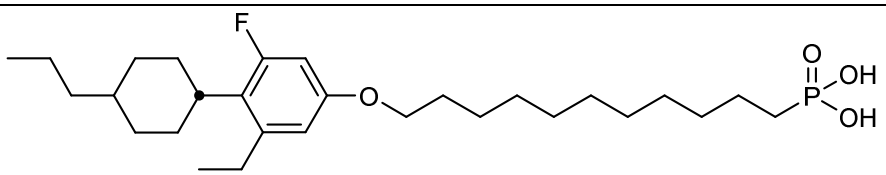
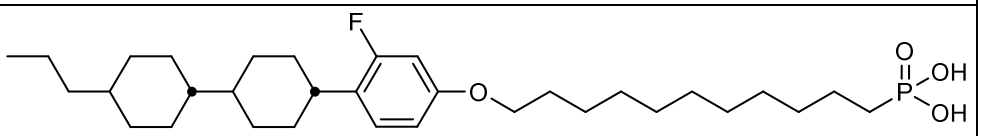
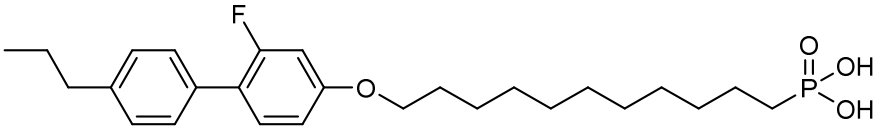
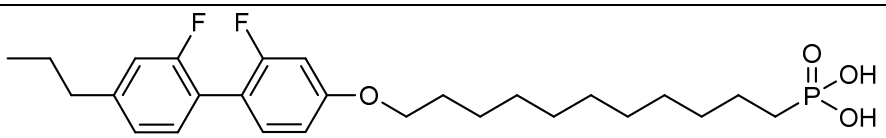
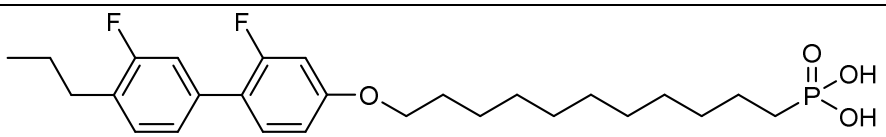
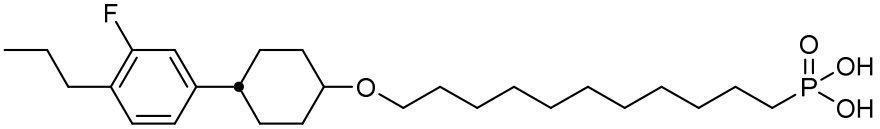
In analogy to Synthesis Example 1, the following compounds are obtained:

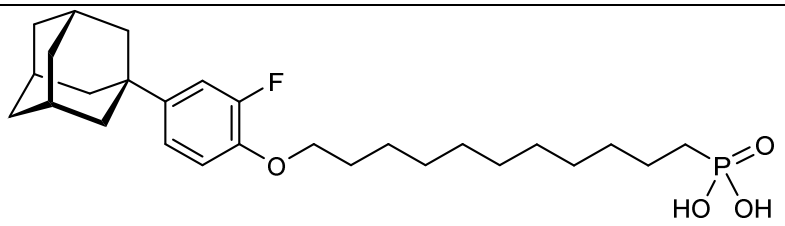
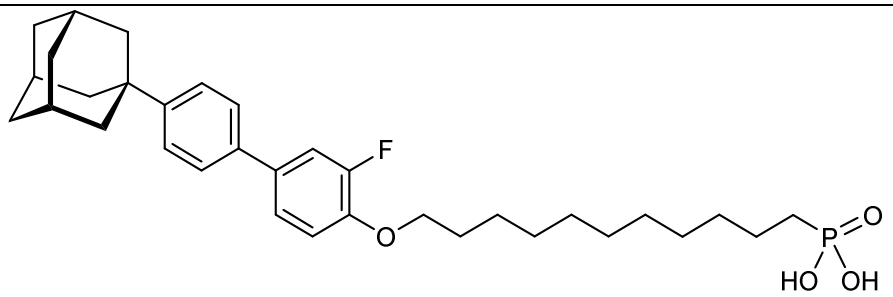
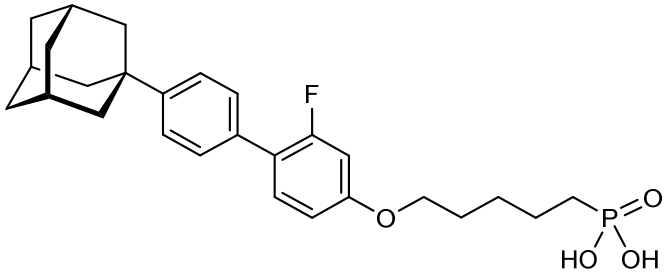
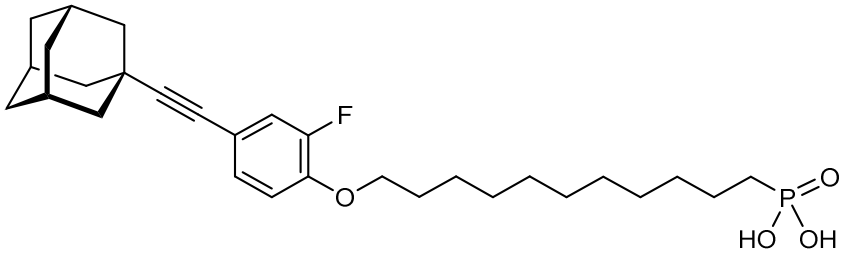
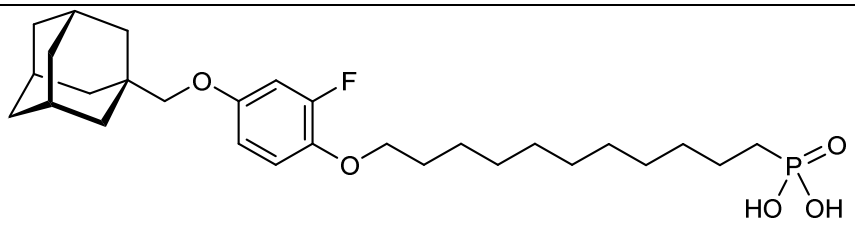
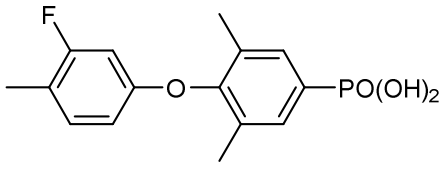
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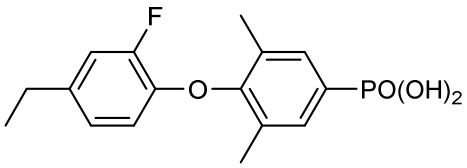
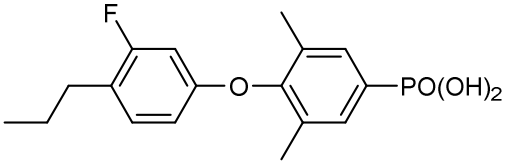
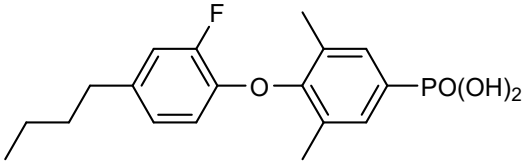
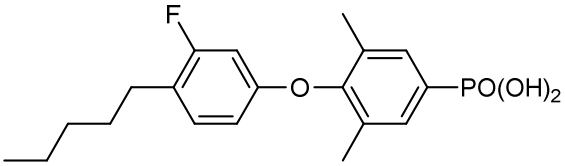
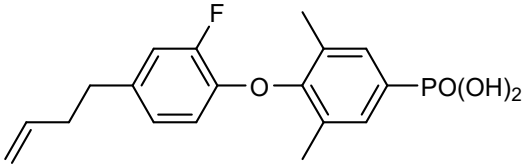
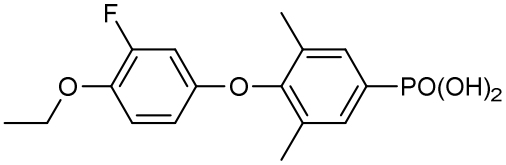
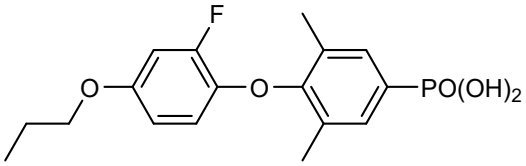
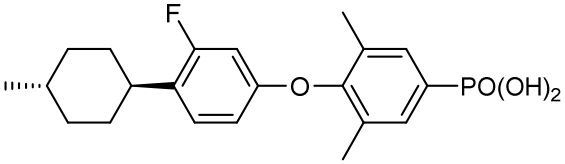
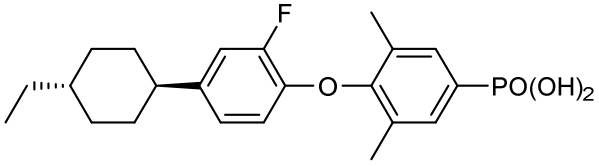
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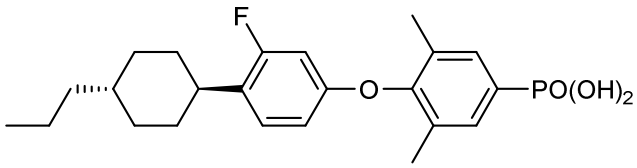
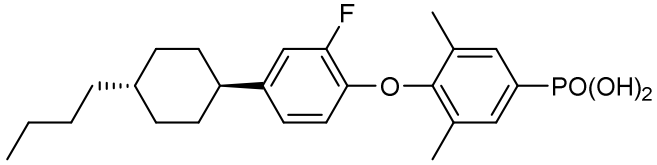
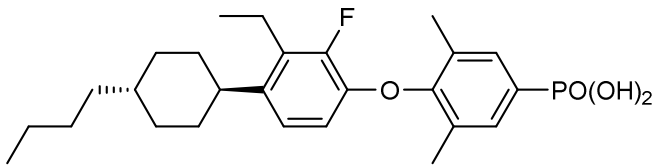
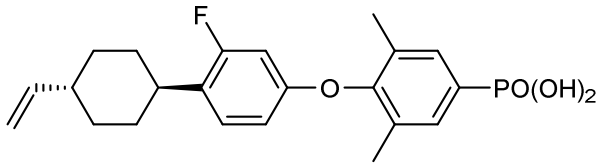
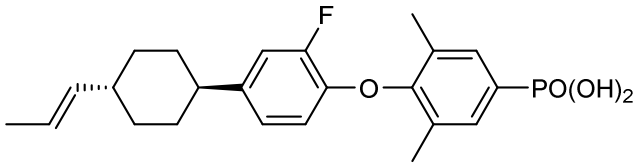
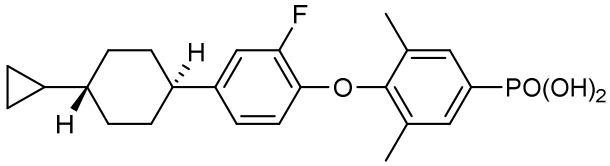
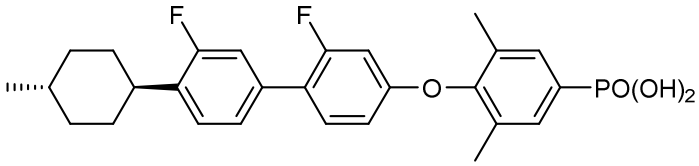
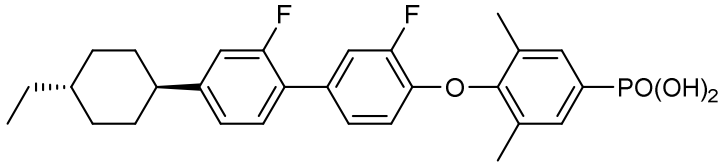
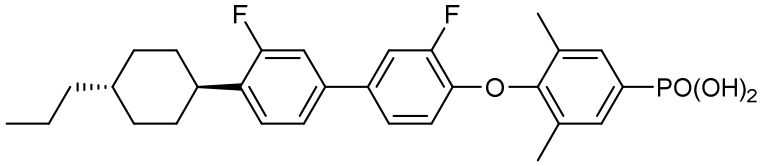
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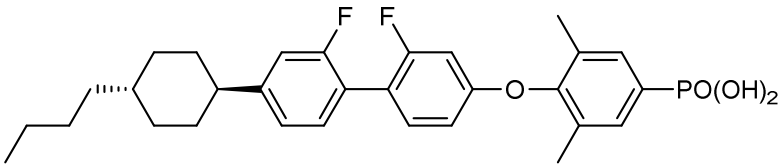
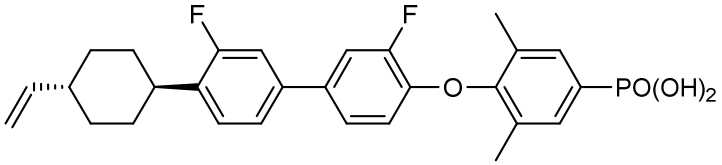
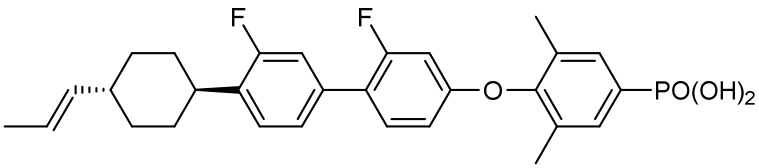
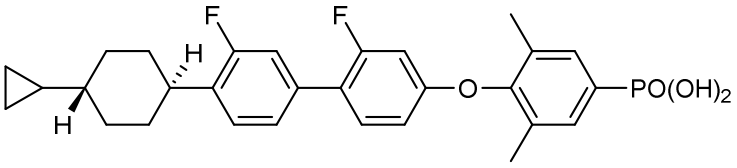
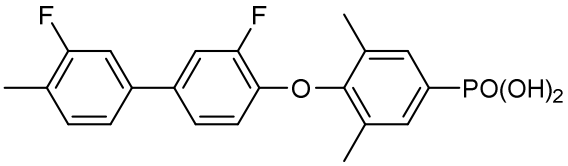
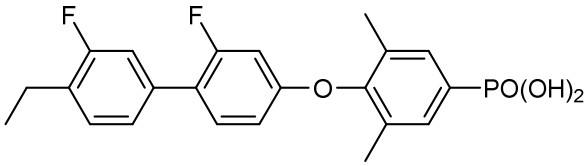
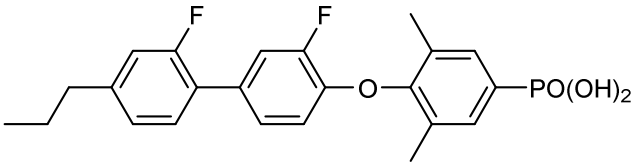
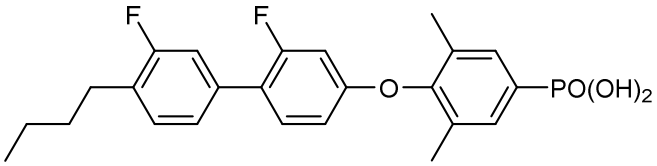
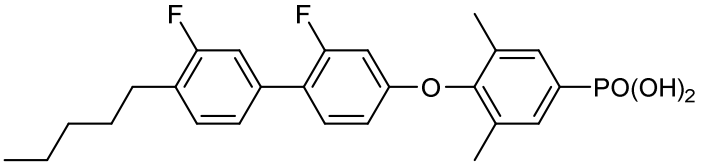
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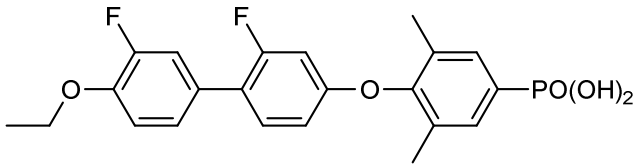
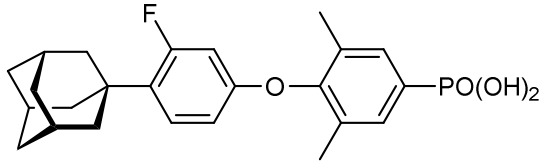
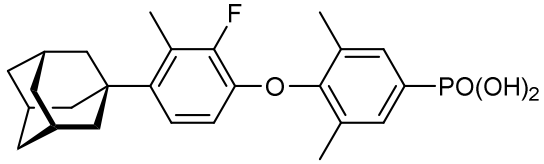
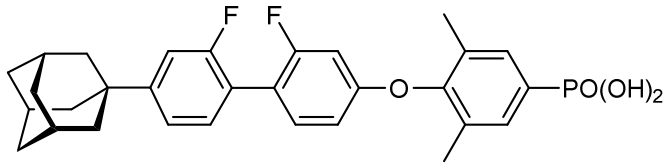
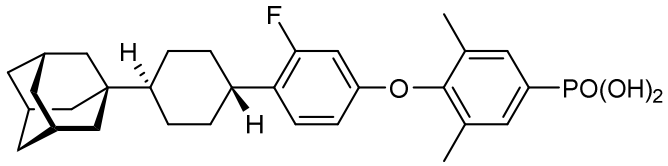
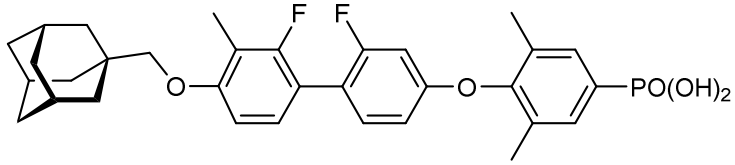
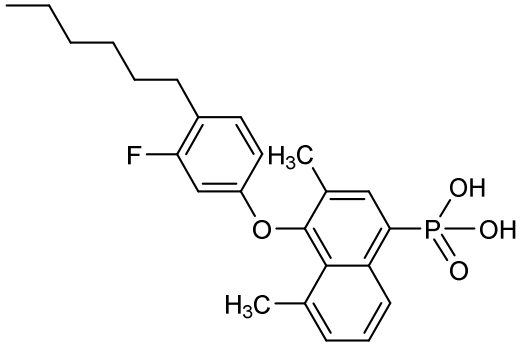
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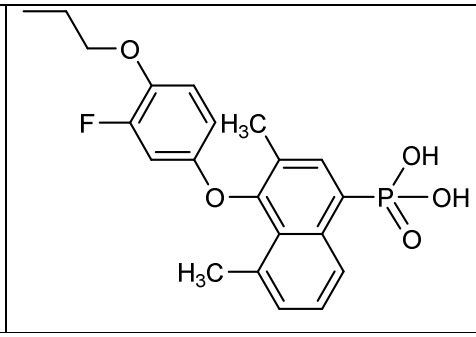
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Device Fabrication

Preparation of Test Chips:

A 45x45 mm silicon wafer with a 4 nm TiO_2 top layer deposited by ALD is treated with ozone for 15 min and then immersed into a 1mM solution of phosphonic acid in THF for 72 h. The chip is dried in a stream of nitrogen and then tempered at 120°C for 1 h. The chip is washed with THF and dried in a stream of nitrogen gas.

Water contact angle measurement

A test chip treated with 11-{2-fluoro-4-[(4-pentylcyclohexyl]phenoxy}undecyl)-phosphonic acid has a water contact angle of 100.8°.

Electrical Characterization

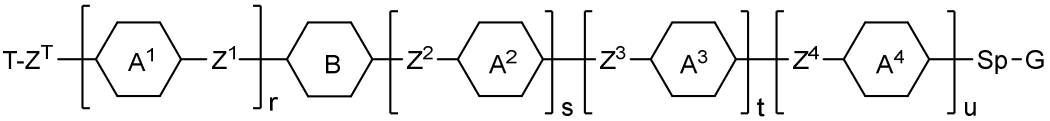
A silicon wafer obtained from treatment with 11-{2-fluoro-4-[(4-pentylcyclohexyl]phenoxy}undecyl)-phosphonic acid is glued with silver conductive paste to a copper plate that has been cleaned by dipping into 1M HCl. The silver conductive paste is annealed at 80°C for 10 min under a flow of nitrogen. The samples are then introduced into a nitrogen glovebox and contacted at the bottom on the copper contact and on the top by a Hg capillary. For each measurement a new fresh Hg drop is generated. The size of the drop is measured with a camera system for determination of the contact area.

4 cycles of current-voltage (I-V) measurements between -3 and +3 V in 40 mV steps are taken per contact area. For retention measurements a half cycle of the I-V measurement from 0 to 3V and back to 0 V for set operation (low resistive state, LRS) is performed. For Reset an I-V measurement from 0 to -3 V and back to 0 V is taken (high resistive state, HRS). After fixed time intervals a short constant voltage measurement at 1 V is done. The resulting current-voltage curves are shown in Fig. 2.

The result of the measurement of a reference device without a molecular monolayer is shown in Fig. 3.

Patent Claims

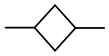
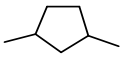
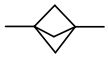
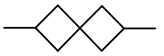
1. A compound of formula I



(I)

in which

T is selected from the group of radicals consisting of the following groups:

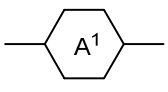
a) straight chain or branched alkyl or alkoxy each having 1 to 20 C atoms, where one or more CH_2 groups in these radicals may each be replaced, independently of one another, by -C≡C- , -CH=CH-,  ,  ,  ,  ,  , -O-, -S-, -CF_2O-, -OCF_2-, -CO-O-, -O-CO- ,-SiR^0R^{00}- , -NH- , -NR^0- or -SO_2- in such a way that O atoms are not linked directly to one another, and in which one or more H atoms may be replaced by halogen, CN, SCN or SF_5,

b) a three- to ten-membered saturated or partially unsaturated aliphatic ring, in which at least one -CH_2- group is replaced with -O-, -S-, -S(O)-, -SO_2-, -NR^x- or -N(O)R^x-, or in which at least one -CH= group is replaced with -N=,

c) a diamondoid radical,

Z^T, Z^1, Z^2, and Z^4, 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_2CF_2-, -CH=CH-,-CF=CF-, -CF=CH-, -CH=CF-, -$(CH_2)_{n3}O$-, -$O(CH_2)_{n4}$-, -C≡C-, -O-, -S-, -CH=N-, -N=CH-, -N=N-, -N=N(O)-, -N(O)=N- or -N=C-C=N-, wherein n1, n2, n3, n4, identically or differently, are 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

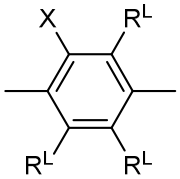
Z^3 denotes -O-, -S-, -CH_2-, -C(O)-, -CF_2-, -CHF-, -$C(R^x)_2$-, -S(O)- or -SO_2-,

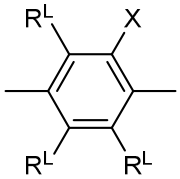
 ,  and  , on each occurrence, identically or differently, denote an aromatic, heteroaromatic, alicyclic or heteroaliphatic ring having 4 to 25 ring atoms, which may also contain condensed rings and which may be monosubstituted by X or which may be mono- or polysubstituted by R^L,



denotes an aromatic or heteroaromatic ring having 5 to 25 ring atoms, which may also contain condensed rings, and which may be monosubstituted by X or which may be mono- or polysubstituted by R^C,



denotes 

or 

,

X denotes F, Cl, Br, I, CN, SF_5, CF_3, OCF_3, or $OCHF_2$, preferably Cl or F, very preferably F,

R^L on each occurrence, identically or differently denotes H, alkyl having 1 to 6 C atoms, alkenyl having 2 to 6 C atoms or alkoxy having 1 to 5 C atoms, preferably H or alkyl having 1 to 4 C atoms, very preferably H, methyl or ethyl,

R^C on each occurrence, identically or differently, denotes straight-chain or branched, in each case optionally fluorinated alkyl, alkoxy, alkylthio, 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, trifluoromethoxy or trifluoromethylthio,

Sp denotes a spacer group or a single bond,

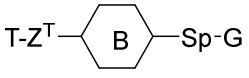
R^0, R^{00}, R^x denotes straight-chain or branched alkyl having 1 to 6 C atoms,

G denotes -OH, -SH, $-SO_2OH$, $-OP(O)(OH)_2$, $-PO(OH)_2$, $-C(OH)(PO(OH)_2)_2$, -COOH, $-Si(OR^x)_3$, $-SiCl_3$, $-CH=CH_2$, $-POCl_2$, $-COH(PO(OH)_2)_2$, -CO(NHOH), $-CO(NR^0OH)$, $-Si(NMe_2)_3$; or straight chain or branched alkyl having 1 to 12 C atoms in which one, two or three not geminal H atoms are substituted by OH; or a group selected from $-O-C(O)-OR^V$, $-O-C(O)-Si(OR^x)_3$, $PO(OR^V)_2$, SO_2OR^V,

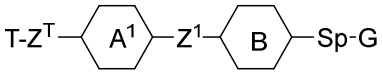
R^V denotes straight chain or branched alkyl having 1 to 12 C atoms, and

r, s, t and u, identically or differently, are 0, 1 or 2.

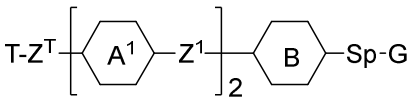
2. The compound according to claim 1, wherein the compound is selected from the group consisting of the formulae IA-1a to IA-1f



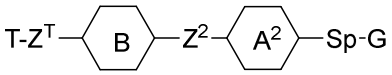
IA-1a



IA-1b



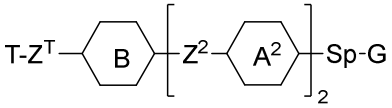
IA-1c



IA-1d



IA-1e



IA-1f

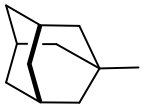
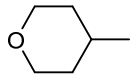
in which T, Z^T, 

, 

, 

, Z^1, Z^2, Sp and G have the meanings given in claim 1.

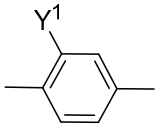
3. The compound according to claim 1 or 2, wherein

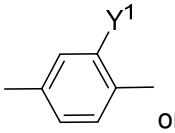
T denotes H, 
, 

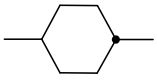
or straight chain or branched alkyl or alkoxy each having 1 to 7 C atoms or straight chain or branched alkenyl having 2 to 7 C atoms,

Z^T denotes CH_2O, OCH_2, CH_2CH_2, or a single bond,

Z^1 and Z^2, identically or differently, denote CH_2O, OCH_2, CH_2CH_2, CF_2O, OCF_2, C(O)O, OC(O) or a single bond,

A^1 and A^2, identically or differently, denote 

, 

or 
,

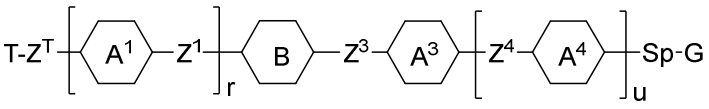
Y^1 on each occurrence, identically or differently, denote H, F of Cl,

Sp denotes branched or unbranched 1,ω-alkylene having 1 to 12 C atoms, in which one or more non-adjacent CH_2-groups may be replaced by O,

G denotes $-OP(O)(OH)_2$, $-PO(OH)_2$, $-COH(PO(OH)_2)_2$ or $-PO(OR^V)_2$, and

R^V denotes methyl, ethyl or secondary or tertiary alkyl having 1 to 6 C atoms.

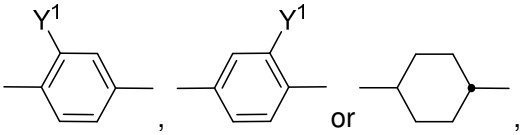
4. The compound according to one or more of claims 1 to 3, wherein the compound is selected from the compounds of the formula IA-2



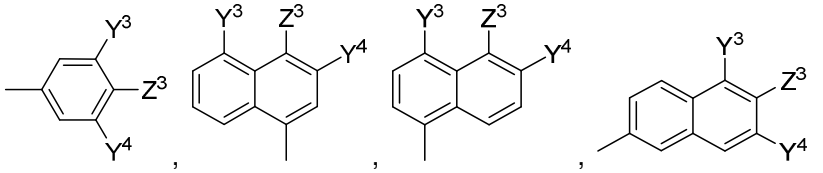
IA-2

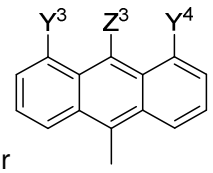
in which the occurring groups and parameters have the meanings given in claim 1.

5.The compound according to claim 4, wherein

A^1 and A^4, identically or differently, denote 

, , or ,

A^3-Z^3 denotes 

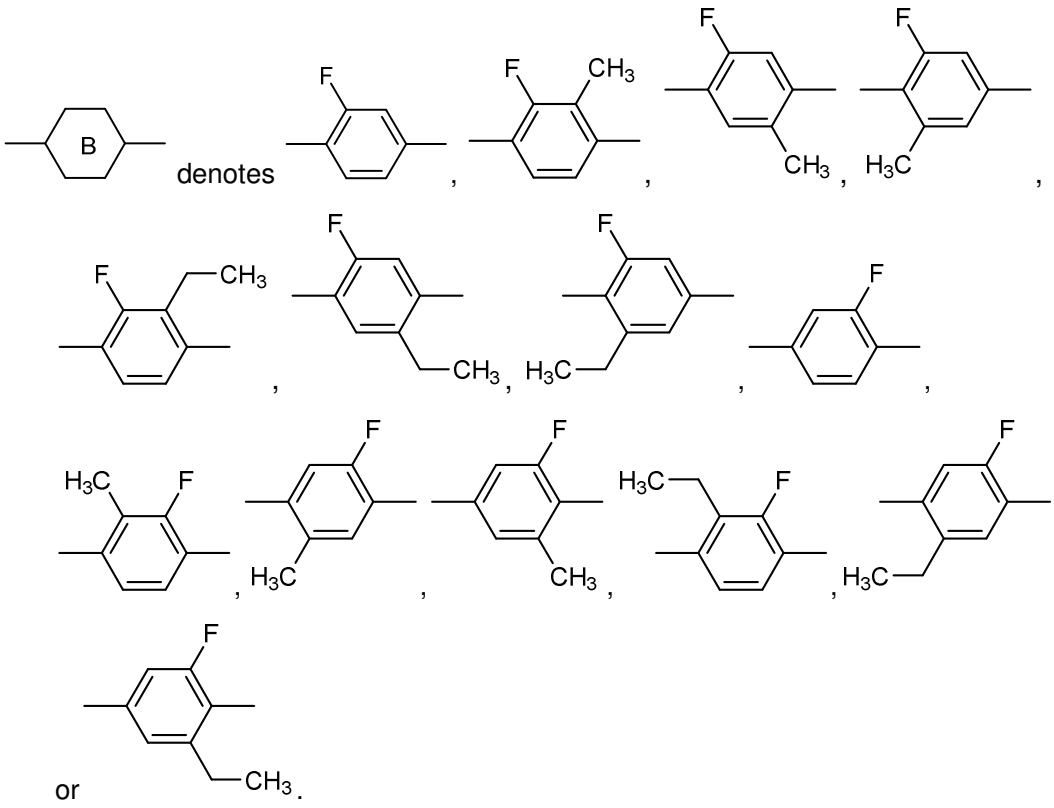
, , , or 

,

Z^T	denotes a single bond, $-CH_2O-$, $-OCH_2-$ or $-CH_2CH_2-$,
L^1 and L^2	identically or differently, denote F, CF_3 or Cl,
Y^2	identically or differently, have one of the meanings of X given above for formula I and preferably denote H, F or Cl,
Y^3 and Y^4,	identically or differently, have one of the meanings of R^C of formula I and preferably denote methyl, ethyl, isopropyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclopentenyl, cyclohexyl, cyclohexenyl, methoxy, trifluoromethyl, trifluoromethoxy, or trifluoromethylthio,
Z^3	denotes CH_2 or O,
Z^1, Z^2,	independently of one another, denote a single bond, -C(O)O-, -OC(O)-, $-CF_2O-$, $-OCF_2-$, $-CH_2O-$, OCH_2- or $-CH_2CH_2-$,
G	denotes $-OP(O)(OH)_2$, $-PO(OH)_2$, $-COH(PO(OH)_2)_2$ or $-PO(OR^V)_2$,

R^V	denotes methyl, ethyl or secondary or tertiary alkyl having 1 to 6 C atoms and
r and u	independently are 0, 1 or 2.

6. The compound according to one or more of claims 1 to 5, wherein the group



or

7. An electronic switching device (100) which comprises, in this sequence,
a first electrode (102),
a molecular layer (103), and
a second electrode (104),
wherein the first and second electrodes, identically or differently, preferably comprise a metal selected from Ag, Al, Au, Co, Cr, Cu, Mo, Nb, Ni, Pt, Ru, Si and W, or a ceramic material selected from CrN, HfN, MoN, NbN, TaN TiN, WN, WCN, VN, ZrN, TiO_2, RuO_2, VO_2 and niobium-doped strontium titanate,
characterised in that the molecular layer is essentially formed from one or more compounds of formula I according to one or more of claims 1 to 6.

8. Electronic switching device (100) according to claim 7, wherein an interlayer (105) is arranged between the first electrode (102) and the molecular layer (103), where the interlayer (105) comprises an oxidic material and where the molecular layer (103) is bonded to said oxidic material, and where the first electrode (102) and the interlayer (105) are operable as a first electrode (102').

9. Electronic switching device (100) according to claim 8, wherein the oxidic interlayer comprises TiO_2, Al_2O_3, ZrO_2, HfO_2, or SiO_2.

10. Electronic switching device (100) according to one or more of claims 7 to 9, wherein the group G of the compounds of the formula I, as defined in claim 1, is bonded to the first electrode (102, 102') by chemisorption or covalently.

11. Electronic switching device (100) according to one or more of claims 8 to 10, wherein the molecular layer (103) is a molecular monolayer.

12. Electronic component comprising one or more switching devices (100) according to one or more of claims 8 to 11.

13. Electronic component according to claim 12, wherein the component has a multitude of switching devices (100), where the first electrodes (102) and second electrodes (104) of the switching devices (100) form a crossbar array.

14. Electronic component according to claim 12 or 13, wherein the switching devices (100) are configured to change between a state having high electrical resistance and a state having low electrical resistance, where the quotient between high electrical resistance and low electrical resistance is between 10 and 100,000.

15. Electronic component according to one or more of claims 12 to 14, wherein the component is a resistive memory device, a sensor, a field-effect transistor or a Josephson junction.

16. Method for operating an electronic component according to one or more of claims 12 to 15, characterised in that a switching device (100) of the electronic component is switched into a state of high electrical resistance by setting a corresponding first electrode (102) to a first electrical potential and setting a

corresponding second electrode (104) to a second electrical potential, where the value of the voltage between the two electrodes (102, 104) is greater than a first switching voltage and the first potential is greater than the second potential, a switching device (100) of the electronic component is switched into a state of low electrical resistance by setting a corresponding first electrode (102) to a third electrical potential and setting a corresponding second electrode (104) to a fourth electrical potential, where the value of the voltage between the two electrodes (102,104) is greater than a second switching voltage and the fourth potential is greater than the third potential, and the state of a switching device is determined by applying a reading voltage whose value is smaller than the first and second switching voltages between corresponding electrodes (102,104) and measuring the current flow.