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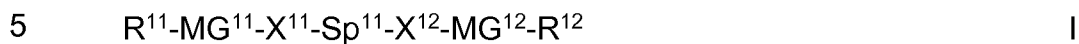
(54) Title: LIQUID CRYSTAL MEDIUM AND LIQUID CRYSTAL DEVICE

(57) Abstract: The invention relates to a compound of formula (I), R^{11} -MG¹¹-X¹¹-Sp¹¹-X¹²-MG¹²-R¹² wherein R¹¹, R²², MG¹¹, MG¹², Sp¹¹, X¹¹ and X¹² have one of the meanings as given herein below. The invention further relates to method of production of a compound of formula I, to the use of said compounds in LC media and to LC media comprising one or more compounds of formula I. Further, the invention relates to a method of production of such LC media, to the use of such media in LC devices, in particular in flexoelectric LC devices and to a flexoelectric LC device comprising a LC medium according to the present invention. P16272 SL -118- Abstract The invention relates to a compound of formula (I), R¹¹-MG¹¹-X¹¹-Sp¹¹-X¹²-MG¹²-R¹² wherein R¹¹, R²², MG¹¹, MG¹², Sp¹¹, X¹¹ and X¹² have one of the meanings as given herein below. The invention further relates to method of production of a compound of formula (I), to the use of said compounds in LC media and to LC media comprising one or more compounds of formula (I). Further, the invention relates to a method of production of such LC media, to the use of such media in LC devices, in particular in flexoelectric LC devices and to a flexoelectric LC device comprising a LC medium according to the present invention.



Liquid Crystal Medium and Liquid Crystal Device

The invention relates to a compound of formula I,



wherein R^{11} , R^{22} , MG^{11} , MG^{12} , Sp^{11} , X^{11} and X^{12} have one of the meanings as given herein below. The invention further relates to method of production of a compound of formula I, to the use of said compounds
10 in LC media and to LC media comprising one or more compounds of formula I. Further, the invention relates to a method of production of such LC media, to the use of such media in LC devices, in particular in flexoelectric LC devices and to a flexoelectric LC device comprising a LC medium according to the present invention.

15

Background and Prior Art

The flexoelectric effect is described, for example, by Chandrasekhar, "Liquid Crystals", 2nd edition, Cambridge University Press (1992) and
20 P.G. deGennes et al., "The Physics of Liquid Crystals", 2nd edition, Oxford Science Publications (1995).

Flexoelectric devices utilizing the flexoelectric effect, for example ULH devices and liquid crystal media that are especially suitable for
25 flexoelectric devices and are known from EP 0 971 016, GB 2 356 629 and Coles, H.J., Musgrave, B., Coles, M.J. and Willmott, J., J. Mater. Chem., **11**, p. 2709-2716 (2001).

The Uniform Lying Helix (ULH) has high potential as a fast switching
30 liquid crystal display mode. It is capable of sub millisecond switching at 35°C and possesses an intrinsically high aperture ratio, resulting in an energy efficient display mode.

The materials commonly used in media suitable for the ULH mode are
35 typically bimesogens. Due to the size of these materials and the presence of polar groups, such as, for example terminal cyano groups,

they normally have high rotational viscosities (γ_1) in the order of many thousands mPa.s at 35°C. The high values for γ_1 are not problematically at increased temperatures of, for example, 35°C, since the switching speed is directly proportional to γ_1 . On the other hand, the values for γ_1 are also proportional to the chiral pitch squared. Since the chiral pitch is normally in the region of 300nm this means that, the switching speeds are still very fast, in the region of 1 millisecond or a few milliseconds.

However, upon reaching lower temperatures, such as room temperature at which the ULH devices are typically operated, the value for γ_1 increases exponentially and even with a short pitch material the switching speeds increase beyond favourable levels.

In order to maintain fast switching speeds at temperatures below 35°C, the value γ_1 of the LC mixtures needs to be reduced and therefore mixture components with lower γ_1 need to be identified.

Accordingly, there is a great demand for new bimesogenic compounds, which exhibit favourable low γ_1 values while preferably at the same time exhibiting:

- favourable e/K (V^{-1}) values,
- favourable broad nematic phase ranges and
- high clearing points.

In addition to those requirements, the corresponding LC media should exhibit favourable low γ_1 values while preferably at the same time exhibiting:

- low melting points,
- high clearing points,
- broad chiral nematic phase ranges,
- short temperature independent pitch lengths,
- high flexoelectric coefficients and
- a favourable low temperature stability without crystallization effects in cells as well as in the bulk.

Other aims of the present invention are immediately evident to the person skilled in the art from the following detailed description.

5 Surprisingly, the inventors have found out that one or more of the above-mentioned aims can be achieved by providing a compound according to claim 1.

Terms and Definitions

10 The term "liquid crystal", "mesomorphic compound" or "mesogenic compound" (also shortly referred to as "mesogen") means a compound that under suitable conditions of temperature, pressure and concentration can exist as a mesophase (nematic, smectic, etc.) or in particular as a LC phase. Non-amphiphilic mesogenic compounds comprise for example one or more calamitic, banana-shaped or discotic mesogenic groups.

15 The term "mesogenic group" means in this context, a group with the ability to induce liquid crystal (LC) phase behaviour. The compounds comprising mesogenic groups do not necessarily have to exhibit an LC phase themselves. It is also possible that they show LC phase behaviour only in mixtures with other compounds. For the sake of simplicity, the term "liquid crystal" is used hereinafter for both mesogenic and LC materials.

25 Throughout the application, unless stated explicitly otherwise, the term "aryl and heteroaryl groups" encompass groups, which can be monocyclic or polycyclic, i.e. they can have one ring (such as, for example, phenyl) or two or more rings, which may also be fused (such as, for example, naphthyl) or covalently linked (such as, for example, biphenyl) or contain a combination of fused and linked rings.

30 Heteroaryl groups contain one or more heteroatoms, preferably selected from O, N, S and Se. Particular preference is given to mono-, bi- or tricyclic aryl groups having 6 to 25 C atoms and mono-, bi- or tricyclic heteroaryl groups having 2 to 25 C atoms, which optionally contain fused rings and which are optionally substituted. Preference is furthermore given to 5, 6 or 7-membered aryl and heteroaryl groups, in which, in

35

- addition, one or more CH groups may be replaced by N, S or O in such a way that O atoms and/or S atoms are not linked directly to one another. Preferred aryl groups are, for example, phenyl, biphenyl, terphenyl, [1,1':3',1'']terphenyl-2'-yl, naphthyl, anthracene, binaphthyl,
- 5 phenanthrene, pyrene, dihydropyrene, chrysene, perylene, tetracene, pentacene, benzopyrene, fluorene, indene, indenofluorene, spirobifluorene, more preferably 1,4-phenylene, 4,4'-biphenylene, 1,4-terphenylene.
- 10 Preferred heteroaryl groups are, for example, 5 membered rings, such as pyrrole, pyrazole, imidazole, 1,2,3-triazole, 1,2,4-triazole, tetrazole, 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, 1,3,4-thiadiazole, 6
- 15 membered rings, such as pyridine, pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, 1,2,4,5-tetrazine, 1,2,3,4-tetrazine, 1,2,3,5-tetrazine or condensed groups, such as indole, isoindole, indolizine, indazole, benzimidazole, benzotriazole, purine, naphthimidazole, phenanthrimidazole, pyridimidazole, pyrazinimidazole,
- 20 quinoxalinimidazole, benzoxazole, naphthoxazole, anthroxazole, phenanthroxazole, isoxazole, benzothiazole, benzofuran, isobenzofuran, dibenzofuran, quinoline, isoquinoline, pteridine, benzo-5,6-quinoline, benzo-6,7-quinoline, benzo-7,8-quinoline, benzoisoquinoline, acridine, phenothiazine, phenoxazine, benzopyridazine, benzopyrimidine,
- 25 quinoxaline, phenazine, naphthyridine, azacarbazole, benzocarboline, phenanthridine, phenanthroline, thieno[2,3b]thiophene, thieno[3,2b]-thiophene, dithienothiophene, isobenzothiophene, dibenzothiophene, benzothiadiazo-thiophene or combinations of these groups. The heteroaryl groups may also be substituted by alkyl, alkoxy, thioalkyl,
- 30 fluorine, fluoroalkyl or further aryl or heteroaryl groups.

- In the context of this application, the term "(non-aromatic) alicyclic and heterocyclic groups" encompass both saturated rings, i.e. those that contain exclusively single bonds and partially unsaturated rings, i.e.
- 35 those that may also contain multiple bonds. Heterocyclic rings contain one or more heteroatoms, preferably selected from Si, O, N, S and Se.

The (non-aromatic) alicyclic and heterocyclic groups can be monocyclic, i.e. contain only one ring (such as, for example, cyclohexane) or polycyclic, i.e. contain a plurality of rings (such as, for example, decahydro-naphthalene or bicyclooctane). Particular preference is given to saturated groups. Preference is furthermore given to mono-, bi- or tricyclic groups having 3 to 25 C atoms, which optionally contain fused rings and that are optionally substituted. Preference is furthermore given to 5-, 6-, 7- or 8-membered carbocyclic groups in which, in addition, one or more C atoms may be replaced by Si and/or one or more CH groups may be replaced by N and/or one or more non-adjacent CH₂ groups may be replaced by -O- and/or -S-. Preferred alicyclic and heterocyclic groups are, for example, 5-membered groups, such as cyclopentane, tetrahydrofuran, tetrahydrothiofuran, pyrrolidine, 6-membered groups, such as cyclohexane, silinane, cyclohexene, tetrahydropyran, tetrahydrothiopyran, 1,3-dioxane, 1,3-dithiane, piperidine, 7-membered groups, such as cycloheptane and fused groups, such as tetrahydronaphthalene, decahydronaphthalene, indane, bicyclo[1.1.1]pentane-1,3-diyl, bicyclo[2.2.2]octane-1,4-diyl, spiro[3.3]heptane-2,6-diyl, octahydro-4,7-methanoindane-2,5-diyl, more preferably 1,4-cyclohexylene 4,4'- bicyclohexylene, 3,17-hexadecahydro-cyclopenta[a]phenanthrene, optionally being substituted by one or more identical or different groups L. Especially preferred aryl-, heteroaryl-, alicyclic- and heterocyclic groups are 1,4-phenylene, 4,4'-biphenylene, 1,4-terphenylene, 1,4-cyclohexylene, 4,4'- bicyclohexylene and 3,17-hexadecahydro-cyclopenta[a]-phenanthrene, optionally being substituted by one or more identical or different groups L.

Preferred substituents of the above-mentioned aryl-, heteroaryl-, alicyclic- and heterocyclic groups (L) are, for example, solubility-promoting groups, such as alkyl or alkoxy and electron-withdrawing groups, such as fluorine, nitro or nitrile.

Particularly preferred substituents are, for example, halogen, CN, NO₂, CH₃, C₂H₅, OCH₃, OC₂H₅, COCH₃, COC₂H₅, COOCH₃, COOC₂H₅, CF₃, OCF₃, OCHF₂ or OC₂F₅.

Above and below "halogen" denotes F, Cl, Br or I.

5 Above and below, the terms "alkyl", "aryl", "heteroaryl", etc., also encompass polyvalent groups, for example alkylene, arylene, heteroarylene, etc.

The term "aryl" denotes an aromatic carbon group or a group derived there from.

10 The term "heteroaryl" denotes "aryl" in accordance with the above definition containing one or more heteroatoms.

15 Preferred alkyl groups are, for example, methyl, ethyl, n propyl, isopropyl, n butyl, isobutyl, s butyl, t butyl, 2 methylbutyl, n pentyl, s pentyl, cyclopentyl, n hexyl, cyclohexyl, 2 ethylhexyl, n heptyl, cycloheptyl, n octyl, cyclooctyl, n nonyl, n decyl, n undecyl, n dodecyl, dodecanyl, trifluoromethyl, perfluoro-n-butyl, 2,2,2-trifluoroethyl, perfluorooctyl, perfluorohexyl, etc.

20 Preferred alkoxy groups are, for example, methoxy, ethoxy, 2-methoxyethoxy, n-propoxy, i-propoxy, n-butoxy, i-butoxy, s-butoxy, t-butoxy, 2-methylbutoxy, n-pentoxy, n-hexoxy, n-heptoxy, n-octoxy, n-nonoxo, n-decoxy, n-undecoxy, n-dodecoxy.

25 Preferred alkenyl groups are, for example, ethenyl, propenyl, butenyl, pentenyl, cyclopentenyl, hexenyl, cyclohexenyl, heptenyl, cycloheptenyl, octenyl, cyclooctenyl.

30 Preferred alkynyl groups are, for example, ethynyl, propynyl, butynyl, pentynyl, hexynyl, octynyl.

35 Oxaalkyl, i.e. where one CH₂ group is replaced by -O-, is preferably straight-chain 2-oxapropyl (= methoxymethyl), 2- (= ethoxymethyl) or 3-oxabutyl (= 2-methoxyethyl), 2-, 3- or 4-oxapentyl, 2-, 3-, 4- or 5-oxahexyl, 2-, 3-, 4-, 5- or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-,

3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl, for example.

5 Preferred amino groups are, for example, dimethylamino, methylamino, methylphenylamino, phenylamino.

The term “chiral” in general is used to describe an object that is non-superimposable on its mirror image.

10 “Achiral” (non- chiral) objects are objects that are identical to their mirror image.

The terms “chiral nematic” and “cholesteric” are used synonymously in this application, unless explicitly stated otherwise.

15 The term “bimesogenic compound” relates to compounds comprising two mesogenic groups in the molecule. Just like normal mesogens, they can form many mesophases, depending on their structure. In particular, bimesogenic compound may induce a second nematic phase, when
20 added to a nematic liquid crystal medium. Bimesogenic compounds are also known as “dimeric liquid crystals”.

The term “director” is known in prior art and means the preferred orientation direction of the long molecular axes (in case of calamitic
25 compounds) or short molecular axes (in case of discotic compounds) of the liquid-crystalline molecules. In case of uniaxial ordering of such anisotropic molecules, the director is the axis of anisotropy.

30 The term “alignment” or “orientation” relates to alignment (orientation ordering) of anisotropic units of material such as small molecules or fragments of big molecules in a common direction named “alignment direction”. In an aligned layer of liquid-crystalline material, the liquid-crystalline director coincides with the alignment direction so that the alignment direction corresponds to the direction of the anisotropy axis of
35 the material.

5 The term "planar orientation/alignment", for example in a layer of an liquid-crystalline material, means that the long molecular axes (in case of calamitic compounds) or the short molecular axes (in case of discotic compounds) of a proportion of the liquid-crystalline molecules are oriented substantially parallel (about 180°) to the plane of the layer.

10 The term "homeotropic orientation/alignment", for example in a layer of a liquid-crystalline material, means that the long molecular axes (in case of calamitic compounds) or the short molecular axes (in case of discotic compounds) of a proportion of the liquid-crystalline molecules are oriented at an angle θ ("tilt angle") between about 80° to 90° relative to the plane of the layer.

15 The terms "uniform orientation" or "uniform alignment" of an liquid-crystalline material, for example in a layer of the material, mean that the long molecular axes (in case of calamitic compounds) or the short molecular axes (in case of discotic compounds) of the liquid-crystalline molecules are oriented substantially in the same direction. In other words, the lines of liquid-crystalline director are parallel.

20 The wavelength of light generally referred to in this application is 550 nm, unless explicitly specified otherwise.

The birefringence Δn herein is defined by the following equation

25
$$\Delta n = n_e - n_o$$

wherein n_e is the extraordinary refractive index and n_o is the ordinary refractive index and the effective average refractive index $n_{av.}$ is given by the following equation

30
$$n_{av.} = [(2 n_o^2 + n_e^2)/3]^{1/2}$$

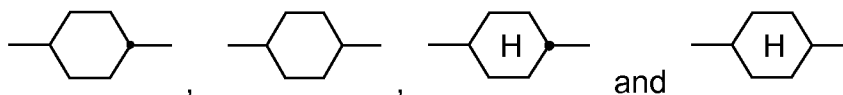
The extraordinary refractive index n_e and the ordinary refractive index n_o can be measured using an Abbe refractometer.

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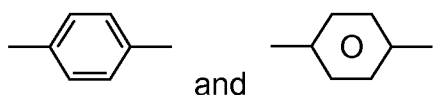
In the present application the term “dielectrically positive” is used for compounds or components with $\Delta\epsilon > 3.0$, “dielectrically neutral” with $-1.5 \leq \Delta\epsilon \leq 3.0$ and “dielectrically negative” with $\Delta\epsilon < -1.5$. $\Delta\epsilon$ is determined at a frequency of 1 kHz and at 20°C. The dielectric anisotropy of the respective compound is determined from the results of a solution of 10 % of the respective individual compound in a nematic host mixture. In case the solubility of the respective compound in the host medium is less than 10 % its concentration is reduced by a factor of 2 until the resultant medium is stable enough at least to allow the determination of its properties. Preferably, the concentration is kept at least at 5 %, however, in order to keep the significance of the results as high as possible. The capacitance of the test mixtures are determined both in a cell with homeotropic and with homogeneous alignment. The cell gap of both types of cells is approximately 20 μm . The voltage applied is a rectangular wave with a frequency of 1 kHz and a root mean square value typically of 0.5 V to 1.0 V; however, it is always selected to be below the capacitive threshold of the respective test mixture.

$\Delta\epsilon$ is defined as $(\epsilon_{||} - \epsilon_{\perp})$, whereas $\epsilon_{\text{av.}}$ is $(\epsilon_{||} + 2 \epsilon_{\perp}) / 3$. The dielectric permittivity of the compounds is determined from the change of the respective values of a host medium upon addition of the compounds of interest. The values are extrapolated to a concentration of the compounds of interest of 100 %. A typical host medium is ZLI-4792 or BL-087 both commercially available from Merck, Darmstadt.

For the present invention,



denote trans-1,4-cyclohexylene,



denote 1,4-phenylene.

Furthermore, the definitions as given in C. Tschierske, G. Pelzl and S. Diele, Angew. Chem. 2004, 116, 6340-6368 shall apply to non-defined terms related to liquid crystal materials in the instant application.

5

Detailed description

The invention relates to a compound of formula I,

10 $R^{11}\text{-MG}^{11}\text{-X}^{11}\text{-Sp}^{11}\text{-X}^{12}\text{-MG}^{12}\text{-R}^{12}$ I

wherein

15 R^{11} and R^{22} are each independently H, F, Cl, CN, NCS or a straight-chain or branched alkyl group, which may be unsubstituted, mono- or polysubstituted by halogen or CN and in which one or more non-adjacent and non-terminal CH_2 groups may be replaced, in each occurrence independently from one another, by -O-,
20 -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-, -O-CO-O-, -S-CO-, -CO-S-, -CH=CH-, -CH=CF-, -CF=CF- or -C≡C- in such a manner that oxygen atoms are not linked directly to one another,
25 preferably F, Cl, CN, a straight-chain or branched alkyl, alkenyl or alkoxy group which may be unsubstituted, mono- or polysubstituted by halogen or CN, more preferably F, CN or OCF_3 ,

30 MG^{11} and MG^{12} are each independently a mesogenic group, preferably, each independently a mesogenic group, which comprises one or more aryl-, heteroaryl-, alicyclic- and heterocyclic groups, which are optionally substituted by F, Cl, CN, OCH_3 , OCF_3 ,
35 preferably each independently a mesogenic group, which comprises two or more aryl-, heteroaryl-, alicyclic- and heterocyclic groups wherein two of these

rings are optionally be linked by a linking group selected from -CO-O-, -O-CO-, -CH₂-O-, -O-CH₂-, -CF₂O- and/or -OCF₂-,

5 Sp¹¹ is a spacer group comprising 1, 3 or 5 to 40 C atoms, wherein one or more non-adjacent and non-terminal CH₂ groups may also be replaced by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -O-CO-, -S-CO-, -O-COO-, -CO-S-, -CO-O-, -CF₂-, -CF₂O-, -OCF₂-, -C(OH)-, -CH(alkyl)-, 10 -CH(alkenyl)-, -CH(alkoxyl)-, -CH(oxaalkyl)-, -CH=CH- or -C≡C-, however in such a way that no two O-atoms are adjacent to one another and no two groups selected from -O-CO-, -S-CO-, -O-COO-, -CO-S-, -CO-O- and -CH=CH- are adjacent to each other, 15 preferably -(CH₂)_n-, with n 1, 3 or an integer from 5 to 15, more preferably from 3 to 11, most preferably an odd integer (i.e. 3, 5, 7, 9 or 11),

20 X¹¹ and X¹² are -CF₂-O-, -O-CF₂- or a single bond, whereby at least one of X¹¹ or X¹² denotes -CF₂-O-, or -O-CF₂-.

Preferably the unit -X¹¹-Sp¹¹-X¹²- denotes -CF₂O-Sp¹¹-CF₂O-, -OCF₂-Sp¹¹-OCF₂-, -OCF₂-Sp¹¹-CF₂O-, -CF₂O-Sp¹¹-OCF₂-, -CF₂O-Sp¹¹-, -OCF₂-Sp¹¹-, -Sp¹¹-CF₂O-, or -Sp¹¹-OCF₂-.

25 Preferred are compounds of formula I wherein the mesogenic groups R¹¹-MG¹¹- and R¹²-MG¹²- are different from each other.

30 In another embodiment, the compounds of formula I are preferably selected from compounds wherein the groups (R¹¹-MG¹¹-) and (R¹²-MG¹²-) in formula I are identical to each other.

Further preferred compounds of formula I are compounds selected from the group of compounds of formulae Ia and/or Ib,

35 R¹¹-MG¹¹-OCF₂-Sp¹¹-CF₂O-MG¹²-R¹² Ia



5 wherein R^{11} , R^{22} , MG^{11} , MG^{12} , Sp^{11} , have one of the meanings as given above under formula I.

Further preferred compounds of formula I are compounds selected from the group of compounds of formulae Ia-1 and/or Ib-1



15 wherein R^{11} , R^{22} , MG^{11} , MG^{12} have one of the meanings as given above under formula I and n denotes 1, 3 or an integer from 5 to 15, more preferably an integer from 3 to 11, most preferably an odd integer (i.e. 3, 5, 7, 9 or 11).

20 If R^{11} or R^{12} is an alkyl or alkoxy radical, this may be straight chain or branched. It is preferably straight-chain, has 2, 3, 4, 5, 6, 7 or 8 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy or octoxy, furthermore methyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradeoxy, for example.

30 If R^{11} or R^{12} is an alkenyl group are, this may be straight-chain or branched, preferably straight-chain, with up to 15 C atoms and more preferably, ethenyl, propenyl, butenyl, pentenyl, cyclopentenyl, hexenyl, cyclohexenyl, heptenyl, cycloheptenyl, octenyl, cyclooctenyl and corresponding isomers.

35 In case of compounds with two non-polar groups, one of R^{11} or R^{12} is preferably alkenyl or alkynyl, preferably alkenyl, with up to 15 C atoms and the other is preferably alkyl, alkenyl or alkynyl, most preferably alky or

alkenyl with 2 to 15 C atoms or alkoxy with 1 to 15, preferably 2 to 15, C atoms.

In addition, compounds of formula I containing an achiral branched group R¹¹ and/or R¹² may occasionally be of importance, for example, due to a reduction in the tendency towards crystallisation. Branched groups of this type generally do not contain more than one chain branch. Preferred achiral branched groups are isopropyl, isobutyl (=methylpropyl), isopentyl (=3-methylbutyl), isopropoxy, 2-methyl-propoxy and 3-methylbutoxy.

In case of a compounds with a terminal polar group, R¹¹ and/or R¹² are selected from CN, NO₂, halogen, OCH₃, OCN, SCN, COR^x, COOR^x or a mono- oligo- or polyfluorinated alkyl or alkoxy group with 1 to 4 C atoms. R^x is optionally fluorinated alkyl with 1 to 4, preferably 1 to 3 C atoms. Halogen is preferably F or Cl.

Especially preferably R¹¹ and R¹² in formula I are selected of H, alkenyl, F, Cl, CN, NO₂, OCH₃, COCH₃, COC₂H₅, COOCH₃, COOC₂H₅, CF₃, C₂F₅, OCF₃, OCHF₂ and OC₂F₅, in particular of ethenyl, propenyl, butenyl, F, Cl, CN, CF₃, OCH₃ and OCF₃, especially of propenyl, butenyl, F, CN and OCF₃.

In a preferred embodiment the compounds of formula Ia-1 are selected from the following compounds:

25	R ¹¹ -Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-R ¹²	Ia-1-	I
	R ¹¹ -PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-R ¹²	Ia-1-	II
	R ¹¹ -PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-R ¹²	Ia-1-	III
30	R ¹¹ -Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	Ia-1-	IV
	R ¹¹ -PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	Ia-1-	V
	R ¹¹ -Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	Ia-1-	VI
	R ¹¹ -Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	Ia-1-	VII
35	R ¹¹ -Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-PheL-R ¹²	Ia-1-	VIII

	R^{11} -PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	la-1- IX
	R^{11} -PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	la-1- X
5	R^{11} -PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-PheL-R ¹²	la-1- XI
	wherein, R ¹¹ , R ¹² have one of the meanings as given above and	

	Phe	is 1,4-phenylene,
	PheL	is 1,4-phenylene, which is substituted by one, two or three fluorine atoms, by one or two Cl atoms or by one Cl atom and one F atom and
10	Z	has one of the meanings of Z ¹¹ as given under partial formula II and if present twice, at least one is preferably selected from -C≡C-, -C=C-, -COO-, -OCO-, -O-CO-O-, -OCH ₂ -, -CH ₂ O-, -OCF ₂ - or -CF ₂ O-.
15		

In a preferred embodiment the compounds of formula Ib-1 are selected from the following compounds:

20	R^{11} -Phe-(CH ₂) _n -CF ₂ O-Phe-R ¹²	Ib-1- I
	R^{11} -PheL-(CH ₂) _n -CF ₂ O-Phe-R ¹²	Ib-1- II
	R^{11} -Phe-(CH ₂) _n -CF ₂ O-PheL-R ¹²	Ib-1- III
	R^{11} -PheL-(CH ₂) _n -CF ₂ O-PheL-R ¹²	Ib-1- IV
25	R^{11} -Phe-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	Ib-1- V
	R^{11} -PheL-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	Ib-1- VI
	R^{11} -Phe-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	Ib-1- VII
	R^{11} -Phe-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	Ib-1- VIII
	R^{11} -Phe-(CH ₂) _n -CF ₂ O-PheL-Z-PheL-R ¹²	Ib-1- IX
30	R^{11} -PheL-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	Ib-1- X
	R^{11} -PheL-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	Ib-1- XI
	R^{11} -PheL-(CH ₂) _n -CF ₂ O-PheL-Z-PheL-R ¹²	Ib-1- XII
35	R^{11} -Phe-OCF ₂ -(CH ₂) _n -Phe-R ¹²	Ib-1- XIII
	R^{11} -PheL-OCF ₂ -(CH ₂) _n -Phe-R ¹²	Ib-1- XIV

	$R^{11}\text{-Phe-OCF}_2\text{-(CH}_2\text{)}_n\text{-PheL-R}^{12}$	lb-1-	XV
	$R^{11}\text{-PheL-OCF}_2\text{-(CH}_2\text{)}_n\text{-PheL-R}^{12}$	lb-1-	XVI
5	$R^{11}\text{-Phe-OCF}_2\text{-(CH}_2\text{)}_n\text{-Phe-Z-Phe-R}^{12}$	lb-1-	XVII
	$R^{11}\text{-PheL-OCF}_2\text{-(CH}_2\text{)}_n\text{-Phe-Z-Phe-R}^{12}$	lb-1-	XVIII
	$R^{11}\text{-Phe-OCF}_2\text{-(CH}_2\text{)}_n\text{-PheL-Z-Phe-R}^{12}$	lb-1-	XIX
	$R^{11}\text{-Phe-OCF}_2\text{-(CH}_2\text{)}_n\text{-Phe-Z-PheL-R}^{12}$		
	$R^{11}\text{-Phe-OCF}_2\text{-(CH}_2\text{)}_n\text{-PheL-Z-PheL-R}^{12}$	lb-1-	XX
10	$R^{11}\text{-PheL-OCF}_2\text{-(CH}_2\text{)}_n\text{-PheL-Z-Phe-R}^{12}$	lb-1-	XXI
	$R^{11}\text{-PheL-OCF}_2\text{-(CH}_2\text{)}_n\text{-Phe-Z-PheL-R}^{12}$	lb-1-	XXII
	$R^{11}\text{-PheL-OCF}_2\text{-(CH}_2\text{)}_n\text{-PheL-Z-PheL-R}^{12}$	lb-1-	XXIII

wherein, R^{11} , R^{12} , Phe, PheL, Z and n have one of the meanings as given above.

15

Further preferred compounds of formula I are compounds in which

MG¹¹ and MG¹² are independently from one another a group of (partial) formula I*

20

$-A^{11}\text{-(Z}^{11}\text{-A}^{12}\text{)}_k-$ I*

Wherein

25 A¹¹ and A¹² each independently in each occurrence denote, 1,4-phenylene, wherein in addition one or more CH groups may be replaced by N, trans-1,4-cyclohexylene in which, in addition, one or two non-adjacent CH₂ groups may be replaced by O and/or S,

30 1,4-cyclohexylene, naphthalene-2,6-diyl, decahydro-naphthalene-2,6-diyl, 1,2,3,4-tetrahydro-naphthalene-2,6-diyl, it being possible for all these groups to be unsubstituted, mono-, di-, tri- or tetrasubstituted with F, Cl, CN or alkyl, alkoxy, alkylcarbonyl or

35 alkoxycarbonyl groups, wherein one or more H atoms may be substituted by F or Cl,

preferably each independently in each occurrence 1,4-phenylene, wherein in addition one or more CH groups may be replaced by N or trans-1,4-cyclohexylene in which, in addition, one or two non-adjacent CH₂ groups may be replaced by O and/or S, it being possible for both ring groups to be unsubstituted, mono-, di-, tri- or tetrasubstituted with F, Cl, CN or alkyl, alkoxy, alkylcarbonyl or alkoxy carbonyl groups, wherein one or more H atoms may be substituted by F or Cl,

Z¹¹ are, independently of each other in each occurrence, a single bond, -COO-, -OCO-, -O-CO-O-, -OCH₂-, -CH₂O-, -OCF₂-, -CF₂O-, -CH₂CH₂-, -(CH₂)₄-, -CF₂CF₂-, -CH=CH-, -CF=CF-, -CH=CH-COO-, -OCO-CH=CH- or -C≡C-, optionally substituted with one or more of F, S and/or Si, preferably a single bond,

k is 0, 1, 2, 3 or 4, preferably 1, 2 or 3 and, most preferably 1 or 2.

A smaller group of preferred mesogenic groups comprising only 6-membered rings is listed below. For reasons of simplicity, Phe in these groups is 1,4-phenylene, PheL is a 1,4-phenylene group which is substituted by 1 to 4 groups L, with L being preferably F, Cl, CN, OH, NO₂ or an optionally fluorinated alkyl, alkoxy or alkanoyl group with 1 to 7 C atoms, very preferably F, Cl, CN, OH, NO₂, CH₃, C₂H₅, OCH₃, OC₂H₅, COCH₃, COC₂H₅, COOCH₃, COOC₂H₅, CF₃, OCF₃, OCHF₂, OC₂F₅, in particular F, Cl, CN, CH₃, C₂H₅, OCH₃, COCH₃ and OCF₃, most preferably F, Cl, CH₃, OCH₃ and COCH₃ and Cyc is 1,4-cyclohexylene. This list comprises the subformulae shown below as well as their mirror images

-Phe-Z-Phe-
-Phe-Z-Cyc-

I*-1

I*-2

	-Cyc-Z-Cyc-	I*-3
	-Phe-Z-PheL-	I*-4
	-PheL-Z-Phe-	I*-5
	-PheL-Z-Cyc-	I*-6
5	-PheL-Z-PheL-	I*-7
	-Phe-Z-Phe-Z-Phe-	I*-8
	-Phe-Z-Phe-Z-Cyc-	I*-9
	-Phe-Z-Cyc-Z-Phe-	I*-10
	-Cyc-Z-Phe-Z-Cyc-	I*-11
10	-Phe-Z-Cyc-Z-Cyc-	I*-12
	-Cyc-Z-Cyc-Z-Cyc-	I*-13
	-Phe-Z-Phe-Z-PheL-	I*-14
	-Phe-Z-PheL-Z-Phe-	I*-15
	-PheL-Z-Phe-Z-Phe-	I*-16
15	-PheL-Z-Phe-Z-PheL-	I*-17
	-PheL-Z-PheL-Z-Phe-	I*-18
	-PheL-Z-PheL-Z-PheL-	I*-19
	-Phe-Z-PheL-Z-Cyc-	I*-20
	-Phe-Z-Cyc-Z-PheL-	I*-21
20	-Cyc-Z-Phe-Z-PheL-	I*-22
	-PheL-Z-Cyc-Z-PheL-	I*-23
	-PheL-Z-PheL-Z-Cyc-	I*-24
	-PheL-Z-Cyc-Z-Cyc-	I*-25
	-Cyc-Z-PheL-Z-Cyc-	I*-26
25	wherein	

	Cyc	is 1,4-cyclohexylene, preferably trans-1,4-cyclohexylene,
	Phe	is 1,4-phenylene,
30	PheL	is 1,4-phenylene, which is substituted by one, two or three fluorine atoms, by one or two Cl atoms or by one Cl atom and one F atom and
	Z	has one of the meanings of Z ¹¹ as given under partial formula II and if present twice, at least one is preferably
35		selected from -C≡C-, -C=C-, -COO-, -OCO-, -O-CO-O-, -OCH ₂ -, -CH ₂ O-, -OCF ₂ - or -CF ₂ O-.

Particularly preferred are the sub-formulae I*-1, I*-4, I*-5, I*-7, I*-8, I*-14, I*-15, I*-16, I*-17, I*-18 and I*-19, wherein Z in each case independently has one of the meanings of Z¹¹ as given under formula I and if present twice, preferably one of Z is -COO-, -OCO-, -CH₂-O-, -O-CH₂-, -CF₂-O- or -O-CF₂-.

In a preferred embodiment the compounds of formula Ia-1 are selected from the following compounds:

10	R ¹¹ -Phe-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	Ia-1-	1
	R ¹¹ -Phe-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	Ia-1-	2
	R ¹¹ -PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	Ia-1-	3
15	R ¹¹ -PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	Ia-1-	4
	R ¹¹ -PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	Ia-1-	5
	R ¹¹ -Phe-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	Ia-1-	6
20	R ¹¹ -PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	Ia-1-	7
	R ¹¹ -PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	Ia-1-	8
	R ¹¹ -PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-PheL-R ¹²	Ia-1-	9
25	R ¹¹ -Phe-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	Ia-1-	10
	R ¹¹ -PheL-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	Ia-1-	11
	R ¹¹ -Phe-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	Ia-1-	12
	R ¹¹ -Phe-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	Ia-1-	13
30	R ¹¹ -Phe-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	Ia-1-	14
	R ¹¹ -Phe-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	Ia-1-	15
	R ¹¹ -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	Ia-1-	16
	R ¹¹ -PheL-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	Ia-1-	17
35	R ¹¹ -PheL-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	Ia-1-	18
	R ¹¹ -PheL-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	Ia-1-	19

5	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	la-1-	20
	R^{11} -Phe-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	la-1-	21
	R^{11} -Phe-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	la-1-	22
	R^{11} -Phe-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	la-1-	23
	R^{11} -Phe-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	la-1-	24
10	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	la-1-	25
	R^{11} -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	la-1-	26
	R^{11} -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	la-1-	27
	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	la-1-	28
	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	la-1-	29
15	R^{11} -Phe-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-PheL-R ¹²	la-1-	30
	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	la-1-	31
	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	la-1-	32
	R^{11} -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-PheL-R ¹²	la-1-	33
	R^{11} -PheL-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-PheL-R ¹²	la-1-	34
20	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-PheL-R ¹²	la-1-	35
	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-PheL-R ¹²	la-1-	36
25	R^{11} -Phe-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-Phe-R ¹²	la-1-	37
	R^{11} -PheL-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-Phe-R ¹²	la-1-	38
	R^{11} -Phe-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-Phe-R ¹²	la-1-	39
	R^{11} -Phe-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-Phe-R ¹²	la-1-	40
	R^{11} -Phe-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-Z-Phe-R ¹²	la-1-	41
30	R^{11} -Phe-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-Z-Phe-R ¹²	la-1-	42
	R^{11} -Phe-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-PheL-R ¹²	la-1-	43
35	R^{11} -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-Phe-R ¹²	la-1-	44
	R^{11} -PheL-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-Phe-R ¹²	la-1-	45
	R^{11} -PheL-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-Z-Phe-R ¹²	la-1-	46

5	R^{11} -PheL-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-Z-Phe-R ¹²	la-1-	47
	R^{11} -PheL-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-PheL-R ¹²	la-1-	48
	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-Phe-R ¹²	la-1-	49
	R^{11} -Phe-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-Z-Phe-R ¹²	la-1-	50
	R^{11} -Phe-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-Z-Phe-R ¹²	la-1-	51
	R^{11} -Phe-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-Z-Phe-R ¹²	la-1-	52
10	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-Phe-R ¹²	la-1-	53
	R^{11} -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-Z-Phe-R ¹²	la-1-	54
	R^{11} -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-Z-Phe-R ¹²	la-1-	55
	R^{11} -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-PheL-R ¹²	la-1-	56
	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-Z-Phe-R ¹²	la-1-	57
	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-Z-Phe-R ¹²	la-1-	58
15	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-Phe-Z-Phe-R ¹²	la-1-	59
	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-Z-Phe-R ¹²	la-1-	60
	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-PheL-R ¹²	la-1-	61
	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-PheL-Z-Phe-R ¹²	la-1-	62
	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Z-PheL-Z-PheL-R ¹²	la-1-	63
	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-PheL-Z-Phe-R ¹²	la-1-	64
20	R^{11} -PheL-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-PheL-Z-PheL-R ¹²	la-1-	65
	R^{11} -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-PheL-Z-PheL-R ¹²	la-1-	66
	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Z-PheL-Z-PheL-R ¹²	la-1-	67

wherein, R¹¹, R¹², Phe, PheL, Z and n have one of the meanings as given above.

30

In a preferred embodiment the compounds of formula Ib-1 are selected from the following compounds:

35	R^{11} -Phe-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	Ib-1-	1
	R^{11} -Phe-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-R ¹²	Ib-1-	2

	R^{11} -PheL-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-R ¹²	lb-1-	3
	R^{11} -Phe-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	lb-1-	4
	R^{11} -PheL-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	lb-1-	5
5	R^{11} -PheL-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-R ¹²	lb-1-	6
	R^{11} -PheL-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-PheL-R ¹²	lb-1-	7
	R^{11} -Phe-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-Phe-R ¹²	lb-1-	8
10	R^{11} -PheL-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	lb-1-	9
	R^{11} -PheL-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	lb-1-	10
	R^{11} -Phe-Z-PheL-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	lb-1-	11
15	R^{11} -PheL-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-Phe-R ¹²	lb-1-	12
	R^{11} -PheL-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-PheL-R ¹²	lb-1-	13
	R^{11} -PheL-Z-PheL-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	lb-1-	14
	R^{11} -PheL-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	lb-1-	15
20	R^{11} -PheL-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-PheL-R ¹²	lb-1-	16
	R^{11} -Phe-Z-Phe-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	lb-1-	17
25	R^{11} -Phe-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-R ¹²	lb-1-	18
	R^{11} -PheL-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-R ¹²	lb-1-	19
	R^{11} -Phe-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-R ¹²	lb-1-	20
	R^{11} -Phe-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-R ¹²	lb-1-	21
30	R^{11} -Phe-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -PheL-Z-Phe-R ¹²	lb-1-	22
	R^{11} -Phe-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-PheL-R ¹²	lb-1-	23
	R^{11} -PheL-Z-Phe-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	lb-1-	24
	R^{11} -Phe-Z-PheL-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	lb-1-	25
35	R^{11} -Phe-Z-Phe-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	lb-1-	26

	R^{11} -Phe-Z-Phe-Z-Phe-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	lb-1-	27
	R^{11} -Phe-Z-Phe-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	lb-1-	28
5	R^{11} -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-R ¹²	lb-1-	29
	R^{11} -PheL-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-R ¹²	lb-1-	30
	R^{11} -PheL-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -PheL-Z-Phe-R ¹²	lb-1-	31
	R^{11} -PheL-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-PheL-R ¹²	lb-1-	32
10	R^{11} -PheL-Z-PheL-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	lb-1-	33
	R^{11} -PheL-Z-Phe-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	lb-1-	34
	R^{11} -PheL-Z-Phe-Z-Phe-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	lb-1-	35
	R^{11} -PheL-Z-Phe-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	lb-1-	36
15	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-R ¹²	lb-1-	37
	R^{11} -Phe-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -PheL-Z-Phe-R ¹²	lb-1-	38
	R^{11} -Phe-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-PheL-R ¹²	lb-1-	39
	R^{11} -Phe-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-Phe-R ¹²	lb-1-	40
	R^{11} -Phe-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-PheL-R ¹²	lb-1-	41
20	R^{11} -Phe-Z-PheL-Z-PheL(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	lb-1-	42
	R^{11} -Phe-Z-PheL-Z-Phe-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	lb-1-	43
	R^{11} -Phe-Z-PheL-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	lb-1-	44
	R^{11} -Phe-Z-Phe-Z-PheL-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	lb-1-	45
	R^{11} -Phe-Z-Phe-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	lb-1-	46
25	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-R ¹²	lb-1-	47
	R^{11} -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -PheL-Z-Phe-R ¹²	lb-1-	48
	R^{11} -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-PheL-R ¹²	lb-1-	49
	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-Phe-R ¹²	lb-1-	50
	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-PheL-R ¹²	lb-1-	51
	R^{11} -Phe-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-PheL-R ¹²	lb-1-	52
30			
35	R^{11} -PheL-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-R ¹²	lb-1-	53

	R ¹¹ -PheL-Z-PheL-Z-Phe-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	lb-1-	54
	R ¹¹ -PheL-Z-PheL-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	lb-1-	55
	R ¹¹ -Phe-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	lb-1-	56
	R ¹¹ -Phe-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	lb-1-	57
5	R ¹¹ -Phe-Z-Phe-Z-PheL-(CH ₂) _n -CF ₂ O-PheL-Z-PheL-R ¹²	lb-1-	58
	R ¹¹ -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-Phe-R ¹²	lb-1-	59
	R ¹¹ -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-PheL-R ¹²	lb-1-	60
10	R ¹¹ -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -PheL-Z-PheL-R ¹²	lb-1-	61
	R ¹¹ -PheL-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-PheL-R ¹²	lb-1-	62
	R ¹¹ -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-PheL-R ¹²	lb-1-	63
	R ¹¹ -PheL-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-R ¹²	lb-1-	64
15	R ¹¹ -PheL-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-R ¹²	lb-1-	65
	R ¹¹ -PheL-Z-PheL-Z-Phe-(CH ₂) _n -CF ₂ O-PheL-Z-PheL-R ¹²	lb-1-	66
	R ¹¹ -PheL-Z-Phe-Z-PheL-(CH ₂) _n -CF ₂ O-PheL-Z-PheL-R ¹²	lb-1-	67
	R ¹¹ -Phe-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-PheL-Z-PheL-R ¹²	lb-1-	68
20	R ¹¹ -PheL-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-PheL-Z-PheL-R ¹²	lb-1-	69
	R ¹¹ -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-PheL-R ¹²	lb-1-	70
	R ¹¹ -Phe-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-Z-Phe-R ¹²	lb-1-	71
25	R ¹¹ -PheL-Z-Phe-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-Phe-R ¹²	lb-1-	72
	R ¹¹ -Phe-Z-PheL-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-Phe-R ¹²	lb-1-	73
	R ¹¹ -Phe-Z-Phe-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-Phe-R ¹²	lb-1-	74
	R ¹¹ -Phe-Z-Phe-Z-Phe-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-Z-Phe-R ¹²	lb-1-	75
30	R ¹¹ -Phe-Z-Phe-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-Z-Phe-R ¹²	lb-1-	76
	R ¹¹ -Phe-Z-Phe-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-PheL-R ¹²	lb-1-	77
	R ¹¹ -PheL-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-Z-Phe-R ¹²	lb-1-	78
35	R ¹¹ -Phe-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-Z-Phe-R ¹²	lb-1-	79
	R ¹¹ -Phe-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-Z-Phe-R ¹²	lb-1-	80

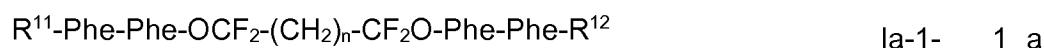
	R^{11} -Phe-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -PheL-Z-Phe-Z-Phe-R ¹²	lb-1-	81
	R^{11} -Phe-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-PheL-Z-Phe-R ¹²	lb-1-	82
	R^{11} -Phe-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-Z-PheL-R ¹²	lb-1-	83
5	R^{11} -PheL-Z-PheL-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-Phe-R ¹²	lb-1-	84
	R^{11} -PheL-Z-Phe-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-Phe-R ¹²	lb-1-	85
	R^{11} -PheL-Z-Phe-Z-Phe-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-Z-Phe-R ¹²	lb-1-	86
	R^{11} -PheL-Z-Phe-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-Z-Phe-R ¹²	lb-1-	87
10	R^{11} -PheL-Z-Phe-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-PheL-R ¹²	lb-1-	88
	R^{11} -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-Z-Phe-R ¹²	lb-1-	89
	R^{11} -PheL-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-Z-Phe-R ¹²	lb-1-	90
	R^{11} -PheL-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -PheL-Z-Phe-Z-Phe-R ¹²	lb-1-	91
15	R^{11} -PheL-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-PheL-Z-Phe-R ¹²	lb-1-	92
	R^{11} -PheL-Z-Phe-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-Z-PheL-R ¹²	lb-1-	93
	R^{11} -Phe-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-Phe-R ¹²	lb-1-	94
	R^{11} -Phe-Z-PheL-Z-Phe-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-Z-Phe-R ¹²	lb-1-	95
20	R^{11} -Phe-Z-PheL-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-Z-Phe-R ¹²	lb-1-	96
	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-Z-Phe-R ¹²	lb-1-	97
	R^{11} -Phe-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -PheL-Z-Phe-Z-Phe-R ¹²	lb-1-	98
	R^{11} -Phe-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-PheL-Z-Phe-R ¹²	lb-1-	99
25	R^{11} -Phe-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-Phe-Z-Phe-R ¹²	lb-1-	100
	R^{11} -PheL-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-Phe-R ¹²	lb-1-	101
	R^{11} -PheL-Z-PheL-Z-Phe-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-Z-Phe-R ¹²	lb-1-	102
30	R^{11} -PheL-Z-PheL-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-Z-Phe-R ¹²	lb-1-	103
	R^{11} -PheL-Z-PheL-Z-Phe-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-PheL-R ¹²	lb-1-	104
	R^{11} -Phe-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-Z-Phe-R ¹²	lb-1-	105
	R^{11} -Phe-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-Z-Phe-R ¹²	lb-1-	106
35	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-Z-Phe-R ¹²	lb-1-	107

	R^{11} -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -PheL-Z-Phe-Z-Phe-R ¹²	lb-1-	108
	R^{11} -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-PheL-Z-Phe-R ¹²	lb-1-	109
	R^{11} -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-Z-PheL-R ¹²	lb-1-	110
	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-Phe-Z-Phe-R ¹²	lb-1-	111
5	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-PheL-Z-Phe-R ¹²	lb-1-	112
	R^{11} -PheL-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-PheL-Z-Phe-Z-Phe-R ¹²	lb-1-	113
	R^{11} -PheL-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-Z-Phe-R ¹²	lb-1-	114
10	R^{11} -PheL-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-Phe-Z-PheL-R ¹²	lb-1-	115
	R^{11} -Phe-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-PheL-Z-PheL-Z-Phe-R ¹²	lb-1-	116
	R^{11} -Phe-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-Phe-Z-PheL-Z-PheL-R ¹²	lb-1-	117
	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-Phe-Z-Phe-R ¹²	lb-1-	118
15	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-PheL-Z-Phe-R ¹²	lb-1-	119
	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-Phe-Z-PheL-R ¹²	lb-1-	120
	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-PheL-Z-Phe-R ¹²	lb-1-	121
	R^{11} -Phe-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -Phe-Z-PheL-Z-PheL-R ¹²	lb-1-	122
20	R^{11} -PheL-Z-PheL-Z-PheL-(CH ₂) _n -CF ₂ O-PheL-Z-PheL-Z-Phe-R ¹²	lb-1-	123
	R^{11} -PheL-Z-Phe-Z-PheL-(CH ₂) _n -CF ₂ O-PheL-Z-PheL-Z-PheL-R ¹²	lb-1-	124
	R^{11} -PheL-Z-PheL-Z-Phe-(CH ₂) _n -CF ₂ O-PheL-Z-PheL-Z-PheL-R ¹²	lb-1-	125
25	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-PheL-Z-Phe-R ¹²	lb-1-	126
	R^{11} -PheL-Z-Phe-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-PheL-Z-PheL-R ¹²	lb-1-	127
	R^{11} -PheL-Z-PheL-Z-Phe-OCF ₂ -(CH ₂) _n -PheL-Z-PheL-Z-PheL-R ¹²	lb-1-	128
30	R^{11} -PheL-Z-PheL-Z-PheL-OCF ₂ -(CH ₂) _n -PheL-Z-PheL-Z-PheL-R ¹²	lb-1-	129

wherein, R¹¹, R¹², Phe, PheL, Z and n have one of the meanings as given above.

Further preferred compounds of formula Ia-1 are selected from the group of compounds with the following formulae:

35



	R^{11} -Phe-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	la-1-	2 a
	R^{11} -PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	la-1-	3 a
5	R^{11} -PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	la-1-	4 a
	R^{11} -PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	la-1-	5 a
	R^{11} -Phe-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	la-1-	6 a
10	R^{11} -PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	la-1-	7 a
	R^{11} -PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	la-1-	8 a
	R^{11} -PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-PheL-R ¹²	la-1-	9 a
15	R^{11} -Phe-Phe-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	la-1-	10 a
	R^{11} -PheL-Phe-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	la-1-	11 a
	R^{11} -Phe-PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	la-1-	12 a
20	R^{11} -Phe-Phe-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	la-1-	13 a
	R^{11} -Phe-Phe-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	la-1-	14 a
	R^{11} -Phe-Phe-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	la-1-	15 a
25	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	la-1-	16 a
	R^{11} -PheL-Phe-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	la-1-	17 a
	R^{11} -PheL-Phe-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	la-1-	18 a
30	R^{11} -PheL-Phe-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	la-1-	19 a
	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	la-1-	20 a
	R^{11} -Phe-PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	la-1-	21 a
35	R^{11} -Phe-PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	la-1-	22 a
	R^{11} -Phe-Phe-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	la-1-	23 a
	R^{11} -Phe-Phe-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	la-1-	24 a
35	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	la-1-	25 a
	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	la-1-	26 a
	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	la-1-	27 a

	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	la-1-	28 a
	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	la-1-	29 a
	R^{11} -Phe-Phe-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-PheL-R ¹²	la-1-	30 a
5	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	la-1-	31 a
	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	la-1-	32 a
	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-PheL-R ¹²	la-1-	33 a
	R^{11} -PheL-Phe-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-PheL-R ¹²	la-1-	34 a
10	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-PheL-R ¹²	la-1-	35 a
	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-PheL-R ¹²	la-1-	36 a
	R^{11} -Phe-Phe-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-Phe-R ¹²	la-1-	37 a
15	R^{11} -PheL-Phe-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-Phe-R ¹²	la-1-	38 a
	R^{11} -Phe-PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-Phe-R ¹²	la-1-	39 a
	R^{11} -Phe-Phe-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-Phe-R ¹²	la-1-	40 a
	R^{11} -Phe-Phe-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Phe-Phe-R ¹²	la-1-	41 a
20	R^{11} -Phe-Phe-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-PheL-Phe-R ¹²	la-1-	42 a
	R^{11} -Phe-Phe-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-PheL-R ¹²	la-1-	43 a
	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-Phe-R ¹²	la-1-	44 a
25	R^{11} -PheL-Phe-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-Phe-R ¹²	la-1-	45 a
	R^{11} -PheL-Phe-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Phe-Phe-R ¹²	la-1-	46 a
	R^{11} -PheL-Phe-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-PheL-Phe-R ¹²	la-1-	47 a
	R^{11} -PheL-Phe-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-PheL-R ¹²	la-1-	48 a
	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-Phe-R ¹²	la-1-	49 a
30	R^{11} -Phe-PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Phe-Phe-R ¹²	la-1-	50 a
	R^{11} -Phe-PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-PheL-Phe-R ¹²	la-1-	51 a
	R^{11} -Phe-Phe-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Phe-Phe-R ¹²	la-1-	52 a
	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-Phe-R ¹²	la-1-	53 a
35	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Phe-Phe-R ¹²	la-1-	54 a

5	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-PheL-Phe-R ¹²	la-1-	55	a
	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-PheL-R ¹²	la-1-	56	a
	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Phe-Phe-R ¹²	la-1-	57	a
	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-PheL-Phe-R ¹²	la-1-	58	a
10	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-Phe-Phe-R ¹²	la-1-	59	a
	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-PheL-Phe-R ¹²	la-1-	60	a
	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-Phe-PheL-R ¹²	la-1-	61	a
	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-PheL-Phe-R ¹²	la-1-	62	a
	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-Phe-PheL-PheL-R ¹²	la-1-	63	a
15	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-PheL-Phe-R ¹²	la-1-	64	a
	R^{11} -PheL-Phe-PheL-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-PheL-PheL-R ¹²	la-1-	65	a
	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -CF ₂ O-PheL-PheL-PheL-R ¹²	la-1-	66	a

wherein, R¹¹, R¹², Phe and PheL have one of the meanings as given above and n denotes 5, 7, 9 or 11.

Further preferred compounds of formula Ib-1 are selected from the following compounds:

25	R^{11} -Phe-Phe-(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	Ib-1-	1	a
	R^{11} -Phe-PheL-OCF ₂ -(CH ₂) _n -Phe-Phe-R ¹²	Ib-1-	2	a
	R^{11} -PheL-Phe-OCF ₂ -(CH ₂) _n -Phe-Phe-R ¹²	Ib-1-	3	a
30	R^{11} -Phe-PheL-(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	Ib-1-	4	a
	R^{11} -PheL-Phe-(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	Ib-1-	5	a
35	R^{11} -PheL-PheL-OCF ₂ -(CH ₂) _n -Phe-Phe-R ¹²	Ib-1-	6	a
	R^{11} -PheL-Phe-OCF ₂ -(CH ₂) _n -Phe-PheL-R ¹²	Ib-1-	7	a
	R^{11} -Phe-PheL-OCF ₂ -(CH ₂) _n -PheL-Phe-R ¹²	Ib-1-	8	a

	R^{11} -PheL-PheL-(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	lb-1-	9	a
	R^{11} -PheL-Phe-(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	lb-1-	10	a
	R^{11} -Phe-PheL-(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	lb-1-	11	a
5	R^{11} -PheL-PheL-OCF ₂ -(CH ₂) _n -PheL-Phe-R ¹²	lb-1-	12	a
	R^{11} -PheL-PheL-OCF ₂ -(CH ₂) _n -Phe-PheL-R ¹²	lb-1-	13	a
	R^{11} -PheL-PheL-(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	lb-1-	14	a
10	R^{11} -PheL-PheL-(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	lb-1-	15	a
	R^{11} -PheL-PheL-OCF ₂ -(CH ₂) _n -PheL-PheL-R ¹²	lb-1-	16	a
	R^{11} -Phe-Phe-Phe-(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	lb-1-	17	a
15	R^{11} -Phe-Phe-Phe-OCF ₂ -(CH ₂) _n -Phe-Phe-R ¹²	lb-1-	18	a
	R^{11} -PheL-Phe-Phe-OCF ₂ -(CH ₂) _n -Phe-Phe-R ¹²	lb-1-	19	a
	R^{11} -Phe-PheL-Phe-OCF ₂ -(CH ₂) _n -Phe-Phe-R ¹²	lb-1-	20	a
	R^{11} -Phe-Phe-PheL-OCF ₂ -(CH ₂) _n -Phe-Phe-R ¹²	lb-1-	21	a
20	R^{11} -Phe-Phe-Phe-OCF ₂ -(CH ₂) _n -PheL-Phe-R ¹²	lb-1-	22	a
	R^{11} -Phe-Phe-Phe-OCF ₂ -(CH ₂) _n -Phe-PheL-R ¹²	lb-1-	23	a
	R^{11} -PheL-Phe-Phe-(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	lb-1-	24	a
25	R^{11} -Phe-PheL-Phe-(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	lb-1-	25	a
	R^{11} -Phe-Phe-PheL-(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	lb-1-	26	a
	R^{11} -Phe-Phe-Phe-(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	lb-1-	27	a
	R^{11} -Phe-Phe-Phe-(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	lb-1-	28	a
30	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -Phe-Phe-R ¹²	lb-1-	29	a
	R^{11} -PheL-Phe-PheL-OCF ₂ -(CH ₂) _n -Phe-Phe-R ¹²	lb-1-	30	a
	R^{11} -PheL-Phe-Phe-OCF ₂ -(CH ₂) _n -PheL-Phe-R ¹²	lb-1-	31	a
	R^{11} -PheL-Phe-Phe-OCF ₂ -(CH ₂) _n -Phe-PheL-R ¹²	lb-1-	32	a
35	R^{11} -PheL-PheL-Phe-(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	lb-1-	33	a

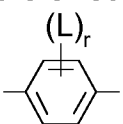
	R^{11} -PheL-Phe-PheL-(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	lb-1-	34	a
	R^{11} -PheL-Phe-Phe-(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	lb-1-	35	a
	R^{11} -PheL-Phe-Phe-(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	lb-1-	36	a
5	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -Phe-Phe-R ¹²	lb-1-	37	a
	R^{11} -Phe-PheL-Phe-OCF ₂ -(CH ₂) _n -PheL-Phe-R ¹²	lb-1-	38	a
	R^{11} -Phe-PheL-Phe-OCF ₂ -(CH ₂) _n -Phe-PheL-R ¹²	lb-1-	39	a
	R^{11} -Phe-Phe-PheL-OCF ₂ -(CH ₂) _n -PheL-Phe-R ¹²	lb-1-	40	a
10	R^{11} -Phe-Phe-PheL-OCF ₂ -(CH ₂) _n -Phe-PheL-R ¹²	lb-1-	41	a
	R^{11} -Phe-PheL-PheL-(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	lb-1-	42	a
	R^{11} -Phe-PheL-Phe-(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	lb-1-	43	a
	R^{11} -Phe-PheL-Phe-(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	lb-1-	44	a
15	R^{11} -Phe-Phe-PheL-(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	lb-1-	45	a
	R^{11} -Phe-Phe-PheL-(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	lb-1-	46	a
	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -Phe-Phe-R ¹²	lb-1-	47	a
	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -PheL-Phe-R ¹²	lb-1-	48	a
20	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -Phe-PheL-R ¹²	lb-1-	49	a
	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -PheL-Phe-R ¹²	lb-1-	50	a
	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -Phe-PheL-R ¹²	lb-1-	51	a
	R^{11} -Phe-Phe-PheL-OCF ₂ -(CH ₂) _n -PheL-PheL-R ¹²	lb-1-	52	a
25	R^{11} -PheL-PheL-PheL-(CH ₂) _n -CF ₂ O-Phe-Phe-R ¹²	lb-1-	53	a
	R^{11} -PheL-PheL-Phe-(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	lb-1-	54	a
	R^{11} -PheL-PheL-Phe-(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	lb-1-	55	a
	R^{11} -Phe-PheL-PheL-(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	lb-1-	56	a
30	R^{11} -Phe-PheL-PheL-(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	lb-1-	57	a
	R^{11} -Phe-Phe-PheL-(CH ₂) _n -CF ₂ O-PheL-PheL-R ¹²	lb-1-	58	a
	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -PheL-Phe-R ¹²	lb-1-	59	a
	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -Phe-PheL-R ¹²	lb-1-	60	a
35	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -PheL-PheL-R ¹²	lb-1-	61	a

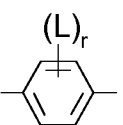
	R^{11} -PheL-Phe-PheL-OCF ₂ -(CH ₂) _n -PheL-PheL-R ¹²	lb-1-	62	a
	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -PheL-PheL-R ¹²	lb-1-	63	a
5	R^{11} -PheL-PheL-PheL-(CH ₂) _n -CF ₂ O-PheL-Phe-R ¹²	lb-1-	64	a
	R^{11} -PheL-PheL-PheL-(CH ₂) _n -CF ₂ O-Phe-PheL-R ¹²	lb-1-	65	a
	R^{11} -PheL-PheL-Phe-(CH ₂) _n -CF ₂ O-PheL-PheL-R ¹²	lb-1-	66	a
	R^{11} -PheL-Phe-PheL-(CH ₂) _n -CF ₂ O-PheL-PheL-R ¹²	lb-1-	67	a
	R^{11} -Phe-PheL-PheL-(CH ₂) _n -CF ₂ O-PheL-PheL-R ¹²	lb-1-	68	a
10	R^{11} -PheL-PheL-PheL-(CH ₂) _n -CF ₂ O-PheL-PheL-R ¹²	lb-1-	69	a
	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -PheL-PheL-R ¹²	lb-1-	70	a
15	R^{11} -Phe-Phe-Phe-OCF ₂ -(CH ₂) _n -Phe-Phe-Phe-R ¹²	lb-1-	71	a
	R^{11} -PheL-Phe-Phe-(CH ₂) _n -CF ₂ O-Phe-Phe-Phe-R ¹²	lb-1-	72	a
	R^{11} -Phe-PheL-Phe-(CH ₂) _n -CF ₂ O-Phe-Phe-Phe-R ¹²	lb-1-	73	a
	R^{11} -Phe-Phe-PheL-(CH ₂) _n -CF ₂ O-Phe-Phe-Phe-R ¹²	lb-1-	74	a
	R^{11} -Phe-Phe-Phe-(CH ₂) _n -CF ₂ O-PheL-Phe-Phe-R ¹²	lb-1-	75	a
20	R^{11} -Phe-Phe-Phe-(CH ₂) _n -CF ₂ O-Phe-PheL-Phe-R ¹²	lb-1-	76	a
	R^{11} -Phe-Phe-Phe-(CH ₂) _n -CF ₂ O-Phe-Phe-PheL-R ¹²	lb-1-	77	a
25	R^{11} -PheL-Phe-Phe-OCF ₂ -(CH ₂) _n -Phe-Phe-Phe-R ¹²	lb-1-	78	a
	R^{11} -Phe-PheL-Phe-OCF ₂ -(CH ₂) _n -Phe-Phe-Phe-R ¹²	lb-1-	79	a
	R^{11} -Phe-Phe-PheL-OCF ₂ -(CH ₂) _n -Phe-Phe-Phe-R ¹²	lb-1-	80	a
	R^{11} -Phe-Phe-Phe-OCF ₂ -(CH ₂) _n -PheL-Phe-Phe-R ¹²	lb-1-	81	a
	R^{11} -Phe-Phe-Phe-OCF ₂ -(CH ₂) _n -Phe-PheL-Phe-R ¹²	lb-1-	82	a
	R^{11} -Phe-Phe-Phe-OCF ₂ -(CH ₂) _n -Phe-Phe-PheL-R ¹²	lb-1-	83	a
30	R^{11} -PheL-PheL-Phe-(CH ₂) _n -CF ₂ O-Phe-Phe-Phe-R ¹²	lb-1-	84	a
	R^{11} -PheL-Phe-PheL-(CH ₂) _n -CF ₂ O-Phe-Phe-Phe-R ¹²	lb-1-	85	a
	R^{11} -PheL-Phe-Phe-(CH ₂) _n -CF ₂ O-PheL-Phe-Phe-R ¹²	lb-1-	86	a
35	R^{11} -PheL-Phe-Phe-(CH ₂) _n -CF ₂ O-Phe-PheL-Phe-R ¹²	lb-1-	87	a
	R^{11} -PheL-Phe-Phe-(CH ₂) _n -CF ₂ O-Phe-Phe-PheL-R ¹²	lb-1-	88	a

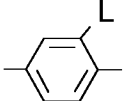
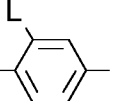
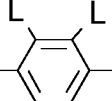
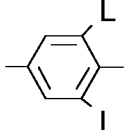
5	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -Phe-Phe-Phe-R ¹²	lb-1-	89	a
	R^{11} -PheL-Phe-PheL-OCF ₂ -(CH ₂) _n -Phe-Phe-Phe-R ¹²	lb-1-	90	a
	R^{11} -PheL-Phe-Phe-OCF ₂ -(CH ₂) _n -PheL-Phe-Phe-R ¹²	lb-1-	91	a
	R^{11} -PheL-Phe-Phe-OCF ₂ -(CH ₂) _n -Phe-PheL-Phe-R ¹²	lb-1-	92	a
	R^{11} -PheL-Phe-Phe-OCF ₂ -(CH ₂) _n -Phe-Phe-PheL-R ¹²	lb-1-	93	a
10	R^{11} -Phe-PheL-PheL-(CH ₂) _n -CF ₂ O-Phe-Phe-Phe-R ¹²	lb-1-	94	a
	R^{11} -Phe-PheL-Phe-(CH ₂) _n -CF ₂ O-PheL-Phe-Phe-R ¹²	lb-1-	95	a
	R^{11} -Phe-PheL-Phe-(CH ₂) _n -CF ₂ O-Phe-PheL-Phe-R ¹²	lb-1-	96	a
15	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -Phe-Phe-Phe-R ¹²	lb-1-	97	a
	R^{11} -Phe-PheL-Phe-OCF ₂ -(CH ₂) _n -PheL-Phe-Phe-R ¹²	lb-1-	98	a
	R^{11} -Phe-PheL-Phe-OCF ₂ -(CH ₂) _n -Phe-PheL-Phe-R ¹²	lb-1-	99	a
	R^{11} -Phe-Phe-PheL-OCF ₂ -(CH ₂) _n -PheL-Phe-Phe-R ¹²	lb-1-	100	a
20	R^{11} -PheL-PheL-PheL-(CH ₂) _n -CF ₂ O-Phe-Phe-Phe-R ¹²	lb-1-	101	a
	R^{11} -PheL-PheL-Phe-(CH ₂) _n -CF ₂ O-PheL-Phe-Phe-R ¹²	lb-1-	102	a
	R^{11} -PheL-PheL-Phe-(CH ₂) _n -CF ₂ O-Phe-PheL-Phe-R ¹²	lb-1-	103	a
	R^{11} -PheL-PheL-Phe-(CH ₂) _n -CF ₂ O-Phe-Phe-PheL-R ¹²	lb-1-	104	a
	R^{11} -Phe-PheL-PheL-(CH ₂) _n -CF ₂ O-PheL-Phe-Phe-R ¹²	lb-1-	105	a
	R^{11} -Phe-PheL-PheL-(CH ₂) _n -CF ₂ O-Phe-PheL-Phe-R ¹²	lb-1-	106	a
25	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -Phe-Phe-Phe-R ¹²	lb-1-	107	a
	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -PheL-Phe-Phe-R ¹²	lb-1-	108	a
	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -Phe-PheL-Phe-R ¹²	lb-1-	109	a
	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -Phe-Phe-PheL-R ¹²	lb-1-	110	a
30	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -PheL-Phe-Phe-R ¹²	lb-1-	111	a
	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -Phe-PheL-Phe-R ¹²	lb-1-	112	a
35	R^{11} -PheL-PheL-PheL-(CH ₂) _n -CF ₂ O-PheL-Phe-Phe-R ¹²	lb-1-	113	a
	R^{11} -PheL-PheL-PheL-(CH ₂) _n -CF ₂ O-Phe-PheL-Phe-R ¹²	lb-1-	114	a
	R^{11} -PheL-PheL-PheL-(CH ₂) _n -CF ₂ O-Phe-Phe-PheL-R ¹²	lb-1-	115	a

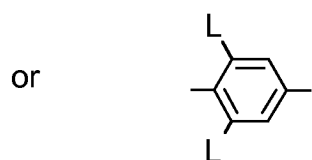
	R^{11} -Phe-PheL-PheL-(CH ₂) _n -CF ₂ O-PheL-PheL-Phe-R ¹²	lb-1-	116	a
	R^{11} -Phe-PheL-PheL-(CH ₂) _n -CF ₂ O-Phe-PheL-PheL-R ¹²	lb-1-	117	a
5	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -PheL-Phe-Phe-R ¹²	lb-1-	118	a
	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -Phe-PheL-Phe-R ¹²	lb-1-	119	a
	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -Phe-Phe-PheL-R ¹²	lb-1-	120	a
	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -PheL-PheL-Phe-R ¹²	lb-1-	121	a
	R^{11} -Phe-PheL-PheL-OCF ₂ -(CH ₂) _n -Phe-PheL-PheL-R ¹²	lb-1-	122	a
10	R^{11} -PheL-PheL-PheL-(CH ₂) _n -CF ₂ O-PheL-PheL-Phe-R ¹²	lb-1-	123	a
	R^{11} -PheL-Phe-PheL-(CH ₂) _n -CF ₂ O-PheL-PheL-PheL-R ¹²	lb-1-	124	a
	R^{11} -PheL-PheL-Phe-(CH ₂) _n -CF ₂ O-PheL-PheL-PheL-R ¹²	lb-1-	125	a
15	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -PheL-PheL-Phe-R ¹²	lb-1-	126	a
	R^{11} -PheL-Phe-PheL-OCF ₂ -(CH ₂) _n -PheL-PheL-PheL-R ¹²	lb-1-	127	a
	R^{11} -PheL-PheL-Phe-OCF ₂ -(CH ₂) _n -PheL-PheL-PheL-R ¹²	lb-1-	128	a
20	R^{11} -PheL-PheL-PheL-OCF ₂ -(CH ₂) _n -PheL-PheL-PheL-R ¹²	lb-1-	129	a
	wherein, R ¹¹ , R ¹² , Phe and PheL have one of the meanings as given above and n denotes 5, 7, 9 or 11.			

In the above given preferred subformulae of formula I, PheL preferably

denotes the group .

The group  is very preferably

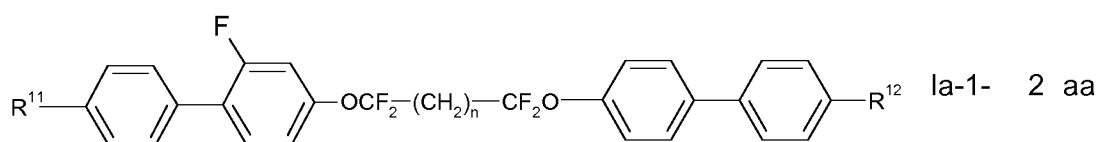
denoting ,  or , furthermore .



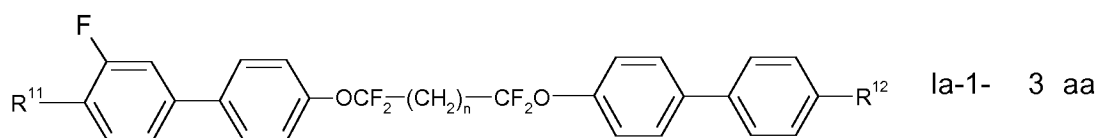
5 wherein L is preferably F, Cl, CH₃, OCH₃ and COCH₃.

Thus, further preferred compounds of formula Ia-1 are selected, for example, from the following compounds:

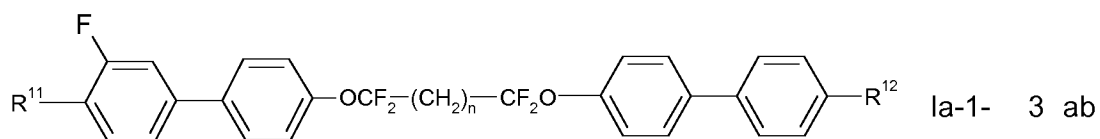
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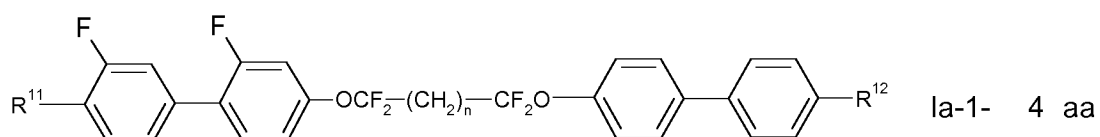
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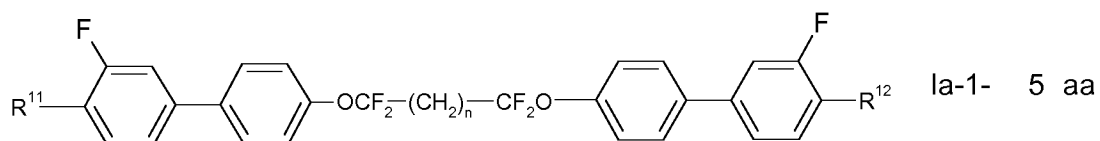
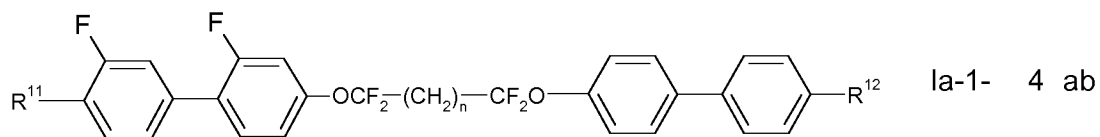
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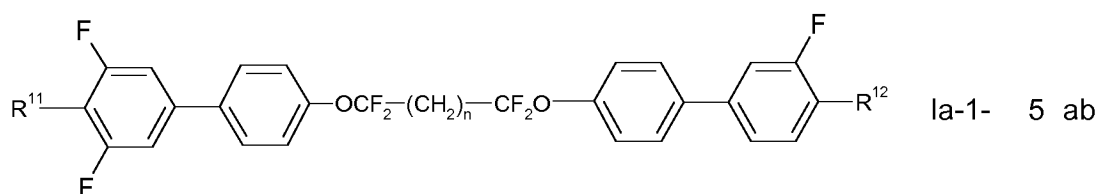
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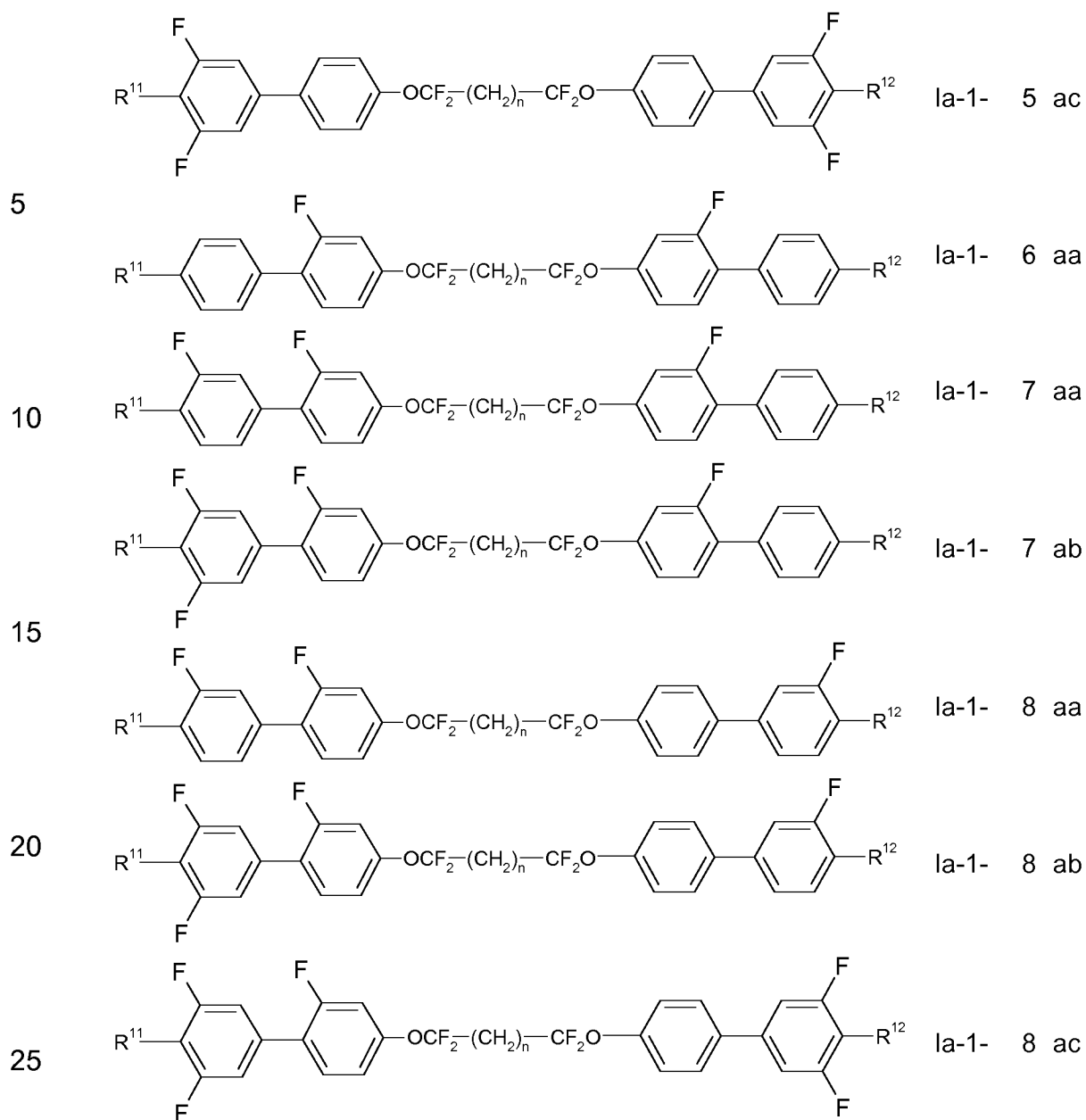


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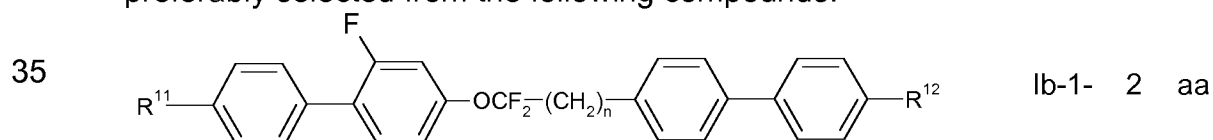
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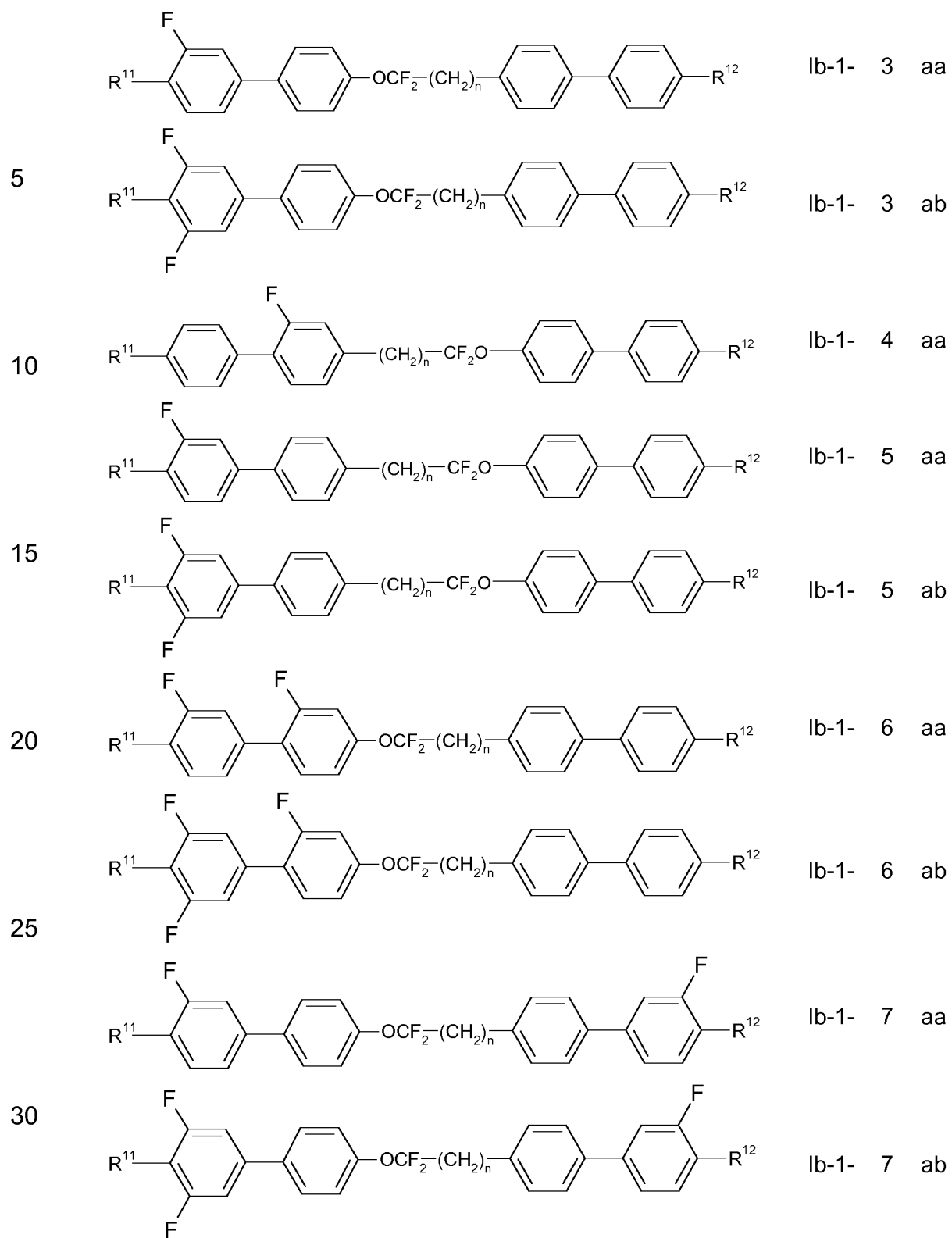


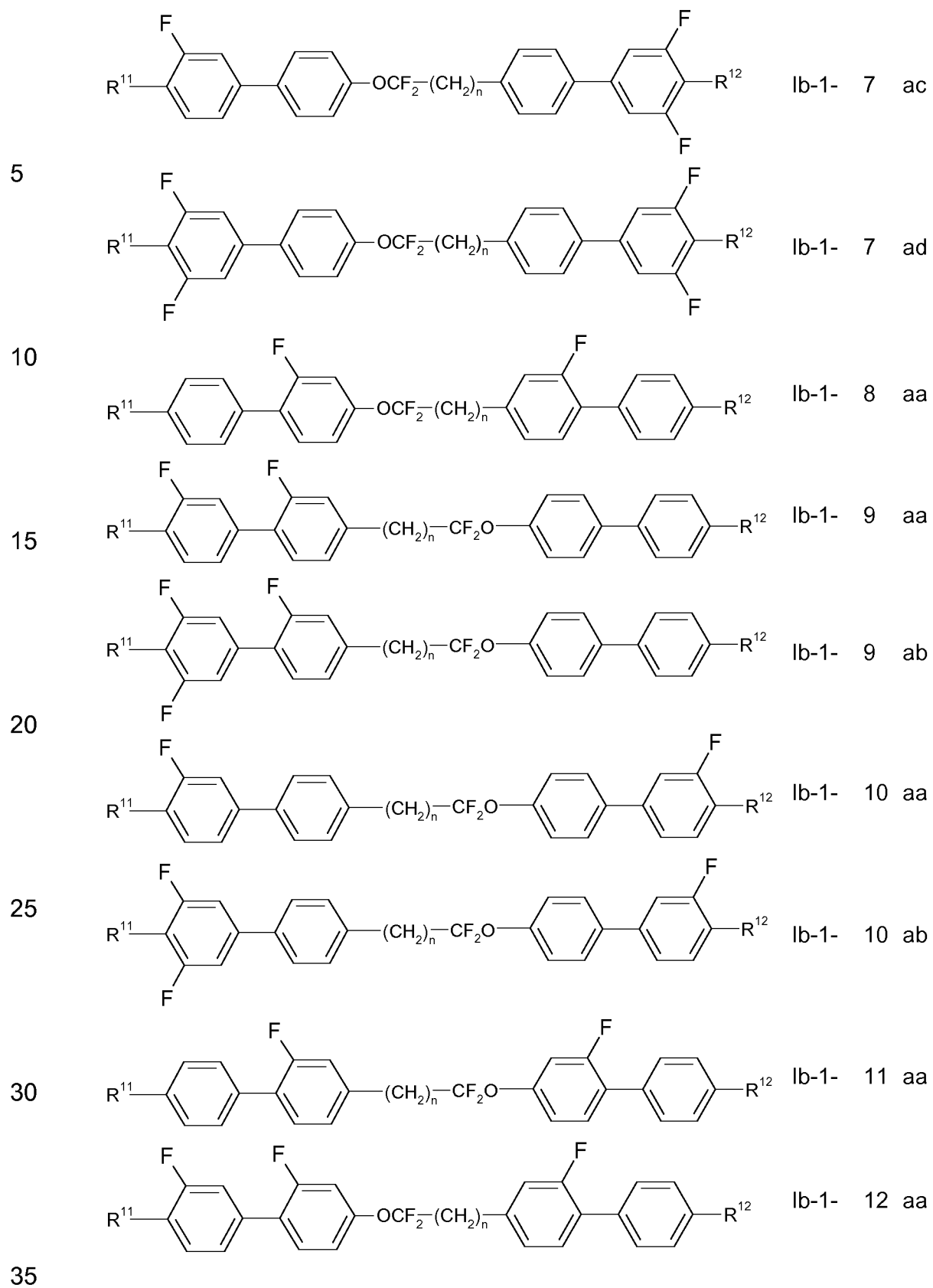


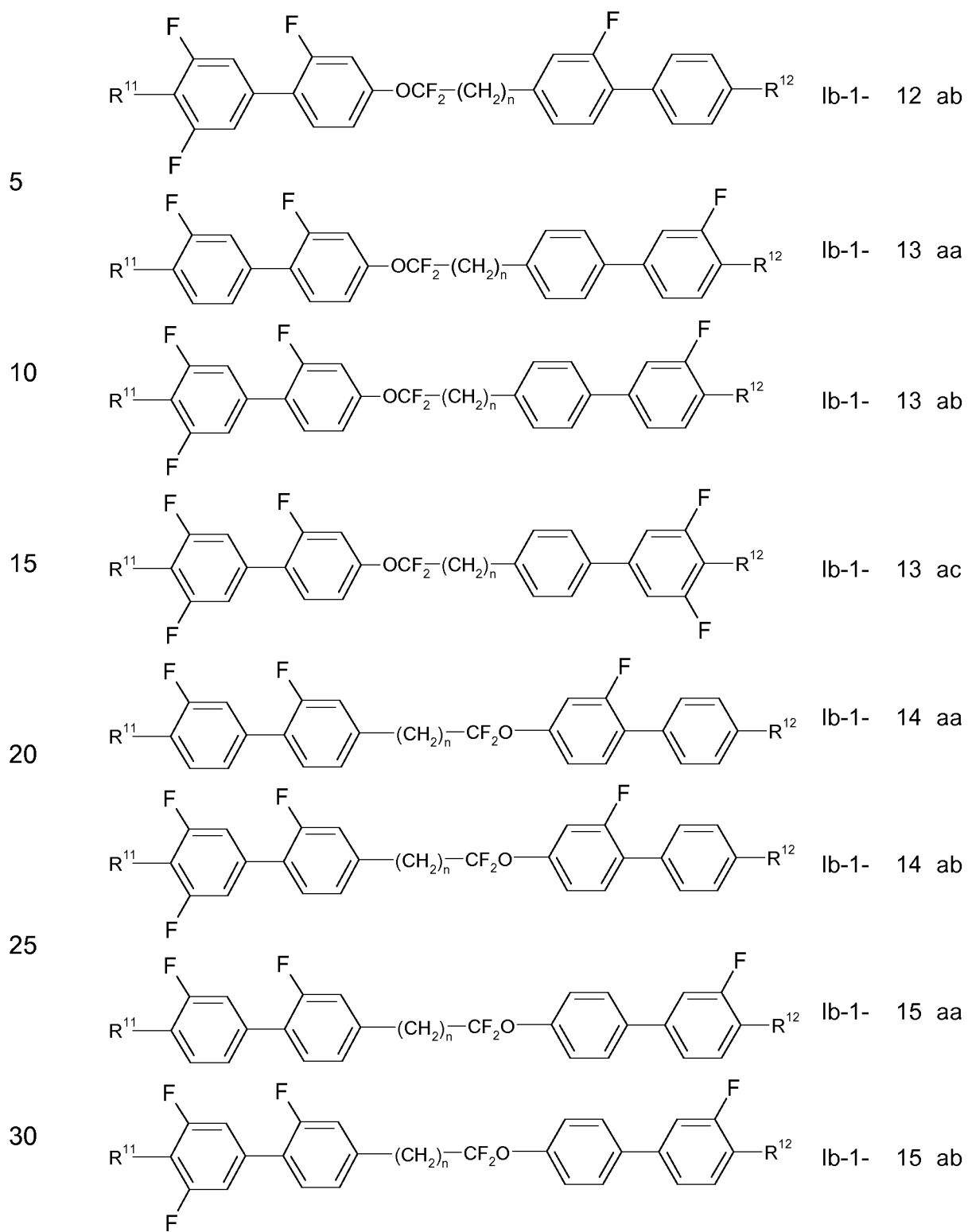
30 R^{11} , R^{12} have one of the meanings as given above, preferably both R^{11} and R^{12} are identical and denote both CN or F, likewise preferably R^{11} and R^{12} are different and at least one of them denote CN or F and n preferably denotes 7 or 9.

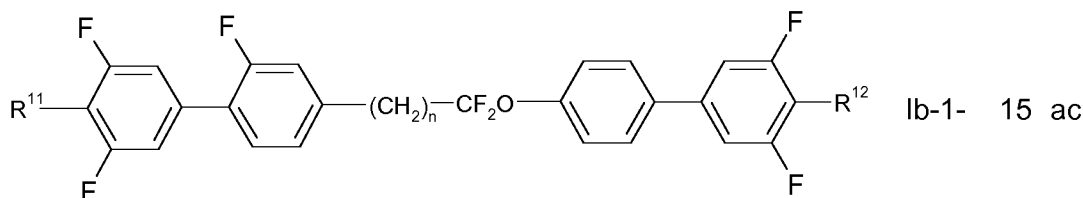
Further preferred compounds are of formula Ib-1, for example, are preferably selected from the following compounds:







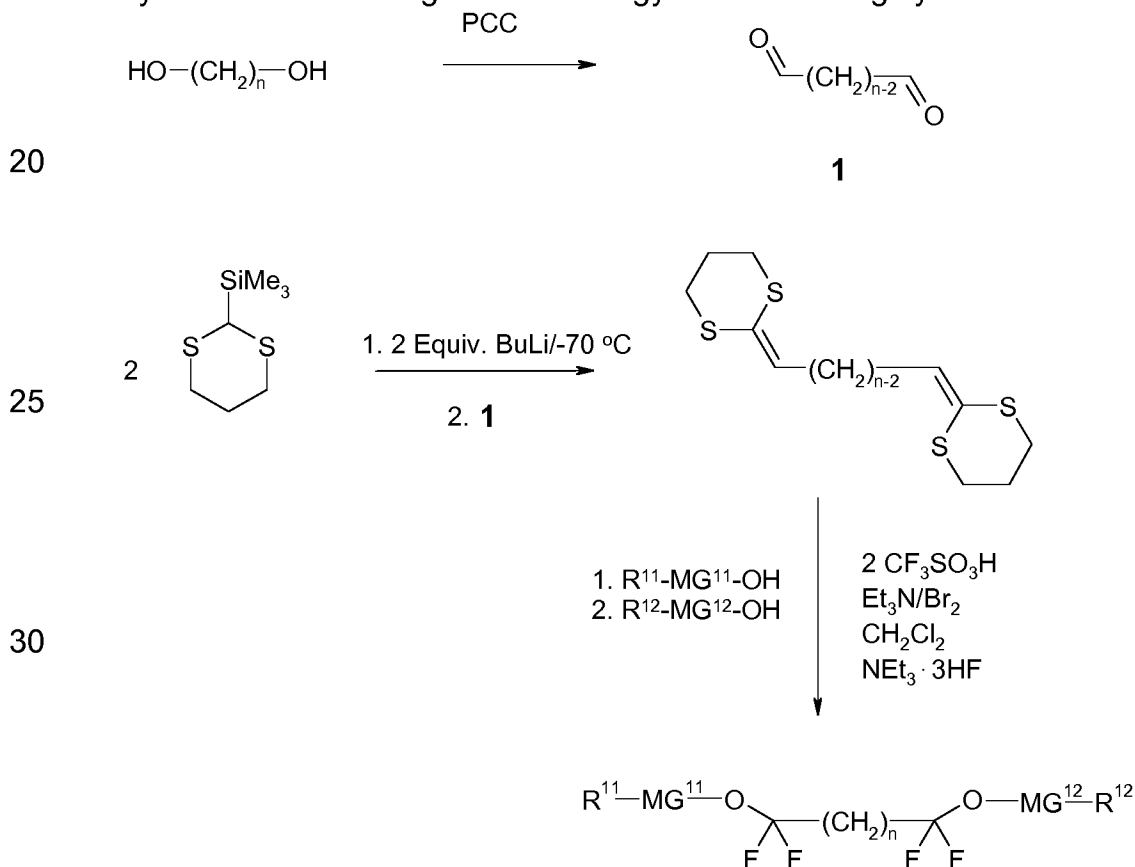




5 R^{11} , R^{12} have one of the meanings as given above, preferably both R^{11} and R^{12} are identical and denote both CN or F, likewise preferably R^{11} and R^{12} are different and at least one of them denote CN or F and n preferably denotes 7 or 9.

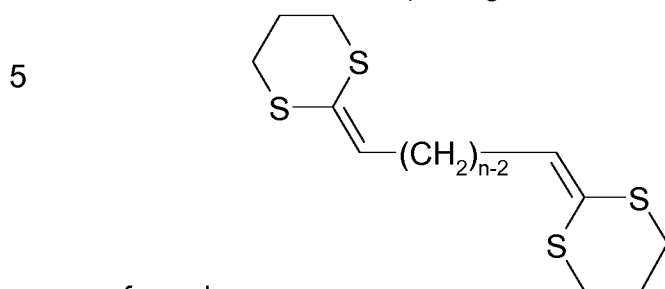
10 The compounds of formula I can be synthesized according to or in analogy to methods which are known per se and which are described in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart.

15 In a preferred embodiment, the compounds of formula Ia-1 can be synthesized according to or in analogy to the following synthesis scheme:



wherein the given parameters have one of the meanings as given above under formula Ia-1.

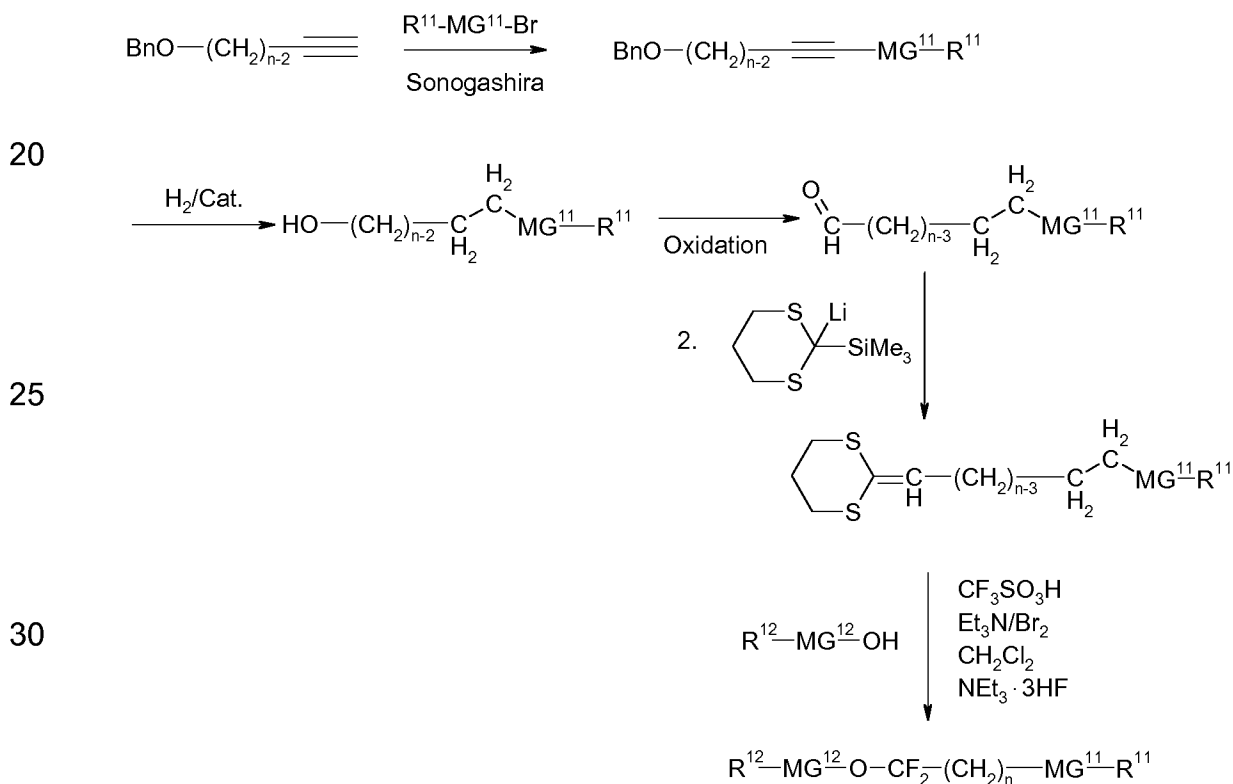
Thus, the invention relates also to a method of production of compounds of formula Ia-1, comprising at least the step of reacting a compound of



10 formula

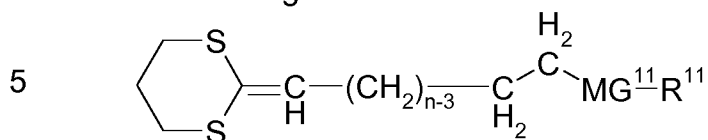
with one or more compounds of formula $R^{11}\text{-MG}^{11}\text{-OH}$ or $R^{12}\text{-MG}^{12}\text{-OH}$, wherein the parameters have one of the meanings as given above under formula Ia-1.

15 In another preferred embodiment, the compounds of formula Ib-1 can be synthesized according to or in analogy to the following synthesis scheme:



35 wherein the parameters have one of the meanings as given above under formula Ib-1.

Thus the invention relates also to a method of production of compounds of formula Ib-1, comprising at least the step of reacting one compound of the following formula:



with at least one compound of formula $\text{R}^{12}\text{-MG}^{12}\text{-OH}$, wherein the parameters have one of the meanings as given above under formula Ib-1.

10

The compounds of formula I and its subformulae can be beneficially utilized in LC media to improve the properties of such media, in particular in LC media for flexoelectric applications.

15

For example, one of the main advantages of using compounds of formula I in LC media for flexoelectric applications is improving the switching speed in the ULH (uniform lying helix) geometry, particularly at temperatures below 35°C. Benefits are also observed in terms of the phase range, in terms of an increased isotropic to nematic clearing point and also in terms of a reduced nematic to nematic twist bend transition temperature below room temperature.

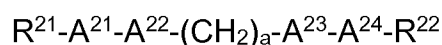
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Therefore, the invention also relates to the use of compounds of formula I in LC media and to a LC media comprising one or more compounds of formula I, as such.

25

In a preferred embodiment, the LC media in accordance with the present invention comprise one or more compounds of formula II,

30



II

wherein

R^{21} and R^{22}

denote independently H, F, Cl, CN, NCS or a straight-chain or branched alkyl group, which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent

35

CH₂ groups to be replaced, in each occurrence independently from one another, by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-, -O-CO-O-, -S-CO-, -CO-S-, -CH=CH-, -CH=CF-, -CF=CF- or -C≡C- in such a manner that oxygen atoms are not linked directly to one another, preferably F, Cl, CN, a straight-chain or branched alkyl or alkoxy group which may be unsubstituted, mono- or polysubstituted by halogen or CN, more preferably F, CN or OCF₃,

A²¹ to A²⁴ denote independently in each occurrence a aryl-, heteroaryl-, alicyclic- and heterocyclic group, preferably 1,4-phenylene, wherein in addition one or more CH groups may be replaced by N, trans-1,4-cyclo-hexylene in which, in addition, one or two non-adjacent CH₂ groups may be replaced by O and/or S, 1,4-cyclohexenylene, 1,4-bicyclo-(2,2,2)-octylene, piperidine-1,4-diyl, naphthalene-2,6-diyl, decahydro-naphthalene-2,6-diyl, 1,2,3,4-tetrahydro-naphthalene-2,6-diyl, cyclobutane-1,3-diyl, spiro[3.3]heptane-2,6-diyl or dispiro[3.1.3.1] decane-2,8-diyl, it being possible for all these groups to be unsubstituted, mono-, di-, tri- or tetrasubstituted with F, Cl, CN or alkyl, alkoxy, alkylcarbonyl or alkoxy carbonyl groups, wherein one or more H atoms may be substituted by F or Cl, more preferably each independently in each occurrence 1,4-phenylene, wherein in addition one or more CH groups may be replaced by N or trans-1,4-cyclohexylene in which, in addition, one or two non-adjacent CH₂ groups may be replaced by O and/or S, it being possible for both ring groups to be unsubstituted, mono-, di-, tri- or tetrasubstituted with F, Cl, CN or alkyl, alkoxy, alkylcarbonyl or

alkoxycarbonyl groups, wherein one or more H atoms may be substituted by F or Cl,

- 5 a denotes an integer from 1 to 15, preferably an odd (i.e. uneven) integer and, more preferably 3, 5, 7, 9 or 11.

Preferred compounds of formula II are selected from compounds in which the groups $(-A^{21}-A^{22}-)$ and $(-A^{23}-A^{24}-)$ are each and independently selected from the following groups

- | | | |
|----|-------------|------|
| 10 | -Phe-Phe- | MG-1 |
| | -Phe-Cyc- | MG-2 |
| | -PheL-PheL- | MG-3 |
| | -Phe-PheL- | MG-4 |
| | -PheL-Phe- | MG-5 |
| 15 | -PheL-Cyc- | MG-6 |
| | -Cyc-PheL- | MG-7 |
| | -Cyc-Cyc- | MG-8 |

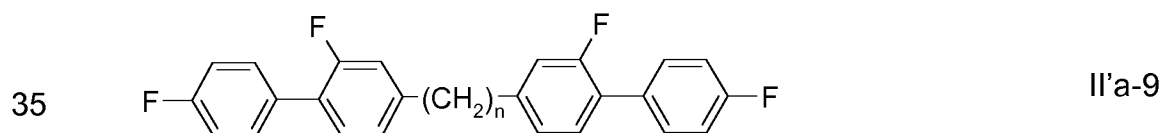
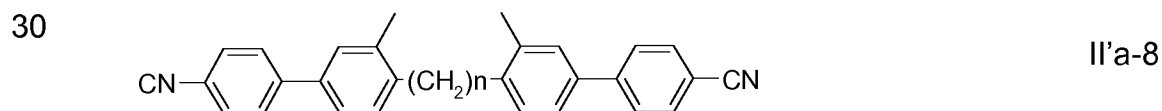
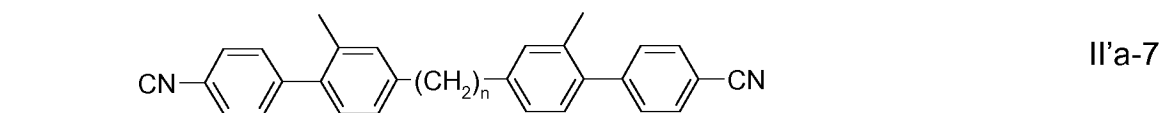
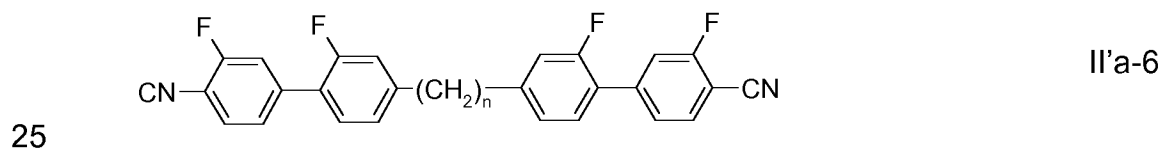
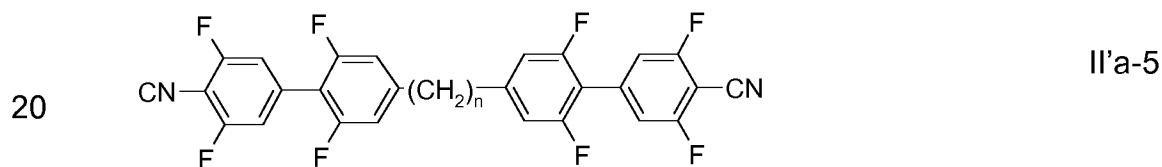
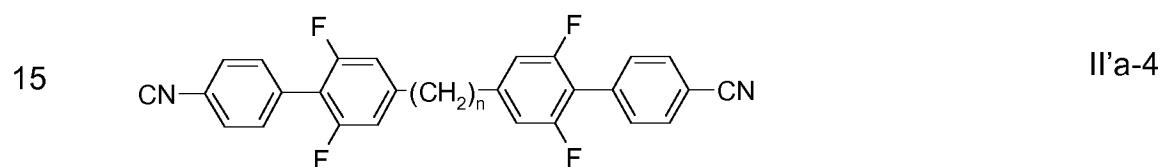
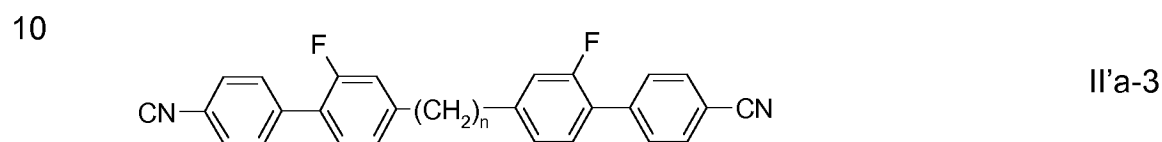
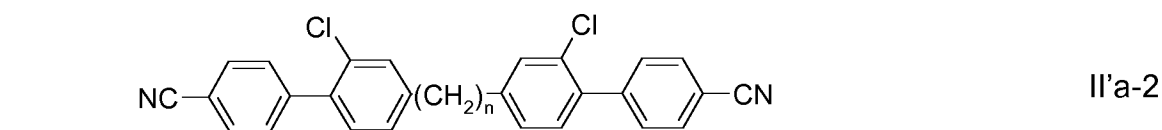
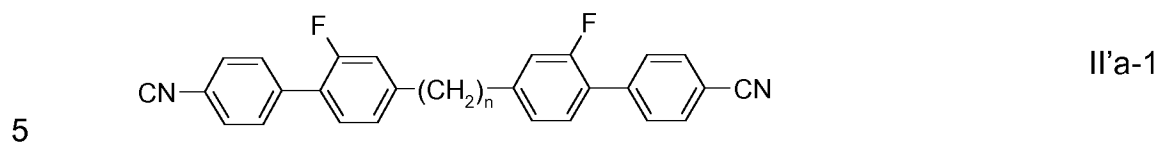
wherein,

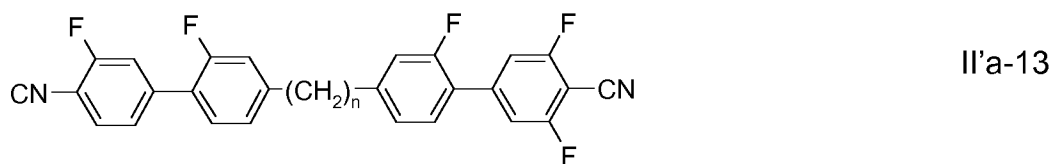
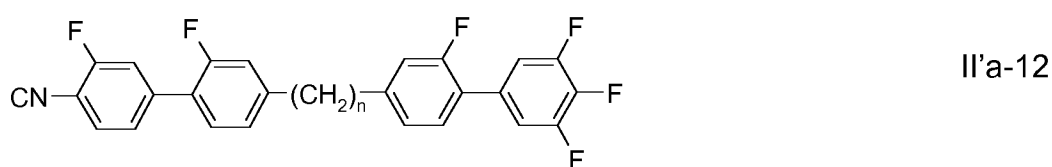
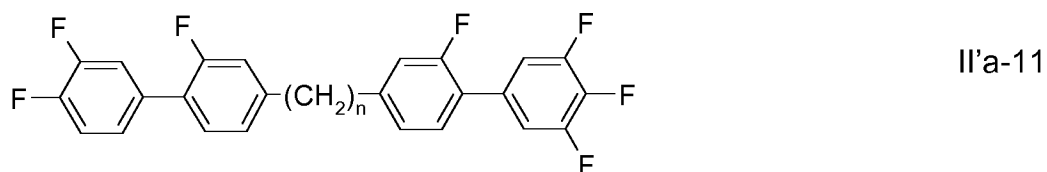
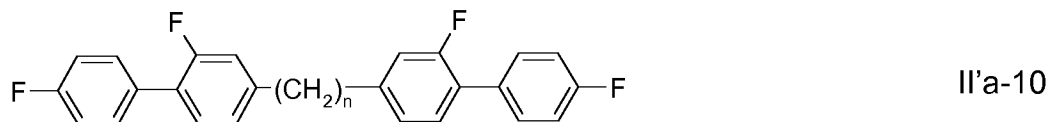
- | | | |
|----|------|--|
| 20 | Phe | in these groups is 1,4-phenylene, |
| | PheL | is a 1,4-phenylene group which is substituted by 1 to 4 groups L, with L being preferably F, Cl, CN, OH, NO ₂ or an optionally fluorinated alkyl, alkoxy or alkanoyl group with 1 to 7 C atoms, very preferably F, Cl, CN, OH, NO ₂ , CH ₃ , C ₂ H ₅ , OCH ₃ , OC ₂ H ₅ , COCH ₃ , COC ₂ H ₅ , COOCH ₃ , COOC ₂ H ₅ , CF ₃ , OCF ₃ , OCHF ₂ , OC ₂ F ₅ , in particular F, Cl, CN, CH ₃ , C ₂ H ₅ , OCH ₃ , COCH ₃ and OCF ₃ , most preferably F, Cl, CH ₃ , OCH ₃ and COCH ₃ and |
| 25 | | |
| | Cyc | is 1,4-cyclohexylene. |
| 30 | | |

Preferred are compounds of formula II wherein the groups $(R^{21}-A^{21}-A^{22}-)$ and $(-A^{23}-A^{24}-R^{22})$ in formula II are identical or mirror images.

- 35 Likewise preferred are compounds of formula II wherein $(R^{21}-A^{21}-A^{22}-)$ and $(-A^{23}-A^{24}-R^{22})$ in formula II are different.

Preferred compounds of formula II are indicated below:





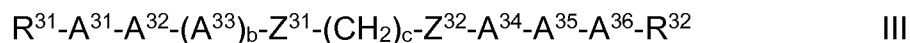
wherein

20 n denotes an integer from 1 to 15, preferably an odd (i.e. uneven) integer and, more preferably 3, 5, 7, 9 or 11.

25 The compounds of formula II can be synthesized according to or in analogy to methods which are known per se and which are described in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart. A preferred method of preparation can be taken from WO 2013/004333 A1.

30 In the mixture according to the present invention, the utilization of compounds of formula II beside compounds of formula I, is especially useful in order to further improve the switching speeds whilst maintaining a good phase range and a favorable value for e/K .

35 In a preferred embodiment, the LC media in accordance with the present invention comprise one or more compounds of formula III,



wherein

5 R^{31} and R^{32} have each and independently from another one of the meanings as given for R^{21} and R^{22} under formula II,

A^{31} to A^{36} have each and independently from another one of the meanings as given for A^{21} to A^{24} under formula II,

10 Z^{31} and Z^{32} are each independently in each occurrence,
 $-COO-$, $-OCO-$, $-O-CO-O-$, $-OCH_2-$, $-CH_2O-$, $-CH_2CH_2-$,
 $-(CH_2)_4-$, $-CF_2CF_2-$, $-CH=CH-$, $-CF=CF-$,
 $-CH=CH-COO-$, $-OCO-CH=CH-$ or $-C\equiv C-$, optionally
substituted with one or more of F, S and/or Si,
15 preferably $-COO-$, $-OCO-$ or $-O-CO-O-$,
more preferably $-COO-$ or $-OCO-$,

b denotes an integer from 1 to 15, preferably an odd (i.e. uneven) integer and, more preferably 3, 5, 7 or 9 and

20 c denotes 0 or 1, preferably 0.

Preferred compounds of formula III are selected from compounds in which c denotes 0 and the group $(-A^{31}-A^{32}-)$ is selected from the groups
25 MG-1 to MG-8 as given above.

Further preferred compounds of formula III are selected from compounds in which c denotes 1 and the groups $(-A^{24}-A^{25}-A^{26}-)$ and $(-A^{21}-A^{22}-A^{23}-)$ are each and independently selected from the following groups

30 $-Cyc-Cyc-Cyc-$ MG-9
 $-Phe-Phe-Cyc-$ MG-10
 $-Phe-Cyc-Phe-$ MG-11
 $-Cyc-Phe-Cyc-$ MG-12
35 $-Phe-Cyc-Cyc-$ MG-13
 $-Phe-Phe-Phe-$ MG-14

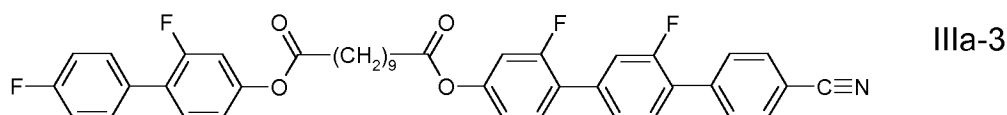
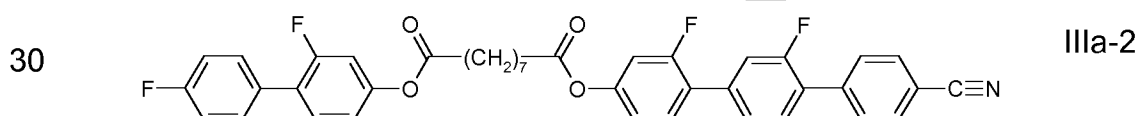
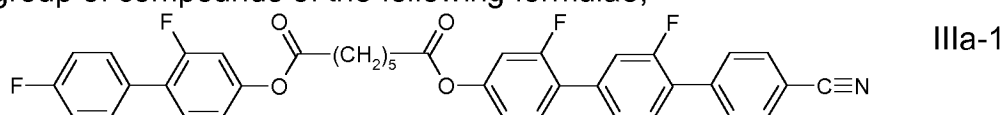
	-Phe-Phe-PheL-	MG-15
	-Phe-PheL-Phe-	MG-16
	-PheL-Phe-Phe-	MG-17
	-PheL-Phe-PheL-	MG-18
5	-PheL-PheL-Phe-	MG-19
	-PheL-PheL-PheL-	MG-20
	-Phe-PheL-Cyc-	MG-21
	-Phe-Cyc-PheL-	MG-22
	-Cyc-Phe-PheL-	MG-23
10	-PheL-Cyc-PheL-	MG-24
	-PheL-PheL-Cyc-	MG-25
	-PheL-Cyc-Cyc-	MG-26
	-Cyc-PheL-Cyc-	MG-27

15 wherein

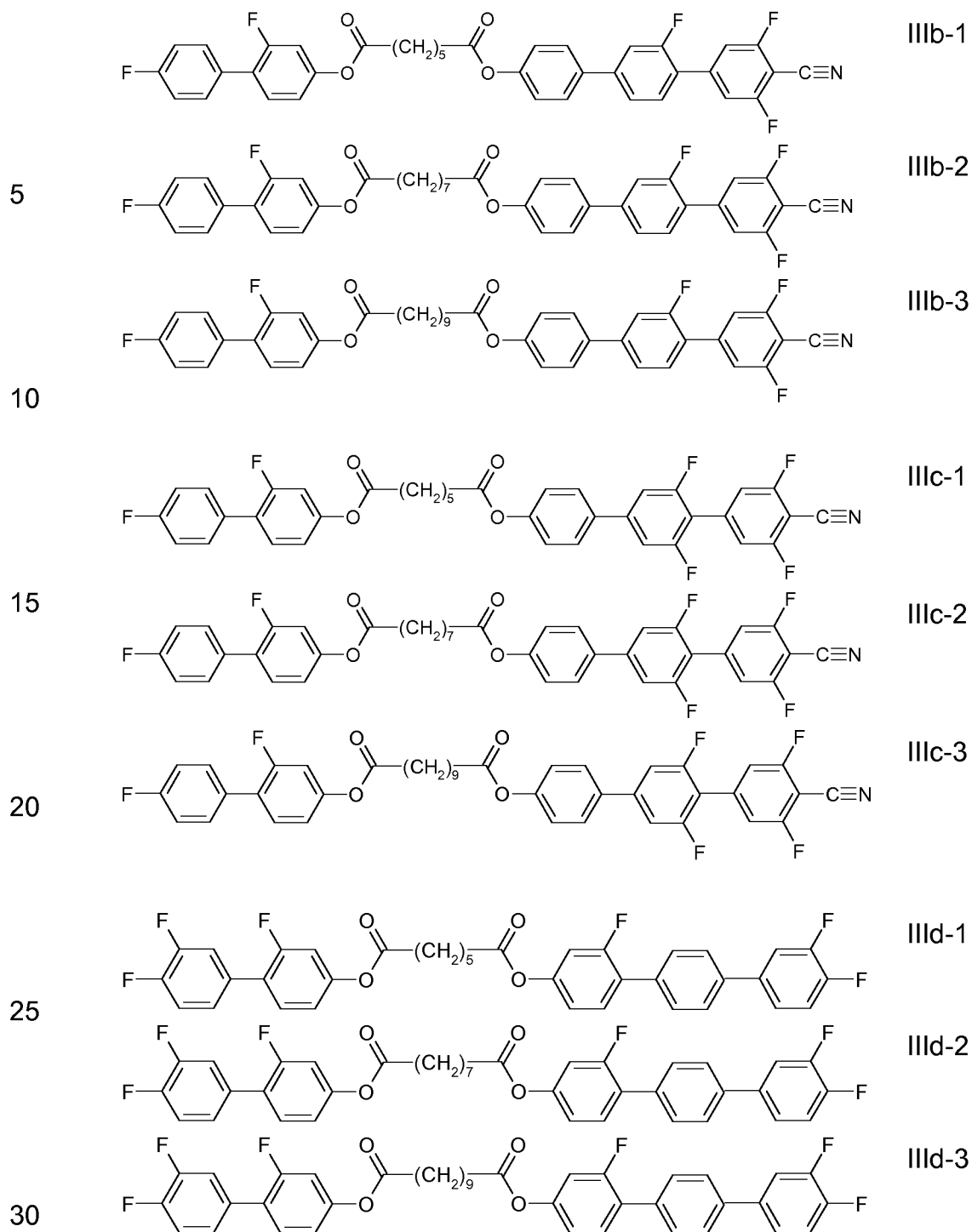
Cyc, Phe, PheL and L have one of the meanings given above for the groups MG-1 to MG-8.

20 Further preferred compounds of formula III are selected from compounds in which c denotes 0 and the group (-A²¹-A²²-) is selected from the groups MG-1 to MG-8 as given above and in which the group (-A²⁴-A²⁵-A²⁶-) is selected from the groups MG-9 to MG-27.

25 Especially preferred compounds of formula III are selected from the group of compounds of the following formulae,



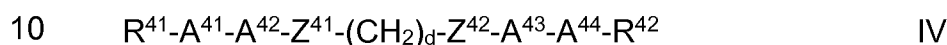
35



The compounds of formula III can be synthesized according to or in analogy to methods which are known per se and which are described in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart.

In the mixture according to the present invention, the utilization of compounds of formula III beside compounds of formula I, is especially useful in order to achieve high stabilities, favourable high clearing points and broad phase ranges, as well as, low appearances of the nematic twist-bend phase.

In further preferred embodiment, the LC medium in accordance with the present invention comprises one or more compounds of formula IV,



wherein

R^{41} and R^{42} have each and independently one of the meanings as given above for R^{21} under formula II,

A^{41} to A^{44} have each and independently one of the meanings as given above for A^{21} under formula II,

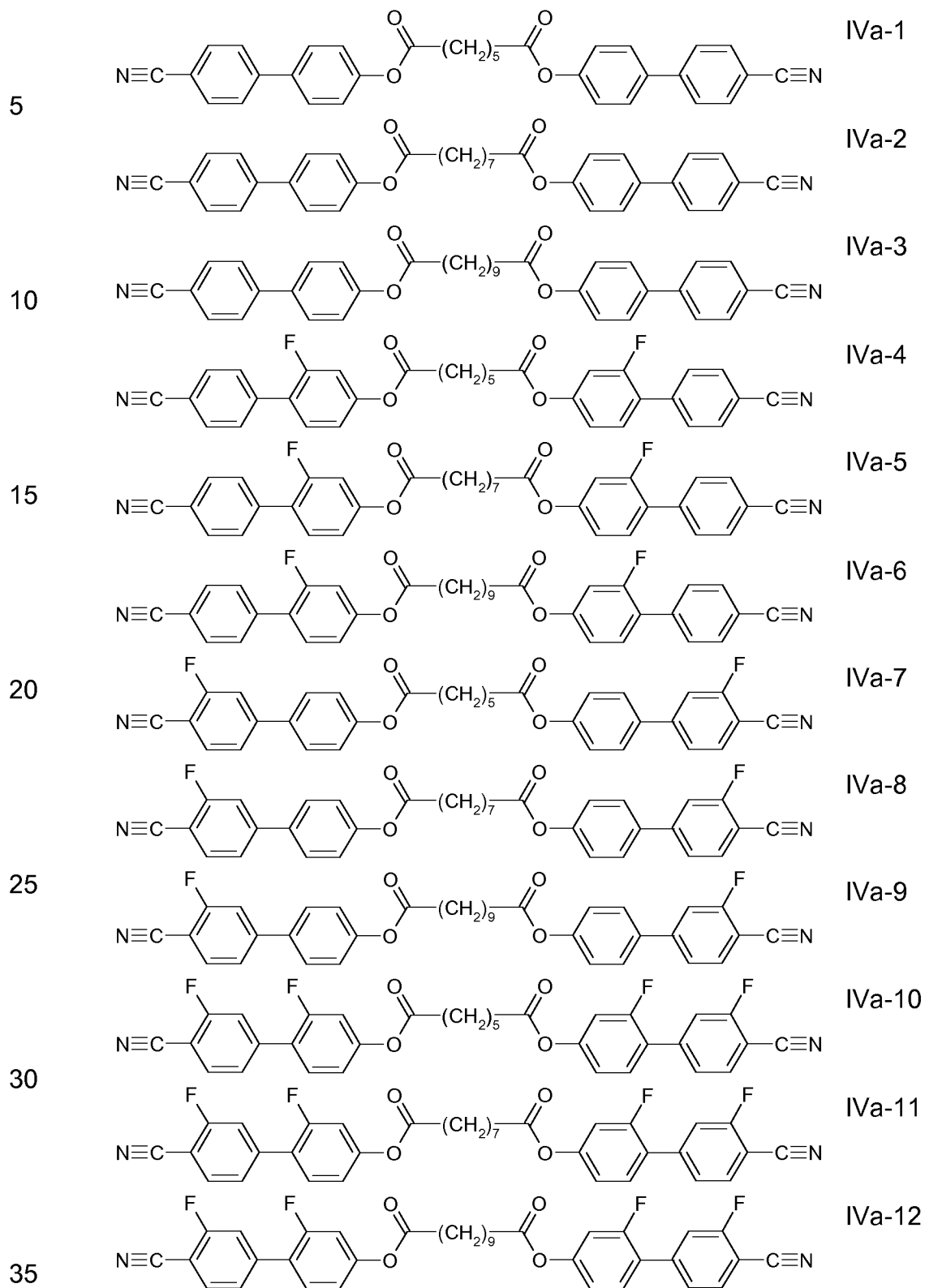
Z^{41} and Z^{42} are each independently in each occurrence, -COO-, -OCO-, -O-CO-O-, -OCH₂-, -CH₂O-, -CH₂CH₂-, -(CH₂)₄-, -CF₂CF₂-, -CH=CH-, -CF=CF-, -CH=CH-COO-, -OCO-CH=CH- or -C≡C-, optionally substituted with one or more of F, S and/or Si, preferably -COO-, -OCO- or -O-CO-O-, more preferably -COO- or -OCO-.

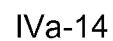
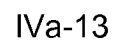
d denotes an integer from 1 to 15, preferably an odd (i.e. uneven) integer and, more preferably 3, 5, 7 or 9.

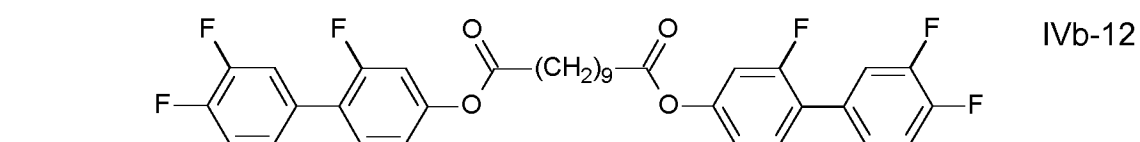
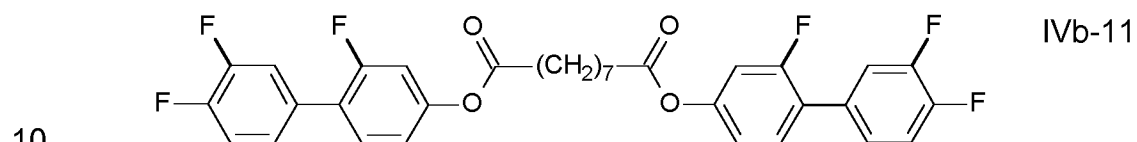
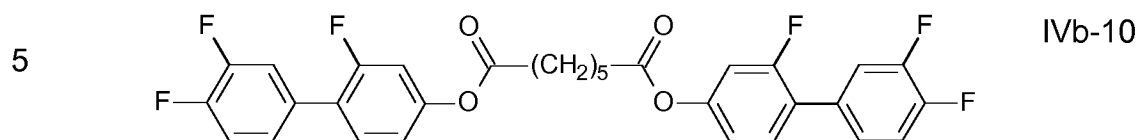
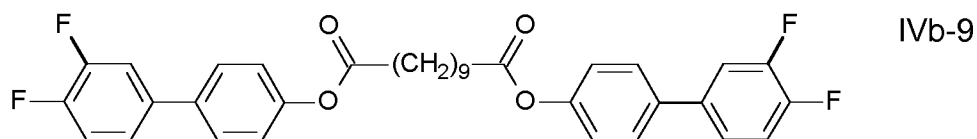
Preferred compounds of formula IV are selected from compounds in which the groups (-A⁴¹-A⁴²-) and (-A⁴³-A⁴⁴-) are each and independently selected from the groups of MG-1 to MG-8 as given above.

Especially preferred compounds of formula IV are selected from the group of compounds of the following formulae:

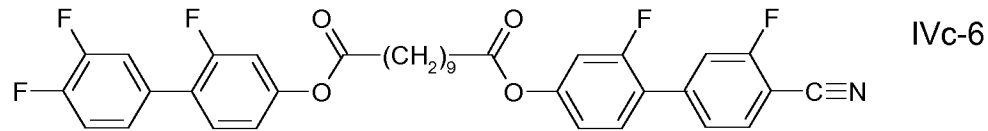
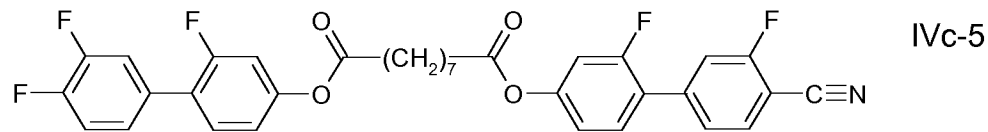
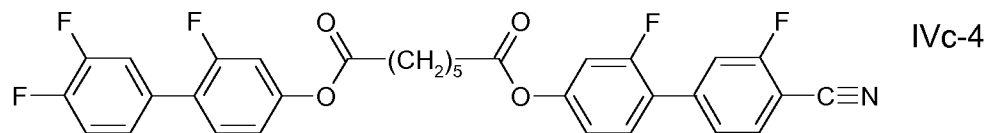
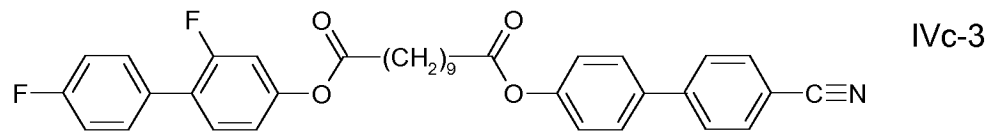
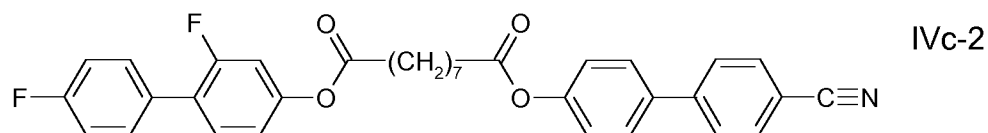
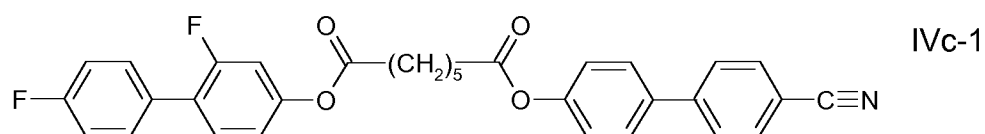
- symmetrical ones (IVa and IVb):

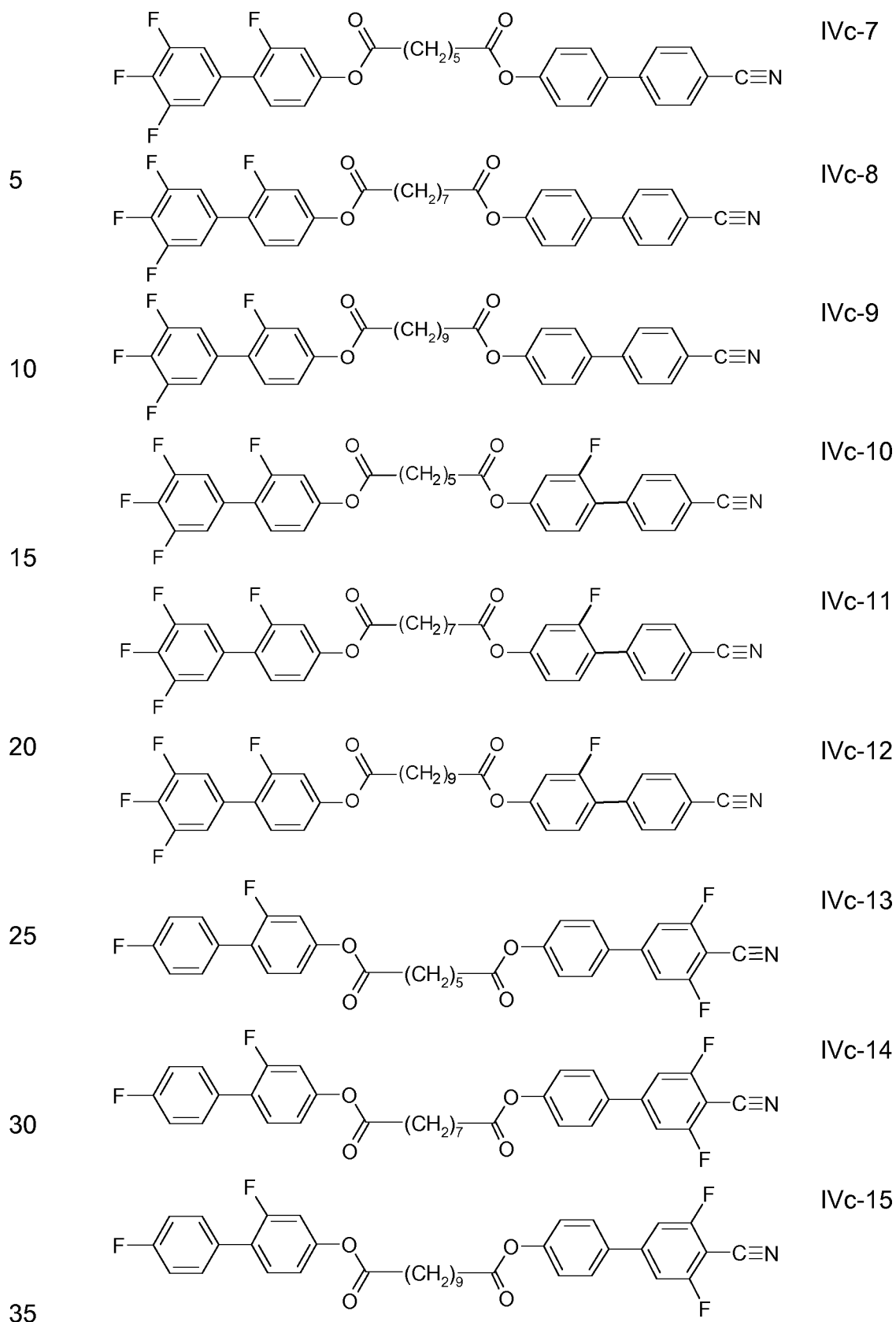






- non-symmetrical ones IVc:



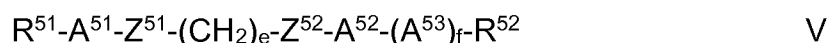


The compounds of formula IV are either known or can be synthesized according to or in analogy to methods which are known per se and which are described in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart.

In the mixture according to the present invention, the utilization of compounds of formula IV beside compounds of formula I, is especially useful in order to reduce the nematic twist bend phase whilst maintaining favorable values for e/K.

In further preferred embodiment, the LC medium in accordance with the present invention additionally comprises one or more compounds of formula V,

15



wherein

R^{51} and R^{52} have each and independently one of the meanings as given above for R^{21} under formula II,

20

A^{51} to A^{53} have each and independently one of the meanings as given above for A^{21} under formula II,

25

Z^{51} and Z^{52} are each independently in each occurrence, -COO-, -OCO-, -O-CO-O-, -OCH₂-, -CH₂O-, -CH₂CH₂-, -(CH₂)₄-, -CF₂CF₂-, -CH=CH-, -CF=CF-, -CH=CH-COO-, -OCO-CH=CH- or -C≡C-, optionally substituted with one or more of F, S and/or Si, preferably -COO-, -OCO- or -O-CO-O-, more preferably -COO- or -OCO-,

30

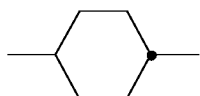
e denotes an integer from 1 to 15, preferably an odd (i.e. uneven) integer and, more preferably 3, 5, 7 or 9 and

35

f denotes 0 or 1.

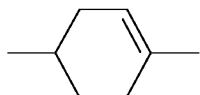
Especially preferred are compounds of formula V wherein the A^{51} is selected from the following group of formulae Va' to Vh' and the mirror images of formulae Vb', Ve' and Vf'

5



Va'

10

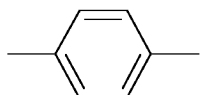


Vb'

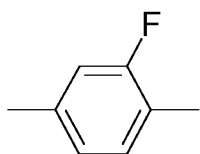


Vc'

15

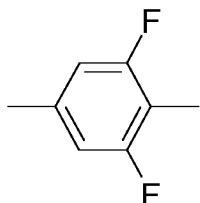


Vd'



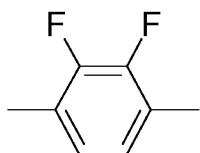
Ve'

20

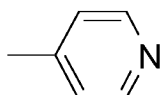


Vf'

25



Vg'



Vh'

30

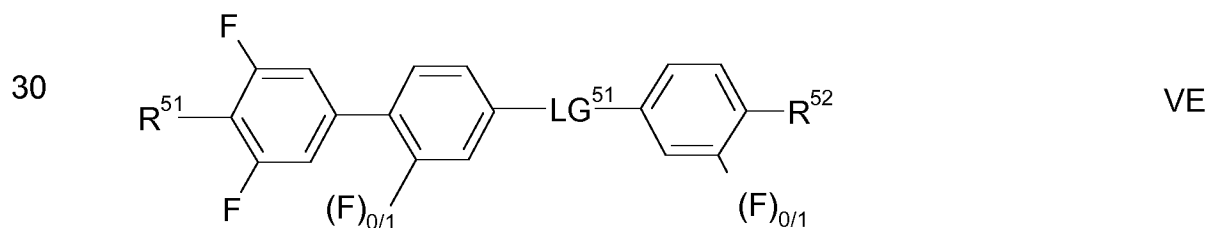
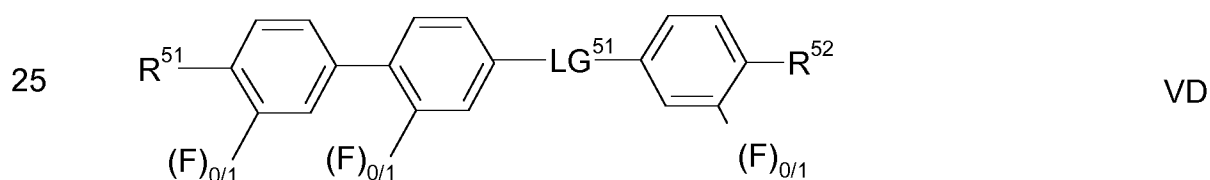
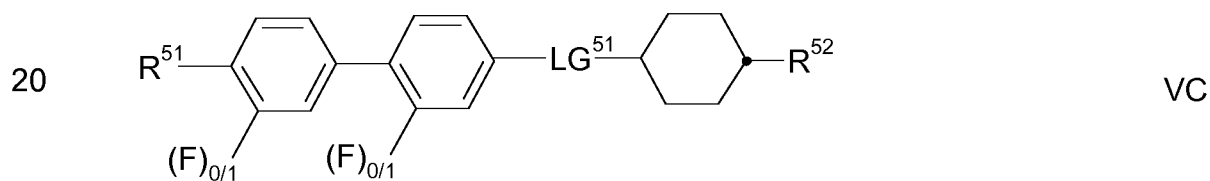
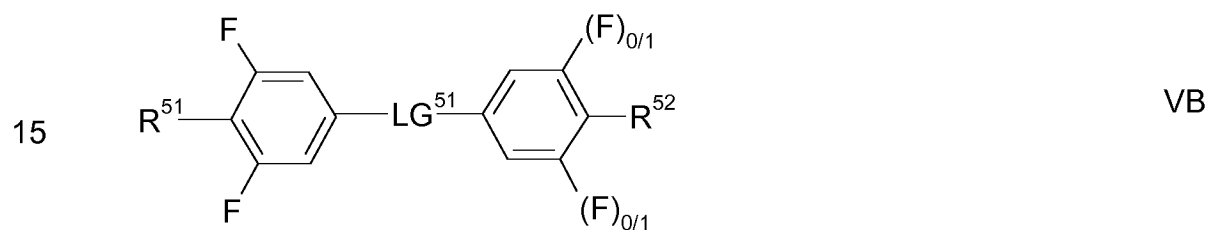
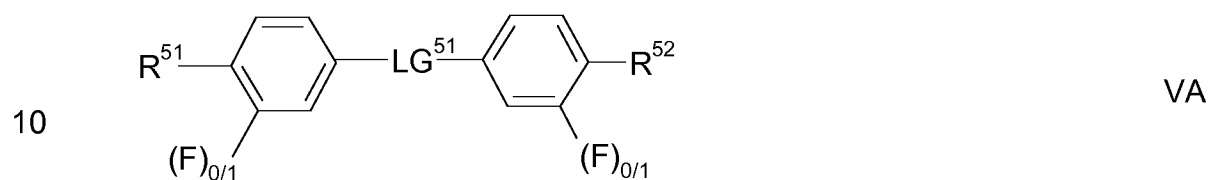
In a preferred embodiment of the present invention are compounds of formula I, wherein A^{51} and is selected from the group of formulae Va' to Vc' or their mirror images.

35

Preferably R^{51} and R^{52} in formula V are selected of H, F, Cl, CN, NO_2 , OCH_3 , COCH_3 , COC_2H_5 , COOCH_3 , COOC_2H_5 , CF_3 , C_2F_5 , OCF_3 , OCHF_2

and OC_2F_5 , in particular of H, F, Cl, CN, OCH_3 and OCF_3 , especially of H, F, CN and OCF_3 .

Preferred compounds of formula V are selected from the group of compounds of formulae VA to VE, preferably of formulae VA and/or VD, most preferably of formula VD,



wherein

35 LG^{51} is $\text{Z}^{51}-(\text{CH}_2)_z-\text{Z}^{52}$,

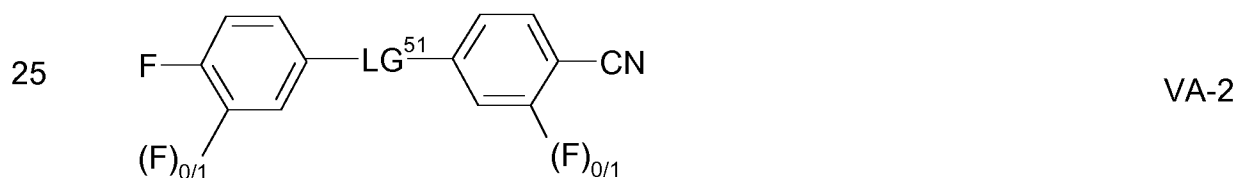
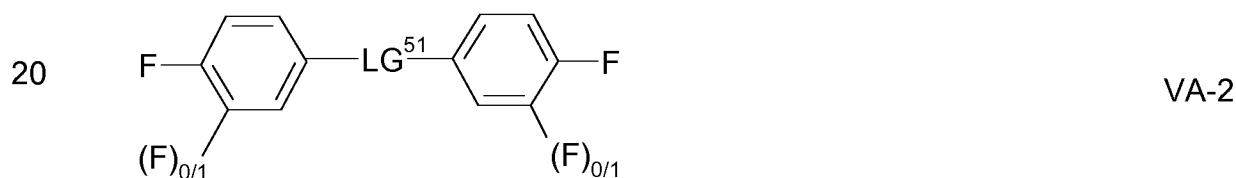
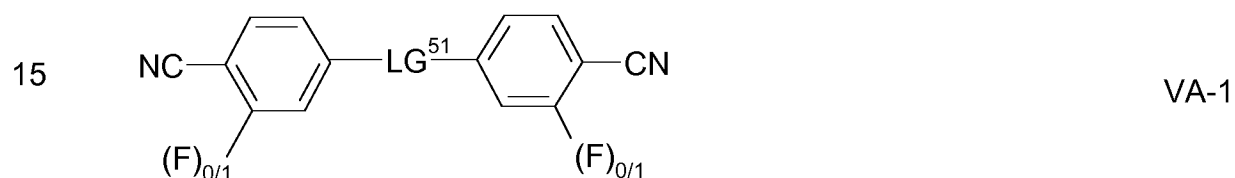
(F)₀ denotes H and
 (F)₁ denotes F.

and the other parameters have the respective meanings given above
 5 including the preferred meanings.

Preferably $Z^{51}-(CH_2)_Z-Z^{52}$ denotes $-O-CO-(CH_2)_n-CO-O-$, $-O-(CH_2)_n-O-$ or
 $-(CH_2)_n-$, more preferably $-O-CO-(CH_2)_n-CO-O-$, wherein n denotes 3, 5,
 7 or 9,

10

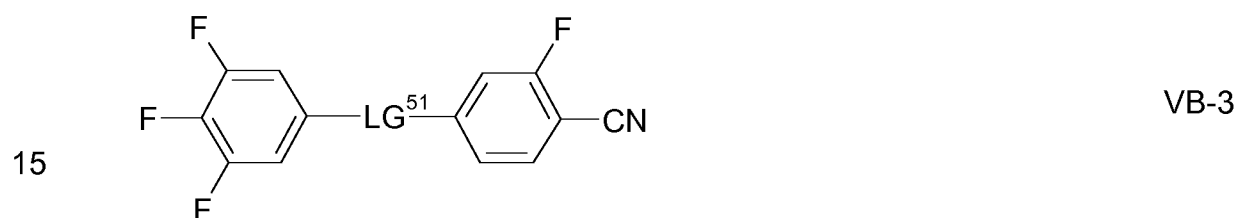
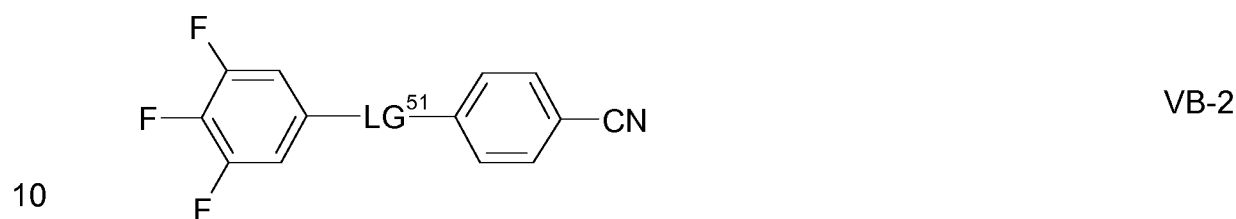
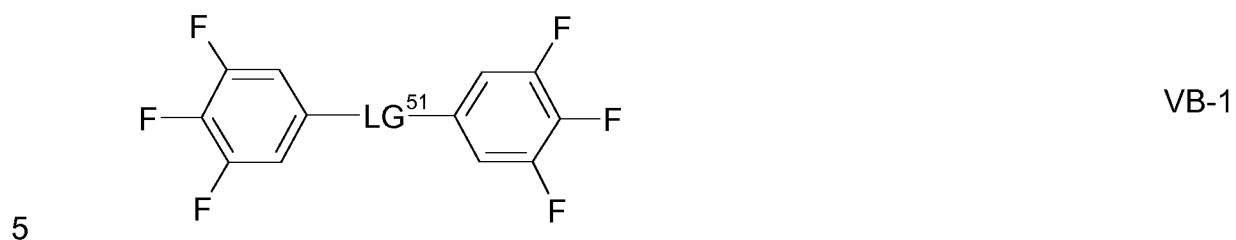
Particularly preferred compounds of formula VA are selected from the
 group of compounds of formulae VA-1 to VA-3



wherein the parameters have the respective meanings given above
 30 including the preferred meanings.

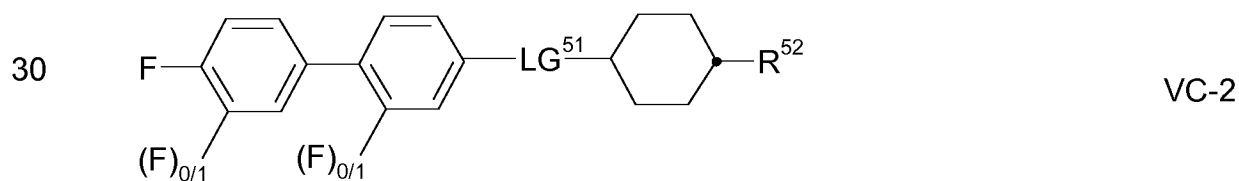
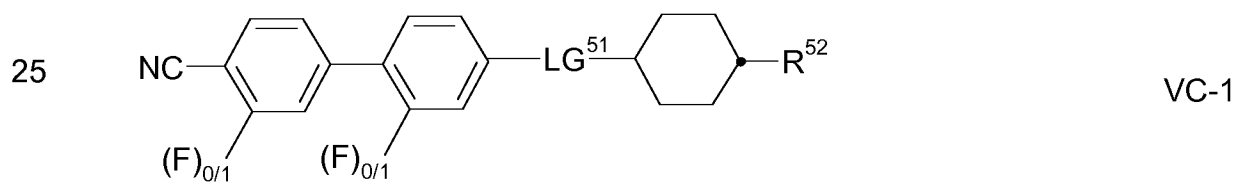
Particularly preferred compounds of formula VB are selected from the
 group of compounds of formulae VB-1 to VB-3

35



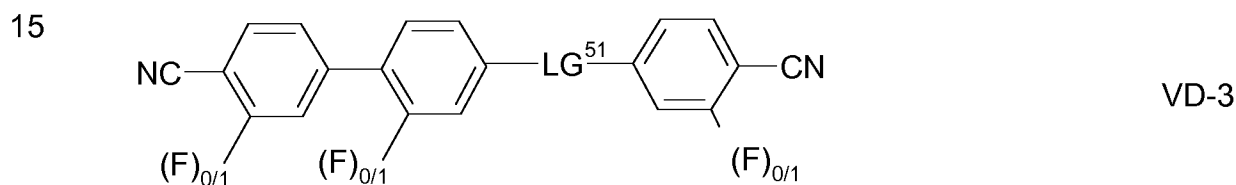
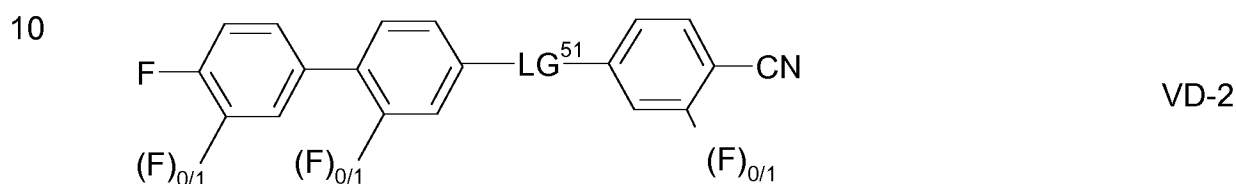
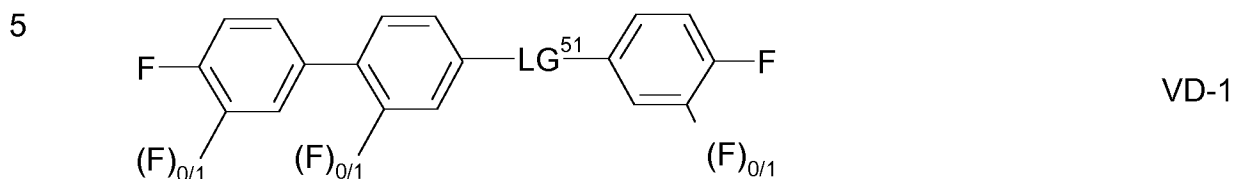
20 wherein the parameters have the respective meanings given above including the preferred meanings.

Particularly preferred compounds of formula VC are selected from the group of compounds of formulae VC-1 and VC-2



35 wherein the parameters have the respective meanings given above including the preferred meanings.

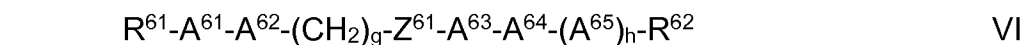
Compounds of formula VD are very much preferred. And of these particularly preferred compounds are selected from the group of compounds of formulae VD-1 to VD-3



20 wherein the parameters have the respective meanings given above including the preferred meanings.

25 The compounds of formula V can be synthesized according to or in analogy to methods which are known per se and which are described in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart. A preferred method of preparation is disclosed for example in WO2015/036079 A1.

30 In a further preferred embodiment, the LC medium in accordance with the present invention additionally comprises one or more compounds of formula VI,

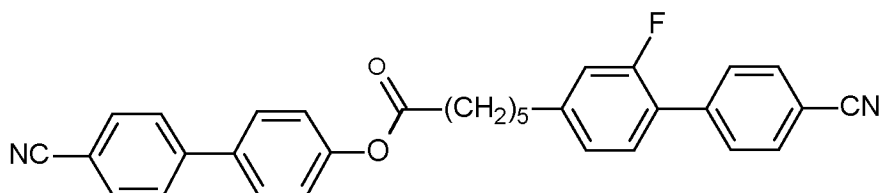


wherein

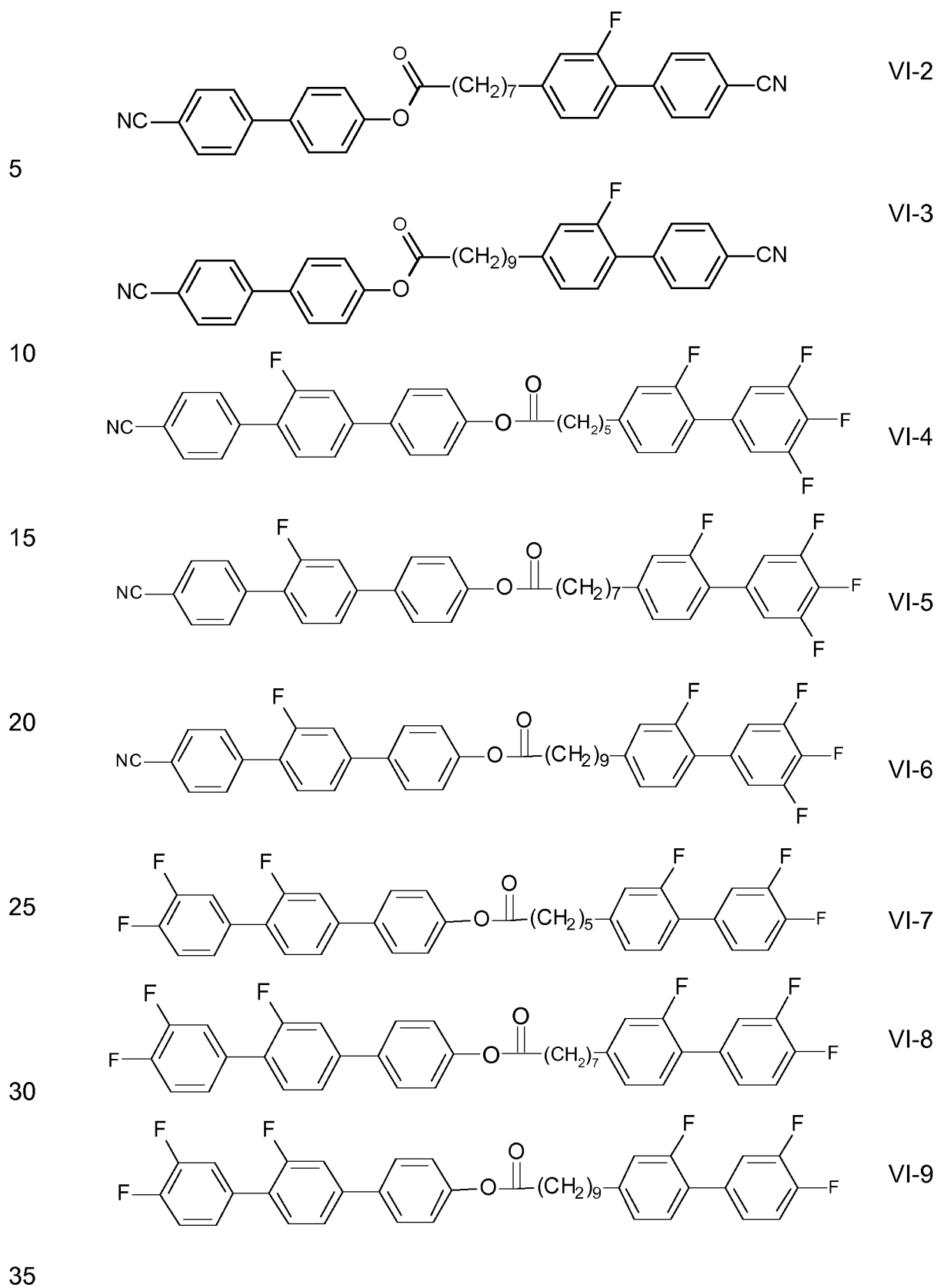
- R^{61} and R^{62} have each and independently one of the meanings as given above for R^{21} under formula II,
- A^{61} to A^{64} have each and independently one of the meanings as given above for A^{21} under formula II,
- Z^{61} denotes -O-, -COO-, -OCO-, -O-CO-O-, -OCH₂-, -CH₂O-, -CH₂CH₂-, -(CH₂)₄-, -CF₂CF₂-, -CH=CH-, -CF=CF-, -CH=CH-COO-, -OCO-CH=CH- or -C≡C-, optionally substituted with one or more of F, S and/or Si, preferably -O-, -COO-, -OCO- or -O-CO-O-, more preferably -O-, -COO- or -OCO-, most preferably -COO- or -OCO-,
- h denotes 0 or 1 and
- g denotes an integer from 1 to 15, preferably an odd (i.e. uneven) integer and, more preferably 3, 5, 7 or 9.
- Preferred compounds of formula VI are selected from compounds in which the groups (- A^{61} - A^{62} -) and (- A^{63} - A^{64} -) are each and independently selected from the groups of MG-1 to MG-8 as given above.

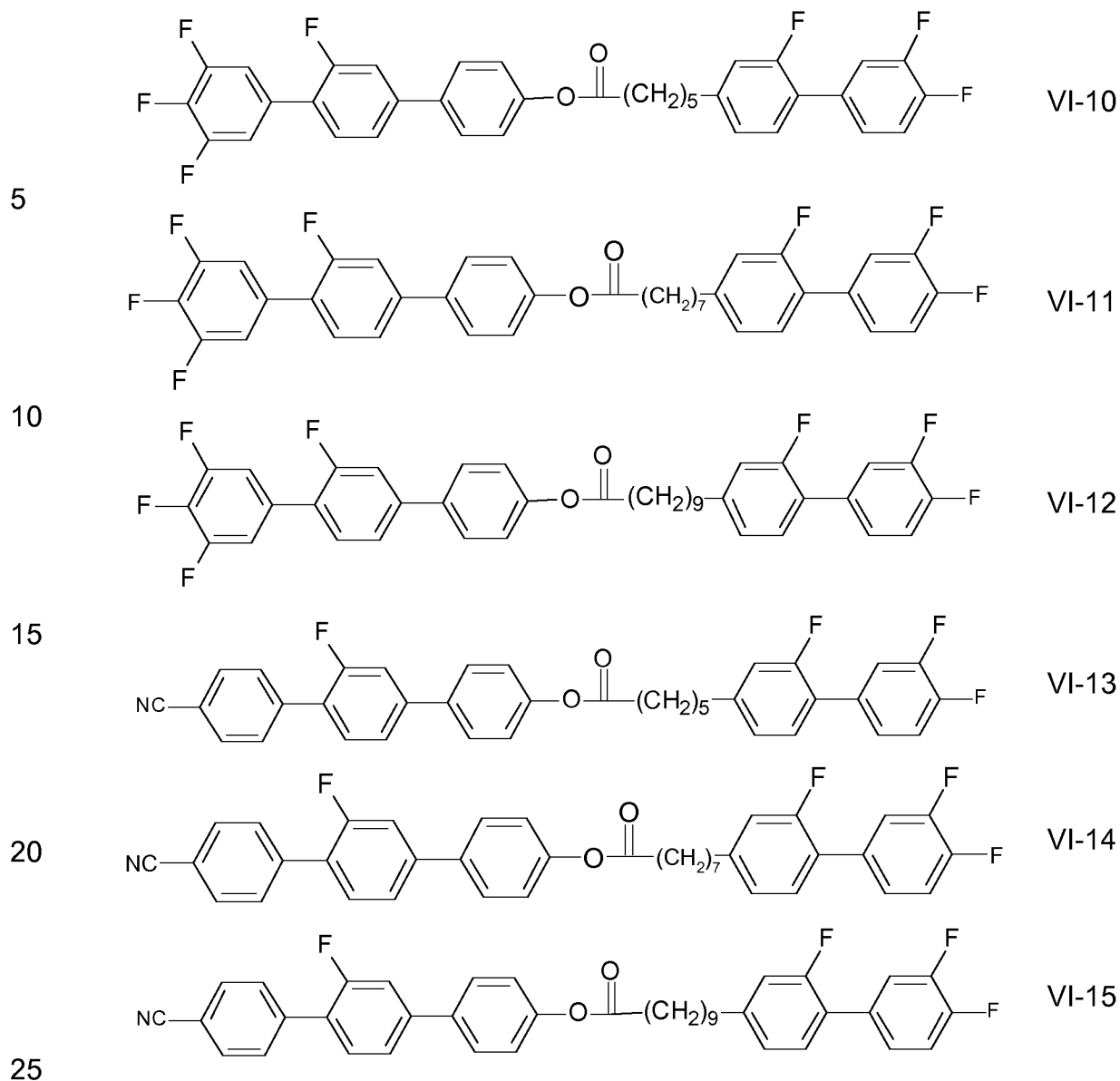
Further preferred are compounds of formula VI wherein h denotes 0 and the groups (- A^{61} - A^{62} -) and (- A^{63} - A^{64} -(A^{65}) _{h}) in formula VI are not identical or not mirror images or wherein h denotes 1

In particular preferred compounds of formula VI are selected from the group of compounds of the following formulae,



VI-1



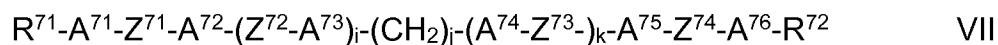


The compounds of formula VI can be synthesized according to or in analogy to methods which are known per se and which are described in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart. Preferably, the compounds of formula VI are synthesized according to or in analogy to methods which are disclosed for example in WO 2014/005672 A1.

In the mixture according to the present invention, the utilization of compounds of formula VI beside compounds of formula I is especially

useful in order to achieve high clearing points and also favorable values for e/K.

5 In a further preferred embodiment, the LC medium in accordance with the present invention additionally comprises one, two, three or more compounds of formula VII,



10 wherein

R^{71} and R^{72} have each and independently one of the meanings as given above for R^{21} under formula II,

15 A^{71} to A^{76} have each and independently one of the meanings as given above for A^{21} under formula II,

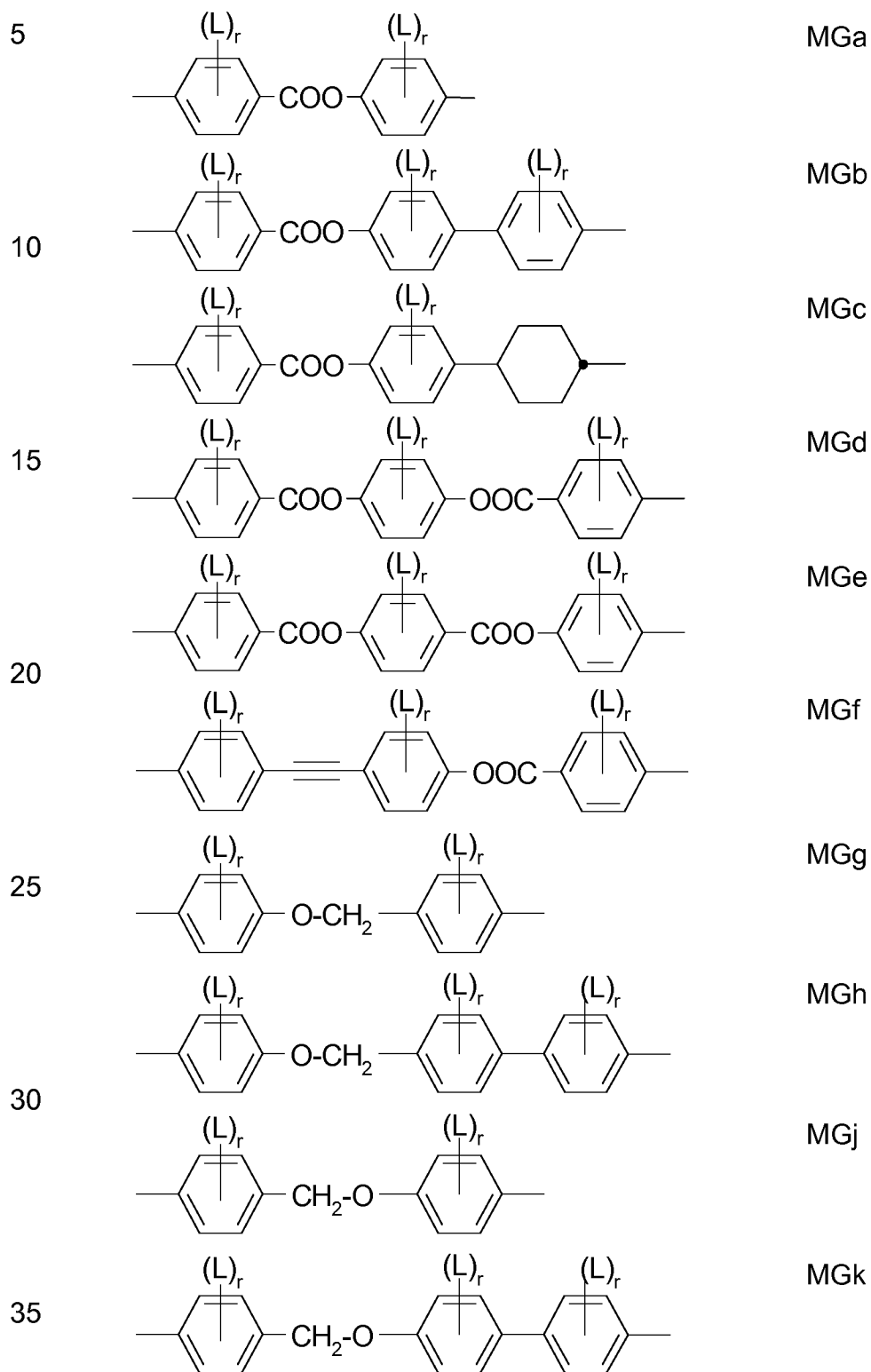
Z^{71} to Z^{74} each and independently denotes -COO-, -OCO-,
-O-CO-O-, -OCH₂-, -CH₂O-, -OCF₂-, -CF₂O-, -CH₂CH₂-,
-(CH₂)₄-, -CF₂CF₂-, -CH=CH-, -CF=CF-, -CH=CH-COO-,
20 -OCO-CH=CH- or -C≡C-, optionally substituted with one or more of F, S and/or Si or a single bond, preferably -COO-, -OCO-, -O-CO-O-, -OCF₂-, -CF₂O- or a single bond
more preferably -COO-, -OCO-, -OCF₂-, -CF₂O- or a
25 single bond,
with the proviso that at least one of Z^{71} to Z^{74} is not a single bond,

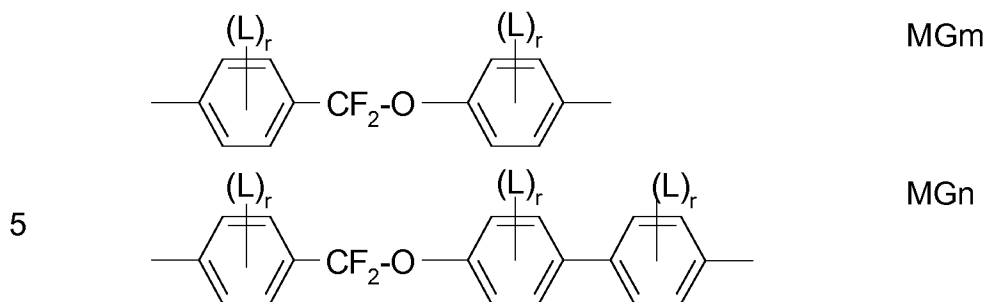
30 j denotes an integer from 1 to 15, preferably an odd (i.e. uneven) integer and, more preferably 3, 5, 7 or 9 and

i and k each and independently denotes 0 or 1.

35 Preferred compounds of formula VII are selected from compounds in which at least one of the groups $-A^{71}-Z^{71}-A^{72}-(Z^{72}-A^{73})_i-$,

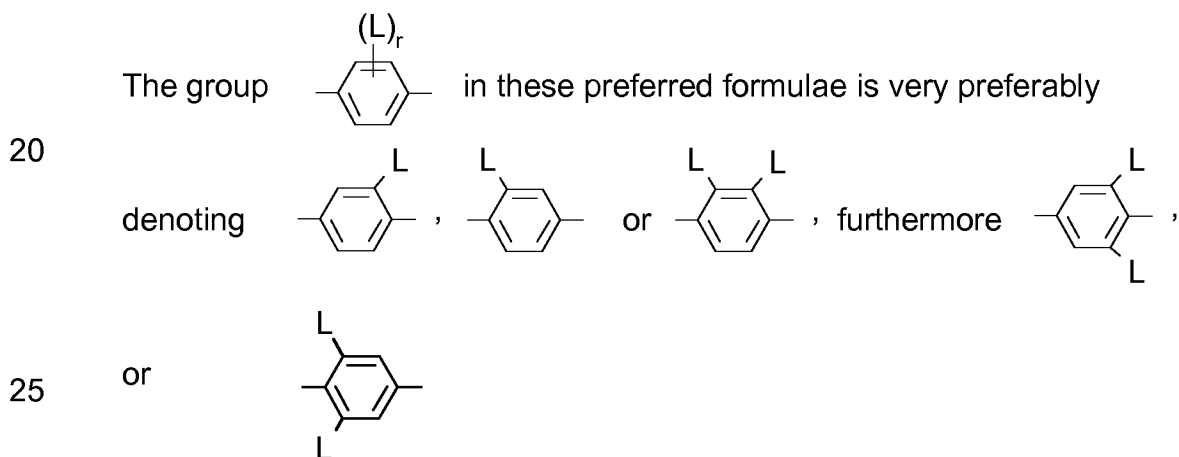
$-(A^{74}-Z^{73})_k-A^{75}-Z^{74}-A^{76}-$ are selected from the groups of MGa to MGn (the two reference Nos. "MG i" and "MG l" being deliberately omitted to avoid any confusion) and their mirror images





wherein

10 wherein L is in each occurrence independently of each other preferably F, Cl, CN or an optionally fluorinated alkyl, alkoxy or alkanoyl group with 1 to 7 C atoms, very preferably F, Cl, CN, CH₃, C₂H₅, OCH₃, OC₂H₅, COCH₃, COC₂H₅, COOCH₃, COOC₂H₅, CF₃, OCF₃, OCHF₂, OC₂F₅, in particular F, Cl, CN, CH₃, C₂H₅, OCH₃, COCH₃ and OCF₃, most
 15 preferably F, Cl, CH₃, OCH₃ and COCH₃ and r is in each occurrence independently of each other 0, 1, 2, 3 or 4, preferably 0, 1 or 2.

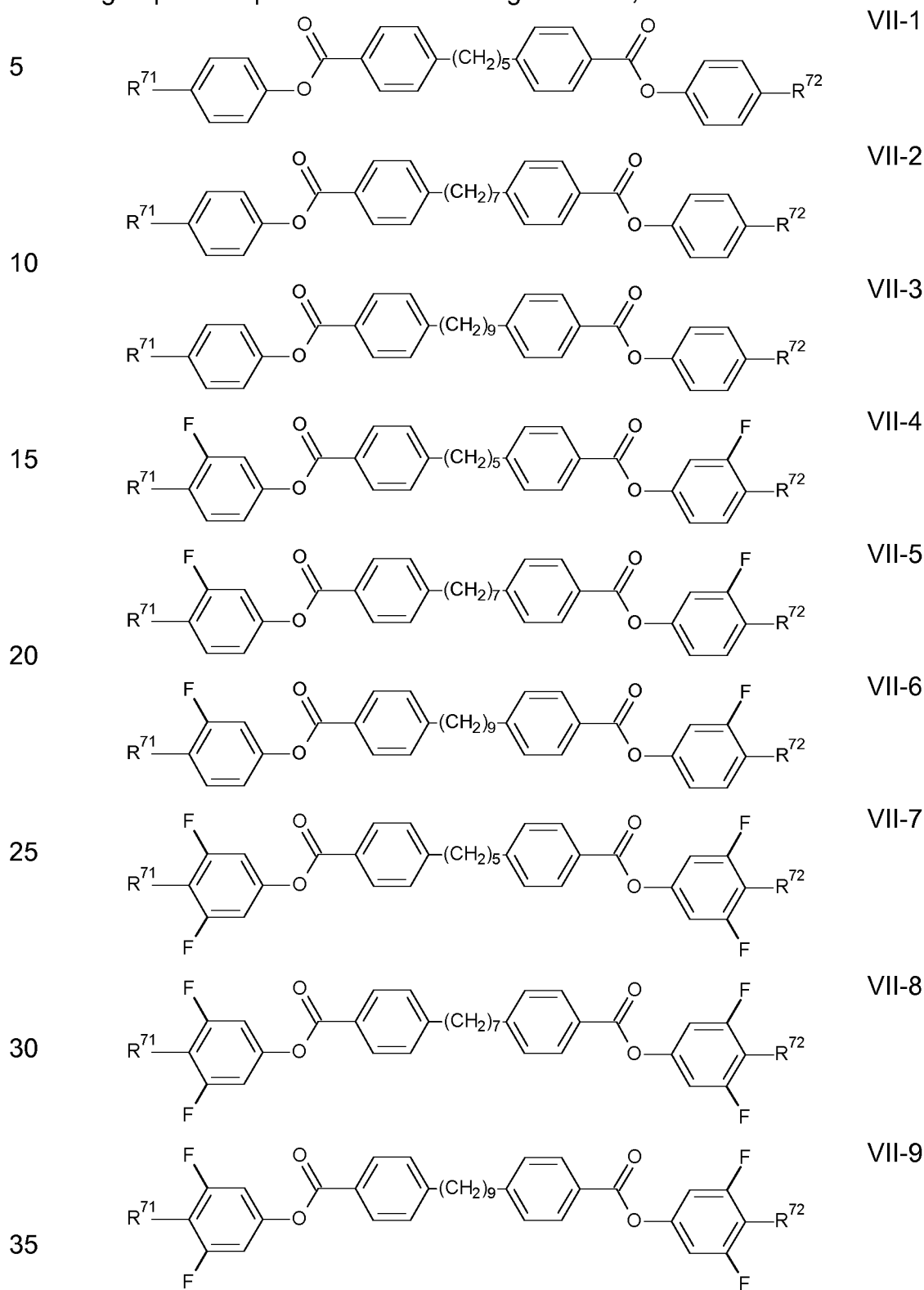


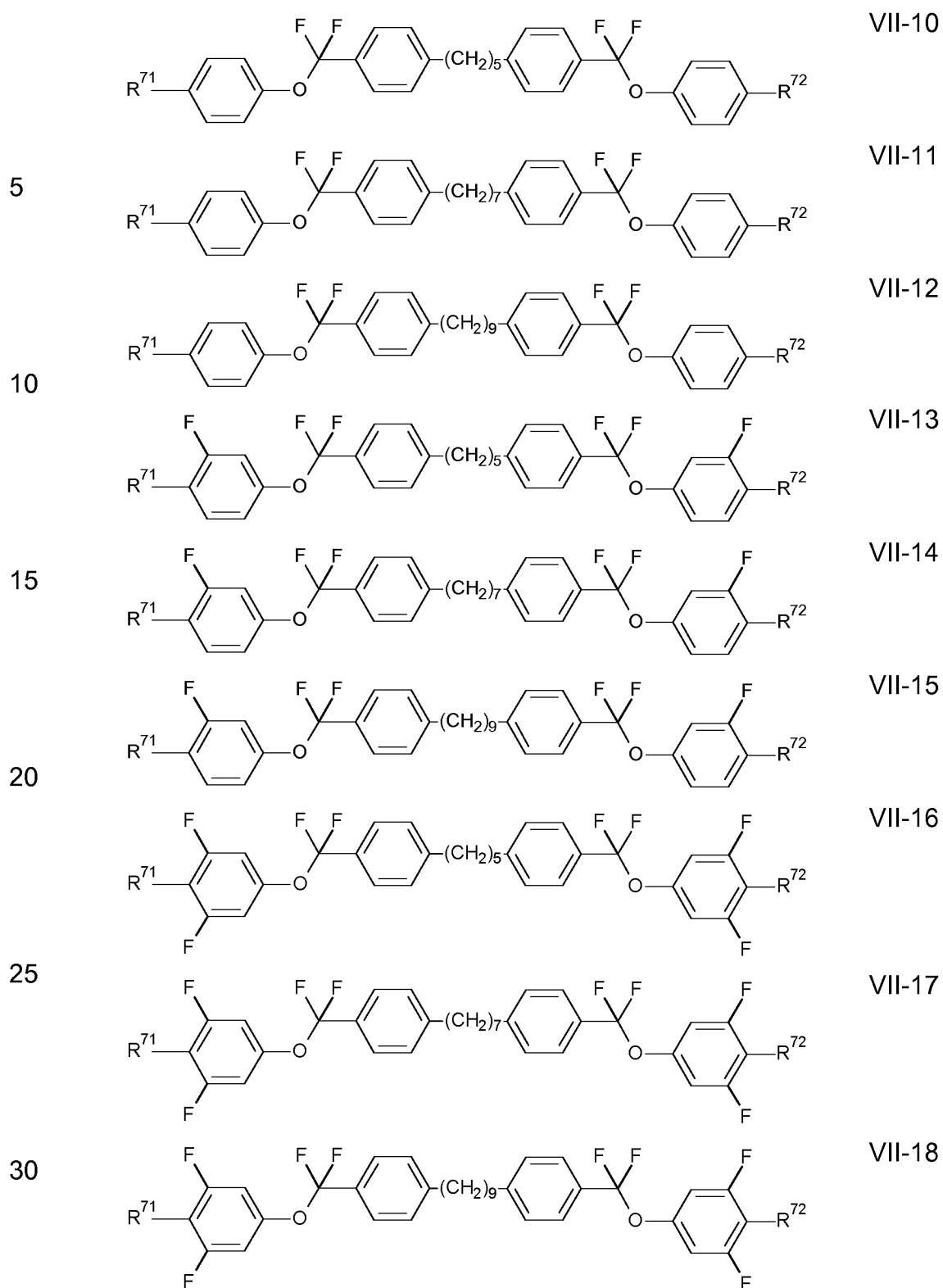
wherein L is preferably F, Cl, CH₃, OCH₃ and COCH₃.

30 Further preferred are compounds of formula VII wherein the groups -A⁷¹-Z⁷¹-A⁷²-(Z⁷²-A⁷³)_i- and -(A⁷⁴-Z⁷³-)_k-A⁷⁵-Z⁷⁴-A⁷⁶- in formula VII are identical or mirror images with the proviso that at least one of Z⁷¹ to Z⁷⁴ is not a single bond.

35 Further preferred are compounds of formula VII, wherein i and k both denote 1, more preferably one of i and k denotes 0 and the other 1, most preferably i and k both denote 0.

Epecially preferred compounds of formula VII are selected from the group of compounds of the following formulae,





wherein R^{71} and R^{72} , each and independently denote F or CN.

The compounds of formula VII can be synthesized according to or in analogy to methods which are known per se and which are described in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart. Preferably, the compounds of formula VII are synthesized according to or in analogy to methods which are disclosed for example in WO 2013/174478 A1.

In a further preferred embodiment, the medium in accordance with the present invention optionally comprises one or more chiral dopants, especially when utilized in a flexoelectric device.

The chiral compounds induce a chiral nematic texture with a pitch (P_0), which is in a first approximation inversely proportional to the concentration (c) of the chiral material used. The constant of proportionality of this relation is called the helical twisting power (HTP) of the chiral substance and defined by the following equation

$$\text{HTP} \equiv 1 / (c \cdot P_0) \quad (1)$$

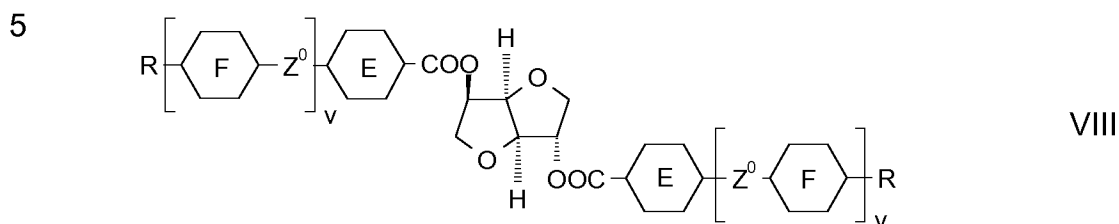
wherein
 c is concentration of the chiral compound.

For example, a uniform lying helix texture is realized using a chiral nematic liquid crystal with a short pitch, typically in the range from 0.2 μm to 1 μm , preferably of 1.0 μm or less, in particular of 0.5 μm or less, which is unidirectional aligned with its helical axis parallel to the substrates, e. g. glass plates, of a liquid crystal cell. In this configuration, the helical axis of the chiral nematic liquid crystal is equivalent to the optical axis of a birefringent plate.

Preferred are chiral dopants with a high helical twisting power (HTP), in particular those disclosed in WO 98/00428.

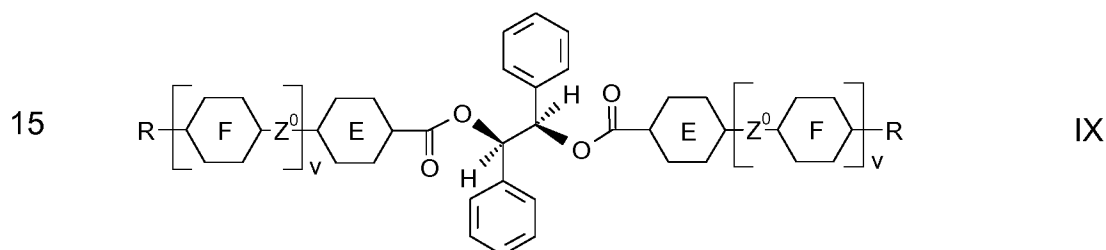
Typically, used chiral dopants are e.g. the commercially available R/S-5011, CD-1, R/S-811 and CB-15 (from Merck KGaA, Darmstadt, Germany).

In another preferred embodiment, the chiral dopants are preferably selected from formula VIII,



10

and/or formula XI,



20

including the respective (S,S) enantiomer,

wherein E and F are each independently 1,4-phenylene or trans-1,4-cyclohexylene, v is 0 or 1, Z⁰ is -COO-, -OCO-, -CH₂CH₂- or a single bond and R is alkyl, alkoxy or alkanoyl with 1 to 12 C atoms.

25

The compounds of formula VIII and their synthesis are described in WO 98/00428. The compounds of formula IX and their synthesis are described in GB 2,328,207.

30

The above-mentioned chiral dopants R/S-5011 and the compounds of formula VIII and IX exhibit a very high helical twisting power (HTP) and are therefore particularly useful for the purpose of the present invention.

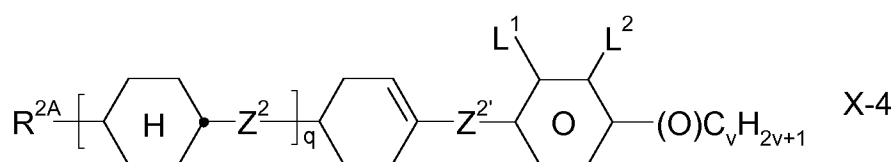
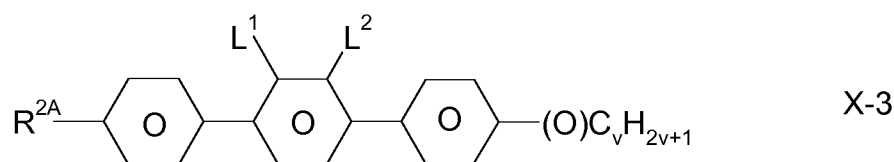
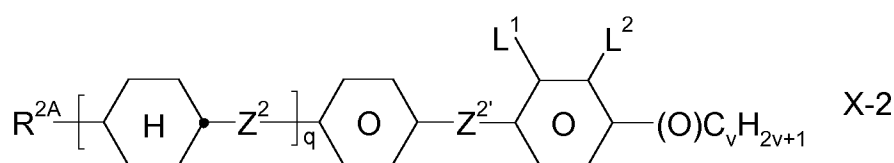
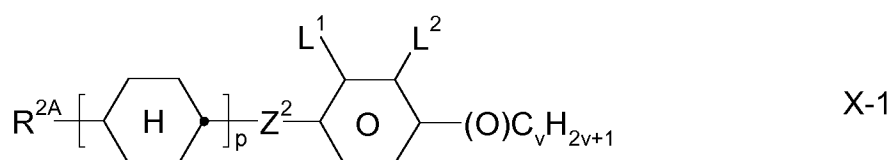
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The liquid crystalline medium preferably comprises preferably 1 to 5, in particular 1 to 3, very preferably 1 or 2 chiral dopants, preferably selected from the above formula VIII, and/or formula IX and/or

R-5011 or S-5011, very preferably, the chiral compound is R-5011, S-5011.

5 The amount of chiral compounds in the liquid crystalline medium is preferably from 0.1 to 15 %, in particular from 0.5 to 10 %, very preferably 1 to 5 % by weight of the total mixture.

10 Preferably, the LC medium comprises one or more nematic LC compounds selected from compounds indicated below:



in which

35 $\text{R}^{2\text{A}}$ denotes H, an alkyl or alkoxy radical having 1 to 15 C atoms, where, in addition, one or more CH_2 groups in these radicals may each be replaced, independently of one another, by $-\text{C}\equiv\text{C}-$, $-\text{CF}_2\text{O}-$, $-\text{CH}=\text{CH}-$, $\text{—}\diamond\text{—}$, $\text{—}\diamond\diamond\text{—}$, $-\text{O}-$, $-\text{CO}-\text{O}-$ or $-\text{O}-\text{CO}-$ in such a way that O atoms are not linked directly to one another and in

which, in addition, one or more H atoms may be replaced by halogen,

- 5 L^1 and L^2 each, independently of one another, denote F, Cl, CF_3 or CHF_2 , preferably each denote F,
- 10 Z^2 and $Z^{2'}$ each, independently of one another, denote a single bond, $-CH_2CH_2-$, $-CH=CH-$, $-C\equiv C-$, $-CF_2O-$, $-OCF_2-$, $-CH_2O-$, $-OCH_2-$, $-COO-$, $-OCO-$, $-C_2F_4-$, $-CF=CF-$ or $-CH=CHCH_2O-$,
- p denotes 0, 1 or 2,
- 15 q denotes 0 or 1,
- $(O)C_vH_{2v+1}$ denotes OC_vH_{2v+1} or C_vH_{2v+1} and
- 20 v denotes 1 to 6.

20 The liquid crystal media may contain further additives like for example stabilizers, inhibitors, surface-active compounds, lubricating agents, wetting agents, dispersing agents, hydrophobing agents, adhesive agents, flow improvers, defoaming agents, deaerators, diluents, reactive

25 diluents, auxiliaries, colourants, dyes, pigments or nanoparticles in usual concentrations. The total concentration of these further constituents is in the range of 0.1 % to 10 %, preferably 0.1 % to 6 %, based on the total mixture. The concentrations of the individual compounds used each are preferably in the range of 0.1 % to 3 %.

30 The concentration of these and of similar additives is not taken into consideration for the values and ranges of the concentrations of the liquid crystal components and compounds of the liquid crystal media in this application. This also holds for the concentration of the dichroic dyes

35 used in the mixtures, which are not counted when the concentrations of the compounds respectively the components of the host medium are

specified. The concentration of the respective additives is always given relative to the final doped mixture.

5 In general, the total concentration of all compounds in the media according to this application is 100 %.

10 The liquid crystal media according to the present invention consists of several compounds, preferably of 2 to 40, more preferably of 3 to 30 and most preferably of 4 to 25 compounds.

The media in accordance with the present invention exhibit high values of the elastic constant k_{11} and a high flexoelectric coefficient e . The liquid crystal media preferably exhibit a $k_{11} \leq 100$ pN, preferably ≤ 20 pN.

15 The liquid crystal media preferably exhibit a $k_{33} \leq 100$ pN, preferably ≤ 15 pN.

20 The liquid crystal media preferably exhibit a flexoelectric coefficient $|e_{11}| \geq 0.2$ pC/m, preferably ≥ 1 pC/m.

The liquid crystal media preferably exhibit a flexoelectric coefficient $|e_{33}| \geq 0.2$ pC/m, preferably ≥ 2 pC/m.

25 The liquid crystal media preferably exhibit a flexo-elastic ratio ($\bar{e} / K$) in the range from 1 to 10 V^{-1} , preferably in the range from 1 to 7 V^{-1} , more preferably in the range from 1 to 5 V^{-1} .

30 The media in accordance with the present invention exhibit high clearing points up to 60°C and higher, preferably up to 65°C and higher and more preferably up to 70°C and higher.

35 The media in accordance with the present invention exhibit broad nematic phases of 30°C and more, preferably 35°C and more or even 40°C or more.

The media in accordance with the present invention exhibit N_{TB} phases below 20°C or less, preferably below 15°C or less and more preferably below 0°C or less.

- 5 The media in accordance with the present invention exhibit high stabilities against crystallization at room temperature of more than 100 h, preferably more than 250 h or more than 1000 h.

- 10 The media in accordance with the present invention exhibit high stabilities against crystallization even at low temperatures (LTS). Accordingly, the media do not crystallize even at temperatures down to 0°C, preferably down to -10°C, more preferably down to -20°C.

- 15 In a preferred embodiment, the LC medium comprises:

- 20 • 1 to 10, preferably 1 to 5, more preferably 1 or 3, most preferably 1 or 2 compounds of formula I, preferably selected from formulae Ia-1-2a, Ia-1-5a, Ib-1-4a and/or Ib-1-9a. The amount of compounds of formula I in the liquid crystalline medium as a whole is preferably in the range from 5 to 50 %, in particular in the range from 6 to 30 %, especially in the range from 7 to 20 % by weight of the total mixture,

25 and

- 30 • optionally 1 to 10, preferably 1 to 5, more preferably 1 or 3, most preferably 1 or 2 compounds of formula II, preferably selected from compounds of formula II wherein (-A²¹-A²²-) and (-A²³-A²⁴-) in formula II are identical or mirror images, more preferably of compounds of formulae II'a-5 and/or II'a-6. The amount of compounds of formula II in the liquid crystalline medium, if present, is preferably in the range from 0 to 30 %, more preferably in the range from 1 to 20 %, even more preferably in the range from 2 to 10 % by weight of the total mixture,

35 and/or

- 5
- optionally 1 to 10, preferably 1 to 5, more preferably 1 or 3, most preferably 1 or 2 compounds of formula III, preferably selected from symmetrical compounds of the above formulae IIIc-2 and/or IIIc-3. The amount of compounds of formula III in the liquid crystalline medium, if present, is preferably in the range from 1 to 50 %, more preferably in the range from 5 to 30 %, even more preferably in the range from 10 to 20 % by weight of the total mixture,

10

and/or

15

 - optionally, 1 to 10, preferably 1 to 5, more preferably 1 or 3, most preferably 1 or 2 compounds of formula IV, preferably selected from the symmetrical ones IVb and/or non-symmetrical ones IVc, more preferably from formulae IVb-5, IVc-2, IVc-3, IVc-12 and or IVc-15. The amount of compounds of formula IV in the liquid crystalline medium, if present, is preferably in the range from 1 to 98 %, more preferably in the range from 20 to 80 %, even more preferably in the range from 30 to 60 % by weight of the total mixture,

20

and/or

25

 - optionally, 1 to 6, in particular 2 to 5, very preferably 3 or 4 compounds of formula V, preferably selected from the above formulae VA-1, VD-2 and/or VD-3. The amount of compounds of formula V in the liquid crystalline medium, if present, is preferably in the range from 1 to 70 %, more preferably in the range from 10 to 60 %, even more preferably in the range from 20 to 50 % by weight of the total mixture,

30

and/or

35

 - optionally 1 to 10, preferably 1 to 5, more preferably 1 or 3, most preferably 1 or 2 compounds from the above formulae VI, preferably from compounds of formula VI-4, VI-5, VI-7 and/or VI-9.

The amount of compounds of formula VI in the liquid crystalline medium, if present, is preferably from 1 to 40 %, in particular from 5 to 25 %, very preferably 10 to 15 % by weight of the total mixture,

5

and/or

- optionally 1 to 10, preferably 1 to 5, more preferably 1 or 3, most preferably 1 or 2 compounds from the above formulae VII, preferably from compounds of formula VII-4, VII-5 and/or VII-8.

10

The amount of compounds of formula VII in the liquid crystalline medium, if present, is preferably from 1 to 35 %, in particular from 5 to 25 %, very preferably 10 to 15 % by weight of the total mixture,

15

and/or

- optionally, 1 to 5, in particular 1 to 3, very preferably 1 or 2 chiral dopants, preferably selected from the above formula VIII and/or formula IX and/or R-5011 or S-5011, very preferably, the chiral compound is R-5011 or S-5011. The amount of chiral compounds in the liquid crystalline medium, if present, is preferably from 1 to 15 %, in particular from 0.5 to 10 %, very preferably 0.1 to 5 % by weight of the total mixture,

20

25

and/or

- optionally up to 25, in particular up to 20, very preferably up to 15, different compounds selected from compounds of formula X. If present, the amount of compounds of formula X in the liquid crystalline medium as a whole, is preferably from 1 to 50 %, in particular from 5 to 30 %, very preferably 10 to 25 % by weight of the total mixture,

30

and/or

35

- optionally further additives, such as for example stabilizers, antioxidants, etc. in usual concentrations. The total concentration of these further constituents, if present, is in the range of 0.1 to 10 %, preferably 0.1 to 6 %, based on the total mixture. The concentrations of the individual compounds used each are preferably in the range of 0.1 to 3 %.

In another preferred embodiment, the LC medium of the present invention consists only of compounds selected from formula I to X, very preferably the LC medium consists only of compounds selected from formula I to IX.

The compounds forming the LC medium in accordance with the present invention are mixed in conventional way. As a rule, the required amount of the compound used in the smaller amount is dissolved in the compound used in the greater amount. In case the temperature is above the clearing point of the compound used in the higher concentration, it is particularly easy to observe completion of the process of dissolution. It is, however, also possible to prepare the media by other conventional ways, e.g. using so-called pre-mixtures, which can be e.g. homologous or eutectic media of compounds or using so-called multi-bottle-systems, the constituents of which are ready to use media themselves. Thus, the invention also relates to a process for the production of an LC medium as described above and below.

In particular, the invention relates to a process for the production of an LC medium comprising the steps of mixing one or more compounds of formula I, with at least one compound selected from compounds of formulae II to X.

The liquid crystalline media in accordance with the present invention can be used in electro optic devices, for example liquid crystal devices, such as STN, TN, AMD-TN, temperature compensation, guest-host, phase change or surface stabilized or polymer stabilized cholesteric texture (SSCT, PSCT) displays, in active and passive optical elements like polarizers, compensators, reflectors, alignment layers, colour filters or

holographic elements, in adhesives, synthetic resins with anisotropic mechanical properties, cosmetics, diagnostics, liquid crystal pigments, for decorative and security applications, in nonlinear optics, optical information storage or as chiral dopants. Thus, another aspect of the present invention is the use of a LC medium, comprising at least one compound of formula I in electro optic devices.

Since the media in accordance with the present invention are particularly beneficially for flexoelectric liquid crystal display applications, such as, for example, devices of the ULH or USH mode.

Thus, another object of the present invention is a liquid crystal device, preferably a flexoelectric device, comprising a medium, which comprises one or more compounds of formula I.

A flexoelectric display according to a preferred embodiment of the present invention comprises two plane parallel substrates, preferably glass plates covered with a transparent conductive layer such as indium tin oxide (ITO) on their inner surfaces, optionally alignment layers and a medium comprising one or more compounds of formula I and a chiral dopant as described above and below.

If an electrical field is applied to this configuration normal to the helical axis, the optical axis is rotated in the plane of the cell, similar as the director of a ferroelectric liquid crystal rotate as in a surface stabilized ferroelectric liquid crystal display.

The field induces a splay bend structure in the director, which is accommodated by a tilt in the optical axis. The angle of the rotation of the axis is in first approximation directly and linearly proportional to the strength of the electrical field. The optical effect is best seen when the liquid crystal cell is placed between crossed polarizers with the optical axis in the unpowered state at an angle of 22.5° to the absorption axis of one of the polarizers. This angle of 22.5° is also the ideal angle of rotation of the electric field, as thus, by the inversion the electrical field, the optical axis is rotated by 45° and by appropriate selection of the

relative orientations of the preferred direction of the axis of the helix, the absorption axis of the polarizer and the direction of the electric field, the optical axis can be switched from parallel to one polarizer to the centre angle between both polarizers. The optimum contrast is then achieved
 5 when the total angle of the switching of the optical axis is 45° . In that case, the arrangement can be used as a switchable quarter wave plate, provided the optical retardation, i. e. the product of the effective birefringence of the liquid crystal and the cell gap, is selected to be the quarter of the wavelength. In this context, the wavelength referred to is
 10 550 nm, the wavelength for which the sensitivity of the human eye is highest, unless explicitly stated otherwise.

The angle of rotation of the optical axis (Φ) is given in good approximation by the formula:

15

$$\tan \Phi = e P_0 E / (2 \pi K)$$

wherein

P_0 is the undisturbed pitch of the cholesteric liquid crystal,
 $\bar{e}$ is the average [$\bar{e} = \frac{1}{2} (e_{11} + e_{33})$] of the splay flexoelectric
 20 coefficient (e_{11}) and the bend flexoelectric coefficient (e_{33}),
 E is the electrical field strength and
 K is the average [$K = \frac{1}{2} (k_{11} + k_{33})$] of the splay elastic constant (k_{11}) and the bend elastic constant (k_{33})

and wherein

25 e / K is called the flexo-elastic ratio.

This angle of rotation is half the switching angle in a flexoelectric switching element.

30 The response time (τ) of this electro-optical effect is given in good approximation by the formula:

$$\tau = [P_0 / (2 \pi)]^2 \cdot \gamma / K$$

35 wherein

γ is the effective viscosity coefficient associated with the distortion of the helix.

5 The flexoelectric effect is characterized by fast response times ($T_{on}+T_{off}$ at 35°C) typically ranging from 1 ms to 10 ms, preferably < 5ms and even more preferably < 3ms. It further features excellent grey scale capability.

There is a critical field (E_c) to unwind the helix, which can be obtained from equation

10

$$E_c = (\pi^2 / P_0) \cdot [k_{22}/(\epsilon_0 \cdot \Delta\epsilon)]^{1/2}$$

wherein

15 k_{22} is the twist elastic constant,
 ϵ_0 is the permittivity of vacuum and
 $\Delta\epsilon$ is the dielectric anisotropy of the liquid crystal.

20 The inventive media in accordance with the present invention can be aligned in their cholesteric phase into different states of orientation by methods that are known to the expert, such as surface treatment or electric fields. For example, they can be aligned into the planar (Grandjean) state, into the focal conic state or into the homeotropic state.

25 The term “planar alignment” or orientation of a liquid crystal or mesogenic material in a display cell or on a substrate means that the mesogenic groups in the liquid crystal or mesogenic material are oriented substantially parallel to the plane of the cell or substrate, respectively.

30

The term “homeotropic alignment” or orientation of a liquid crystal or mesogenic material in a display cell or on a substrate means that the mesogenic groups in the liquid crystal or mesogenic material are oriented substantially perpendicular to the plane of the cell or substrate, respectively.

35

The switching between different states of orientation according to a preferred embodiment of the present invention is exemplarily described below in detail.

5 According to this preferred embodiment, the sample is placed into a cell comprising two plane-parallel glass plates coated with electrode layers, e.g. ITO layers and aligned in its cholesteric phase into a planar state wherein the axis of the cholesteric helix is oriented normal to the cell walls. This state is also known as Grandjean state and the texture of the sample,
10 which is observable e.g. in a polarization microscope, as Grandjean texture. Planar alignment can be achieved e.g. by surface treatment of the cell walls, for example by rubbing and/or coating with an alignment layer such as polyimide.

15 A Grandjean state with a high quality of alignment and only few defects can further be achieved by heating the sample to the isotropic phase, subsequently cooling to the chiral nematic phase at a temperature close to the chiral nematic-isotropic phase transition and flow alignment by lightly pressing the cell.

20 In the planar state, the sample shows selective reflection of incident light, with the central wavelength of reflection depending on the helical pitch and the mean refractive index of the material.

25 When an electric field is applied to the electrodes, for example with a frequency from 10 Hz to 1 kHz and an amplitude of up to $12 V_{\text{rms}}/\mu\text{m}$, the sample is being switched into a homeotropic state where the helix is unwound and the molecules are oriented parallel to the field, i.e. normal to the plane of the electrodes. In the homeotropic state, the sample is
30 transmissive when viewed in normal daylight and appears black when being put between crossed polarizers.

Upon reduction or removal of the electric field in the homeotropic state, the sample adopts a focal conic texture, where the molecules exhibit a
35 helically twisted structure with the helical axis being oriented perpendicular to the field, i.e. parallel to the plane of the electrodes. A

focal conic state can also be achieved by applying only a weak electric field to a sample in its planar state. In the focal conic state the sample is scattering when viewed in normal daylight and appears bright between crossed polarizers.

5

A sample of a medium in accordance with the present invention in different states of orientation exhibits different transmission of light. Therefore, the respective state of orientation, as well as its quality of alignment, can be controlled by measuring the light transmission of the sample depending on the strength of the applied electric field. Thereby it is also possible to determine the electric field strength required to achieve specific states of orientation and transitions between these different states.

10

15

In a sample of a medium in accordance with the present invention, the above-described focal conic state consists of many disordered birefringent small domains. By applying an electric field greater than the field for nucleation of the focal conic texture, preferably with additional shearing of the cell, a uniformly aligned texture is achieved where the helical axis is parallel to the plane of the electrodes in large, well-aligned areas. In accordance with the literature on state of the art chiral nematic materials, such as P. Rudquist et al., *Liq. Cryst.* **23** (4), 503 (1997), this texture is also called uniformly lying helix (ULH) texture. This texture is required to characterize the flexoelectric properties of the inventive compound.

20

25

Starting from the ULH texture, the inventive media can be subjected to flexoelectric switching by application of an electric field. This causes rotation of the optic axis of the material in the plane of the cell substrates, which leads to a change in transmission when placing the material between crossed polarizers. The flexoelectric switching of inventive materials is further described in detail in the introduction above and in the examples.

30

It is also possible to obtain the ULH texture, starting from the focal conic texture, by applying an electric field with a high frequency, of for example 10 kHz, to the sample whilst cooling slowly from the isotropic phase into

35

the cholesteric phase and shearing the cell. The field frequency may differ for different compounds.

5 Apart from the use in flexoelectric devices, the media in accordance with the present invention are also suitable for other types of displays and other optical and electro optical applications, such as optical compensation or polarizing films, colour filters, reflective cholesterics, optical rotatory power and optical information storage.

10 Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention fully. The following examples are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever.

15 Unless the context clearly indicates otherwise, as used herein plural forms of the terms herein are to be construed as including the singular form and vice versa.

20 Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of the words, for example "comprising" and "comprises", mean "including but not limited to" and are not intended to (and do not) exclude other components.

25 Throughout the present application it is to be understood that the angles of the bonds at a C atom being bound to three adjacent atoms, e.g. in a C=C or C=O double bond or e.g. in a benzene ring, are 120° and that the angles of the bonds at a C atom being bound to two adjacent atoms, e.g. in a C≡C or in a C≡N triple bond or in an allylic position C=C=C are
30 180°, unless these angles are otherwise restricted, e.g. like being part of small rings, like 3-, 4- or 5-atomic rings, notwithstanding that in some instances in some structural formulae these angles are not represented exactly.

35 It will be appreciated that variations to the foregoing embodiments of the invention can be made while still falling within the scope of the invention.

Each feature disclosed in this specification, unless stated otherwise, may be replaced by alternative features serving the same, equivalent or similar purpose. Thus, unless stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

5

All of the features disclosed in this specification may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. In particular, the preferred features of the invention are applicable to all aspects of the invention and may be used in any combination. Likewise, features described in non-essential combinations may be used separately (not in combination).

10

The parameter ranges indicated in this application all include the limit values including the maximum permissible errors as known by the expert. The different upper and lower limit values indicated for various ranges of properties in combination with one another give rise to additional preferred ranges.

15

The total concentration of all compounds in the media according to this application is 100 %. All concentrations are given in % w/w, unless explicitly stated otherwise.

20

In the foregoing and in the following examples, unless otherwise indicated, all temperatures are set forth uncorrected in degrees Celsius and all parts and percentages are by weight.

25

It goes without saying to the person skilled in the art that the LC media may also comprise compounds in which, for example, H, N, O, Cl, F have been replaced by the corresponding isotopes.

30

The following abbreviations are used to illustrate the liquid crystalline phase behaviour of the compounds: $T_{N,I}$ = clearing point; K = crystalline; N = nematic; N_{TB} = second nematic; S or Sm = smectic; Ch = cholesteric; I = isotropic; T_g = glass transition. The numbers between the symbols indicate the phase transition temperatures in °C.

35

In the present application and especially in the following examples, the structures of the liquid crystal compounds are represented by abbreviations, which are also called “acronyms”. The transformation of the abbreviations into the corresponding structures is straightforward according to the following three tables A to C.

All groups C_nH_{2n+1} , C_mH_{2m+1} and C_lH_{2l+1} are preferably straight chain alkyl groups with n , m and l C-atoms, respectively, all groups C_nH_{2n} , C_mH_{2m} and C_lH_{2l} are preferably $(CH_2)_n$, $(CH_2)_m$ and $(CH_2)_l$, respectively and $-CH=CH-$ preferably is *trans*- respectively *E* vinylene. Preferably n , m and l denote an integer between 1 and 12.

Table A lists the symbols used for the ring elements, table B those for the linking groups and table C those for the symbols for the left hand and the right hand end groups of the molecules.

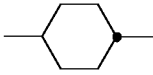
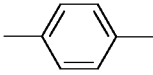
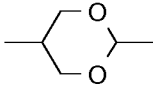
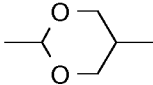
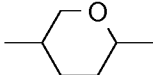
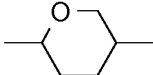
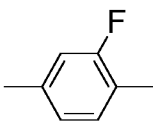
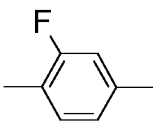
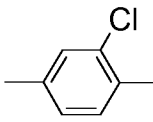
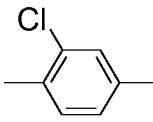
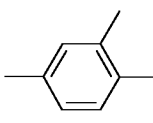
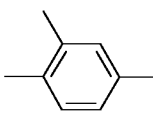
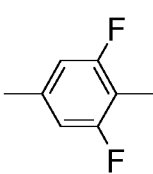
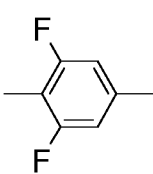
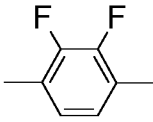
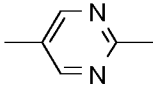
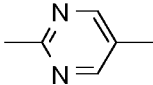
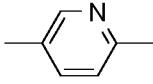
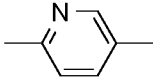
20

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Table A: Ring Elements

	C		P	
5	D		DI	
	A		AI	
10	G		GI	
	G(Cl)		GI(Cl)	
15	G(1)		GI(1)	
20	U		UI	
25	Y			
	M		MI	
30	N		NI	
35				

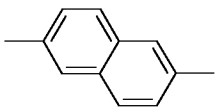
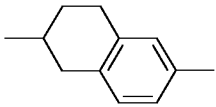
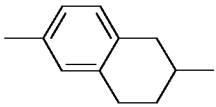
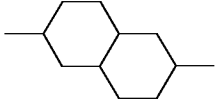
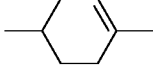
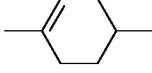
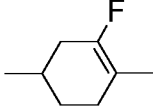
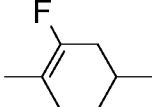
	np			
5	th		thl	
10	dh			
	L		LI	
15	F		FI	

Table B: Linking Groups

20	n	$(-\text{CH}_2-)_n$	"n" is an integer between 1 and 13 except 2	
	E	$-\text{CH}_2-\text{CH}_2-$		
	V	$-\text{CH}=\text{CH}-$		
	T	$-\text{C}\equiv\text{C}-$		
	W	$-\text{CF}_2-\text{CF}_2-$		
	B	$-\text{CF}=\text{CF}-$		
25	Z	$-\text{CO}-\text{O}-$	ZI	$-\text{O}-\text{CO}-$
	X	$-\text{CF}=\text{CH}-$	XI	$-\text{CH}=\text{CF}-$
	1O	$-\text{CH}_2-\text{O}-$	O1	$-\text{O}-\text{CH}_2-$
	Q	$-\text{CF}_2-\text{O}-$	QI	$-\text{O}-\text{CF}_2-$

30

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Table C: End Groups

	Left hand side, used alone or in combination with others		Right hand side, used alone or in combination with others	
5	-n-	$C_nH_{2n+1}-$	-n	$-C_nH_{2n+1}$
	-nO-	$C_nH_{2n+1}-O-$	-nO	$-O-C_nH_{2n+1}$
	-V-	$CH_2=CH-$	-V	$-CH=CH_2$
	-nV-	$C_nH_{2n+1}-CH=CH-$	-nV	$-C_nH_{2n}-CH=CH_2$
	-Vn-	$CH_2=CH-C_nH_{2n}-$	-Vn	$-CH=CH-C_nH_{2n+1}$
	-nVm-	$C_nH_{2n+1}-CH=CH-C_mH_{2m}-$	-nVm	$-C_nH_{2n}-CH=CH-C_mH_{2m+1}$
	-N-	$N\equiv C-$	-N	$-C\equiv N$
10	-S-	$S=C=N-$	-S	$-N=C=S$
	-F-	$F-$	-F	$-F$
	-CL-	$Cl-$	-CL	$-Cl$
	-M-	CFH_2-	-M	$-CFH_2$
	-D-	CF_2H-	-D	$-CF_2H$
	-T-	CF_3-	-T	$-CF_3$
	-MO-	CFH_2O-	-OM	$-OCFH_2$
15	-DO-	CF_2HO-	-OD	$-OCF_2H$
	-TO-	CF_3O-	-OT	$-OCF_3$
	-A-	$H-C\equiv C-$	-A	$-C\equiv C-H$
	-nA-	$C_nH_{2n+1}-C\equiv C-$	-An	$-C\equiv C-C_nH_{2n+1}$
	-NA-	$N\equiv C-C\equiv C-$	-AN	$-C\equiv C-C\equiv N$
20	Left hand side, used in combination with others only		Right hand side, used in combination with others only	
	-...n...	$(-CH_2-)_n$	-...n...	$(-CH_2-)_n$
	-...M...	$-CFH-$	-...M...	$-CFH-$
	-...D...	$-CF_2-$	-...D...	$-CF_2-$
	-...V...	$-CH=CH-$	-...V...	$-CH=CH-$
	-...Z...	$-CO-O-$	-...Z...	$-CO-O-$
25	-...ZI...	$-O-CO-$	-...ZI...	$-O-CO-$
	-...K...	$-CO-$	-...K...	$-CO-$
	-...W...	$-CF=CF-$	-...W...	$-CF=CF-$

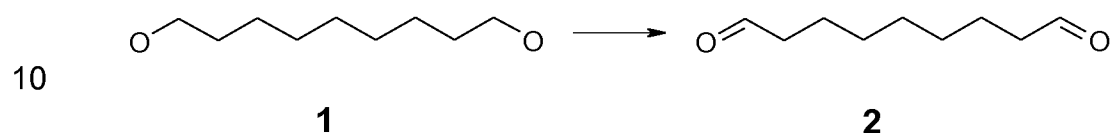
wherein n und m each are integers and three points “...” indicate a space for other symbols of this table.

Examples

A. Compound examples:

5 A.1. Synthesis of BM-1 (7) and BM-2 (8)

Step 1.1



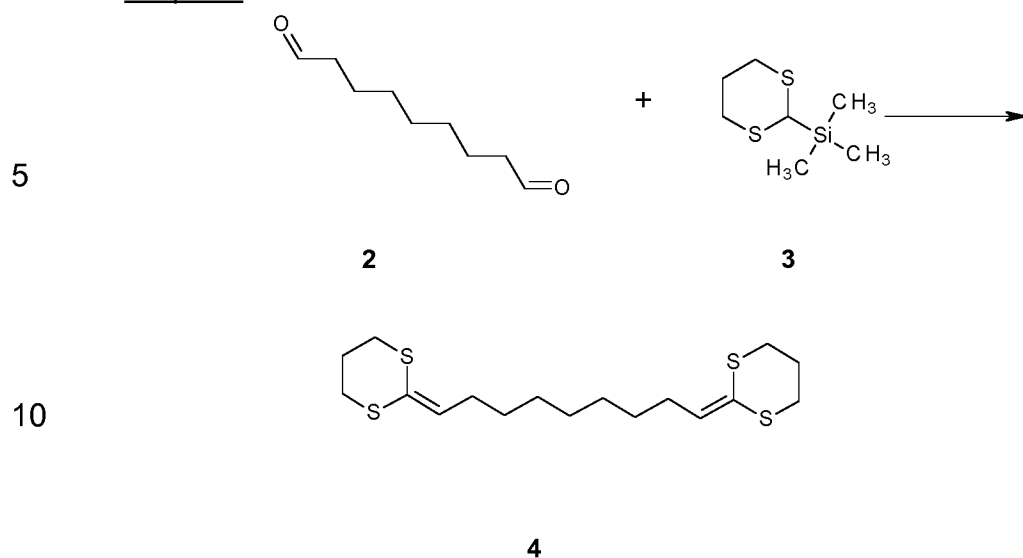
Pyridinium chlorochromate (103.6 g, 480 mmol) and 140 g Celite are suspended in 480 ml dichloromethane at room temperature. While stirring, 1,9-nonanediol **1** (35 g, 218 mmol) dissolved in 50 ml tetrahydrofuran and 150 ml dichloromethane is added dropwise between 20 and 30°C. The mixture is filtered, the solvent removed in vacuum and the residue chromatographed on silica gel/dichloromethane; 20 g of crude dialdehyde **2** is obtained and is used in the next step without further purification.

20

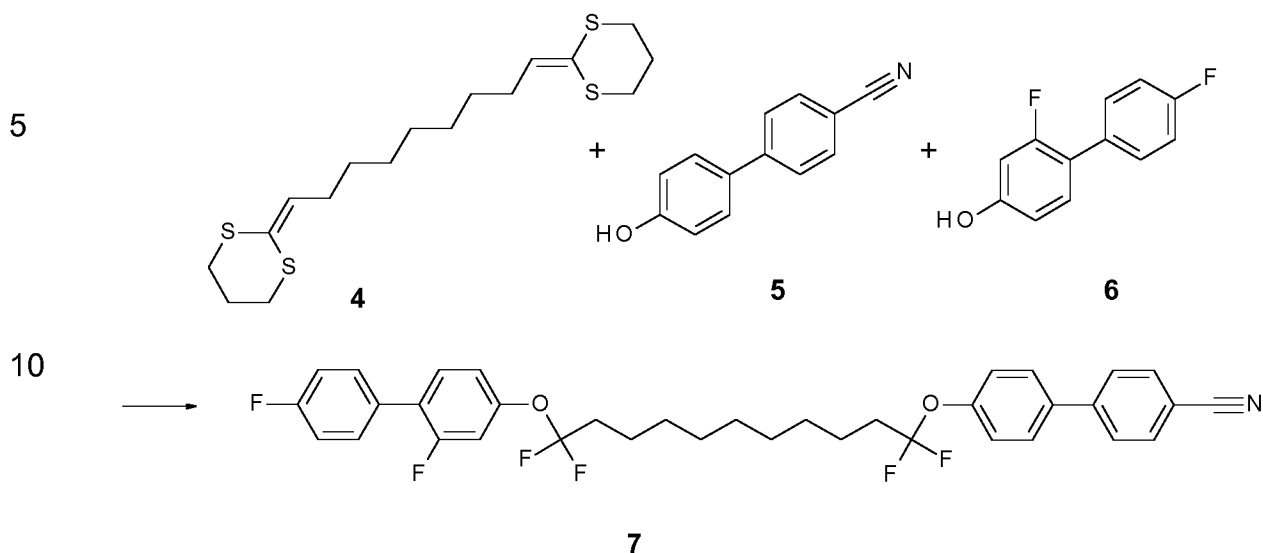
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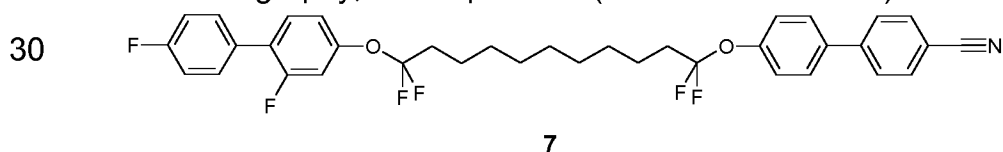
35

Step 1.2

2-Trimethylsilyl-1,3-dithiane **3** (52.8 g, 269 mmol) is dissolved in 190 ml tetrahydrofuran and cooled to -70°C. Butyllithium (107.5 ml of a 2.5 M solution in hexanes, 269 mmol) is slowly added. After the addition is complete, the mixture is warmed to room temperature for 2 hours and then cooled again to -70°C. 20 g of dialdehyde **2** in 80 ml tetrahydrofuran is slowly added at that temperature. After the addition is complete, the mixture is warmed to room temperature and worked up as usual. The residue is distilled under reduced pressure and gave 22.9 g of product **4** with a boiling point of 67-74°C at a pressure of 0.1 mbar.

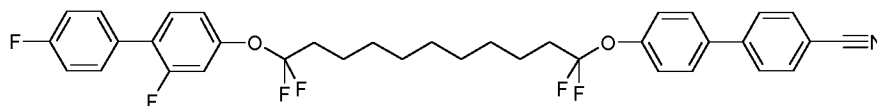
Step 1.3

15 Bis(dithiane) **4** (15.4 mmol) is suspended in 200 ml dichloromethane and cooled to -30°C. Trifluoromethane sulfonic acid (2.98 ml, 34 mmol) is added dropwise while stirring and the mixture is warmed to room temperature for 30 min. It is then cooled again to -70°C, the two phenols **5** (3.1 g, 15.4 mmol) and **6** (3.3 g, 15.4 mmol) together with triethylamine (7.7 ml, 56 mmol) and 70 ml dichloromethane are added dropwise to the mixture. Triethylamine trishydrofluoride (24.9 ml, 154 mmol) is added and subsequently within a period of 60 min bromine (7.9 ml, 154 mmol) in 65 ml dichloromethane. After stirring for one hour at -70°C, the mixture is allowed to warm to -30°C and morpholine (13.5 ml, 154 mmol) is added below -20°C. After warming to 0°C, the mixture is poured onto 200 ml ice water and 19.7 ml aqueous KOH (47 %). The pH is adjusted to approximately 9.0 with additional small amounts of the KOH solution. The organic phase is separated and worked up as usual. After chromatography, of compound **7** (F-PGI-QI-9-Q-PP-N) is isolated.



In addition, the symmetrical difluoroether **8** (N-PP-QI-9-Q-PP-N) is isolated.

- 91 -



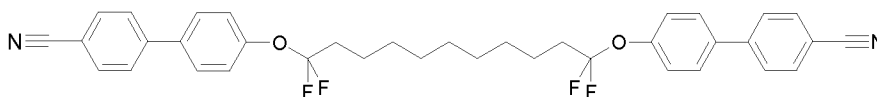
7

7: K 66 N 101.6 I

5

^1H NMR (500 MHz, Chloroform-*d*) δ 7.75 – 7.69 (m), 7.68 – 7.60 (m), 7.59 – 7.50 (m), 7.48 (ddt, J = 6.9, 5.3, 1.6 Hz), 7.32 – 7.24 (m), 7.17 – 7.08 (m), 7.08 – 6.99 (m), 2.16 (qt, J = 11.3, 5.8 Hz), 1.66 (ddd, J = 11.9, 6.8, 3.3 Hz), 1.39 (dt, J = 24.3, 6.1 Hz).

10



8

8: K 131 N 154.1 I

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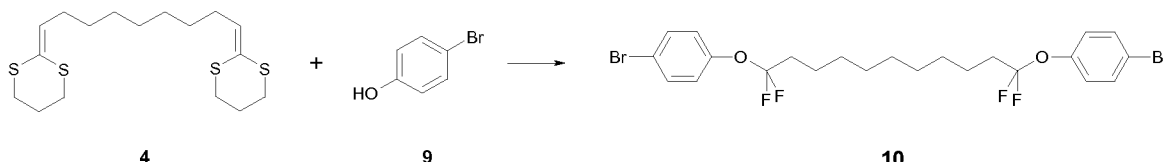
^1H NMR (500 MHz, Chloroform-*d*) δ 7.75 – 7.69 (m), 7.68 – 7.62 (m), 7.58 – 7.52 (m), 7.29 (d, J = 8.5 Hz), 3.73 (dtd, J = 14.1, 6.8, 5.4 Hz), 2.23 – 2.11 (m), 1.62 (s), 1.46 – 1.34 (m), 1.31 – 1.21 (m).

20

2. Synthesis of BM-3 (12)

Step 2.1

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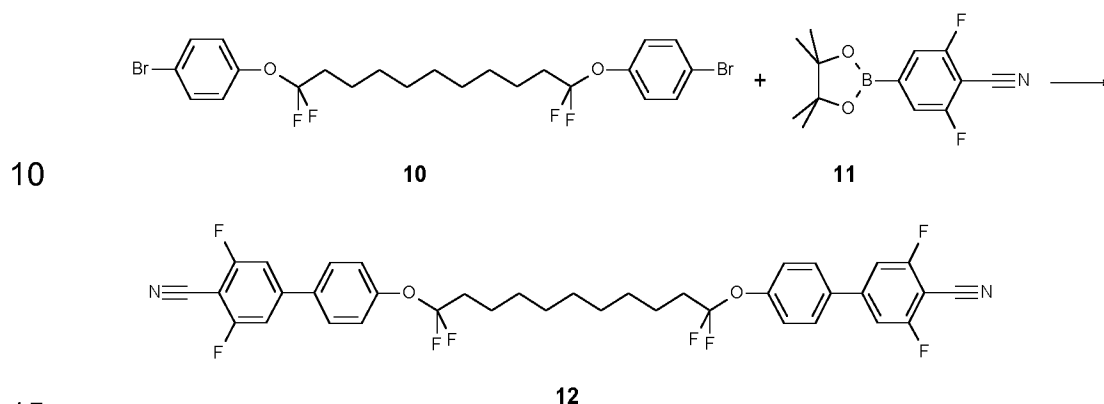
10

Dithiane **4** (18.3 mmol) is suspended in 230 ml dichloromethane, cooled to -30°C and trifluoromethane sulfonic acid (3.5 ml, 40.3 mmol) is added dropwise. The mixture is allowed to warm to room temperature, stirred for 30 min and cooled again to -70°C . A mixture of 4-bromophenol **9** (7 g, 40.3 mmol) and triethylamine (9.1 ml, 65.9 mmol) dissolved in 100 ml dichloromethane is added. After the addition is complete, the mixture is stirred at -70°C for one hour. Triethylamine trihydrofluoride (29.5 ml, 183 mmol) is added and after one hour bromine (9.4 ml, 183 mmol) in 50 ml dichloromethane. Stirring is continued for one hour and the mixture is

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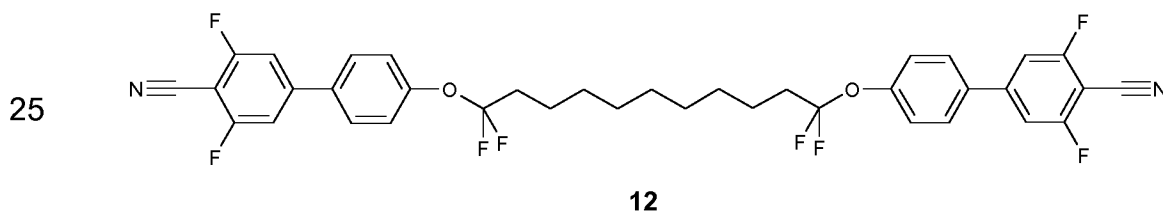
warmed to -30°C. Morpholine (15.9 ml, 183 mmol) is added below -20°C. Workup is carried out as described above for compound **7** and gave compound **10**.

5 Step 2.2



15 Sodium bicarbonate (1.4 g, 16.8 mmol) is dissolved in 12 ml water; dibromide **10** (2.4 g, 4.2 mmol) and boronic ester **11** (2.4 g, 8.8 mmol) are dissolved in 20 ml tetrahydrofuran and the two solutions are combined and degassed by bubbling a stream of nitrogen through it.

20 Bis(tri-(tert-butyl)phosphino)palladium(0) (11 mg, 0.021 mmol) is added and the mixture is heated to reflux for 3 hours. After the usual workup, 2.6 g **12** (N-UIP-QI-9-Q-PU-N) is obtained as a colorless powder.



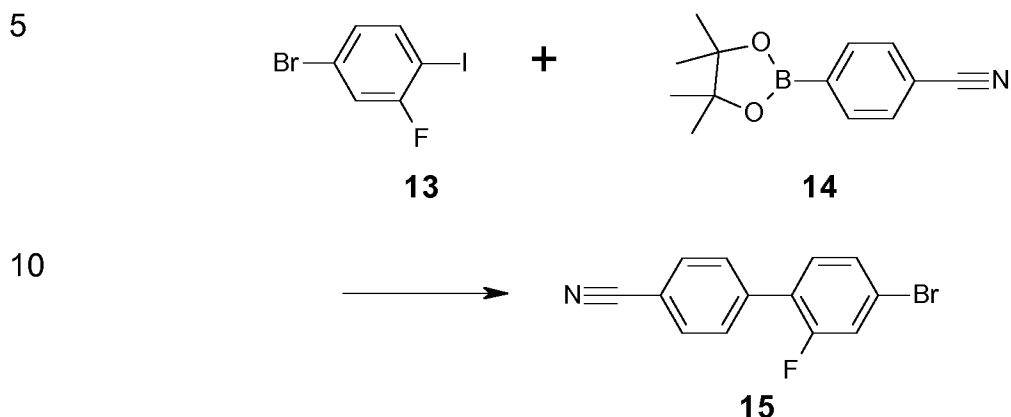
12: K 83 N 83.2 I

30 ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.7 Hz), 7.25 (s), 7.21 – 7.12 (m), 2.10 (tdd, *J* = 11.3, 8.0, 5.6 Hz), 1.64 – 1.55 (m), 1.39 – 1.26 (m).

35

A.3. Synthesis of BM-4 (21)

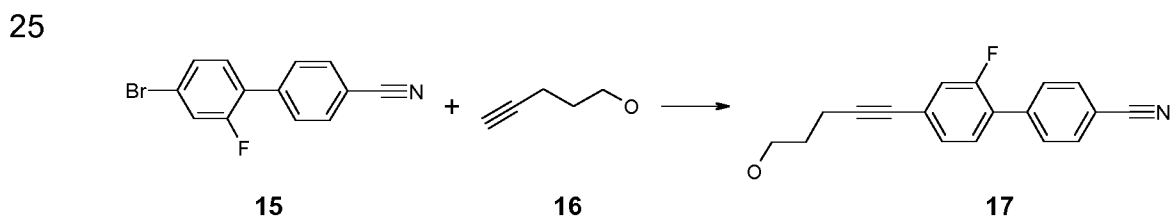
Step 3.1



15 Sodium metaborate tetrahydrate (45.3 g, 322 mmol) is dissolved in 290 ml water and 300 ml tetrahydrofuran, bis(triphenylphosphino)palladium(II)chloride (4.6 g, 6 mmol) and hydrazinium hydroxide (0.3 ml, 6 mmol) are added and the mixture is stirred for 5 min at room temperature. 1-Bromo-3-fluoro-4-iodobenzene

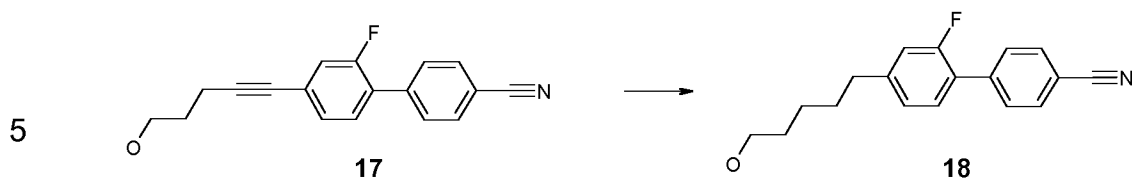
20 **13** (100 g, 322 mmol), boronic acid ester **14** (81.3 g, 355 mmol) and 330 ml tetrahydrofuran are added and the mixture is heated to reflux overnight. After the usual workup crude **15** is obtained.

Step 3.2



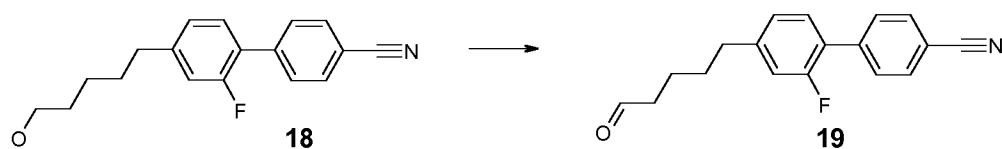
30 **15** (126 mmol), bis(triphenylphosphino)palladium(II)chloride (8.4 g, 12 mmol), copper(I)iodide (2.5 g, 13.2 mmol) and diisopropylamine (84.1 ml, 0.6 mol) are combined with 600 ml tetrahydrofuran and warmed to 60°C. Pent-4-yn-1-ol **16** (15.2 ml, 151 mmol) is dissolved in 170 ml tetrahydrofuran and is added dropwise within 15 min and the mixture is

35 then heated to reflux overnight. After the usual workup **17** is obtained as a yellow solid.

Step 3.3

Crude **17** (31.9 g) is dissolved in 100 ml tetrahydrofuran and hydrogenated (2.2 kPa H₂, 1 h) over platinum on carbon (5 %).

10

Step 3.4

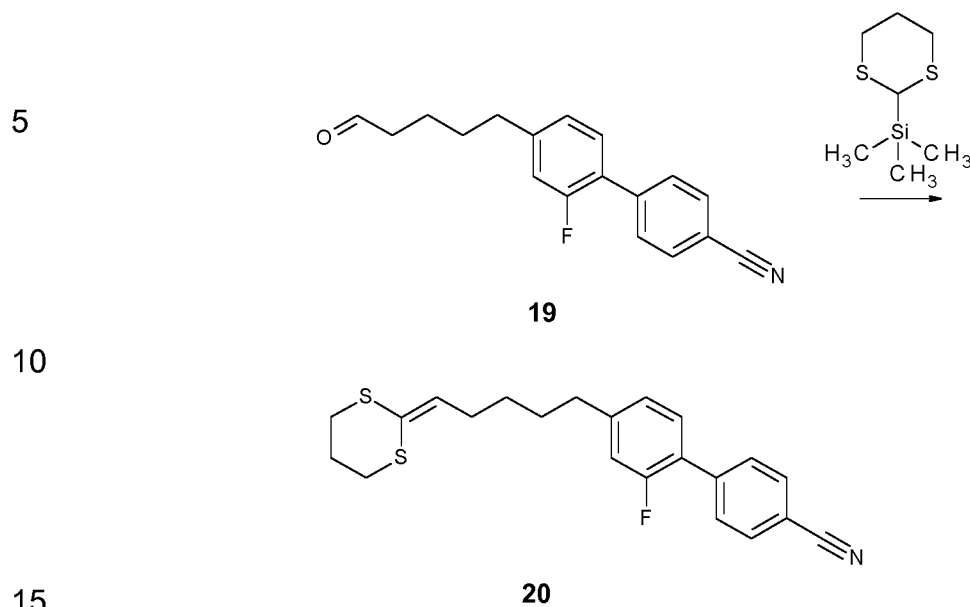
15 Pyridinium chlorochromate (12.1 g, 56.2 mmol) and Celite (30 g) are suspended in 100 ml dichloromethane and **18** (47 mmol) dissolved in 60 ml dichloromethane is added dropwise between 20 and 30°C. After filtration and the usual workup **19** is obtained as a colorless oil.

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Step 3.5

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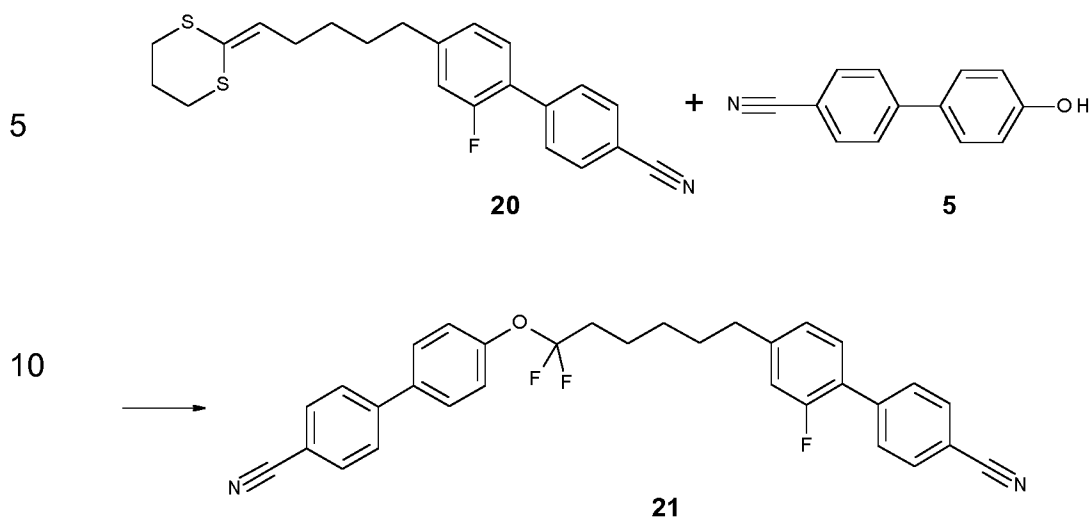
2-Trimethylsilyl-1,3-dithiane (6.7 ml, 35.4 mmol) is dissolved in 40 ml tetrahydrofuran and cooled to -70°C. Butyllithium in hexanes (23.4 ml of a 15 % solution, 37.2 mmol) is added dropwise and the mixture is warmed to -20°C and stirred for 4 hours. It is then cooled again to -70°C and **19** (37.2 mmol) dissolved in 40 ml dichloromethane is added dropwise. After warming to room temperature followed by the usual workup, **20** is obtained as a yellow oil.

25

30

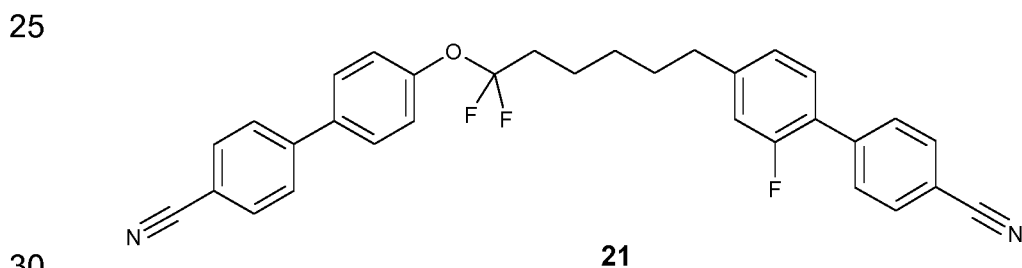
35

Step 3.6



15 **20** (17.2 mmol) is suspended in 200 ml dichloromethane, cooled to -15°C and trifluoromethane sulfonic acid (1.7 ml, 18.9 mmol) is added. The mixture is allowed to warm to room temperature, stirred for 30 min and then cooled to -70°C . 4'-Hydroxy-4-cyano-1,1'-biphenyl **5** (3.8 g, 18.9 mmol), triethylamine (4.3 ml, 31 mmol) and 100 ml dichloromethane are added dropwise and the mixture is stirred for 1 hour at -70°C .

20 Triethylamine trishydrofluoride (13.9 ml, 86 mmol) is added dropwise and after 1 hour 4.4 ml (86 mmol) bromine in 100 ml dichloromethane. The mixture is stirred for 1 hour at -70°C . After warming to -20°C , morpholine (7.5 ml, 86 mmol) is added and stirring is continued for 1h at 0°C . After the usual workup **21** (N-PP-QI-5-GP-N) is obtained as a white powder.



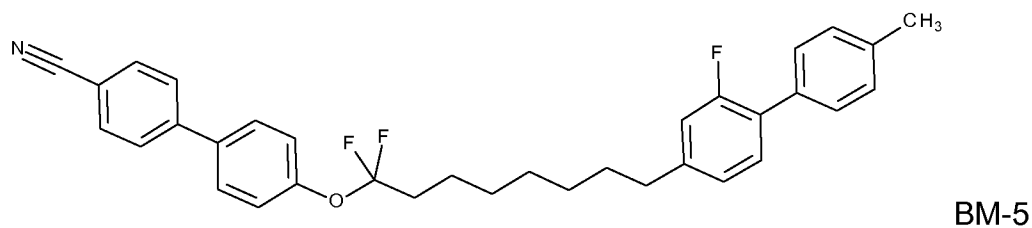
21: K 138 (N 117.1) I

35 ^1H NMR (500 MHz, Chloroform-*d*) δ 7.72 (dd, $J = 8.5, 2.4$ Hz), 7.65 (d, $J = 8.3$ Hz), 7.58 – 7.52 (m), 7.34 (t, $J = 8.0$ Hz), 7.28 (d, $J = 8.5$ Hz), 7.11 – 6.99 (m), 2.70 (t, $J = 7.6$ Hz), 2.24 – 2.12 (m), 1.72 (dtd, $J = 12.3, 8.0, 5.9$ Hz), 1.53 – 1.46 (m).

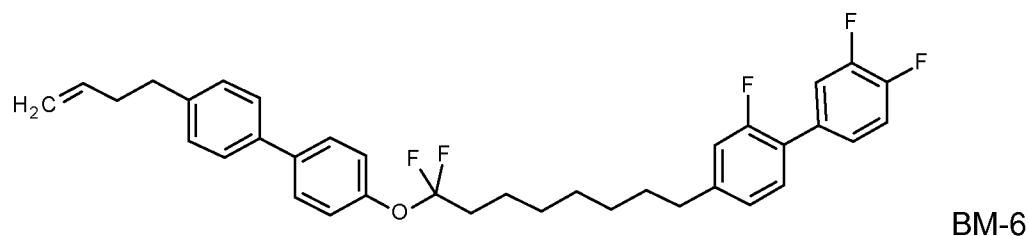
A.4. BM-5, BM-6 and BM-7

In an analogue manner to the synthesis as described under 3. Synthesis of BM-4 (21), the following compounds BM-5, BM-6 and BM-7 are obtained:

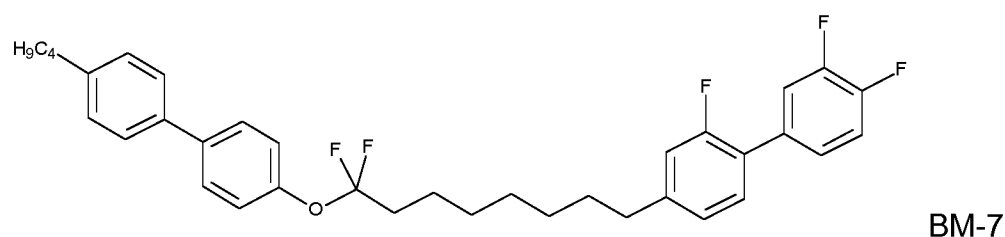
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B. Test cells and methods

Typically a 3 μm thick cell, having an anti-parallel rubbed PI alignment layer, is filled on a hotplate at a temperature at which the flexoelectric mixture in the isotropic phase.

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After the cell has been filled, the phase transitions including clearing point and the crystallization behavior are determined using Differential Scanning Calorimetry (DSC) and verified by optical inspection. For optical phase transition measurements, a Mettler FP90 hot-stage controller connected to a FP82 hot-stage is used to control the

35

temperature of the cell. The temperature is increased from ambient temperature at a rate of 5 degrees C per minute, until the onset of the isotropic phase is observed. The texture change is observed through crossed polarizers using an Olympus BX51 microscope and the
5 respective temperature noted.

Wires are then attached to the ITO electrodes of the cell using indium metal. The cell is secured in a Linkam THMS600 hot-stage connected to a Linkam TMS93 hot-stage controller. The hot-stage is secured to a
10 rotation stage in an Olympus BX51 microscope.

The cell is heated until the liquid crystal is completely isotropic. The cell is then cooled under an applied electric field until the sample is completely nematic. The driving waveform is supplied by a Tektronix
15 AFG3021B arbitrary function generator, which is sent through a Newtons4th LPA400 power amplifier before being applied to the cell. The cell response is monitored with a Thorlabs PDA55 photodiode. Both input waveforms and optical response are measured using a Tektronix TDS
20 2024B digital oscilloscope.

In order to measure the flexoelectric response of the material, the change in the size of the tilt of the optic axis is measured as a function of increasing voltage at a temperature of 35°C, unless stated explicitly otherwise. This is achieved by using the equation:

25
$$\tan \varphi = (P_0/2\pi) (e/K) E$$

wherein φ is the tilt in the optic axis from the original position (i.e. when $E = 0$), E is the applied field, K is the elastic constant (average of K_1 and K_3) and e is the flexoelectric coefficient (where $e = e_1 + e_3$). The applied
30 field is monitored using a HP 34401A multimeter. The tilt angle is measured using the aforementioned microscope and oscilloscope. The undisturbed cholesteric pitch, P_0 , is measured using an Ocean Optics USB4000 spectrometer attached to a computer. The selective reflection
35 band is obtained and the pitch determined from the spectral data.

The media shown in the following examples are well suitable for use in ULH-displays. To that end, an appropriate concentration of the chiral dopant or dopants used has to be applied in order to achieve a typical cholesteric pitch of 350 to 275 nm.

5

C. Mixture examples

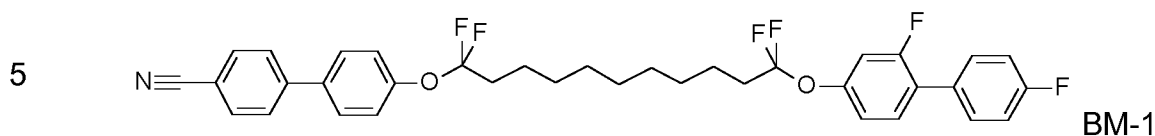
Host Mixture H-1

10 The following mixture H1 is prepared.

	Compound	Amount %-w/w
	N-PP-ZI-9-Z-GP-F	9.520
	F-PGI-ZI-7-Z-PP-N	9.520
15	F-PGI-ZI-9-Z-PU-N	6.600
	F-PGI-ZI-7-Z-PUU-N	10.250
	N-UIUI-9-UU-N	5.860
	N-GIGI-9-GG-N	2.920
20	N-PGI-ZI-9-Z-GU-F	8.780
	N-GI-ZI-9-Z-G-N	7.330
	F-PGI-ZI-9-Z-G-N	3.320
	N-PP-ZI-9-Z-G-N	3.320
	F-PGI-ZI-9-Z-P-N	3.320
25	F-PGI-ZI-9-PUU-N	12.460
	CY-3-O2	2.336
	CCY-3-O1	1.168
	CCY-3-O2	1.168
	CPY-2-O2	1.460
30	CPY-3-O2	1.460
	CLY-3-O2	1.168
	Y-4O-O4	1.752
	CPTP-3-OD	1.168
	CZY-3-O2	1.460
35	CZY-5-O2	1.460
	R-5011	2.200

C.1.1 Mixture example M-1

15 % w/w of the compound BM-1,



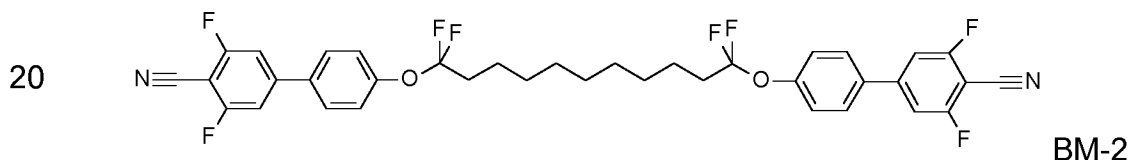
are added to 85 % w/w of host mixture H-1.

10 The resulting mixture is homogenized and filled into a test cell as described above. Measurements with respect to the switching performance, the clearing point, the flexo elastic constant and the N_{TB} transition temperature are performed and the results are summarized in the table under C.1.4.

15

C.1.2 Mixture example M-2

15 % w/w of the compound BM-3,



are added to 85 % w/w of host mixture H-1.

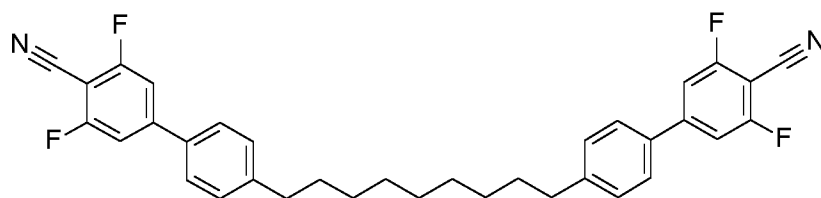
25 The resulting mixture is homogenized and filled into a test cell as described above. Measurements with respect to the switching performance, the clearing point, the flexo elastic constant and the N_{TB} transition temperature are performed and the results are summarized in the table under C.1.4.

30

C.1.3 Comparative Mixture Example CM-1

15 % w/w of the compound CM*-1,

35



CM*-1

are added to 85 % w/w of host mixture H-1.

The resulting mixture is homogenized and filled into a test cell as described above. Measurements with respect to the switching performance, the clearing point, the flexo elastic constant and the N_{TB} transition temperature are performed and the results are summarized in the table under C.1.4

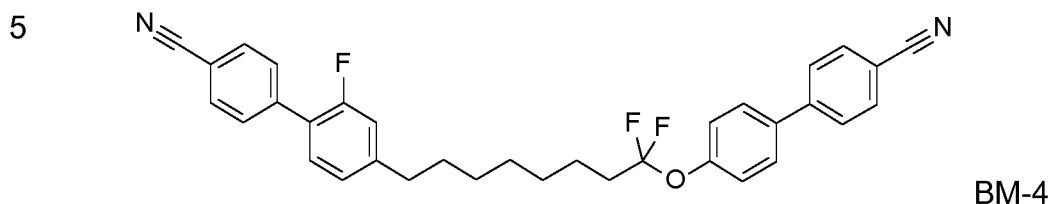
C.1.4 Summary

Composition	M-1	M-2	CM-1
$T_{on}+T_{off}$ (at 35°C)	3.89 ms	4.01 ms	4.25 ms
e/K	2.77 V ⁻¹	2.99 V ⁻¹	3.19 V ⁻¹
T_{NI}	76.5°C	72.4°C	63.7°C
N_{TB}	<-10°C	<-10°C	-2°C

It is clear from the above given results of the measurement that the materials M-1 and M-2 show an advantage both in terms of phase range and also switching speeds when compared to the material CM-1. At the same time, the flexo elastic constant stays at an acceptable level. In addition, the N_{TB} transition temperature can be favourably lowered by utilizing compounds according to the present invention. Furthermore, it is particularly surprising that the T_{NI} of the mixture M-2 is significantly higher (+8.7°C) than the T_{NI} of the mixture CM-1.

C.2.1 Mixture example M-3

15 % w/w of the compound BM-4,

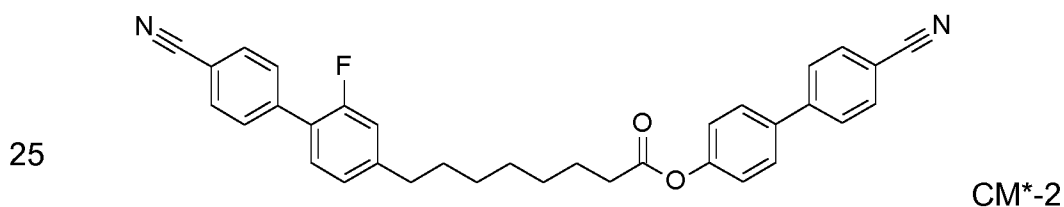


10 are added to 85 % w/w of host mixture H-1.

The resulting mixture is homogenized and filled into a test cell as described above. Measurements with respect to the switching performance, the clearing point, the flexo elastic constant and the N_{TB} transition temperature are performed and the results are summarized in the table under C.2.3.

C.2.2 Comparative Mixture Example CM-2

20 15 % w/w of the compound CM*-2,



are added to 85 % w/w of host mixture H-1.

30 The resulting mixture is homogenized and filled into a test cell as described above. Measurements with respect to the switching performance, the clearing point, the flexo elastic constant and the N_{TB} transition temperature are performed and the results are summarized in the table under C.2.3.

35

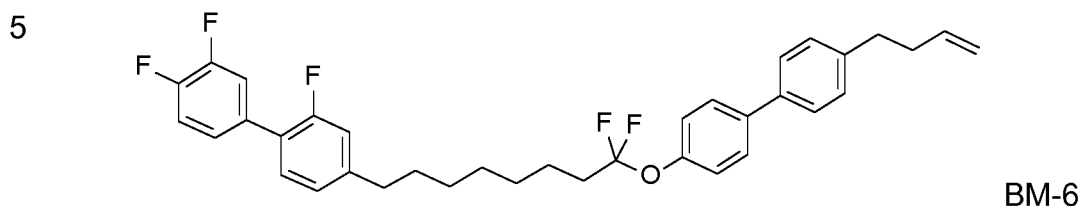
C.2.3 Summary

Composition	M-3	CM-2
T_{on}+T_{off} (at 35°C)	4.07 ms	5.16 ms
e/K	3.08 V ⁻¹	2.96 V ⁻¹
T_{NI}	77.9°C	79.8°C
N_{TB}	+6°C	+9°C

From the results of the measurement, it is clear that the material containing BM-4 in accordance with the present has a significant advantage with respect to the switching speed when compared to material comprising a compound of the prior art (CM*-2). The T_{NI} is also similar, something that is surprising when considering conventional liquid crystal materials with differing switching speeds when normally a strong inverse relationship between T_{NI} and switching speeds is observed (i.e. higher T_{NI} leads to reduced switching speeds).

C.3.1 Mixture example M-4

15 % w/w of the compound BM-4,

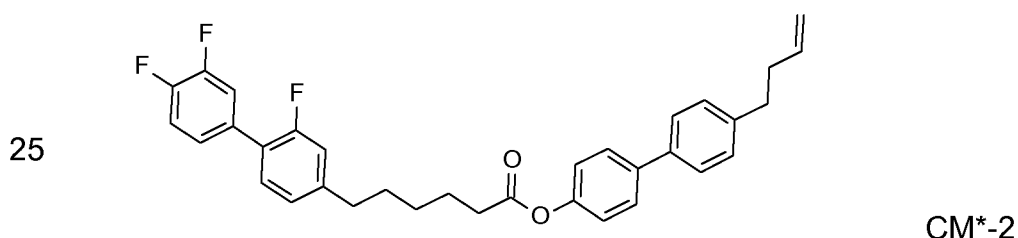


10 are added to 85 % w/w of host mixture H-1.

15 The resulting mixture is homogenized and filled into a test cell as described above. Measurements with respect to the switching performance, the clearing point, the flexo elastic constant and the N_{TB} transition temperature are performed and the results are summarized in the table under C.3.3

C.3.2 Comparative Mixture Example CM-3

20 15 % w/w of the compound CM*-3,



are added to 85 % w/w of host mixture H-1. The resulting mixture is homogenized and filled into a test cell as described above. Measurements with respect to the switching performance, the clearing point, the flexo elastic constant and the N_{TB} transition temperature are performed and the results are summarized in the table under C.3.3

35

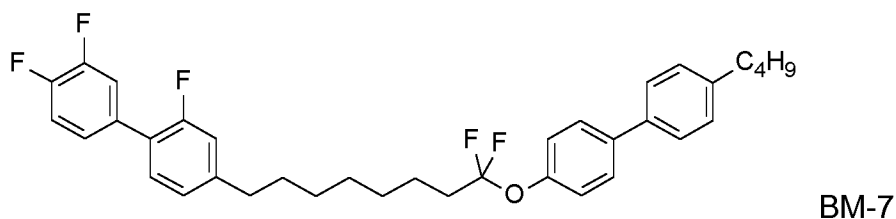
C.3.3 Summary

Composition	M-4	CM-3
$T_{on}+T_{off}$ (at 35°C)	2.95 ms	3.57 ms
e/K	2.88 V ⁻¹	2.96 V ⁻¹
T_{NI}	66.0°C	65.8°C
N_{TB}	-1°C	-4°C

From the results of the measurement, it is clear that the material containing BM-6 in accordance with the present has a significant advantage with respect to the switching speed when compared to material comprising a compound of the prior art (CM*-3). The T_{NI} is also similar, something that is surprising when considering conventional liquid crystal materials with differing switching speeds when normally a strong inverse relationship between T_{NI} and switching speeds is observed (i.e. higher T_{NI} leads to reduced switching speeds).

C.4.1 Mixture example M-5

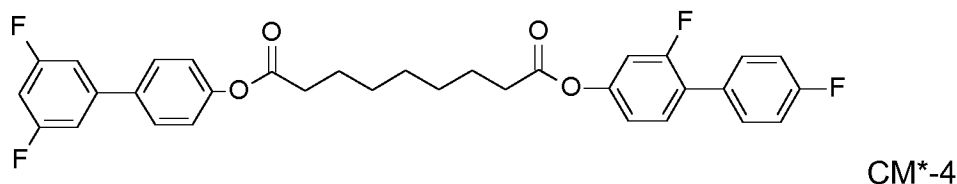
15 % w/w of the compound BM-7,



are added to 85 % w/w of host mixture H-1. The resulting mixture is homogenized and filled into a test cell as described above. Measurements with respect to the switching performance, the clearing point, the flexo elastic constant and the N_{TB} transition temperature are performed and the results are summarized in the table under C.4.3

C.4.2 Comparative Mixture Example CM-4

15 % w/w of the compound CM*-4,



are added to 85 % w/w of host mixture H-1. The resulting mixture is homogenized and filled into a test cell as described above. Measurements with respect to the switching performance, the clearing point, the flexo elastic constant and the N_{TB} transition temperature are performed and the results are summarized in the table under C.4.3

C.4.3 Summary

	Composition	M-5	CM-4
	T_{on}+T_{off} (at 35°C)	3.08 ms	3.94 ms
5	e/K	2.85 V ⁻¹	2.82 V ⁻¹
	T_{NI}	63.7°C	65.4°C
	N_{TB}	-3°C	<-10°C

10 From the results of the measurement, it is clear that the material containing BM-7 in accordance with the present has a significant advantage with respect to the switching speed and the T_{NI} when compared to material comprising a compound of the prior art (CM*-4).

15

20

25

30

35

C.5.1 Comparative Mixture Example CM-5

The following comparative mixture example is prepared CM-5

5	Compound	Amount %-w/w
	N-PGIP-ZI-5-GU-F	14.70
	N-PP-ZI-Z-GP-F	16.70
	N-PP-ZI-9-Z-G-N	11.80
	N-GIGI-9-GG-N	3.90
10	F_PGI-ZI-9-Z-G-N	9.80
	N-GI-ZI-9-Z-G-N	8.80
	F-PGI-ZI-7-Z-GP-F	16.70
	N-PP-ZI-7-Z-G-N	15.70
	R-5011	1.90

15 The mixture is homogenized and filled into a test cell. Measurements with respect to the switching performance, the clearing point, the flexo elastic constant and the N_{TB} transition temperature are performed .

20 The results are summarized in the table under C.5.3.

C.5.1 Mixture Example M-6

The following mixture example is prepared CM-6

25	Compound	Amount %-w/w
	N-PGIP-ZI-5-GU-F	14.70
	N-PP-ZI-Z-GP-F	16.70
	N-PP-ZI-9-Z-G-N	4.90
30	N-GIGI-9-GG-N	3.90
	F_PGI-ZI-9-Z-G-N	8.80
	N-GI-ZI-9-Z-G-N	6.90
	F-PGI-ZI-7-Z-GP-F	17.70
	N-PP-ZI-7-Z-G-N	16.70
35	Compound BM-7	7.80
	R-5011	1.90

The mixture is homogenized and filled into a test cell. Measurements with respect to the switching performance, the clearing point, the flexo elastic constant and the N_{TB} transition temperature are performed.

5 The results are summarized in the table under C.5.3

C.5.3 Summary

10	Composition	CM-5	M-6
	$T_{on}+T_{off}$ (at 35°C)	5.51 ms	4.28 ms
	e/K	3.53 V ⁻¹	3.38 V ⁻¹
	T_{NI}	68.4°C	66.5°C
15	N_{TB}	+10°C	+12°C

It can be clearly seen from the data in the table that the addition of the compound BM-7 results in over a 20 % improvement in the switching speed. This is a considerable advantage for ULH mixtures, especially for applications such as field sequential colour driving. Only a small

20 reduction in T_{NI} and e/K are observed due to the addition of BM-7, which means that the overall benefit to the performance is still significant.

25

30

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Patent Claims

1. Compound of formula I,

5 $R^{11}-MG^{11}-X^{11}-Sp^{11}-X^{12}-MG^{12}-R^{12}$ I

wherein

10 R^{11} and R^{22} are each independently H, F, Cl, CN, NCS or a straight-chain or branched alkyl group, which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH_2 groups to be replaced, in each occurrence independently from one another, by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-,
15 -O-CO-O-, -S-CO-, -CO-S-, -CH=CH-, -CH=CF-, -CF=CF- or -C≡C- in such a manner that oxygen atoms are not linked directly to one another,

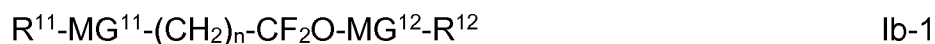
20 MG^{11} and MG^{12} are each independently a mesogenic group,

25 Sp^{11} is a spacer group comprising 1, 3 or 5 to 40 C atoms, wherein one or more non-adjacent and non-terminal CH_2 groups may also be replaced by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -O-CO-, -S-CO-, -O-COO-, -CO-S-, -CO-O-, -CF₂-, -CF₂O-, -OCF₂-,
30 -C(OH)-, -CH(R¹¹)-, -CH=CH- or -C≡C-, however in such a way that no two O-atoms are adjacent to one another and no two groups selected from -O-CO-, -S-CO-, -O-COO-, -CO-S-, -CO-O- and -CH=CH- are adjacent to each other,

35 X^{11} and X^{12} denote -CF₂-O-, -O-CF₂- or a single bond, whereby at least one of X^{11} or X^{12} denotes -CF₂-O-, or -O-CF₂-.

2. Compound according to claim 1 characterized in that it is selected from the group of compounds of formulae Ia-1 or Ib-1

5

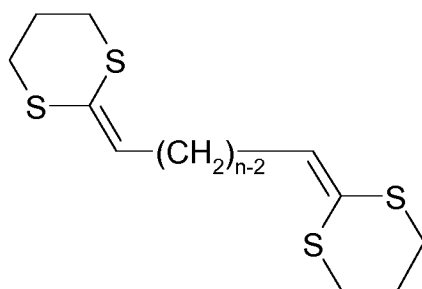


10

wherein R^{11} , R^{22} , MG^{11} , MG^{12} have one of the meanings as given above in claim 1 and n denotes 1, 3 or an integer from 5 to 15.

3. Method of production of compounds of formula Ia-1, comprising at least the step of reacting one compound of the following formula,

15



20

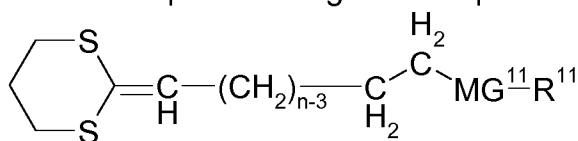
with one or more compounds of formulae $R^{11}-MG^{11}-OH$ or $R^{12}-MG^{12}-OH$,

wherein the parameters have one of the meanings as given above in claim 2.

25

4. Method of production of compounds of formula Ib-1, comprising at least the step of reacting one compound of the formula:

30



with at least one compound of formula $R^{12}-MG^{12}-OH$,
wherein the parameters have one of the meanings as given above in claim 2.

35

5. Use of the compounds of formula I in a liquid crystalline medium.

6. LC medium comprising one or more compounds of formula I.

5 7. LC medium according to claim 6, comprising one or more compounds of formula II,



wherein

10 R^{21} and R^{22} denote each and independently H, F, Cl, CN, NCS or a straight-chain or branched alkyl group, which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH_2 groups to be replaced, in each
15 occurrence independently from one another, by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-, -O-CO-O-, -S-CO-, -CO-S-, -CH=CH-, -CH=CF-, -CF=CF- or -C≡C- in such a manner that oxygen atoms are not linked directly to one another,

20 A^{21} to A^{24} denote each and independently in each occurrence a aryl-, heteroaryl-, alicyclic- and heterocyclic group and

25 a denotes an integer from 1 to 15.

8. LC medium according to claim 6 or 7, comprising one or more compounds of formula III,



30 wherein
 R^{31} and R^{32} have each and independently from another one of the meanings as given for R^{21} under formula II,

35 A^{31} to A^{36} have each and independently from another one of the meanings as given for A^{21} under formula II,

5 Z^{31} and Z^{32} denote each and independently in each occurrence,
 -COO-, -OCO-, -O-CO-O-, -OCH₂-, -CH₂O-,
 -CH₂CH₂-, -(CH₂)₄-, -CF₂CF₂-, -CH=CH-, -CF=CF-,
 -CH=CH-COO-, -OCO-CH=CH- or -C≡C-, optionally
 substituted with one or more of F, S and/or Si

10 c denotes an integer from 1 to 15 and
 a denotes 0 or 1.

9. LC medium according to one or more of claims 6 to 8, comprising
 one or more compounds of formula IV,

15 $R^{41}-A^{41}-A^{42}-Z^{41}-(CH_2)_d-Z^{42}-A^{43}-A^{44}-R^{42}$ IV

wherein

20 R^{41} and R^{42} have each and independently from another one of
 the meanings as given for R^{21} under formula II,

A^{41} to A^{44} have each and independently from another one of
 the meanings as given for A^{21} under formula II,

25 Z^{41} and Z^{42} are each independently in each occurrence,
 -COO-, -OCO-, -O-CO-O-, -OCH₂-, -CH₂O-,
 -CH₂CH₂-, -(CH₂)₄-, -CF₂CF₂-, -CH=CH-, -CF=CF-,
 -CH=CH-COO-, -OCO-CH=CH- or -C≡C-, optionally
 substituted with one or more of F, S and/or Si,

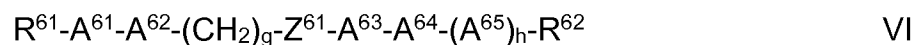
30 d denotes an integer from 1 to 15,

10. LC medium according to one or more of claims 6 to 9, comprising
 one or more compounds of formula V,

35 $R^{51}-A^{51}-Z^{51}-(CH_2)_e-Z^{52}-A^{52}-(A^{53})_f-R^{52}$ V

- wherein
- 5 R^{51} and R^{52} have each and independently from another one of the meanings as given for R^{21} under formula II,
- A^{51} to A^{53} have each and independently from another one of the meanings as given for A^{21} under formula II,
- 10 Z^{51} and Z^{52} are each independently in each occurrence,
 $-\text{COO}-$, $-\text{OCO}-$, $-\text{O}-\text{CO}-\text{O}-$, $-\text{OCH}_2-$, $-\text{CH}_2\text{O}-$,
 $-\text{CH}_2\text{CH}_2-$, $-(\text{CH}_2)_4-$, $-\text{CF}_2\text{CF}_2-$, $-\text{CH}=\text{CH}-$, $-\text{CF}=\text{CF}-$,
 $-\text{CH}=\text{CH}-\text{COO}-$, $-\text{OCO}-\text{CH}=\text{CH}-$ or $-\text{C}\equiv\text{C}-$, optionally substituted with one or more of F, S and/or Si,
- 15 f denotes 0 or 1,
- e denotes an integer from 1 to 15,

- 20 11. LC medium according to one or more of claims 6 to 10, comprising one or more compounds of formula VI,



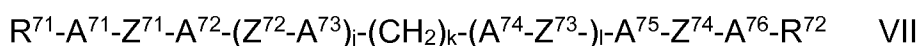
- 25 wherein
- R^{61} and R^{62} have each and independently from another one of the meanings as given for R^{21} and R^{22} under formula II,
- 30 A^{61} to A^{64} have each and independently one of the meanings as given above for A^{21} under formula II,
- Z^{61} denotes $-\text{O}-$, $-\text{COO}-$, $-\text{OCO}-$, $-\text{O}-\text{CO}-\text{O}-$, $-\text{OCH}_2-$,
 $-\text{CH}_2\text{O}$, $-\text{CH}_2\text{CH}_2-$, $-(\text{CH}_2)_4-$, $-\text{CF}_2\text{CF}_2-$, $-\text{CH}=\text{CH}-$,
- 35

-CF=CF-, -CH=CH-COO-, -OCO-CH=CH- or -C≡C-, optionally substituted with one or more of F, S and/or Si,

5 h denotes 0 or 1 and

g denotes an integer from 1 to 15.

10 12. LC medium according to one or more of claims 6 to 11, comprising one or more compounds of formula VII,



wherein

15 R^{71} and R^{72} have each and independently one of the meanings as given above for R^{21} under formula II,

A^{71} to A^{76} have each and independently one of the meanings as given above for A^{21} under formula II,

20 Z^{71} to Z^{74} each and independently denotes -COO-, -OCO-, -O-CO-O-, -OCH₂-, -CH₂O-, -OCF₂-, -CF₂O-, -CH₂CH₂-, -(CH₂)₄-, -CF₂CF₂-, -CH=CH-, -CF=CF-, -CH=CH-COO-, -OCO-CH=CH- or -C≡C-, optionally substituted with one or more of F, S and/or Si or a single bond, with the proviso that at least one of Z^{71} to Z^{74} is not a single bond,

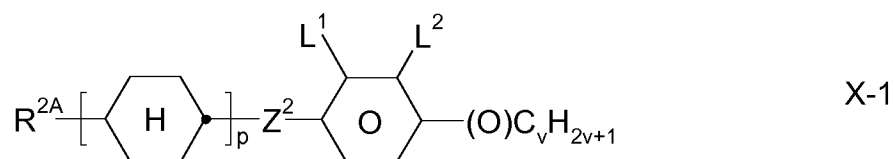
30 j denotes an integer from 1 to 15 and

i and k denotes 0 or 1.

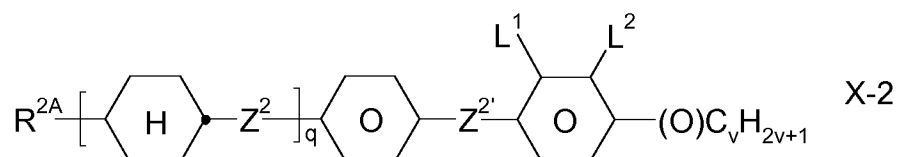
35 13. LC medium according to one or more of claims 6 to 12, comprising one or more chiral dopants.

14. LC medium according to one or more of claims 6 to 13, comprising one or more nematic LC compounds selected from compounds of formula X-1 to X-4,

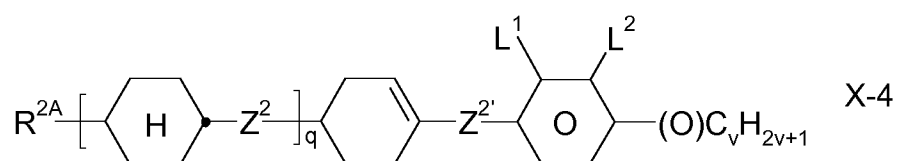
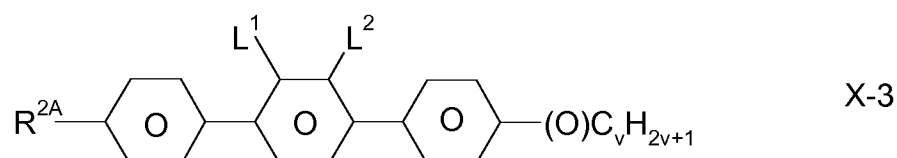
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10



15



20

in which

 R^{2A}

denotes H, an alkyl, alkenyl or alkoxy radical having 1 to 15 C atoms, where, in addition, one or more CH_2 groups in these radicals may each be replaced, independently of one another, by $-\text{C}\equiv\text{C}-$, $-\text{CF}_2\text{O}-$, $-\text{CH}=\text{CH}-$, $\text{---} \text{C}_6\text{H}_4 \text{---}$, $\text{---} \text{C}_6\text{H}_2 \text{---}$, $-\text{O}-$, $-\text{CO}-\text{O}-$ or $-\text{O}-\text{CO}-$ in such a way that O atoms are not linked directly to one another and in which, in addition, one or more H atoms may be replaced by halogen,

25

 L^1 and L^2

each, independently of one another, denote F, Cl, CF_3 or CHF_2 , preferably each denote F,

35

 Z^2 and $Z^{2'}$

each, independently of one another, denote a single bond, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}=\text{CH}-$, $-\text{C}\equiv\text{C}-$

, -CF₂O-, -OCF₂-, -CH₂O-, -OCH₂-, -COO-, -OCO-,
-C₂F₄-, -CF=CF- or -CH=CHCH₂O-,

5 p denotes 0, 1 or 2,

 q denotes 0 or 1,

 (O)C_vH_{2v+1} denotes OC_vH_{2v+1} or C_vH_{2v+1} and

10 v denotes 1 to 6.

15 15. Method for the production of an LC medium according to one or more
of claims 6 to 14, comprising the step of mixing one or more
compounds of formula I, with at least one compound selected from
compounds of formulae II to X.

20 16. Use of a LC medium according to one or more of claims 6 to 14, in
electro optic devices.

17. Electro optical device comprising a medium according to one or more
of claims 6 to 14.

25 18. Electro optical device according to claim 17, characterized in that it is
a flexoelectric device.

30

35

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/081471

A. CLASSIFICATION OF SUBJECT MATTER INV. C09K19/02 C09K19/04 C09K19/20 C09K19/06 C09K19/30 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C09K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2016/096112 A1 (MERCK PATENT GMBH [DE]) 23 June 2016 (2016-06-23) claims; examples; compounds -----	1-18
A	WO 2006/066688 A1 (MERCK PATENT GMBH [DE]; GOULDING MARK JOHN [GB]; ADLEM KEVIN [GB]; DUF) 29 June 2006 (2006-06-29) claims; examples; compounds -----	1-18
A	WO 2014/005672 A1 (MERCK PATENT GMBH [DE]) 9 January 2014 (2014-01-09) cited in the application claims; examples; compounds -----	1-18
A	WO 2013/004333 A1 (MERCK PATENT GMBH [DE]; ADLEM KEVIN [GB]; WILKES DAVID [DE]; SAXTON PA) 10 January 2013 (2013-01-10) cited in the application claims; examples; compounds -----	1-18
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 6 February 2018	Date of mailing of the international search report 13/02/2018	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Serbetsoglou, A	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/081471

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