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(54) **Title**: MESOGENIC COMPOUNDS COMPRISING DISCOTIC AND CALAMITIC GROUPS

(57) **Abstract**: The invention relates to novel calamitic mesogenic compounds which are especially suitable for use in birefringent films with negative optical dispersion, to novel liquid crystal (LC) formulations and polymer films comprising them, and to the use of the compounds, formulations and films in optical, electrooptical, electronic, semiconducting or luminescent components or devices.

Mesogenic Compounds comprising Discotic and Calamitic Groups

Field of the Invention

The invention relates to novel mesogenic compounds comprising discotic and calamitic groups which are especially suitable for use in birefringent films with negative optical dispersion, to novel liquid crystal (LC) formulations and polymer films comprising them, and to the use of the compounds, formulations and films in optical, electrooptical, electronic, semiconducting or luminescent components or devices.

Background and Prior Art

There is a need for anisotropic optical films that demonstrate negative optical retardation dispersion. For example, a quarter wave film made with negative dispersion birefringent materials will be largely achromatic. Devices such as reflective LCDs that utilise such a quarter wave film will have a dark state that is not coloured. Currently such devices have to use two retarder films to achieve this effect.

The dispersive power of such a negative dispersion birefringent film can be defined in many ways, however one common way is to measure the optical retardation at 450nm and divide this by the optical retardation measured at 550nm (R_{450}/R_{550}). If the on-axis retardation of a negative retardation dispersion film at 550nm is 137.5nm and the R_{450}/R_{550} value is 0.82, then such a film will be a largely a quarter wave for all wavelengths of visible light and a liquid crystal display device (LCD) using this film as, for example, a circular polarizer would have a substantially black appearance. On the other hand, a film made with an on axis of 137.5nm which had normal positive dispersion (typically $R_{450}/R_{550} = 1.13$) would only be a quarter wave for one wavelength (550nm), and an LCD device using this film as, for example, a circular polarizer would have a purple appearance. Another way of representing this information is to plot the change in birefringence as a function of wavelength. **Figure 1** shows a typical birefringence against wavelength plot for a polymerized film made

from the commercially available reactive mesogen RM257 (Merck KgaA, Darmstadt, Germany). The R_{450}/R_{550} for this compound is around 1.115.

In an anisotropic optical film formed by rod-shaped, optically anisotropic molecules, the origin of the retardation dispersion is due to the fact that the two refractive indices n_e, n_o, of the anisotropic molecules (wherein n_e is the "extraordinary refractive index" in the direction parallel to the long molecular axis, and n_o is the "ordinary refractive index" in the directions perpendicular to the long molecular axis) are changing with wavelength at different rates, with n_e changing more rapidly than n_o towards the blue end of the visible wavelength spectrum. One way of preparing material with low or negative retardation dispersion is to design molecules with increased n_o dispersion and decreased n_e dispersion. This is schematically shown in **Figure 2**. Such an approach has been demonstrated in prior art to give LC's with negative birefringence and positive dispersion as well as compounds with positive birefringence and negative dispersion.

If the compounds are polymerizable, or are mixed with a polymerizable host material comprising for example polymerizable mesogenic compounds (also known as "reactive mesogens" or "RMs"), it is possible to prepare anisotropic optical polymer films with negative dispersion. This can easily be carried out by in situ polymerization, e.g. by exposure to heat or UV radiation, of the polymerizable material when being uniformly oriented in its mesophase, thereby permanently fixing the macroscopically uniform orientation. Suitable polymerization methods are well-known to the person skilled in the art, and are described in the literature.

Molecules that can be formed into anisotropic films that demonstrate the property of negative or reverse retardation dispersion have been disclosed in prior art. For example, JP 2005-208146 A1 and WO 2006/052001 A1 disclose polymerisable materials largely based on compounds with a "cardo" core group.

Another class of compounds which is claimed to demonstrate negative birefringence is described in US 6,139,771. These compounds generally

consist of two rod-shaped mesogenic groups connected by an acetylenic or bis-acetylenic bridging group. The bridging group is connected to the two rod-shaped groups using a benzene ring on the rod-shaped part of the molecule, resulting in the bridge having an angle of approximately 60° to the rods.

US 6,203,724 discloses molecules generally consisting of two rod-shaped mesogenic groups connected by a highly dispersive bridging group. The bridge is connected to the rod-shaped groups via a the axial position of a cyclohexane ring.

WO 2005/085222 A1 and WO 2006/137599 A1 disclose molecules that have two lower refractive index parts connected by a higher refractive index bridge part. The bridge is predominantly connected to the rods via a fused five-membered heterocyclic ring.

In the compounds descibed in the above-mentioned documents, where the rods are connected to a highly polarisable bridge, only a maximum of two rods is connected to the polarisable bridging group.

However, many of the materials disclosed in the literature have drawbacks, like for example thermal properties that are not suitable for processing under standard industrial processes, limited solubility in the solvents commonly used in standard industrial processes, or are not compatible with host RM materials commonly used in standard industrial processes, or are too expensive to manufacture.

JP 2005-208414 A1 discloses molecules comprising rod-shaped groups that are covalently bonded to a central discotic group. However in the compounds specifically disclosed in that document, the rod-shaped molecules are connected via an ester group to the discotic ring. The presence of such an ester group gives the rod freedom to rotate in at least two directions relative to the ring. This decreases the probability that the rods and disc will, on average, retain the correct orientation relative to each other, and thus prevents that the desired optical effect can be maximised.

This invention has the aim of providing improved compounds for use in LC formulations and polymer films having negative dispersion, which do not have the drawbacks of the prior art materials.

In particular, there is a need for compounds that demonstrate reduced or negative dispersion, and are also available at reduced cost and with improved properties such as solubility and thermal properties.

Another aim of the invention is to extend the pool of materials and polymer films having negative dispersion that are available to the expert. Other aims are immediately evident to the expert from the following description.

It has been found that these aims can be achieved by providing compounds, materials and films as claimed in the present invention.

Summary of the Invention

The invention relates to compounds of formula I

$$D[-(B)_q-M]_z \qquad I$$

wherein

D is a discotic group, or forms a discotic group together with $(B)_q$,

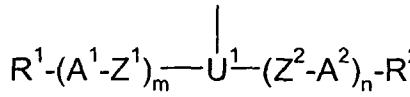
z is an integer from 3 to 10, very preferably 3, 4, 5 or 6,

B is, in each occurrence independently of one another, a bivalent group having high polarizability, preferably selected from the group consisting of $-C\equiv C-$, $-CY^1=CY^2-$ and optionally substituted aromatic or heteroaromatic groups,

$Y^{1,2}$ are independently of each other H, F, Cl, CN or R^0,

q is, in each occurrence independently of one another, 0 or an integer from 1 to 10, preferably 0, 1, 2, 3, 4, 5 or 6,

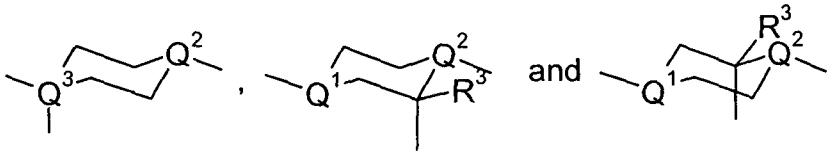
M is a group of formula II



II

wherein the individual radicals have, in case of multiple occurrence independently of one another, the following meanings

U^1 is selected from the group consisting of the following rings



including their mirror images, wherein the ring U^1 is bonded to the group $-(B)_q-$ via the axial bond, and one or two non-adjacent CH_2 groups in these rings are optionally replaced by O and/or S, and the ring U^1 is optionally substituted,

$Q^{1,2}$ are independently of each other CH or SiH,

Q^3 is C or Si,

$A^{1,2}$ are independently of each other selected from non-aromatic, aromatic or heteroaromatic carbocylic or heterocyclic groups, which are optionally substituted, and wherein $-(A^1-Z^1)_m-U^1-(Z^2-A^2)_n-$ does not contain more aromatic groups than non-aromatic groups and preferably does not contain more than one aromatic group,

$Z^{1,2}$ are independently of each other -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, $-CO-NR^0-$, $-NR^0-CO-$, $-NR^0-CO-NR^0-$, $-OCH_2-$, $-CH_2O-$, $-SCH_2-$, $-CH_2S-$, $-CF_2O-$, $-OCF_2-$, $-CF_2S-$, -

SCF_2-, $-CH_2CH_2$-, $-(CH_2)_3$-, $-(CH_2)_4$-, $-CF_2CH_2$-, $-CH_2CF_2$-, $-CF_2CF_2$-, -CH=CH-, $-CY^1=CY^2$-, -CH=N-, -N=CH-, -N=N-, $-CH=CR^0$-, -C≡C-, -CH=CH-COO-, -OCO-CH=CH-, CR^0R^{00} or a single bond,

R^0 and R^{00} are independently of each other H or alkyl with 1 to 12 C-atoms,

m and n are independently of each other 0, 1, 2, 3 or 4, with m+n > 0,

R^{1-3} are independently of each other identical or different groups selected from H, halogen, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-NH_2$, $-NR^0R^{00}$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-SF_5$, P-Sp-, optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, or denote P or P-Sp-, or are substituted by P or P-Sp-,

P is a polymerizable group,

Sp is a spacer group or a single bond.

These compounds have the capability to induce or enhance a negative optical dispersion in liquid crystalline materials, and can be used for the manufacture of polymer films exhibiting a negative dispersion.

The invention further relates to an LC formulation comprising one or more compounds as described above and below.

The invention further relates to a polymerizable LC formulation comprising one or more compounds as described above and below and one or more further compounds, wherein at least one of the compounds is polymerizable.

The invention further relates to a birefringent polymer obtainable by polymerizing a compound or LC formulation as described above and below, preferably in its LC phase in an oriented state in form of a thin film.

The invention further relates to a birefringent polymer film with $R_{450}/R_{550} < 1$, wherein R_{450} is the optical on-axis retardation at a wavelength of 450nm and R_{550} is the optical on-axis retardation at a wavelength of 550nm, said film being obtainable by polymerizing one or more compounds or LC formulations as described above and below.

The invention further relates to the use of compounds, LC formulations and polymers as described above and below in optical, electronic and electrooptical components and devices, preferably in optical films, retarders or compensators having negative optical dispersion.

The invention further relates to an optical, electronic or electrooptical component or device, comprising a compound, LC formulation or or polymer as described above and below.

Said devices and components include, without limitation, electrooptical displays, LCDs, optical films, polarizers, compensators, beam splitters, reflective films, alignment layers, colour filters, holographic elements, hot stamping foils, coloured images, decorative or security markings, LC pigments, adhesives, non-linear optic (NLO) devices, optical information storage devices, electronic devices, organic semiconductors, organic field effect transistors (OFET), integrated circuits (IC), thin film transistors (TFT), Radio Frequency Identification (RFID) tags, organic light emitting diodes (OLED), organic light emitting transistors (OLET), electroluminescent displays, organic photovoltaic (OPV) devices, organic solar cells (O-SC), organic laser diodes (O-laser), organic integrated circuits (O-IC), lighting devices, sensor devices, electrode materials, photoconductors, photodetectors, electrophotographic recording devices, capacitors, charge injection layers, Schottky diodes, planarising layers, antistatic films, conducting substrates, conducting patterns, photoconductors, electrophotographic applications, electrophotographic recording, organic memory devices, biosensors, biochips, optoelectronic

devices requiring similar phase shift at multiple wavelengths, combined CD/DVD/HD-DVD/Blu-Rays, reading, writing re-writing data storage systems, or cameras.

Brief Description of the Drawings

Figure 1 shows the birefringence versus wavelength plot for a polymerized film made from a reactive mesogen of prior art.

Figure 2 shows the refractive index versus wavelength plot of a modelled molecule with low or negative retardation dispersion, showing increased n_o dispersion and decreased n_e dispersion.

Figure 3a and **Figure 3b** show the birefringence versus wavelenght plot for a compound with negative optical dispersion (3a) and positive optical dispersion (3b), respectively.

Figure 4 exemplarily and schematically illustrates the structure of a compound according to the present invention.

Figure 5 exemplarily and schematically illustrates the structure of a compound according to prior art.

Definitions of Terms

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 or in particular as a LC phase. Non-amphiphilic mesogenic compounds comprise for example one or more calamitic, banana-shaped or discotic mesogenic groups.

The term "calamitic " means a rod- or board/lath-shaped compound or group. The term "banana-shaped" means a bent group in which two, usually calamitic, mesogenic groups are linked through a semi-rigid group in such a way as not to be collinear.

The term "discotic" means a disc- or sheet-shaped compound or group.

The term "mesogenic group" means a group with the ability to induce liquid crystal (LC) phase behaviour. Mesogenic groups, especially those of the non-amphiphilic type, are usually either calamitic or discotic. 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, or when the mesogenic compounds or the mixtures thereof are polymerized. For the sake of simplicity, the term "liquid crystal" is used hereinafter for both mesogenic and LC materials.

A calamitic mesogenic compound is usually comprising a calamitic, i.e. rod- or lath-shaped, mesogenic group consisting of one or more aromatic or alicyclic groups connected to each other directly or via linkage groups, optionally comprising terminal groups attached to the short ends of the rod, and optionally comprising one or more lateral groups attached to the long sides of the rod, wherein these terminal and lateral groups are usually selected e.g. from carbyl or hydrocarbyl groups, polar groups like halogen, nitro, hydroxy, etc., or polymerizable groups.

A discotic mesogenic compound is usually comprising a discotic, i.e. relatively flat disc- or sheet-shaped mesogenic group consisting for example of one or more condensed aromatic or alicyclic groups, like for example triphenylene, and optionally comprising one or more terminal groups that are attached to the mesogenic group and are selected from the terminal and lateral groups mentioned above.

For an overview of terms and definitions in connection with liquid crystals and mesogens see Pure Appl. Chem. 73(5), 888 (2001) and C. Tschierske, G. Pelzl and S. Diele, Angew. Chem. 2004, 116, 6340-6368.

The term "reactive mesogen" (RM) means a polymerizable mesogenic or liquid crystal compound.

Polymerizable compounds with one polymerizable group are also referred to as "monoreactive" compounds, compounds with two polymerizable groups as "direactive" compounds, and compounds with more than two polymerizable groups as "multireactive" compounds. Compounds without a polymerizable group are also referred to as "non-reactive" compounds.

The term "spacer" or "spacer group", also referred to as "Sp" below, is known to the person skilled in the art and is described in the literature, see, for example, Pure Appl. Chem. 73(5), 888 (2001) and C. Tschierske, G. Pelzl, S. Diele, Angew. Chem. 2004, 116, 6340-6368. Unless stated otherwise, the term "spacer" or "spacer group" above and below denotes a flexible organic group, which in a polymerisable mesogenic compound ("RM") connects the mesogenic group and the polymerisable group(s).

The term "film" includes rigid or flexible, self-supporting or free-standing films with mechanical stability, as well as coatings or layers on a supporting substrate or between two substrates.

The term "pi-conjugated" means a group containing mainly C atoms with sp^2-hybridisation, or optionally also sp-hybridisation, which may also be replaced by hetero atoms. In the simplest case this is for example a group with alternating C-C single and double bonds, or triple bonds, but does also include groups like 1,3- or 1,4-phenylene. Also included in this meaning are groups like for example aryl amines, aryl phosphines and certain heterocycles (i.e. conjugation via N-, O-, P- or S-atoms).

The term "carbyl group" means any monovalent or multivalent organic radical moiety which comprises at least one carbon atom either without any non-carbon atoms (like for example -C≡C-), or optionally combined with at least one non-carbon atom such as N, O, S, P, Si, Se, As, Te or Ge (for example carbonyl etc.). The term "hydrocarbyl group" denotes a carbyl group that does additionally contain one or more H atoms and optionally contains one or more hetero atoms like for example N, O, S, P, Si, Se, As, Te or Ge. A carbyl or hydrocarbyl group comprising a chain of 3 or more C atoms may also be linear, branched and/or cyclic, including spiro and/or fused rings.

On the molecular level, the birefringence of a liquid crystal depends on the anisotropy of the polarizability ($\Delta\alpha=\alpha_{\parallel}-\alpha_{\perp}$). "Polarizability" means the ease with which the electron distribution in the atom or molecule can be distorted. The polarizability increases with greater number of electrons and a more diffuse electron cloud. The polarizability can be calculated using a method described in eg Jap. J. Appl. Phys. 42, (2003) p3463.

The "optical retardation" at a given wavelength $R(\lambda)$ (in nm) of a layer of liquid crystalline or birefringent material is defined as the product of birefringence at that wavelength $\Delta n(\lambda)$ and layer thickness d (in nm) according to the equation

$$R(\lambda) = \Delta n(\lambda) \cdot d$$

The optical retardation R represents the difference in the optical path lengths in nanometres travelled by S-polarised and P-polarised light whilst passing through the birefringent material. "On-axis" retardation means the retardation at normal incidence to the sample surface.

The term "negative (optical) dispersion" refers to a birefringent or liquid crystalline material or layer that displays reverse birefringence dispersion where the magnitude of the birefringence (Δn) increases with increasing wavelength (λ). i.e $|\Delta n(450)| < |\Delta n(550)|$, or $\Delta n(450)/\Delta n(550) < 1$, where $\Delta n(450)$ and $\Delta n(550)$ are the birefringence of the material measured at wavelengths of 450nm and 550nm respectively. In contrast, positive (optical) dispersion" means a material or layer having $|\Delta n(450)| > |\Delta n(550)|$ or $\Delta n(450)/\Delta n(550) > 1$. See also for example A. Uchiyama, T. Yatabe "Control of Wavelength Dispersion of Birefringence for Oriented Copolycarbonate Films Containing Positive and Negative Birefringent Units". J. Appl. Phys. Vol. 42 pp 6941-6945 (2003).

This is shown schematically in **Figure 3a**.

Since the optical retardation at a given wavelength is defined as the product of birefringence and layer thickness as described above [$R(\lambda)$ =

$\Delta n(\lambda) \cdot d$], the optical dispersion can be expressed either as the "birefringence dispersion" by the ratio $\Delta n(450)/\Delta n(550)$, or as "retardation dispersion" by the ratio R(450)/R(550), wherein R(450) and R(550) are the retardation of the material measured at wavelengths of 450nm and 550nm respectively. Since the layer thickness d does not change with the wavelength, R(450)/R(550) is equal to $\Delta n(450)/\Delta n(550)$. Thus, a material or layer with negative or reverse dispersion has R(450)/R(550) < 1 or $|R(450)| < |R(550)|$, and a material or layer with positive or normal dispersion has R(450)/R(550) > 1 or $|R(450)| > |R(550)|$.

In the present invention, unless stated otherwise "optical dispersion" means the retardation dispersion i.e. the ratio (R(450)/R(550).

The retardation ($R(\lambda)$) of a material can be measured using a spectroscopic ellipsometer, for example the M2000 spectroscopic ellipsometer manufactured by J. A. Woollam Co., This instrument is capable of measuring the optical retardance in nanometres of a birefringent sample e.g. Quartz over a range of wavelengths typically, 370nm to 2000nm. From this data it is possible to calculate the dispersion (R(450)/R(550) or $\Delta n(450)/\Delta n(550)$) of a material.

A method for carrying out these measurements was presented at the National Physics Laboratory (London, UK) by N. Singh in October 2006 and entitled "Spectroscopic Ellipsometry, Part1-Theory and Fundamentals, Part 2 – Practical Examples and Part 3 - measurements". In accordance with the measurement procedures described Retardation Measurement (RetMeas) Manual (2002) and Guide to WVASE (2002) (Woollam Variable Angle Spectroscopic Ellipsometer) published by J. A. Woollam Co. Inc (Lincoln, NE, USA). Unless stated otherwise, this method is used to determine the retardation of the materials, films and devices described in this invention.

Detailed Description of the Invention

The prior art documents cited above demonstrate the general feasibility of making negative dispersion films using polymerisable LCs. However, in

addition to the need for negative dispersion additives to demonstrate good solubility and thermal properties, it is also desired for these additives to show the desired optical effect with a minimum concentration in the final LC mixture. Therefore it is desired to have available compounds that impart an increased negative dispersion to the LC host mixture.

The inventors of the present invention have now found that this can be achieved by modifying the molecular structure of the negative dispersion compounds. **Figure 4** shows a typical compound of prior art as disclosed for example in US 6,203,724, comprising a highly polarisable bridge, typically with an aromatic ring and two alkinyl groups, between two rod shaped groups with low polarisability, which essentailly consist of cyclohexane rings. It was found that the highly polarisable bridge is a key component that allows a film formed from such molecules to demonstrate negative birefringence dispersion. Restricting the freedom of the bridge to move relative to the rods should increase the effectiveness of the negative dispersion additives. Furthermore, if the aromatic rings in the bridge have the freedom to rotate in and out of the plane, as schematically depicted by the arrow in **Figure 4**, then this part of the bridge can contribute to both n_e and n_o. Thus, limiting the contribution of the bridge to n_e should increase the effectiveness of the negative dispersion additive. With three or more rods around each central highly polarisable part of the molecule, any aromatic rings will be predominantly orientated such as to maximise its contribution to n_o. In addition, increasing the number of rods attached to the central aromatic ring should also help to increase the LC properties of the molecule.

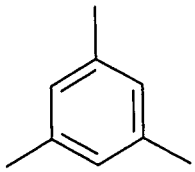
To summarise, there are the following reasons why it is expected that the structurally modified compounds according to the present invention will show improved performance over the prior art compounds:

1. Restricting the freedom of the bridge to move relative to the rods will increase the effectiveness of the negative dispersion additives. Therefore, linking the two moieties via a suitably substituted axial cyclohexane linking group should achieve this effect better than linking it via an ester group.

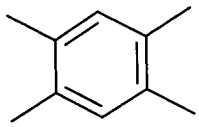
2. Limiting the contribution the bridge makes to n_e will increase the effectiveness of the negative dispersion dopant. Further restricting the freedom of any aromatic rings to rotate out of plane by predominantly anchoring the orientation with three rather than two rods should maximise its contribution to n_o whilst minimising its contribution to n_e.
3. Increasing the number of rods attached to a central ring should help to increase the liquid crystalline properties of the molecule.

The above modifications were realised by providing compounds of formula I according to the present invention. These compounds do generally consist of two distinct molecular parts as exemplarily and schematically shown in **Figure 5**: A central discotic core (1), for example a ring structure or a group comprising two or more rings, surrounded by three or more rod shaped groups (2). The molecular geometry of the system increases the probability that the plane of the ring will be held largely perpendicular to the long axis of the rod-shaped molecular part. The rod-shaped groups (2) do preferably consist predominantly of groups with low polarisability such as cyclohexane rings. At the end of the rods polymerisable groups (3) can be attached. The distribution of the polymerisable groups is random and they can also be all at the same side of the molecule. The number of polymerisable groups can be as low as one. The central part of the molecule (1) predominantly consists of highly polarisable groups like for example aromatic rings. The rods (2) are connected via a lateral group to the core (1). The lateral group connecting the rod (2) to the core (1) is chosen so that it restricts the freedom of the rod to revolve relative to the core. Overall, the molecule will have low birefringence in long axis of the molecule and high birefringence in the lateral part of the molecule (= the discotic core).

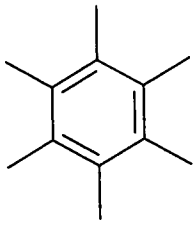
In the compounds of formula I, the discotic group D preferably denotes benzene, which is preferably tri-, tetra or hexavalent, or triphenylene, which is preferably hexavalent. Very preferably the discotic group D is selected from the group consisting of the following formulae:



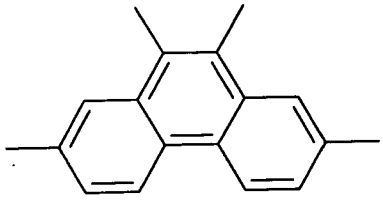
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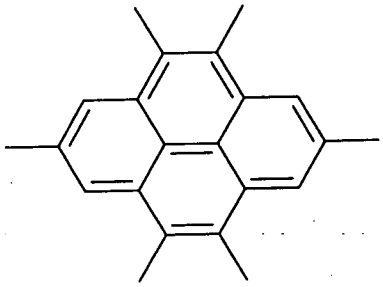
D2



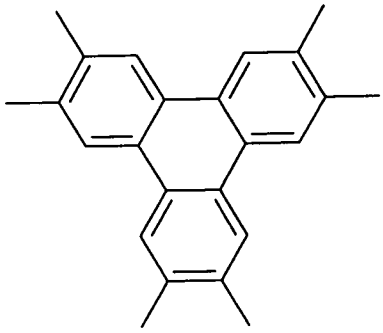
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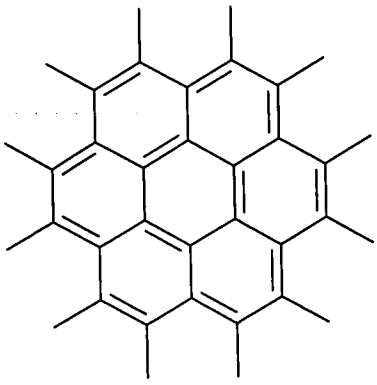
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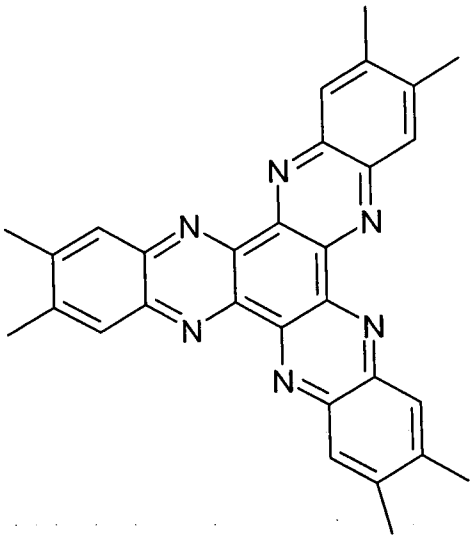
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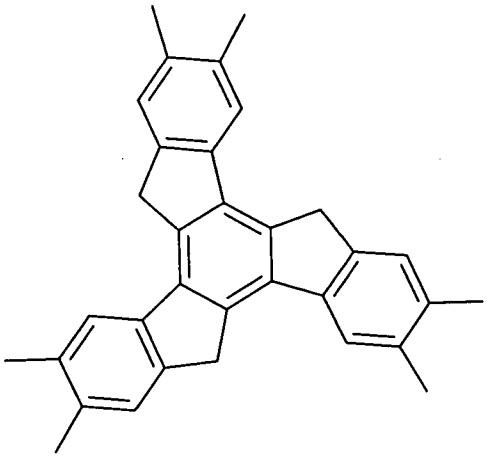
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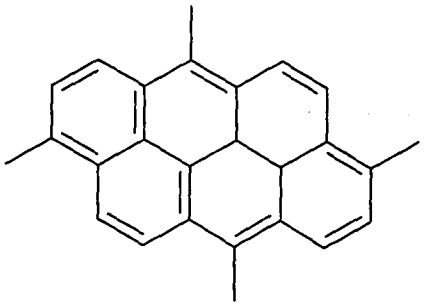
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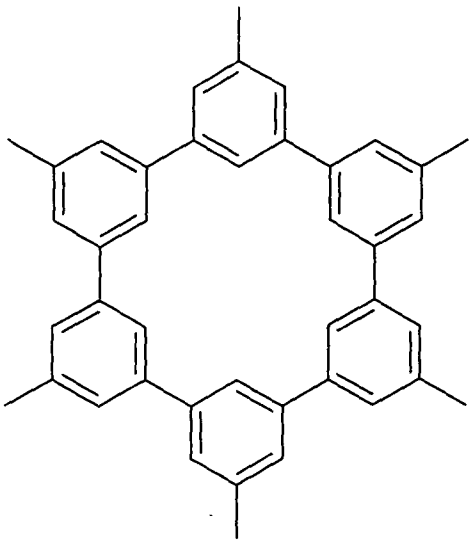
D8



D9



D10



D11

The group $(B)_q$ having high polarizability is preferably consisting mainly, very preferably exclusively, of one or more subgroups B, which are selected from pi-conjugated linear groups, aromatic and heteroaromatic groups.

Preferably the group $(B)_q$ consists, very preferably exclusively, of one or more subgroups B selected from groups having a bonding angle of 120° or more, preferably in the range of 180°. Suitable and preferred subgroups B include, without limitation, groups comprising sp-hybridised C-atoms, like -C≡C-, or divalent aromatic groups connected to their neighboured groups in para-position, like e.g. 1,4-phenylene, naphthalene-2,6-diyl, indane-2,6-diyl or thieno[3,2-b]thiophene-2,5-diyl.

In the groups $(B)_q$ q may also be 0, so that $(B)_q$ is a single bond and the corresponding group M is attached directly to the discotic group.

Preferably, however, the compounds of formula I comprise at least one, more preferably at least two groups $(B)_q$ wherein q is different from 0. Further preferred are compounds of formula I wherein each q is different from 0.

The group $(B)_q$ is preferably a linear group consisting of subgroups B having bonding angles of approx. 180°, and is linked to the calamitic compound via an sp^3-hybridised C-atom (i.e. with a bonding angle of approx. 109°). Thereby it is posible to achieve a structure where the long axis of the calamitic mesogenic groups M are largely perpendicular to the plane of the ring of the discotic group D.

The group $(B)_q$, which essentially consists of subgroups B with pi-conjugation, has a high polarizability and a high refractive index. If the mesogenic groups M are selected to have a low polarizability and a low refractive index, then as a result the compounds show, depending on their exact structure, either positive birefringence and negative dispersion, as schematically depicted in **Figure 3a**, or negative birefringence with positive dispersion, as schematically depicted in **Figure 3b.**

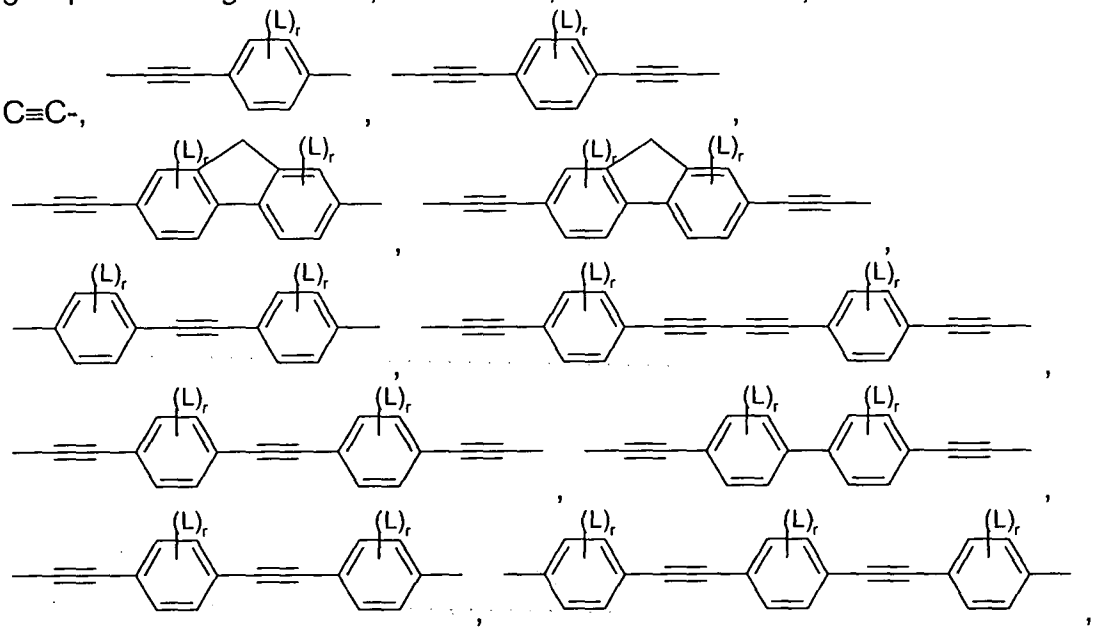
As a reference, normal calamitic materials have positive birefringence and positive dispersion. It is desirable to have materials where the magnitude of Δn decreases at shorter wavelength, and compounds with both positive dispersion and negative birefringence can be mixed with a host material to give a mixture which possesses a range of dispersion (depending on the concentration of the dopant and host) varying from positive birefringence with positive dispersion through to positive birefringence with negative dispersion.

The subgroups B are preferably selected from groups having a bonding angle of 120° or more, preferably in the range of 180°. Very preferred are -C≡C- groups or divalent aromatic groups connected to their adjacent groups in para-position, like e.g. 1,4-phenylene, naphthalene-2,6-diyl, indane-2,6-diyl or thieno[3,2-b]thiophene-2,5-diyl.

Further possible subgroups B include -CH=CH-, $-CY^1=CY^2-$, and $-CH=CR^0-$ wherein Y^1, Y^2, R^0 have the meanings given above.

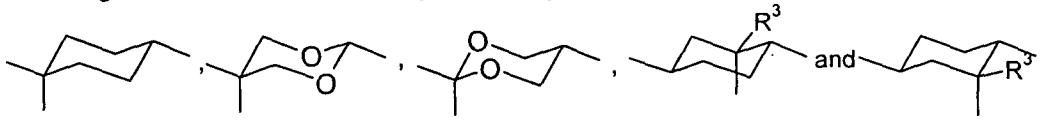
Preferably the bridging group $-(B)_q-$ in formula I comprises one or more groups selected from the group consisting of -C≡C-, optionally substituted 1,4-phenylene and optionally substituted 9H-fluorene-2,7-diyl. The subgroups, or B in formula I, are preferably selected from the group consisting of -C≡C-, optionally substituted 1,4-phenylene and optionally substituted 9H-fluorene-2,7-diyl, wherein in the fluorene group the H-atom in 9-position is optionally replaced by a carbyl or hydrocarbyl group.

Very preferably the bridging group $-(B)_q-$ in formula I is selected from the group consisting of -C≡C-, -C≡C-C≡C-, -C≡C-C≡C-C≡C-, -C≡C-C≡C-C≡C-C≡C-,



wherein r is 0, 1, 2, 3 or 4 and L has the meaning as described below.

The rings U^1 in formula II are preferably selected from



wherein R^3 is as defined in formula I.

The groups M are preferably calamitic mesogenic groups, very preferably rod-shaped mesogenic groups.

Preferably the groups M comprise one or more groups selected from aromatic or heteroaromatic rings, and non-aromatic, e.g. fully or partially saturated, carbocyclic or heterocyclic groups, said groups being linked to each other either directly or via linkage groups.

Preferably the groups M are selected such that they exhibit a low polarizability. This can be achieved e.g. by using mesogenic groups that are preferably comprising mainly non-aromatic, most preferably fully saturated, carbocyclic or heterocyclic groups which are connected directly or via linkage groups, wherein "mainly" means that each mesogenic group comprises more saturated rings than unsaturated or aromatic rings, and very preferably does not comprise more than one unsaturated or aromatic ring.

Especially preferred are compounds of formula I, wherein all groups M are identical.

Further preferred are compounds of formula I, wherein in one or more groups M, very preferably in each group M, the subgroups $-(Z^1-A^1)_m-R^1$ and $-(Z^2-A^2)_n-R^2$ are different from each other.

Further preferred are compounds of formula I, wherein at least one of the the groups A^1 or A^2 linked to the central ring U^1 is cyclohexylene, and very preferably said group A^1 or A^2 is directly attached to U^1, i.e. the corresponding group Z^1 or Z^2 between U^1 and said group A^1 or A^2 is a single bond.

The aromatic groups, like $A^{1,2}$, may be mononuclear, i.e. having only one aromatic ring (like for example phenyl or phenylene), or polynuclear, i.e. having two or more fused rings (like for example napthyl or naphthylene). Especially preferred are mono-, bi- or tricyclic aromatic or heteroaromatic groups with up to 25 C atoms that may also comprise fused rings and are optionally substituted.

Preferred aromatic groups include, without limitation, benzene, biphenylene, triphenylene, [1,1':3',1"]terphenyl-2'-ylene, naphthalene, anthracene, binaphthylene, phenanthrene, pyrene, dihydropyrene, chrysene, perylene, tetracene, pentacene, benzpyrene, fluorene, indene, indenofluorene, spirobifluorene, etc.

Preferred heteroaromatic groups include, without limitation, 5-membered rings like 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-membered rings like 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, and fused systems like carbazole, indole, isoindole, indolizine, indazole, benzimidazole, benzotriazole, purine, naphthimidazole, phenanthrimidazole, pyridimidazole, pyrazinimidazole, 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, quinoxaline, phenazine, naphthyridine, azacarbazole, benzocarboline, phenanthridine, phenanthroline, thieno[2,3b]thiophene, thieno[3,2b]thiophene, dithienothiophene, dithienopyridine, isobenzothiophene, dibenzothiophene, benzothiadiazothiophene, or combinations thereof.

The non-aromatic carbocyclic and heterocyclic groups, like A^{1-4}, include those which are saturated (also referred to as "fully saturated"), i.e. they do only contain C-atoms or hetero atoms connected by single bonds, and those which are unsaturated (also referred to as "partially saturated"), i.e. they also comprise C-atoms or hetero atoms connected by double bonds. The non-aromatic rings may also comprise one or more hetero atoms, preferably selected from Si, O, N and S.

The non-aromatic carbocyclic and heterocyclic groups may be mononuclear, i.e. having only one ring (like for example cyclohexane), or polynuclear, i.e. having two or more fused rings (like for example decahydronaphthalene or bicyclooctane). Especially preferred are fully saturated groups. Further preferred are mono-, bi- or tricyclic non-aromatic groups with up to 25 C atoms that optionally comprise fused rings and are optionally substituted. Very preferred are 5-, 6-, 7- or 8-membered carbocyclic rings wherein one or more C-atoms are optionally replaced by Si and/or one or more CH groups are optionally replaced by N and/or one or more non-adjacent CH_2 groups are optionally replaced by -O- and/or -S-, all of which are optionally substituted.

Preferred non-aromatic rings include, without limitation, 5-membered rings like cyclopentane, tetrahydrofuran, tetrahydrothiofuran, pyrrolidine, 6-membered rings like cyclohexane, silinane, cyclohexene, tetrahydropyran, tetrahydrothiopyran, 1,3-dioxane, 1,3-dithiane, piperidine, 7- membered rings like cycloheptane, and fused systems like 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-methano-indan-2,5-diyl, or combinations thereof.

Preferably the non-aromatic and aromatic rings, like $A^{1,2}$, are selected from trans-1,4-cyclohexylene and 1,4-phenylene that is optionally substituted with one or more groups L.

Very preferably the mesogenic groups M comprise not more than one aromatic ring.

Very preferred are compounds of formula I and II wherein m and n are 0, 1 or 2, in particular wherein one of m and n is 1 and the other is 0 or 1.

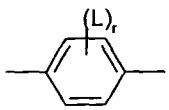
In the calamitic compounds of the present invention, the linkage groups connecting the aromatic and non-aromatic cyclic groups in the mesogenic groups, like $Z^{1,2}$, are preferably selected from -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, -CO-NR^0-, -NR^0-CO-, -NR^0-CO-NR^0-, -OCH_2-, -CH_2O-, -SCH_2-, -CH_2S-, -CF_2O-, -OCF_2-, -CF_2S-, -SCF_2-, -CH_2CH_2-, -$(CH_2)_3$-, -

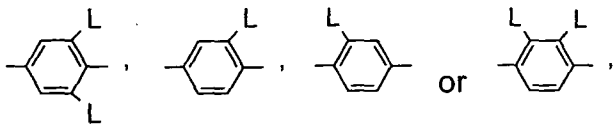
$(CH_2)_4$-, -CF_2CH_2-, -CH_2CF_2-, -CF_2CF_2-, -CH=CH-, -CY^1=CY^2-, -CH=N-, -N=CH-, -N=N-, -CH=CR^0-, -C≡C-, -CH=CH-COO-, -OCO-CH=CH-, CR^0R^{00} or a single bond, very preferably from -COO-, -OCO- and a single bond.

In the calamitic compounds of the present invention, the substituents on the groups B, U^1, $A^{1,2}$ and R^{1-3} , also referred to as "L", are preferably selected from P-Sp-, F, Cl, Br, I, -CN, -NO_2 , -NCO, -NCS, -OCN, -SCN, -C(=O)NR^0R^{00}, -C(=O)X, -C(=O)OR^0, -C(=O)R^0, -NR^0R^{00}, -OH, -SF_5, optionally substituted silyl, aryl or heteroaryl with 1 to 12, preferably 1 to 6 C atoms, and straight chain or branched alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy with 1 to 12, preferably 1 to 6 C atoms, wherein one or more H atoms are optionally replaced by F or Cl, wherein R^0 and R^{00} are as defined in formula I and X is halogen.

Preferred substituents L are selected from F, Cl, CN, NO_2 or straight chain or branched alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonlyoxy or alkoxycarbonyloxy with 1 to 12 C atoms, wherein the alkyl groups are optionally perfluorinated, or P-Sp-.

Very preferred substituents are selected from F, Cl, CN, NO_2, CH_3, C_2H_5, $C(CH_3)_3$, $CH(CH_3)_2$, $CH_2CH(CH_3)C_2H_5$, OCH_3, OC_2H_5, $COCH_3$, COC_2H_5, $COOCH_3$, $COOC_2H_5$, CF_3, OCF_3, $OCHF_2$, OC_2F_5 or P-Sp-, in particular F, Cl, CN, CH_3, C_2H_5, $C(CH_3)_3$, $CH(CH_3)_2$, OCH_3, $COCH_3$ or OCF_3, most preferably F, Cl, CH_3, $C(CH_3)_3$, OCH_3 or $COCH_3$, or P-Sp-.



is preferably


or

with L having each independently one of the meanings given above.

The carbyl and hydrocarbyl groups R^{1-3} are preferably selected from straight-chain, branched or cyclic alkyl with 1 to 40, preferably 1 to 25 C-atoms, which is unsubstituted, mono- or polysubstituted by F, Cl, Br, I or CN, and wherein one or more non-adjacent CH_2 groups are optionally replaced, in each case independently from one another, by -O-, -S-, -NH-,

$-NR^0-$, $-SiR^0R^{00}-$, -CO-, -COO-, -OCO-, -O-CO-O-, -S-CO-, -CO-S-, $-SO_2-$, $-CO-NR^0-$, $-NR^0-CO-$, $-NR^0-CO-NR^{00}-$, $-CY^1=CY^2-$ or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, wherein Y^1 and Y^2 are independently of each other H, F, Cl or CN, and R^0 and R^{00} are independently of each other H or an optionally substituted aliphatic or aromatic hydrocarbon with 1 to 20 C atoms.

Very preferably R^1 and R^2 are selected from , C_1-C_{20}-alkyl, C_1-C_{20}-oxaalkyl, C_1-C_{20}-alkoxy, C_2-C_{20}-alkenyl, C_2-C_{20}-alkynyl, C_1-C_{20}-thioalkyl, C_1-C_{20}-silyl, C_1-C_{20}-ester, C_1-C_{20}-amino, C_1-C_{20}-fluoroalkyl.

R^3 is preferably H or methyl.

An alkyl or alkoxy radical, i.e. where the terminal CH_2 group is replaced by -O-, can 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 tetradecoxy, for example.

Oxaalkyl, i.e. where one CH_2 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.

An alkyl group wherein one or more CH_2 groups are replaced by -CH=CH- can be straight-chain or branched. It is preferably straight-chain, has 2 to 10 C atoms and accordingly is preferably vinyl, prop-1-, or prop-2-enyl, but-1-, 2- or but-3-enyl, pent-1-, 2-, 3- or pent-4-enyl, hex-1-, 2-, 3-, 4- or hex-5-enyl, hept-1-, 2-, 3-, 4-, 5- or hept-6-enyl, oct-1-, 2-, 3-, 4-, 5-, 6- or oct-7-enyl, non-1-, 2-, 3-, 4-, 5-, 6-, 7- or non-8-enyl, dec-1-, 2-, 3-, 4-, 5-, 6-, 7-, 8- or dec-9-enyl.

Especially preferred alkenyl groups are C_2-C_7-1E-alkenyl, C_4-C_7-3E-alkenyl, C_5-C_7-4-alkenyl, C_6-C_7-5-alkenyl and C_7-6-alkenyl, in particular C_2-C_7-1E-alkenyl, C_4-C_7-3E-alkenyl and C_5-C_7-4-alkenyl. Examples for particularly preferred alkenyl groups are vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 1E-heptenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-heptenyl, 4-pentenyl, 4Z-hexenyl, 4E-hexenyl, 4Z-heptenyl, 5-hexenyl, 6-heptenyl and the like. Groups having up to 5 C atoms are generally preferred.

In an alkyl group wherein one CH_2 group is replaced by -O- and one by -CO-, these radicals are preferably neighboured. Accordingly these radicals together form a carbonyloxy group -CO-O- or an oxycarbonyl group -O-CO-. Preferably this group is straight-chain and has 2 to 6 C atoms. It is accordingly preferably acetyloxy, propionyloxy, butyryloxy, pentanoyloxy, hexanoyloxy, acetyloxymethyl, propionyloxymethyl, butyryloxymethyl, pentanoyloxymethyl, 2-acetyloxyethyl, 2-propionyloxyethyl, 2-butyryloxyethyl, 3-acetyloxypropyl, 3-propionyloxypropyl, 4-acetyloxybutyl, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, butoxycarbonyl, pentoxycarbonyl, methoxycarbonylmethyl, ethoxycarbonylmethyl, propoxycarbonylmethyl, butoxycarbonylmethyl, 2-(methoxycarbonyl)ethyl, 2-(ethoxycarbonyl)ethyl, 2-(propoxycarbonyl)ethyl, 3-(methoxycarbonyl)propyl, 3-(ethoxycarbonyl)propyl, 4-(methoxycarbonyl)-butyl.

An alkyl group wherein two or more CH_2 groups are replaced by -O- and/or -COO- can be straight-chain or branched. It is preferably straight-chain and has 3 to 12 C atoms. Accordingly it is preferably bis-carboxymethyl, 2,2-bis-carboxy-ethyl, 3,3-bis-carboxy-propyl, 4,4-bis-carboxybutyl, 5,5-bis-carboxy-pentyl, 6,6-bis-carboxy-hexyl, 7,7-bis-carboxyheptyl, 8,8-bis-carboxy-octyl, 9,9-bis-carboxy-nonyl, 10,10-bis-carboxydecyl, bis-(methoxycarbonyl)-methyl, 2,2-bis-(methoxycarbonyl)-ethyl, 3,3-bis-(methoxycarbonyl)-propyl, 4,4-bis-(methoxycarbonyl)-butyl, 5,5-bis-(methoxycarbonyl)-pentyl, 6,6-bis-(methoxycarbonyl)-hexyl, 7,7-bis-(methoxycarbonyl)-heptyl, 8,8-bis-(methoxycarbonyl)-octyl, bis-(ethoxycarbonyl)-methyl, 2,2-bis-(ethoxycarbonyl)-ethyl, 3,3-bis-

(ethoxycarbonyl)-propyl, 4,4-bis-(ethoxycarbonyl)-butyl, 5,5-bis-(ethoxycarbonyl)-hexyl.

An alkyl or alkenyl group that is monosubstituted by CN or CF_3 is preferably straight-chain. The substitution by CN or CF_3 can be in any desired position.

An alkyl or alkenyl group that is at least monosubstituted by halogen is preferably straight-chain. Halogen is preferably F or Cl, in case of multiple substitution preferably F. The resulting groups include also perfluorinated groups. In case of monosubstitution the F or Cl substituent can be in any desired position, but is preferably in ω-position. Examples for especially preferred straight-chain groups with a terminal F substituent are fluoromethyl, 2-fluoroethyl, 3-fluoropropyl, 4-fluorobutyl, 5-fluoropentyl, 6-fluorohexyl and 7-fluoroheptyl. Other positions of F are, however, not excluded.

R^0 and R^{00} are preferably selected from H, straight-chain or branched alkyl with 1 to 12 C atoms.

$-CY^1=CY^2-$ is preferably -CH=CH-, -CF=CF- or -CH=C(CN)-.

Halogen is F, Cl, Br or I, preferably F or Cl.

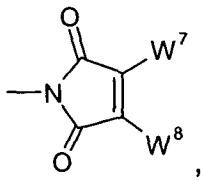
R^{1-3} can be an achiral or a chiral group. Particularly preferred chiral groups are 2-butyl (=1-methylpropyl), 2-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, in particular 2-methylbutyl, 2-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy, 2-octyloxy, 2-oxa-3-methylbutyl, 3-oxa-4-methylpentyl, 4-methylhexyl, 2-hexyl, 2-octyl, 2-nonyl, 2-decyl, 2-dodecyl, 6-methoxyoctoxy, 6-methyloctoxy, 6-methyloctanoyloxy, 5-methylheptyloxycarbonyl, 2-methylbutyryloxy, 3-methylvaleroyloxy, 4-methylhexanoyloxy, 2-chlorpropionyloxy, 2-chloro-3-methylbutyryloxy, 2-chloro-4-methylvaleryloxy, 2-chloro-3-methylvaleryloxy, 2-methyl-3-oxapentyl, 2-methyl-3-oxahexyl, 1-methoxypropyl-2-oxy, 1-ethoxypropyl-2-oxy, 1-propoxypropyl-2-oxy, 1-butoxypropyl-2-oxy, 2-fluorooctyloxy, 2-fluorodecyloxy, 1,1,1-trifluoro-2-octyloxy, 1,1,1-trifluoro-2-octyl, 2-fluoromethyloctyloxy for example. Very

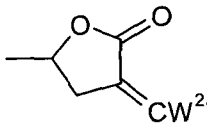
preferred are 2-hexyl, 2-octyl, 2-octyloxy, 1,1,1-trifluoro-2-hexyl, 1,1,1-trifluoro-2-octyl and 1,1,1-trifluoro-2-octyloxy.

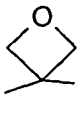
Preferred achiral branched groups are isopropyl, isobutyl (=methylpropyl), isopentyl (=3-methylbutyl), isopropoxy, 2-methyl-propoxy and 3-methylbutoxy.

The polymerizable group P is a group that is capable of participating in a polymerization reaction, like radical or ionic chain polymerization, polyaddition or polycondensation, or capable of being grafted, for example by condensation or addition, to a polymer backbone in a polymer analogous reaction. Especially preferred are polymerizable groups for chain polymerization reactions, like radical, cationic or anionic polymerization. Very preferred are polymerizable groups comprising a C-C double or triple bond, and polymerizable groups capable of polymerization by a ring-opening reaction, like oxetanes or epoxides.

Suitable and preferred polymerizable groups include, without limitation,

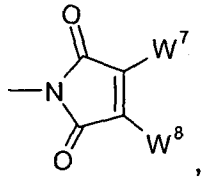
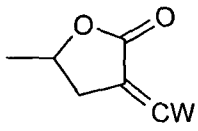
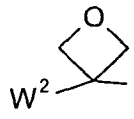


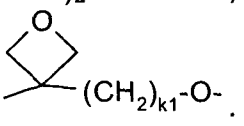




$CH_2=CW^1\text{-}COO\text{-}$, $CH_2=CW^1\text{-}CO\text{-}$, W^2HC , , CW^2W^3, W^2 $(CH_2)_{k1}\text{-}O\text{-}$, $CH_2=CW^2\text{-}(O)_{k1}\text{-}$, $CH_3\text{-}CH=CH\text{-}O\text{-}$, $(CH_2=CH)_2CH\text{-}OCO\text{-}$, $(CH_2=CH\text{-}CH_2)_2CH\text{-}OCO\text{-}$, $(CH_2=CH)_2CH\text{-}O\text{-}$, $(CH_2=CH\text{-}CH_2)_2N\text{-}$, $(CH_2=CH\text{-}CH_2)_2N\text{-}CO\text{-}$, $HO\text{-}CW^2W^3\text{-}$, $HS\text{-}CW^2W^3\text{-}$, $HW^2N\text{-}$, $HO\text{-}CW^2W^3\text{-}NH\text{-}$, $CH_2=CW^1\text{-}CO\text{-}NH\text{-}$, $CH_2=CH\text{-}(COO)_{k1}\text{-}Phe\text{-}(O)_{k2}\text{-}$, $CH_2=CH\text{-}(CO)_{k1}\text{-}Phe\text{-}(O)_{k2}\text{-}$, Phe-CH=CH-, HOOC-, OCN-, and $W^4W^5W^6Si\text{-}$, with W^1 being H, F, Cl, CN, CF_3, phenyl or alkyl with 1 to 5 C-atoms, in particular H, Cl or CH_3, W^2 and W^3 being independently of each other H or alkyl with 1 to 5 C-atoms, in particular H, methyl, ethyl or n-propyl, W^4, W^5 and W^6 being independently of each other Cl, oxaalkyl or oxacarbonylalkyl with 1 to 5 C-atoms, W^7 and W^8 being independently of each other H, Cl or alkyl with 1 to 5 C-atoms, Phe being 1,4-phenylene that is optionally substituted, preferably by one or more groups L as defined above (except

for the meaning P-Sp-), and k_1 and k_2 being independently of each other 0 or 1.

Very preferred polymerizable groups are selected from $CH_2=CW^1$-COO-, $CH_2=CW^1$-CO-, W^2HC(O)$CH-$, , , $(CH_2)_{k1}$-O-, $(CH_2=CH)_2CH$-OCO-, $(CH_2=CH-CH_2)_2CH$-OCO-, $(CH_2=CH)_2CH$-O-, $(CH_2=CH-CH_2)_2N$-, $(CH_2=CH-CH_2)_2N$-CO-, HO-CW^2W^3-, HS-CW^2W^3-, HW^2N-, HO-CW^2W^3-NH-, $CH_2=CW^1$-CO-NH-, $CH_2=CH$-$(COO)_{k1}$-Phe-$(O)_{k2}$-, $CH_2=CH$-$(CO)_{k1}$-Phe-$(O)_{k2}$-, Phe-CH=CH-, HOOC-, OCN-, and $W^4W^5W^6Si$-, with W^1 being H, F, Cl, CN, CF_3, phenyl or alkyl with 1 to 5 C-atoms, in particular H, F, Cl or CH_3, W^2 and W^3 being independently of each other H or alkyl with 1 to 5 C-atoms, in particular H, methyl, ethyl or n-propyl, W^4, W^5 and W^6 being independently of each other Cl, oxaalkyl or oxacarbonylalkyl with 1 to 5 C-atoms, W^7 and W^8 being independently of each other H, Cl or alkyl with 1 to 5 C-atoms, Phe being 1,4-phenylene that is optionally substituted preferably by one or more groups L as defined above (except for the meaning P-Sp-), and k_1 and k_2 being independently of each other 0 or 1.

Most preferred polymerizable groups are selected from $CH_2=CH$-COO-, $CH_2=C(CH_3)$-COO-, $CH_2=CF$-COO-, $(CH_2=CH)_2CH$-OCO-, $(CH_2=CH)_2CH$-O-, W^2HC(O)$CH-$ and .

Polymerization can be carried out according to methods that are known to the ordinary expert and described in the literature, for example in D. J. Broer; G. Challa; G. N. Mol, *Macromol. Chem*, 1991, **192**, 59.

The spacer group Sp is preferably selected of formula Sp'-X', such that P-Sp- is P-Sp'-X'-, wherein

Sp' is alkylene with 1 to 20 C atoms, preferably 1 to 12 C-atoms, which is optionally mono- or polysubstituted by F, Cl, Br, I or CN, and wherein one or more non-adjacent CH_2 groups are optionally replaced, in each case independently from one another, by -O-, -S-, -NH-, $-NR^0-$, $-SiR^0R^{00}-$, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, $-NR^0$-CO-O-, -O-CO-NR^0-, $-NR^0$-CO-NR^0-, -CH=CH- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another,

X' is -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, $-CO-NR^0-$, $-NR^0$-CO-, $-NR^0$-CO-NR^0-, $-OCH_2-$, $-CH_2O-$, $-SCH_2-$, $-CH_2S-$, $-CF_2O-$, $-OCF_2-$, $-CF_2S-$, $-SCF_2-$, $-CF_2CH_2-$, $-CH_2CF_2-$, $-CF_2CF_2-$, -CH=N-, -N=CH-, -N=N-, $-CH=CR^0-$, $-CY^1=CY^2-$, -C≡C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond,

R^0 and R^{00} are independently of each other H or alkyl with 1 to 12 C-atoms, and

Y^1 and Y^2 are independently of each other H, F, Cl or CN.

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

Typical groups Sp' are, for example, $-(CH_2)_{p1}-$, $-(CH_2CH_2O)_{q1}-CH_2CH_2-$, $-CH_2CH_2-S-CH_2CH_2-$ or $-CH_2CH_2-NH-CH_2CH_2-$ or $-(SiR^0R^{00}-O)_{p1}-$, with p1 being an integer from 2 to 12, q1 being an integer from 1 to 3 and R^0 and R^{00} having the meanings given above.

Preferred groups Sp' are ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, octadecylene, ethyleneoxyethylene, methyleneoxy-butylene, ethylene-thioethylene, ethylene-N-methyl-iminoethylene, 1-methylalkylene, ethenylene, propenylene and butenylene for example. Further preferred are chiral sapcer groups.

Further preferred are compounds wherein the polymerizable group is directly attached to the mesogenic group without a spacer group Sp.

In case of compounds with two or more groups P-Sp-, the polymerizable groups P and the spacer groups Sp can be identical or different.

In another preferred embodiment the calamitic compounds comprise one or more terminal groups $R^{1,2}$ or substituents L or R^3 that are substituted by two or more polymerizable groups P or P-Sp- (multifunctional polymerizable groups). Suitable multifunctional polymerizable groups of this type are disclosed for example in US 7,060,200 B1 oder US 2006/0172090 A1. Very preferred are compounds comprising one or more multifunctional polymerizable groups selected from the following formulae:

-X-alkyl-CHP^1-CH_2-CH_2P^2 P1

-X'-alkyl-$C(CH_2P^1)(CH_2P^2)$-CH_2P^3 P2

-X'-alkyl-CHP^1CHP^2-CH_2P^3 P3

-X'-alkyl-$C(CH_2P^1)(CH_2P^2)$-$C_{aa}H_{2aa+1}$ P4

-X'-alkyl-CHP^1-CH_2P^2 P5

-X'-alkyl-CHP^1P^2 P5

-X'-alkyl-CP^1P^2-$C_{aa}H_{2aa+1}$ P6

-X'-alkyl-$C(CH_2P^1)(CH_2P^2)$-CH_2OCH_2-$C(CH_2P^3)(CH_2P^4)CH_2P^5$ P7

-X'-alkyl-$CH((CH_2)_{aa}P^1)((CH_2)_{bb}P^2)$ P8

-X'-alkyl-CHP^1CHP^2-$C_{aa}H_{2aa+1}$ P9

wherein

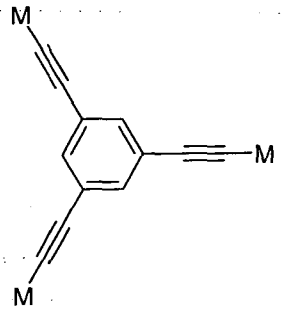
alkyl is straight-chain or branched alkylene having 1 to 12 C-atoms which is unsubstituted, mono- or polysubstituted by F, Cl, Br, I or CN, and wherein one or more non-adjacent CH_2 groups are optionally replaced, in each case independently from one another, by -O-, -S-, -NH-, $-NR^0-$, $-SiR^0R^{00}-$, -CO-, -COO-, -OCO-, -O-CO-O-, -S-CO-, -CO-S-, $-SO_2-$, $-CO-NR^0-$, $-NR^0-CO-$, $-NR^0-CO-NR^{00}-$, $-CY^1=CY^2-$ or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, with R^0 and R^{00} having the meanings given above, or denotes a single bond,

aa and bb are independently of each other 0, 1, 2, 3, 4, 5 or 6,

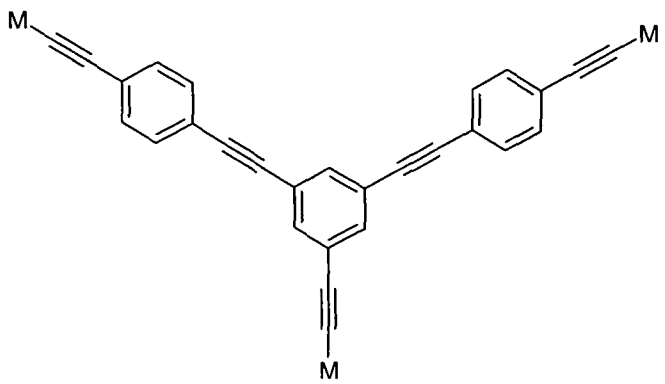
X' is as defined above, and

P^{1-5} independently of each other have one of the meanings given for P above.

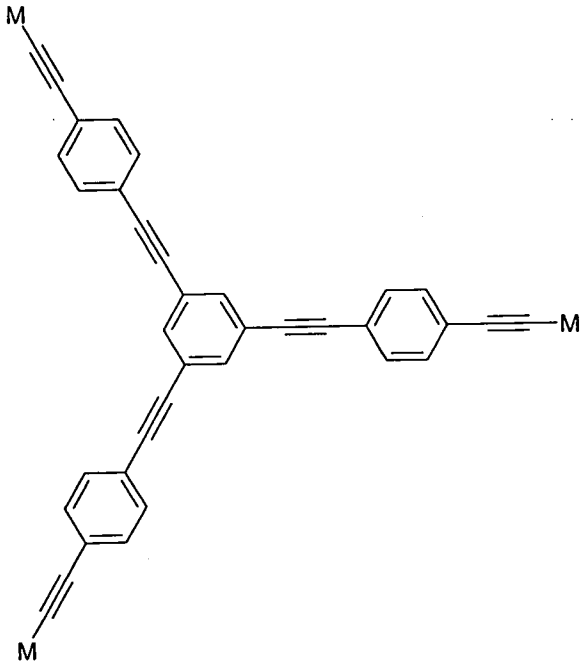
Preferred compounds of formula I are selected from the group consisting of the following subformulae:



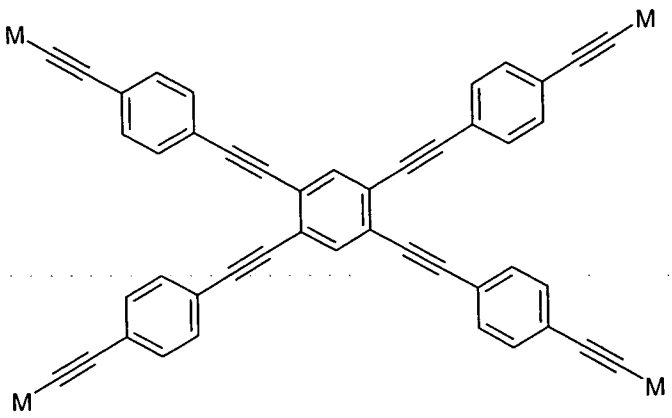
Ia



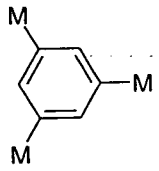
Ib



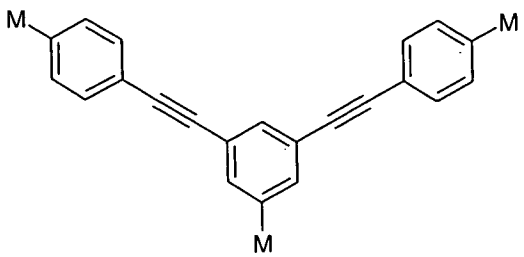
Ic



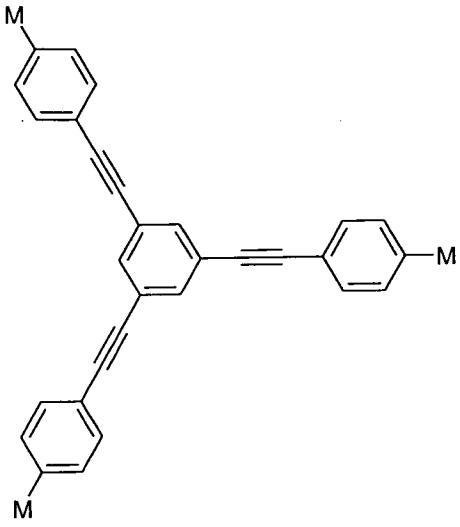
Id



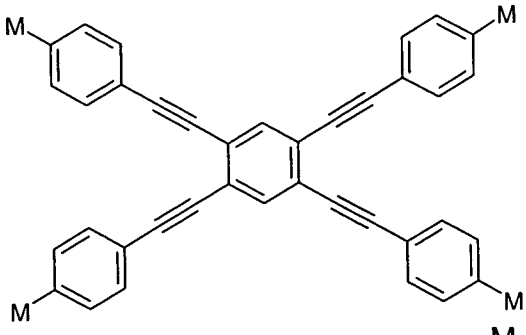
Ie



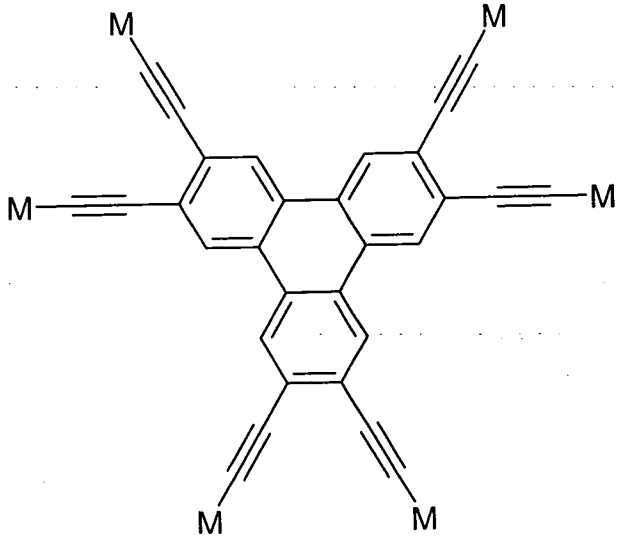
If



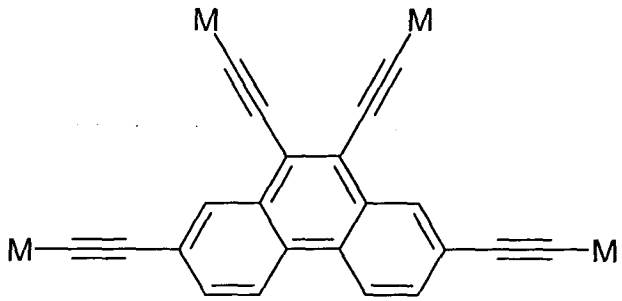
Ig



Ih



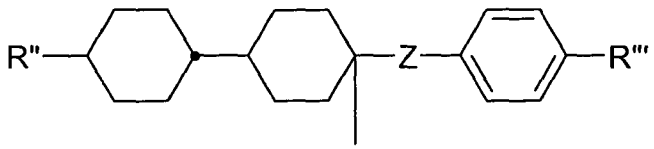
Ii



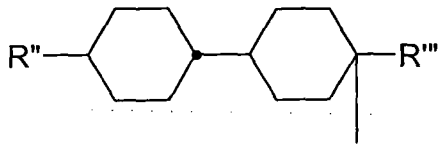
Ik

wherein M is as defined above and below, and the phenylene rings are optionally substituted by one or more groups L as defined above.

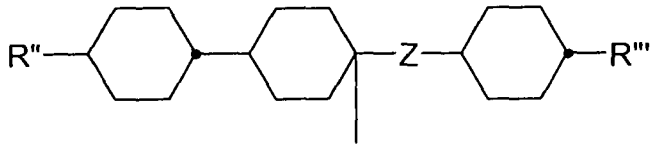
The groups M are preferably selected from the group consisting of the following subformulae:



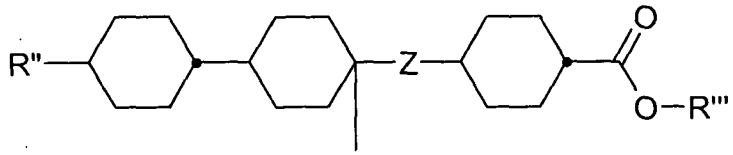
IIa



IIb



IIc



IId

wherein R" and R''' have independently of each other one of the meanings of R^1 given above, and Z has in each occurrence independently of one another one of the meanings of Z^1 given above. Preferably one or more of R" and R''', very preferably both groups R" and/or both groups R''', denote P- or P-Sp-. Z is preferably -COO-, -OCO- or a single bond. The phenyl

rings are optionally substituted by one or more, preferably one or two groups L as defined above.

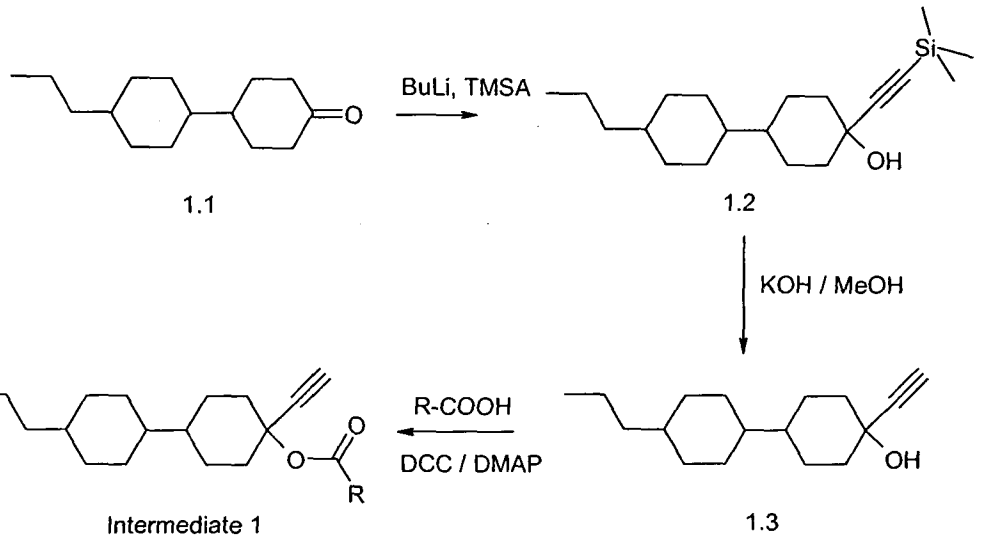
P-Sp- in these preferred compounds is preferably P-Sp'-X', with X' preferably being -O-, -COO- or -OCOO-. Z is preferably -COO-, -OCO- or a single bond.

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 the literature and in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart. Especially suitable methods are disclosed in US 6,203,724. Further suitable methods of synthesis are also described belwo and in the examples.

The compounds of formula I can be generally synthesized by initially reacting a suitably substituted acetylene, e.g. (trimethylsilyl)acetylene, with a suitable cyclohexanone in the presence of butyllithium, as described e.g. in ACS Symposium Series (2001), 798 (Anisotropic Organic Materials), 195-205. Esterification of the resulting tertiary alcohol with a suitable carboxylic acid yields an ester product. The axial acetylenic substituent is then coupled to a reactive discotic derivative of the formula $D(B\text{-}G)_z$, wherein D, B and Z have the meanings of formula I and G is a suitable reactive group or leaving group, e.g. bromine or iodine, via a palladium catalyzed coupling reaction in analogy to the method as described e.g. in either J Org. Chem. 1997, 62, 7471, or Tetrahedron Lett. 1993, 6403.

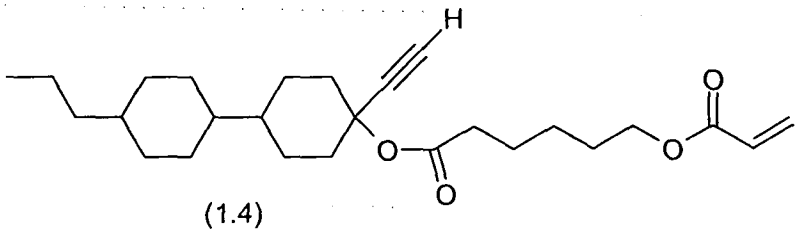
The method for making the key intermediates is exemplarily shown below in Scheme 1

Scheme 1

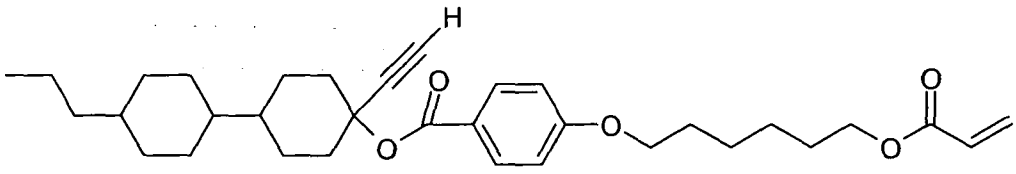


Intermediate 1 is prepared as shown in Scheme 1 above. Compound 1.3 is prepared in two steps by reacting the ketone 1.1 with trimethylacetylene in the presence of butyl lithium, and then removing the TMS group using potassium hydroxide. Compound 1.3 is then reacted with a suitable carboxylic acid in the presence of DCC and catalytic amount of DMAP.

Typical examples of Intermediate 1 are shown below:



(1.4)



(1.5)

Intermediate 1 (for example compound 1.4 or 1.5) is then coupled with a halogenated discotic group preferably in a Sonogashira reaction. For example, intermediate 1 can be coupled with 1,3,5-triiodo- or 1,3,5-tribromobenzene or other discotic groups as mentioned below, in the presence of a suitable catalyst, for example a Pd(II) catalyst like

$Pd(PPh3)_2Cl_2$ and in the presence of a base, like for example triethylamine.

The methods of preparing a compound of formula I as described above and below are another aspect of the invention. Especially preferred is a method comprising the following steps:

a) reacting a suitably substituted acetylene with an optionally substituted cyclohexanone in the presence of butyllithium,

b) separating the isomers thereby formed,

c) esterification the tertiary alcohol of the isolated isomer of step b) with a suitable aromatic or aliphatic carboxylic acid,

d) coupling the resulting compound via its axial acetylenic substituent to an aromatic ring.

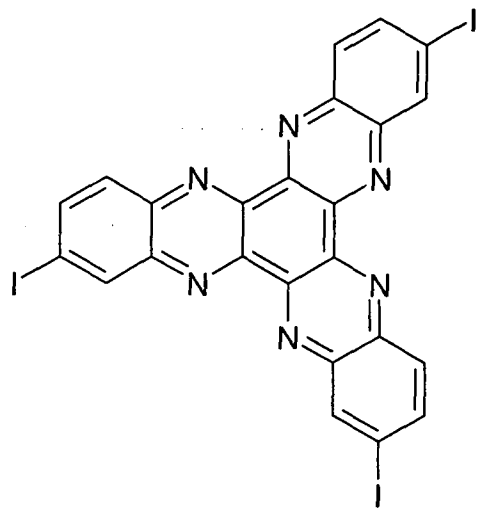
The discotic groups D1-D6 are well-known in prior art. The discotic groups D7-D11 can be prepared according to or in analogy to the methods described in the references cited below:

D7: See US 2008/087879A1, which describes the synthesis of tetrabromocoronenes like 1,4,7,10- tetrabromocoronene.

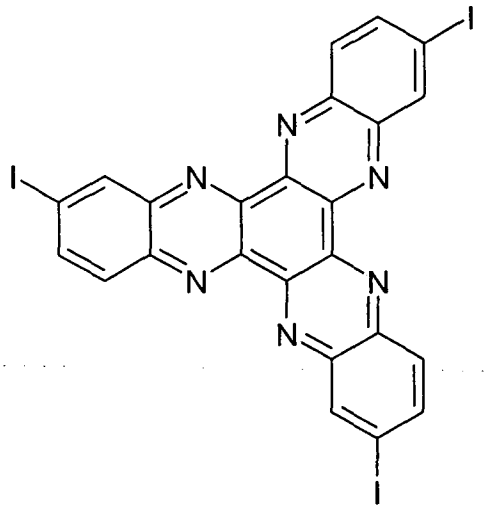
D8: The synthesis of the isomers 2,8,15-Triiodo-5,6,1 1,12,17,1 8-hexaaza-trinaphthylene and 2,8,14-Triiodo-5,6,11,12,17,18-hexaazatrinaphthylene as shown below is described in WO 2005/123737 A2.

D9: The synthesis of 2,7,12-Tribromotruxene is described in A. W. Amick et al., J. Org. Chem. 2007, 72(9), 3412-3418, and B. Gomez-Lor et al., Eur. J. Org. Chem. 2001, 11, 2107-2114.

2,8,14-Triiodo-5,6,11,12,17,18-hexaazatrinaphthylene:



2,8,15-Triiodo-5,6,1 1,12,17,1 8-hexaaza-trinaphthylene:



D10: See US 2005/048313 A1, which describes the synthesis of 3,6,9,12-tetrahalogenatedanthanthrene.

D11: See "Columnar mesophase formation of cyclohexa-m-phenylene-based macrocycles", W. Pisula et al. "Chemistry-An Asian Journal" (2007), 2(1), 51-56. Publisher: Wiley-VCH Verlag GmbH & Co. KGaA, CODEN: CAAJBI, ISSN: 1861-4728; CAN 147:395541, AN 2007:94977, which describes the synthesis of 5,5',5'',5''',5'''',5'''''-Hexaiodohexa-m-phenylene.

The methods of preparing a compound of formula I as described above and below, the novel intermediates used therein and obtained thereby,

and their use for preparing compounds of formula I, are further aspects of the invention.

Preferably the birefringent polymer film according to the present invention is prepared by polymerizing an LC formulation comprising one or more compounds of formula I, hereinafter referred to as "guest component" or "guest compound", and further comprising an LC material, which may be a single compound or a mixture of compounds, hereinafter referred to as "host component" or "host mixture", preferably a polymerizable LC host mixture having a nematic phase. The terms "guest" and "host" do not exclude the possibility that the amount of the guest component in the final LC mixture is > 50 % by weight, and the amount of the host component in the final LC mixture is < 50 % by weight.

The birefringent polymer film according to the present invention preferably has positive birefringence and negative (or "reverse") dispersion.

The host component preferably has positive birefringence and positive (or "normal") dispersion.

The guest component preferably has:

(1) Negative birefringence at 550nm and normal (positive) birefringence dispersion or

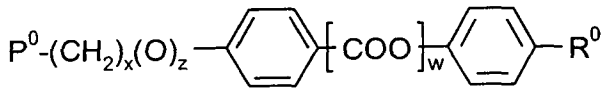
(2) Positive birefringence at 550nm and reverse (negative) birefringence dispersion. In this case $\Delta n(450)/\Delta n(550)$ can be negative if the guest component has a negative birefringence at 450nm.

Another aspect of the invention is a polymerizable formulation, preferably a polymerizable LC formulation, comprising one or more guest compounds as described above and below, and one or more additional compounds, which are preferably mesogenic or liquid crystalline and/or polymerizable. Very preferably the LC formulation comprises one or more additional compounds selected from reactive mesogens (RMs), most preferably selected from mono- and direactive RMs. These additional compounds constitute the polymerizable LC host component.

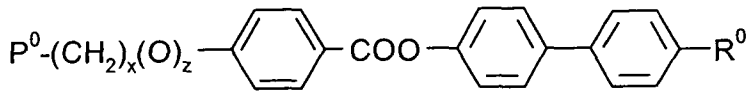
Preferably the polymer films according to the present invention are crosslinked, and the polymerizable guest compounds and/or the polymerizable host components comprise at least one compound with two or more polymerizable groups (di- or multireactive).

The concentration of the guest compound(s) of the present invention in the polymerizable LC formulation (including both the guest and host component) is preferably from 5 to 90 wt. %, very preferably from 30 to 70 wt. %.

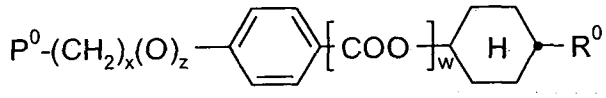
The additional RMs of the polymerizable LC host formulation can be prepared by methods which are known per se and which are described in standard works of organic chemistry like for example Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart. Suitable RMs are disclosed for example in WO 93/22397, EP 0 261 712, DE 195 04 224, WO 95/22586, WO 97/00600, US 5,518,652, US 5,750,051, US 5,770,107 and US 6,514,578. Examples of particularly suitable and preferred RMs are shown in the following list.



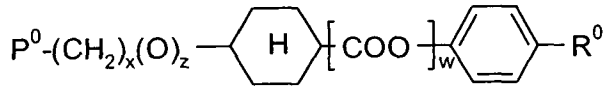
(MR1)



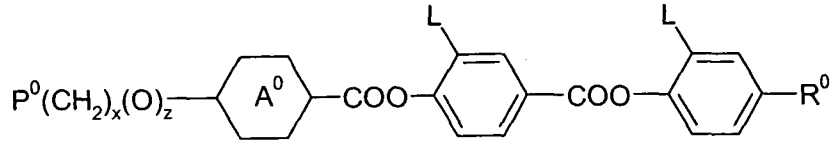
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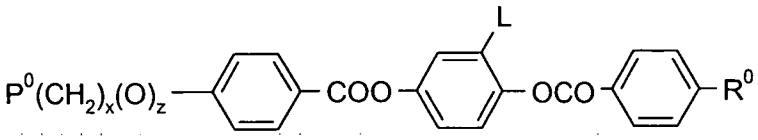
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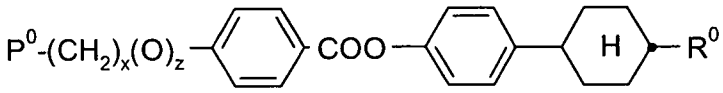
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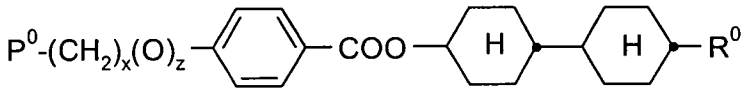
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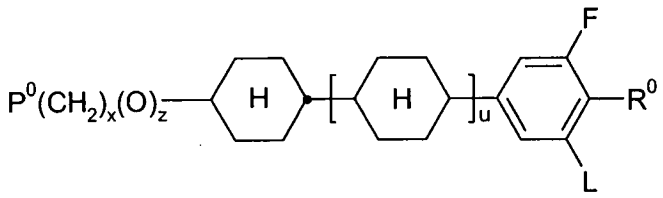
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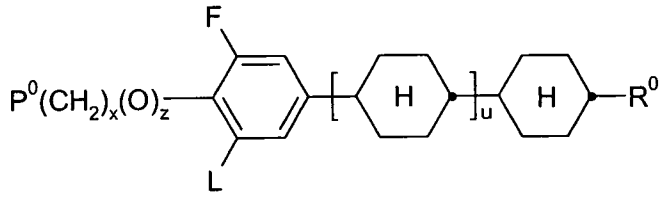
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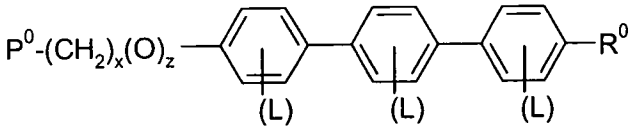
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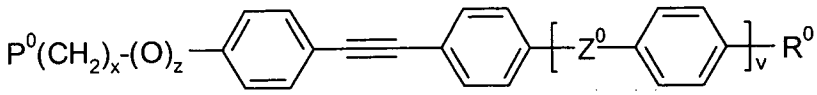
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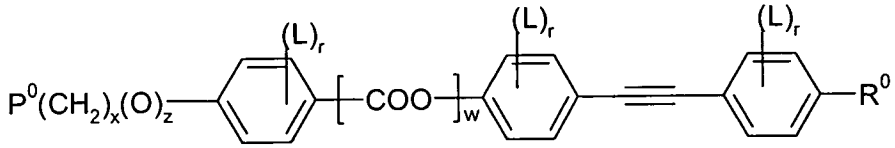
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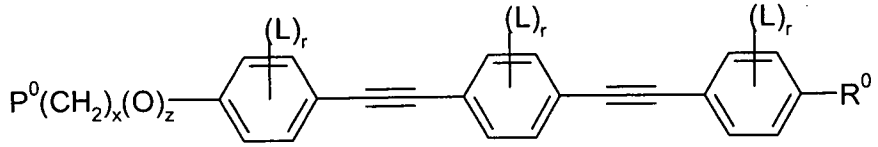
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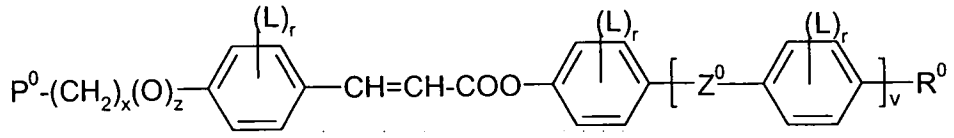
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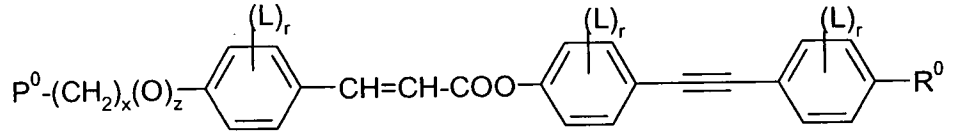
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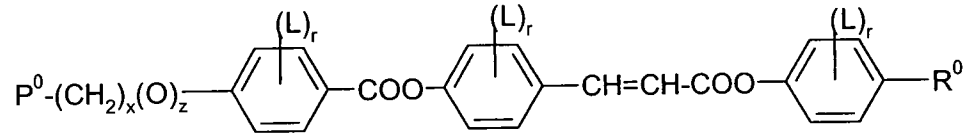
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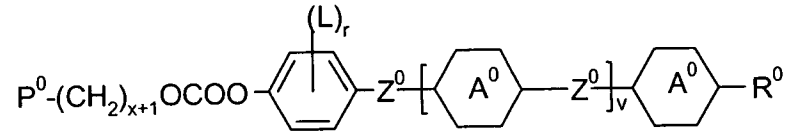
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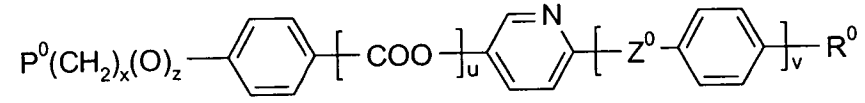
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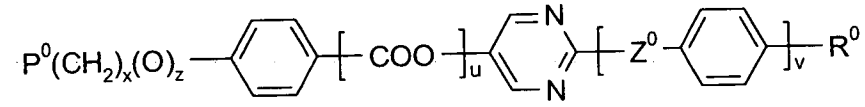
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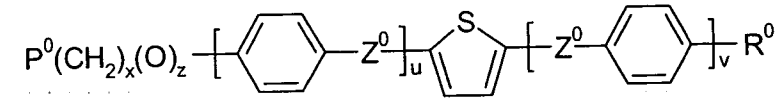
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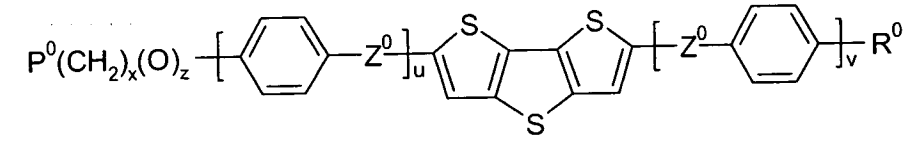
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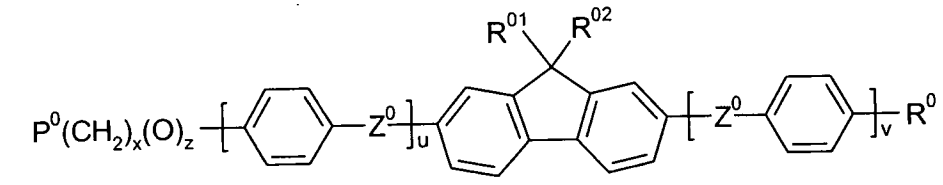
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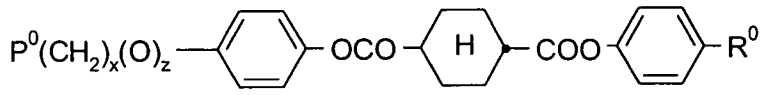
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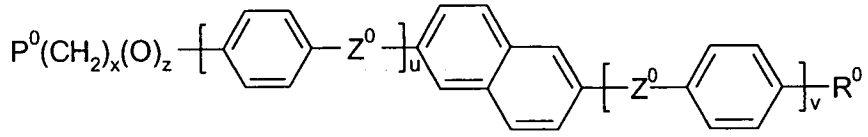
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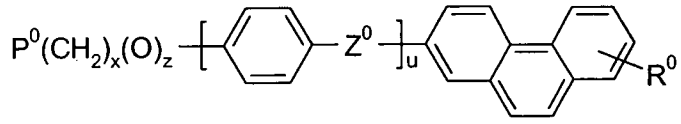
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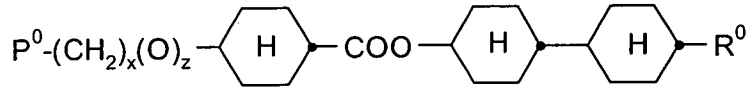
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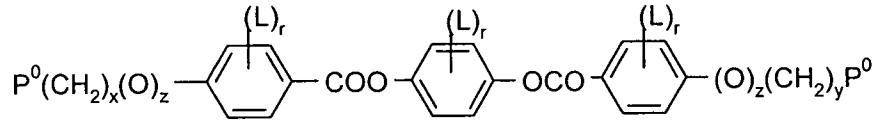
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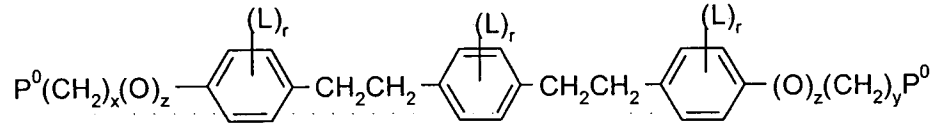
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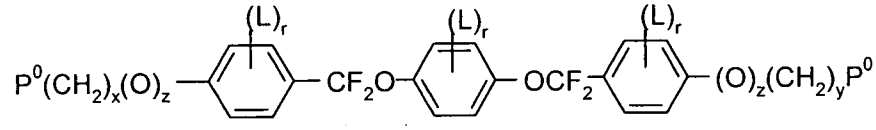
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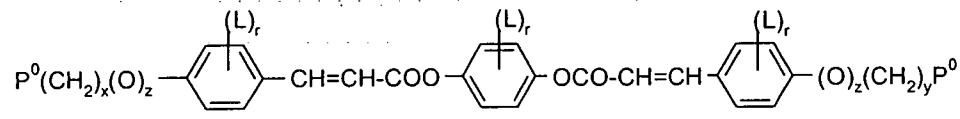
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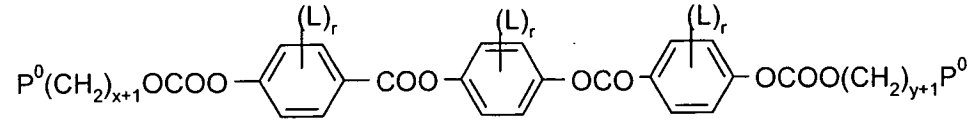
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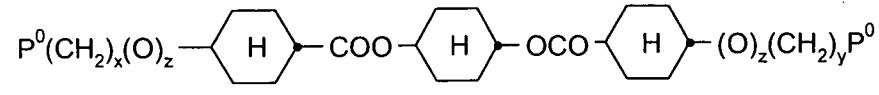
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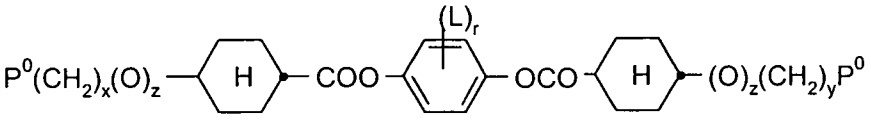
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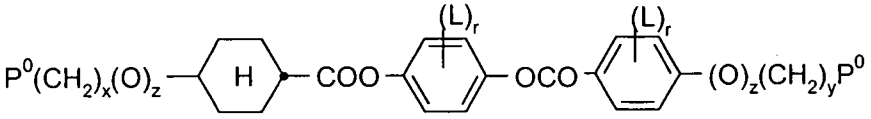
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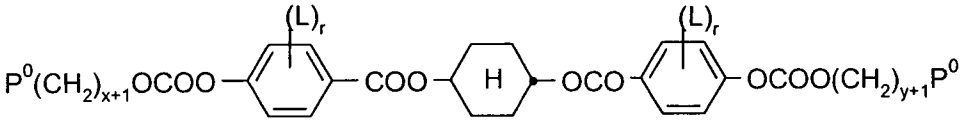
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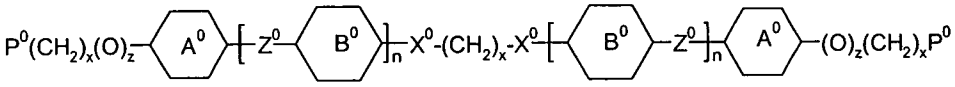
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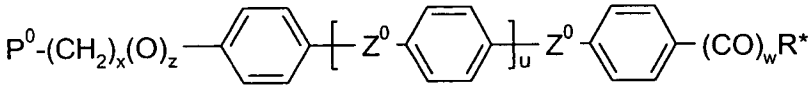
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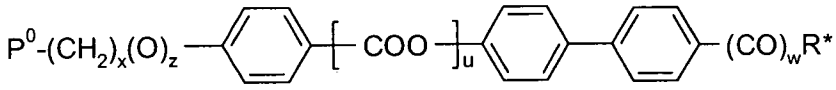
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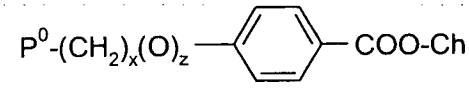
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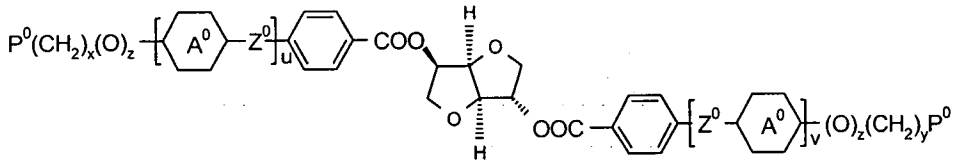
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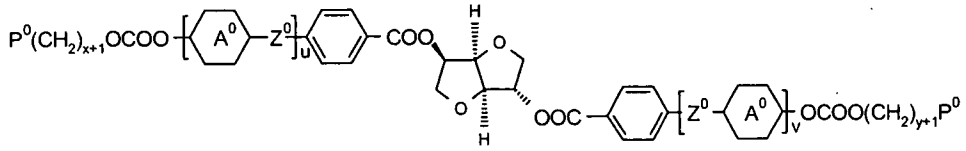
(CR2



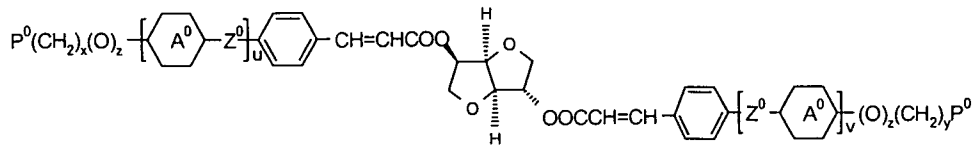
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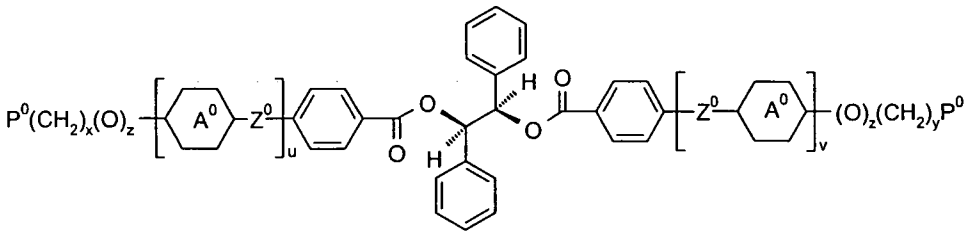
(CR4)



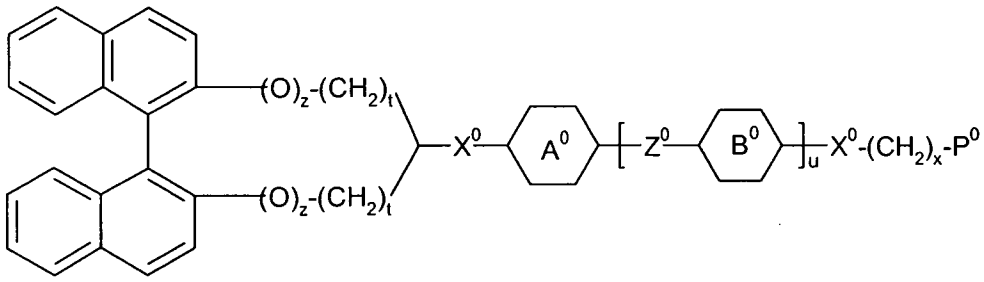
(CR5)



(CR6)



(CR7)



(CR8)

wherein

P^0 is, in case of multiple occurrence independently of one another, a polymerizable group, preferably an acryl, methacryl, oxetane, epoxy, vinyl, vinyloxy, propenyl ether or styrene group,

A^0 and B^0 are, in case of multiple occurrence independently of one another, 1,4-phenylene that is optionally substituted with 1, 2, 3 or 4 groups L, or trans-1,4-cyclohexylene,

Z^0 is, in case of multiple occurrence independently of one another, -COO-, -OCO-, $-CH_2CH_2-$, -C≡C-, -CH=CH-, -CH=CH-COO-, -OCO-CH=CH- or a single bond,

R^0 is alkyl, alkoxy, thioalkyl, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy with 1 or more, preferably 1 to 15 C atoms which is optionally fluorinated, or is Y^0 or $P-(CH_2)_y-(O)_z-$,

X^0 is -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, $-CO-NR^{01}-$, $-NR^{01}-CO-$, $-NR^{01}-CO-NR^{01}-$, $-OCH_2-$, $-CH_2O-$, $-SCH_2-$, $-CH_2S-$, $-CF_2O-$, $-OCF_2-$, $-CF_2S-$, $-SCF_2-$, $-CF_2CH_2-$, $-CH_2CF_2-$, $-CF_2CF_2-$, -CH=N-, -N=CH-, -N=N-, $-CH=CR^{01}-$, -CF=CF-, -C≡C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond

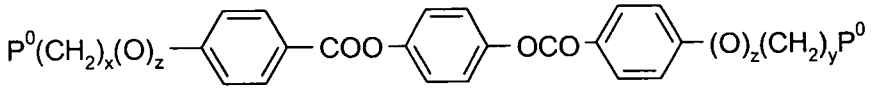
	Y^0	is F, Cl, CN, NO_2, OCH_3, OCN, SCN, SF_5, optionally fluorinated alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy with 1 to 4 C atoms, or mono- oligo- or polyfluorinated alkyl or alkoxy with 1 to 4 C atoms,
	$R^{01,02}$	are independently of each other H, R^0 or Y^0,
	R*	is a chiral alkyl or alkoxy group with 4 or more, preferably 4 to 12 C atoms, like 2-methylbutyl, 2-methyloctyl, 2-methylbutoxy or 2-methyloctoxy,
	Ch	is a chiral group selected from cholesteryl, estradiol, or terpenoid radicals like menthyl or citronellyl,
	L	is, in case of multiple occurrence independently of one another, H, F, Cl, CN or optionally halogenated alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy with 1 to 5 C atoms,
	r	is 0, 1, 2, 3 or 4,
	t	is, in case of multiple occurrence independently of one another, 0, 1, 2 or 3,
	u and v	are independently of each other 0, 1 or 2,
	w	is 0 or 1,
	x and y	are independently of each other 0 or identical or different integers from 1 to 12,
	z	is 0 or 1, with z being 0 if the adjacent x or y is 0,

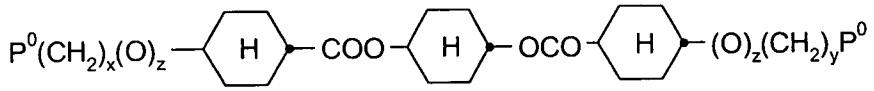
and wherein the benzene and napthalene rings can additionally be substituted with one or more identical or different groups L.

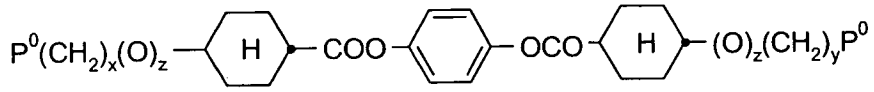
Especially preferably the polymerizable LC host component contains only achiral compounds and no chiral compounds.

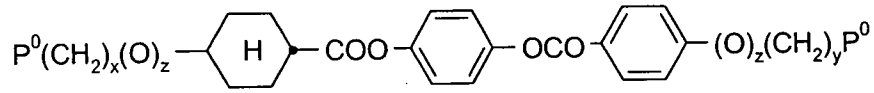
Further preferably the polymerizable LC host component comprises one or more componds selectred from formual MR3, MR4, MR7, MR8, MR9, MR10, MR18, MR27, DR6, DR7, DR8, DR9 and DR10, furthermore DR1 and DR5.

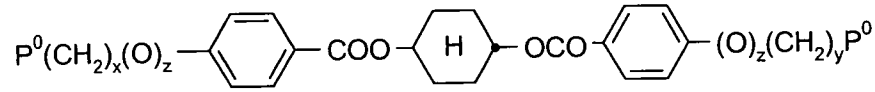
Further preferably the polymerizable LC host component comprises one or more compounds selected from the following formulae:

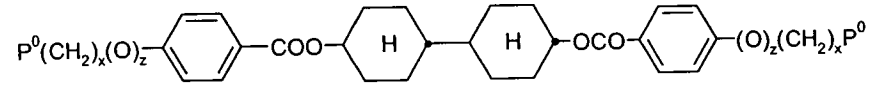

(DR1a)

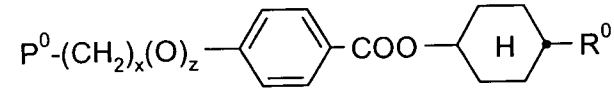

(DR6)

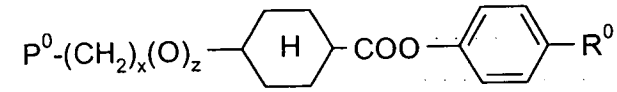

(DR7a)

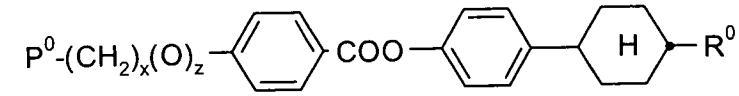

(DR8a)

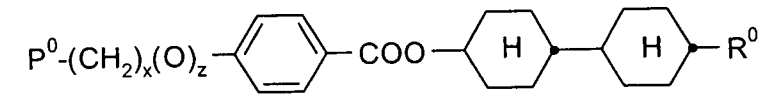

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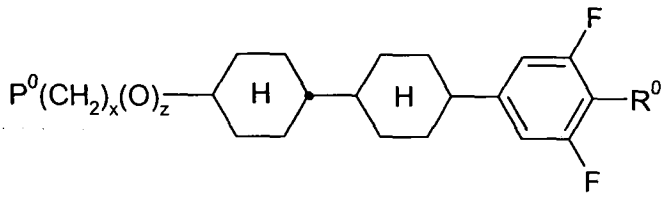

(DR10a)


(MR3a)

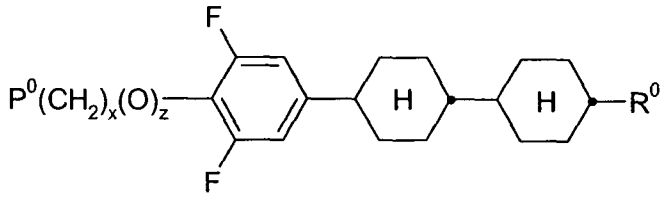

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(MR7a)

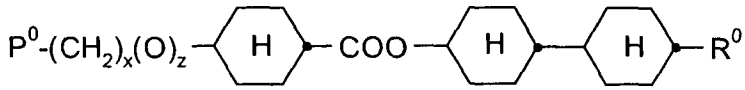

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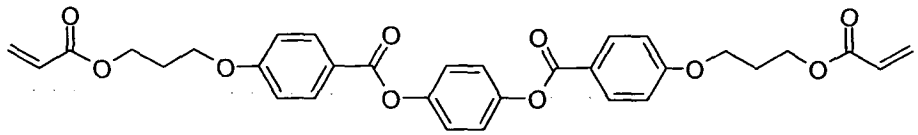
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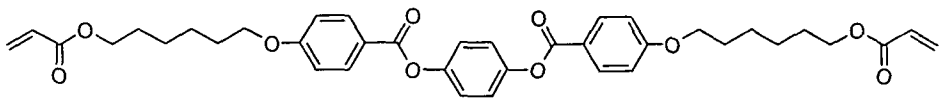
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wherein P^0, R^0, x, y, and z are as defined above.

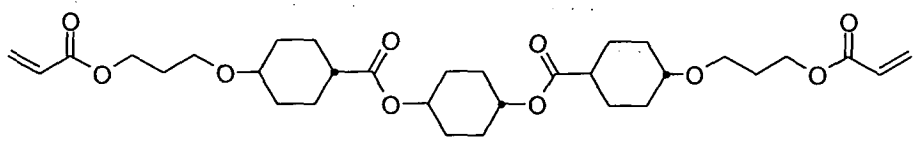
Further preferably the polymerizable LC host component comprises one or more compounds selected from the following formulae:



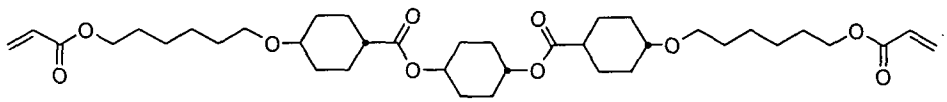
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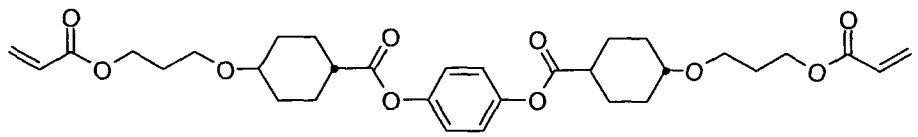
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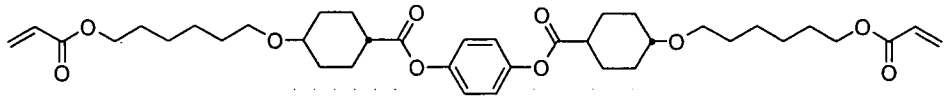
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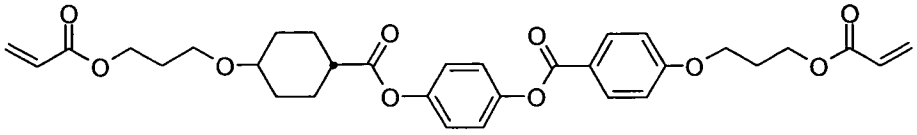
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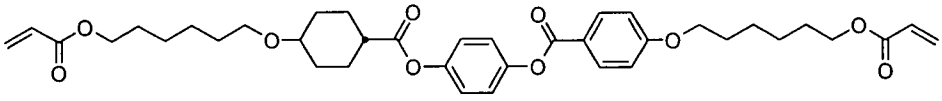
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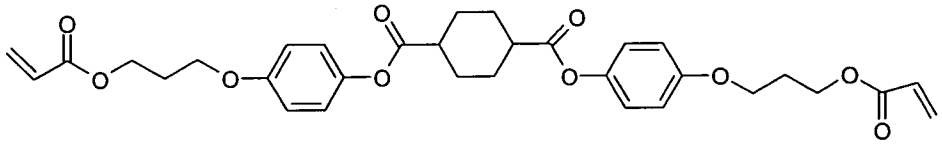
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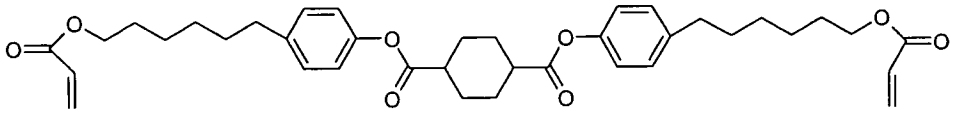
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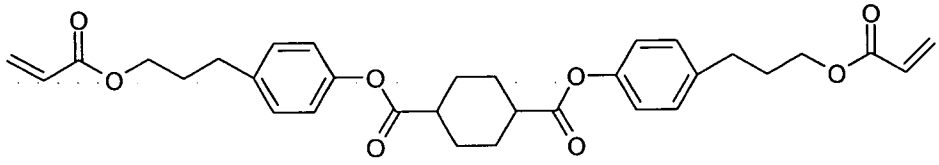
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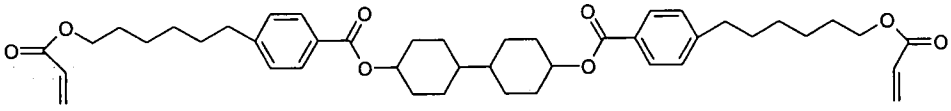
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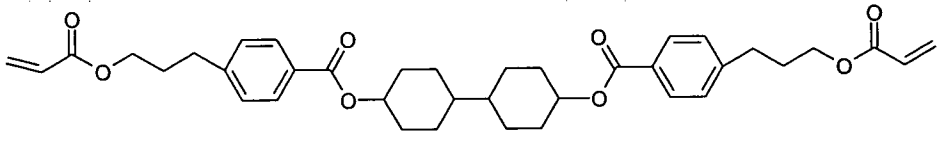
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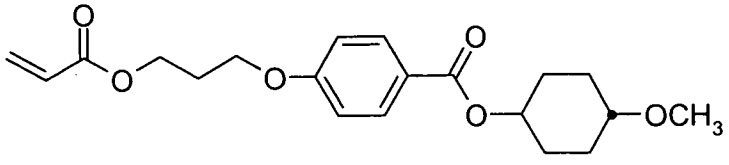
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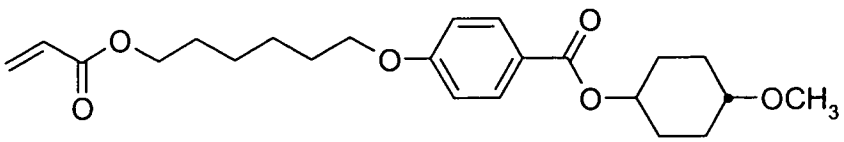
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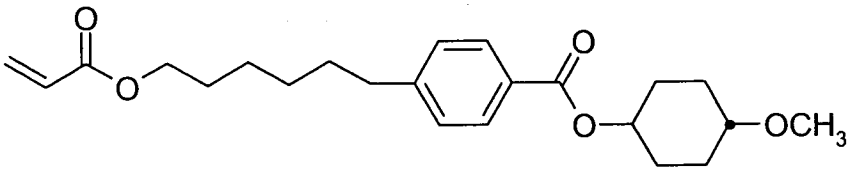
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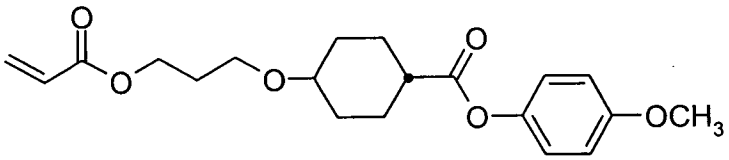
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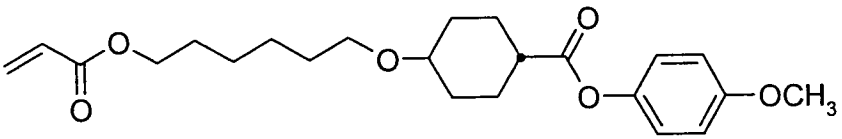
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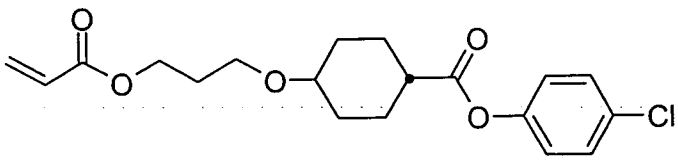
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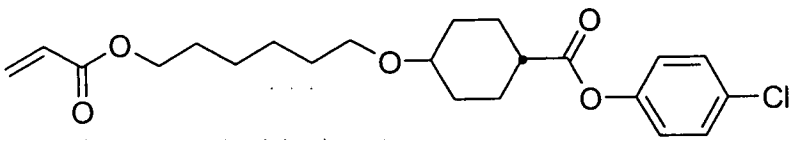
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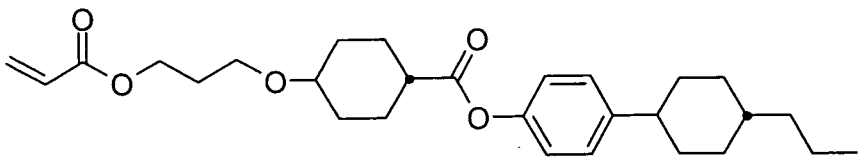
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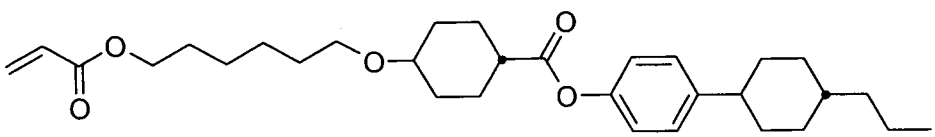
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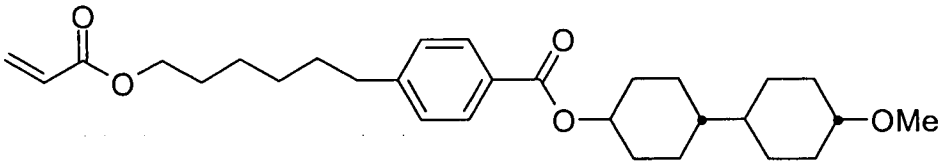
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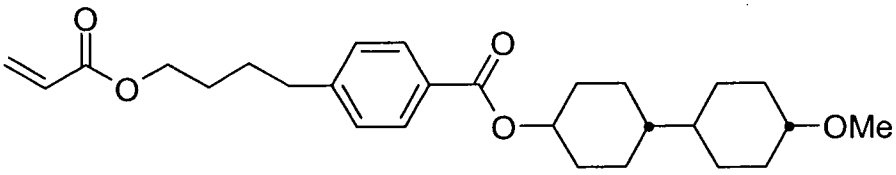
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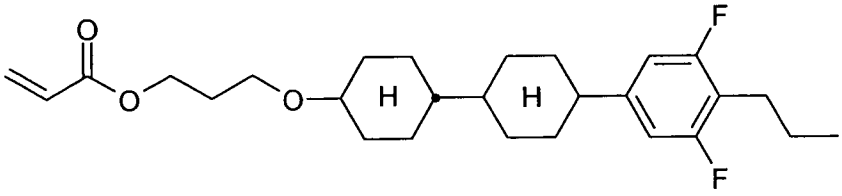
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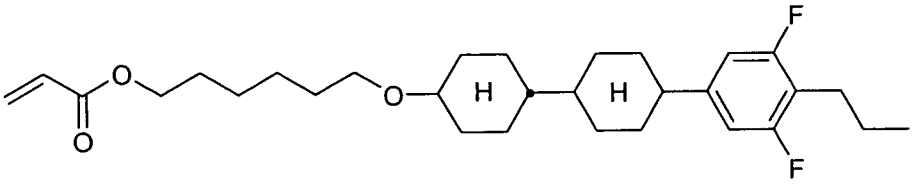
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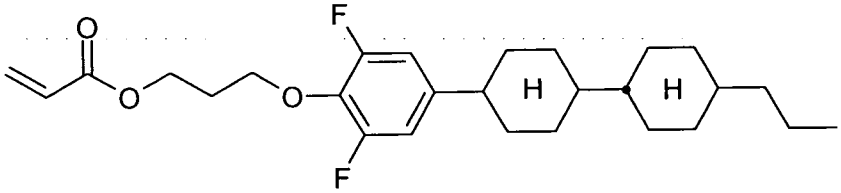
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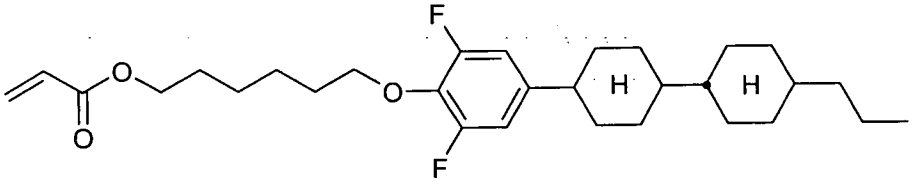
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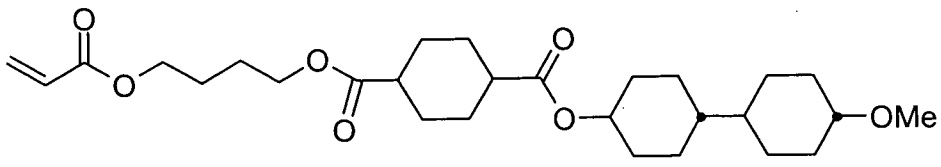
(MR9a2)



(MR10a1)



(MR10a2)



(MR27a1)

Preferably the polymerizable compounds of the polymerizable LC host component are selected from compounds, very preferably mono- or direactive RMs, having low birefringence.

Especially preferred is a polymerizable host component having an absolute value of the birefringence from 0.01 to 0.2, very preferably from 0.04 to 0.16.

The general preparation of polymer LC films according to this invention is known to the ordinary expert and described in the literature, for example in D. J. Broer; G. Challa; G. N. Mol, *Macromol. Chem*, 1991, **192**, 59. Typically a polymerizable LC material (i.e. a compound or a mixture or formulation) is coated or otherwise applied onto a substrate where it aligns into uniform orientation, and polymerized in situ in its LC phase at a selected temperature for example by exposure to heat or actinic radiation, preferably by photo-polymerization, very preferably by UV-photopolymerization, to fix the alignment of the LC molecules. If necessary, uniform alignment can promoted by additional means like shearing or annealing the LC material, surface treatment of the substrate, or adding surfactants to the LC material.

As substrate for example glass or quartz sheets or plastic films can be used. It is also possible to put a second substrate on top of the coated material prior to and/or during and/or after polymerization. The substrates can be removed after polymerization or not. When using two substrates in case of curing by actinic radiation, at least one substrate has to be transmissive for the actinic radiation used for the polymerization. Isotropic or birefringent substrates can be used. In case the substrate is not removed from the polymerized film after polymerization, preferably isotropic substrates are used.

Suitable and preferred plastic substrates are for example films of polyester such as polyethyleneterephthalate (PET) or polyethylene-naphthalate (PEN), polyvinylalcohol (PVA), polycarbonate (PC) or triacetylcellulose (TAC), very preferably PET or TAC films. As birefringent substrates for example uniaxially stretched plastics film can be used. PET films are commercially available for example from DuPont Teijin Films under the trade name Melinex ®.

The polymerizable material can be applied onto the substrate by conventional coating techniques like spin-coating or blade coating. It can also be applied to the substrate by conventional printing techniques which are known to the expert, like for example screen printing, offset printing, reel-to-reel printing, letter press printing, gravure printing, rotogravure printing, flexographic printing, intaglio printing, pad printing, heat-seal printing, ink-jet printing or printing by means of a stamp or printing plate.

It is also possible to dissolve the polymerizable material in a suitable solvent. This solution is then coated or printed onto the substrate, for example by spin-coating or printing or other known techniques, and the solvent is evaporated off before polymerization. In many cases it is suitable to heat the mixture in order to facilitate the evaporation of the solvent. As solvents for example standard organic solvents can be used. The solvents can be selected for example from ketones such as acetone, methyl ethyl ketone, methyl propyl ketone or cyclohexanone; acetates such as methyl, ethyl or butyl acetate or methyl acetoacetate; alcohols such as methanol, ethanol or isopropyl alcohol; aromatic solvents such as toluene or xylene; halogenated hydrocarbons such as di- or trichloromethane; glycols or their esters such as PGMEA (propyl glycol monomethyl ether acetate), γ-butyrolactone, and the like. It is also possible to use binary, ternary or higher mixtures of the above solvents.

Initial alignment (e.g. planar alignment) of the polymerizable LC material can be achieved for example by rubbing treatment of the substrate, by shearing the material during or after coating, by annealing the material before polymerization, by application of an alignment layer, by applying a magnetic or electric field to the coated material, or by the addition of surface-active compounds to the material. Reviews of alignment techniques are given for example by I. Sage in "Thermotropic Liquid Crystals", edited by G. W. Gray, John Wiley & Sons, 1987, pages 75-77; and by T. Uchida and H. Seki in "Liquid Crystals - Applications and Uses Vol. 3", edited by B. Bahadur, World Scientific Publishing, Singapore 1992, pages 1-63. A review of alignment materials and techniques is given by J. Cognard, Mol. Cryst. Liq. Cryst. 78, Supplement 1 (1981), pages 1-77.

Especially preferred is a polymerizable material comprising one or more surfactants that promote a specific surface alignment of the LC molecules. Suitable surfactants are described for example in J. Cognard, Mol.Cryst.Liq.Cryst. **78**, Supplement 1, 1-77 (1981). Preferred aligning agents for planar alignment are for example non-ionic surfactants, preferably fluorocarbon surfactants such as the commercially available Fluorad FC-171® (from 3M Co.) or Zonyl FSN ® (from DuPont), multiblock surfactants as described in GB 2 383 040 or polymerizable surfactants as described in EP 1 256 617.

It is also possible to apply an alignment layer onto the substrate and provide the polymerizable material onto this alignment layer. Suitable alignment layers are known in the art, like for example rubbed polyimide or alignment layers prepared by photoalignment as described in US 5,602,661, US 5,389,698 or US 6,717,644.

It is also possible to induce or improve alignment by annealing the polymerizable LC material at elevated temperature, preferably at its polymerization temperature, prior to polymerization.

Polymerization is achieved for example by exposing the polymerizable material to heat or actinic radiation. Actinic radiation means irradiation with light, like UV light, IR light or visible light, irradiation with X-rays or gamma rays or irradiation with high energy particles, such as ions or electrons. Preferably polymerization is carried out by UV irradiation. As a source for actinic radiation for example a single UV lamp or a set of UV lamps can be used. When using a high lamp power the curing time can be reduced. Another possible source for actinic radiation is a laser, like for example a UV, IR or visible laser.

Polymerization is preferably carried out in the presence of an initiator absorbing at the wavelength of the actinic radiation. For this purpose the polymerizable LC material preferably comprises one or more initiators, preferably in a concentration from 0.01 to 10 %, very preferably from 0.05 to 5 %. For example, when polymerizing by means of UV light, a

photoinitiator can be used that decomposes under UV irradiation to produce free radicals or ions that start the polymerization reaction. For polymerizing acrylate or methacrylate groups preferably a radical photoinitiator is used. For polymerizing vinyl, epoxide or oxetane groups preferably a cationic photoinitiator is used. It is also possible to use a thermal polymerization initiator that decomposes when heated to produce free radicals or ions that start the polymerization. Typical radical photoinitiators are for example the commercially available Irgacure® or Darocure® (Ciba Geigy AG, Basel, Switzerland). A typical cationic photoinitiator is for example UVI 6974 (Union Carbide).

The polymerizable material may also comprise one or more stabilizers or inhibitors to prevent undesired spontaneous polymerization, like for example the commercially available Irganox® (Ciba Geigy AG, Basel, Switzerland).

The curing time depends, inter alia, on the reactivity of the polymerizable material, the thickness of the coated layer, the type of polymerization initiator and the power of the UV lamp. The curing time is preferably ≤ 5 minutes, very preferably ≤ 3 minutes, most preferably ≤ 1 minute. For mass production short curing times of ≤ 30 seconds are preferred.

Preferably polymerization is carried out in an inert gas atmosphere like nitrogen or argon.

The polymerizable material may also comprise one or more dyes having an absorption maximum adjusted to the wavelength of the radiation used for polymerization, in particular UV dyes like e.g. 4,4"-azoxy anisole or Tinuvin® dyes (from Ciba AG, Basel, Switzerland).

In another preferred embodiment the polymerizable material comprises one or more monoreactive polymerizable non-mesogenic compounds, preferably in an amount of 0 to 50 %, very preferably 0 to 20 %. Typical examples are alkylacrylates or alkylmethacrylates.

In another preferred embodiment the polymerizable material comprises one or more di- or multireactive polymerizable non-mesogenic compounds, preferably in an amount of 0 to 50 %, very preferably 0 to 20 %, alternatively or in addition to the di- or multireactive polymerizable mesogenic compounds. Typical examples of direactive non-mesogenic compounds are alkyldiacrylates or alkyldimethacrylates with alkyl groups of 1 to 20 C atoms. Typical examples of multireactive non-mesogenic compounds are trimethylpropanetrimethacrylate or pentaerythritoltetraacrylate.

It is also possible to add one or more chain transfer agents to the polymerizable material in order to modify the physical properties of the polymer film. Especially preferred are thiol compounds, for example monofunctional thiols like dodecane thiol or multifunctional thiols like trimethylpropane tri(3-mercaptopropionate). Very preferred are mesogenic or LC thiols as disclosed for example in WO 96/12209, WO 96/25470 or US 6,420,001. By using chain transfer agents the length of the free polymer chains and/or the length of the polymer chains between two crosslinks in the polymer film can be controlled. When the amount of the chain transfer agent is increased, the polymer chain length in the polymer film decreases.

The polymerizable material may also comprise a polymeric binder or one or more monomers capable of forming a polymeric binder, and/or one or more dispersion auxiliaries. Suitable binders and dispersion auxiliaries are disclosed for example in WO 96/02597. Preferably, however, the polymerizable material does not contain a binder or dispersion auxiliary.

The polymerizable material can additionally comprise one or more additives like for example catalysts, sensitizers, stabilizers, inhibitors, chain-transfer agents, co-reacting monomers, surface-active compounds, lubricating agents, wetting agents, dispersing agents, hydrophobing agents, adhesive agents, flow improvers, defoaming agents, deaerators, diluents, reactive diluents, auxiliaries, colourants, dyes, pigments or nanoparticles.

The thickness of a polymer film according to the present invention is preferably from 0.3 to 5 microns, very preferably from 0.5 to 3 microns, most preferably from 0.7 to 1.5 microns. For use as alignment layer, thin films with a thickness of 0.05 to 1, preferably 0.1 to 0.4 microns are preferred.

The polymer films and materials of the present invention can be used as retardation or compensation film for example in LCDs to improve the contrast and brightness at large viewing angles and reduce the chromaticity. It can be used outside the switchable LC cell of the LCD or between the substrates, usually glass substrates, forming the switchable LC cell and containing the switchable LC medium (incell application).

The polymer film and materials of the present invention can be used in conventional LC displays, for example displays with vertical alignment like the DAP (deformation of aligned phases), ECB (electrically controlled birefringence), CSH (colour super homeotropic), VA (vertically aligned), VAN or VAC (vertically aligned nematic or cholesteric), MVA (multi-domain vertically aligned), PVA (patterned vertically aligned) or PSVA (polymer stabilised vertically aligned) mode; displays with bend or hybrid alignment like the OCB (optically compensated bend cell or optically compensated birefringence), R-OCB (reflective OCB), HAN (hybrid aligned nematic) or pi-cell (π-cell) mode; displays with twisted alignment like the TN (twisted nematic), HTN (highly twisted nematic), STN (super twisted nematic), AMD-TN (active matrix driven TN) mode; displays of the IPS (in plane switching) mode, or displays with switching in an optically isotropic phase.

The layers, films and materials of the present invention can be used for various types of optical films, preferably selected from optically uniaxial films (A-plate, C-plate, negative C-plate, O-plate), twisted optical retarders, like for example twisted quarter wave foils (QWF), achromatic retarders, achromatic QWFs or half wave foils (HWF), and optically biaxial films. The LC phase structure in the layers and materials can be selected from cholesteric, smectic, nematic and blue phases. The alignment of the LC material in the layer can be selected from homeotropic, splayed, tilted,

planar and blue-phase alignment. The layers can be uniformly oriented or exhibit a pattern of different orientations.

The films can be used as optical compensation film for viewing angle enhancement of LCD's or as a component in a brightness enhancement films, furthermore as an achromatic element in reflective or transflective LCD's. Further preferred applications and devices include

- retarding components in optoelectronic devices requiring similar phase shift at multiple wavelengths, such as combined CD/DVD/HD-DVD/Blu-Ray, including reading, writing re-writing data storage systems
- achromatic retarders for optical devices such as cameras
- achromatic retarders for displays including OLED and LCD's.

The following examples are intended to explain the invention without restricting it. The methods, structures and properties described hereinafter can also be applied or transferred to materials that are claimed in this invention but not explicitly described in the foregoing specification or in the examples.

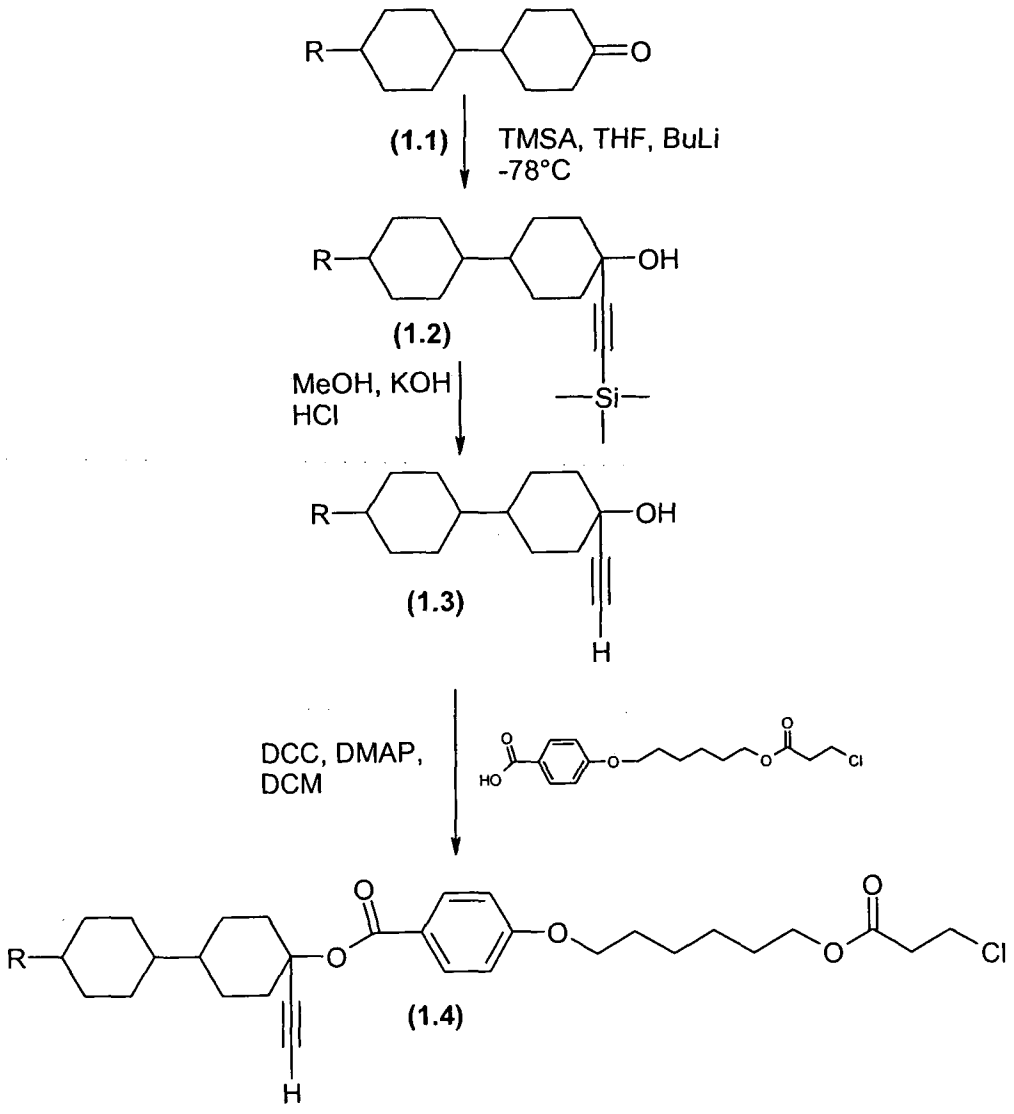
Above and below, percentages are per cent by weight. All temperatures are given in degrees Celsius. m.p. denotes melting point, cl.p. denotes clearing point, T_g denotes glass transition temperature. Furthermore, C = crystalline state, N = nematic phase, S = smectic phase and I = isotropic phase. The data between these symbols represent the transition temperatures. Δn denotes the optical anisotropy ($\Delta n = n_e - n_o$, where n_o denotes the refractive index parallel to the longitudinal molecular axes and n_e denotes the refractive index perpendicluar thereto), measured at 589 nm and 20°C. The optical and electrooptical data are measured at 20°C, unless expressly stated otherwise.

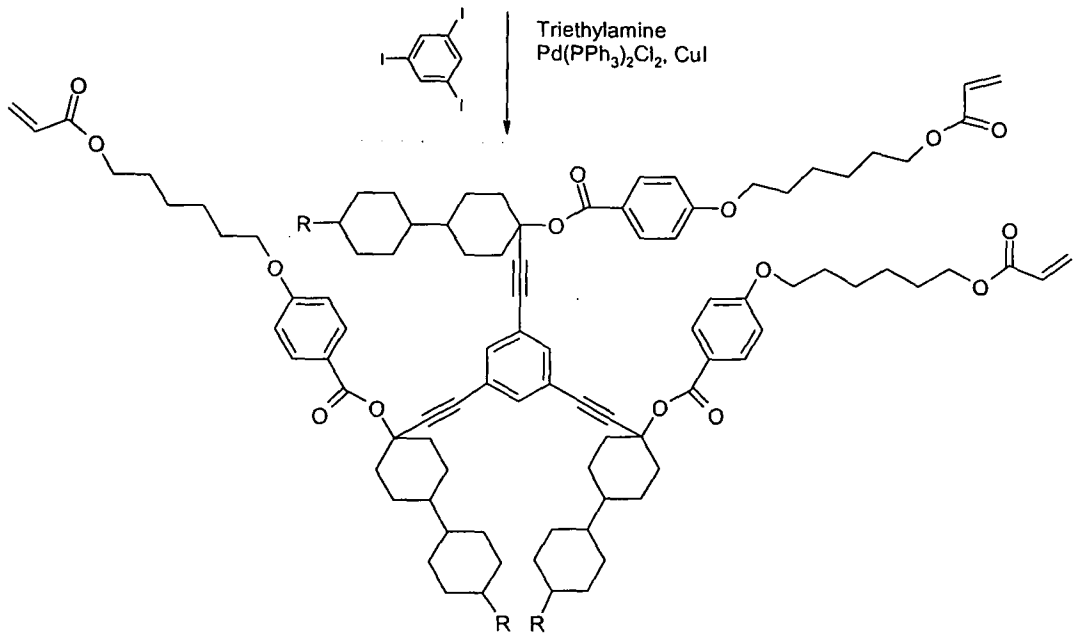
In the description and claims of this specification, unless stated otherwise the retardation and dispersion are determined by the methods as described above.

Unless stated otherwise, the precentages of components of a polymerizable mixture as given above and below refer to the total amount of solids in the mixture polymerizable mixture, i.e. not including solvents.

Example 1

Compound **1**, wherein R is n-propyl, is prepared as described below. Intermediate **1.4** is prepared by the method described in Scheme 1, and is then reacted with 1,3,5-triiodobenzene under Sonogashira conditions to give **1**.





(1)

(R = n-C_3H_7)

The synthesis of **1.3** has been described in the literature, see e.g. US 1999-0452166. Trans-4'-propyl- [1,1'-Bicyclohexyl]-4-one (**1.1**) is commercially available. Trans,trans)- 4'-propyl-4-[2-(trimethylsilyl)ethynyl]-[1,1'-Bicyclohexyl]-4-ol (**1.2**) was prepared by reacting **1.1** with trimethylsilylacetylene and butyl lithium. The reaction produces two isomers and the trans-trans isomer is isolated by column chromatography. (trans,trans)- 4-ethynyl-4'-propyl-[1,1'-Bicyclohexyl]-4-ol (**1.3**) is prepared by reacting **1.2** with potassium hydroxide in methanol.

Synthesis of **1.4**

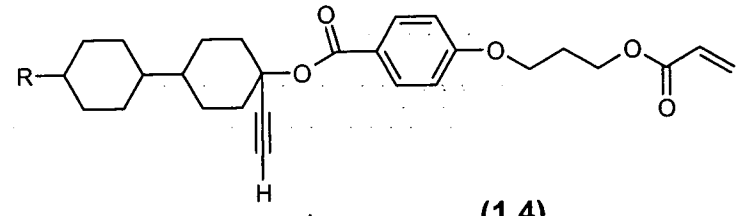
To a stirring dichloromethane solution of the tertiary alcohol – compound 3, was added a premixed solution of Trifluoroacetic anhydride and 4-[6-(3-chloropropionyloxy)hexyloxy]benzoic acid in dichloromethane. After stirring overnight at 25°C the reaction mixture was diluted with water and the organic layer separated. After extracting the aqueous layer with DCM, the combined organics were washed with sodium hydrogen carbonate solution and water until neutral pH. The material was purified using silica gel column chromatography, eluting with 20% DCM in petrol 40-60°C, affording an off-white solid (NMR shows expected signals, 98% yield).

Synthesis of **1**

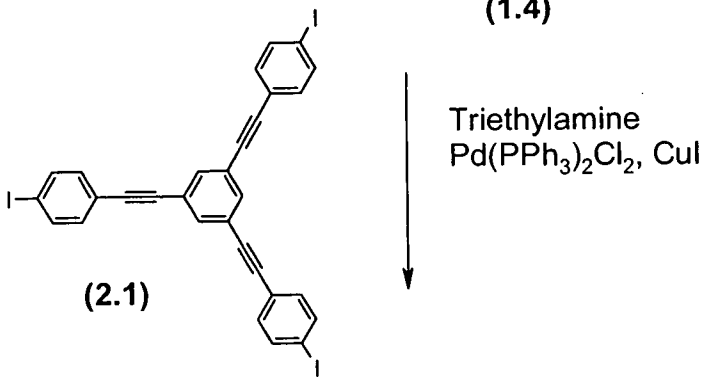
A round bottom flask was charged with the ester-compound **1.4**, 1,3,5-triiodobenzene, CuI, $Pd(PPh_4)_2Cl_2$ and triethylamine in tetrahydrofuran and treated with sonication before being heated with stirring at 50°C under nitrogen for 72hours. After cooling, the reaction mixture was acidified by adding dilute HCl, the organic layer was seperated and washed with water. The organic layer was dried using sodium sulphate, and concentrated to give a brown oil. The oil was purified using silica gel column chromatography eluting with ethyl acetate-petrol 40-60°C (1:10). The fractions containing the product were collected to give a dark brown solid which was redissolved in dichloromethane and added to stirring acetonitrile pre-cooled to -20°C. The dark brown precipitate was collected and recrystallised from ethyl acetate/denatured ethanol to give a yellow solid (96.1% by HPLC, 22% yield)

Example 2

1,3,5-tris[(4-iodophenyl)ethynyl]benzene is prepared via the method described in Nature (1999), 398, 796-799. Compound **1.4** of Example 1 is reacted with 1,3,5-tris[(4-iodophenyl)ethynyl]benzene under Sonogashira conditions to give compound **2** as shown below.

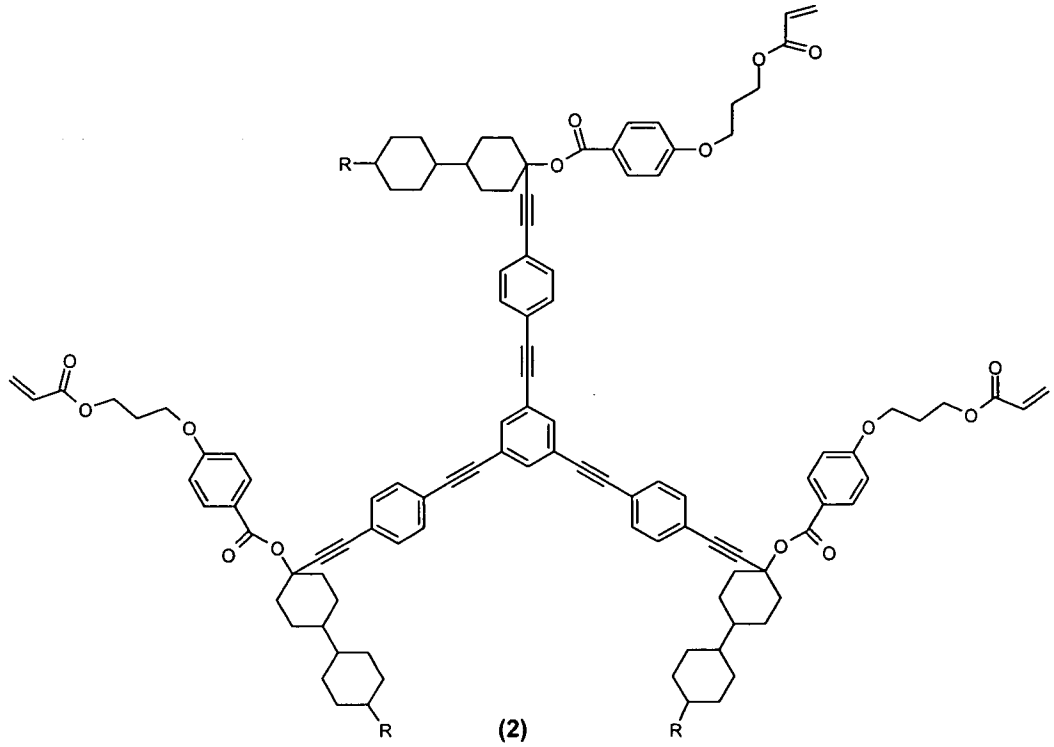


(1.4)



(2.1)

Triethylamine
$Pd(PPh_3)_2Cl_2$, CuI



(2)

(R = n-C_3H_7

Patent Claims

1. Compounds of formula I

$$D[-(B)_q-M]_z \qquad I$$

wherein

D is a discotic group, or forms a discotic group together with $(B)_q$,

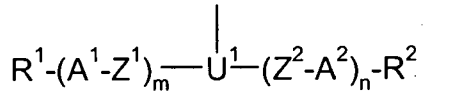
z is an integer from 3 to 10,

B is, in each occurrence independently of one another, a bivalent group having high polarizability, preferably selected from the group consisting of $-C\equiv C-$, $-CY^1=CY^2-$ and optionally substituted aromatic or heteroaromatic groups,

$Y^{1,2}$ are independently of each other H, F, Cl, CN or R^0,

q is, in each occurrence independently of one another, 0 or an integer from 1 to 10,

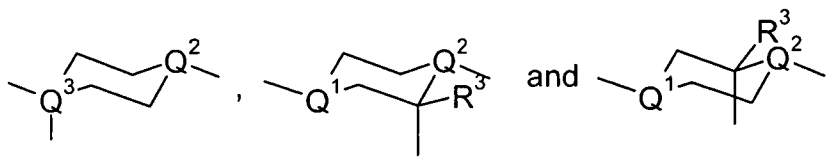
M is a group of formula II



$$R^1-(A^1-Z^1)_m-U^1-(Z^2-A^2)_n-R^2 \qquad II$$

wherein the individual radicals have, in case of multiple occurrence independently of one another, the following meanings

U^1 is selected from the group consisting of the following rings



including their mirror images, wherein the ring U^1 is bonded to the group $-(B)_q-$ via the axial bond, and one or two non-adjacent CH_2 groups in these rings are optionally replaced by O and/or S, and the ring U^1 is optionally substituted,

$Q^{1,2}$ are independently of each other CH or SiH,

Q^3 is C or Si,

$A^{1,2}$ are independently of each other selected from non-aromatic, aromatic or heteroaromatic carbocylic or heterocyclic groups, which are optionally substituted, and wherein $-(A^1-Z^1)_m-U^1-(Z^2-A^2)_n-$ does not contain more aromatic groups than non-aromatic groups and preferably does not contain more than one aromatic group,

$Z^{1,2}$ are independently of each other -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, $-CO-NR^0-$, $-NR^0-CO-$, $-NR^0-CO-NR^0-$, $-OCH_2-$, $-CH_2O-$, $-SCH_2-$, $-CH_2S-$, $-CF_2O-$, $-OCF_2-$, $-CF_2S-$, $-SCF_2-$, $-CH_2CH_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-CF_2CH_2-$, $-CH_2CF_2-$, $-CF_2CF_2-$, -CH=CH-, $-CY^1=CY^2-$, -CH=N-, -N=CH-, -N=N-, $-CH=CR^0-$, -C≡C-, -CH=CH-COO-, -OCO-CH=CH-, CR^0R^{00} or a single bond,

R^0 and R^{00} are independently of each other H or alkyl with 1 to 12 C-atoms,

m and n are independently of each other 0, 1, 2, 3 or 4, with $m+n > 0$,

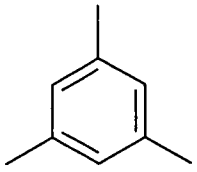
R^{1-3} are independently of each other identical or different groups selected from H, halogen, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-NH_2$, $-NR^0R^{00}$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-SF_5$, P-Sp-, optionally substituted silyl, or carbyl or

hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, or denote P or P-Sp-, or are substituted by P or P-Sp-,

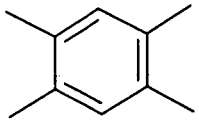
P is a polymerizable group,

Sp is a spacer group or a single bond.

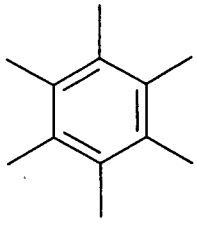
2. Compounds according to claim 1, characterized in that D is selected from the group consisting of the following subformulae:



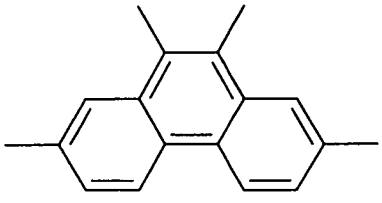
D1



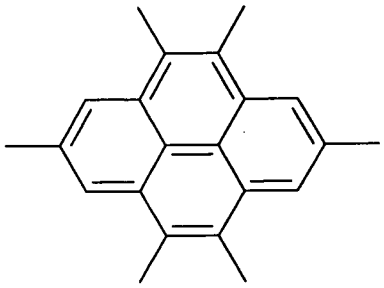
D2



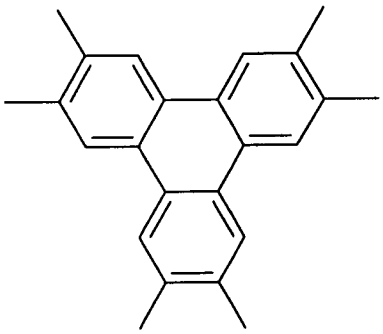
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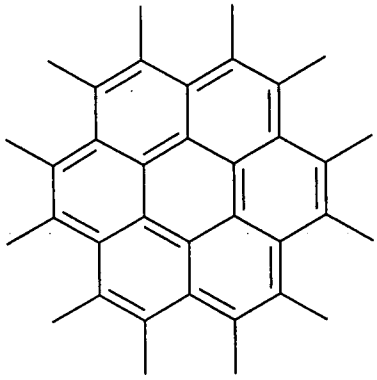
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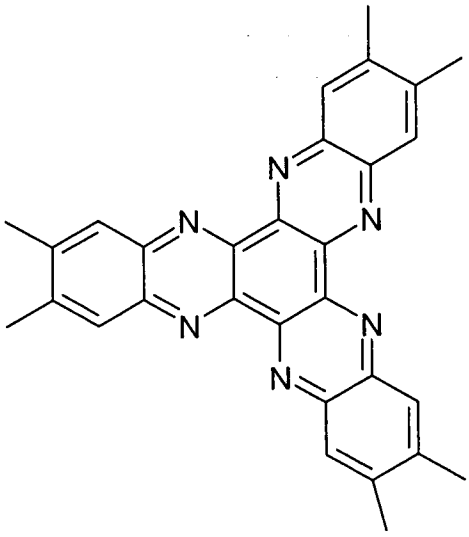
D5



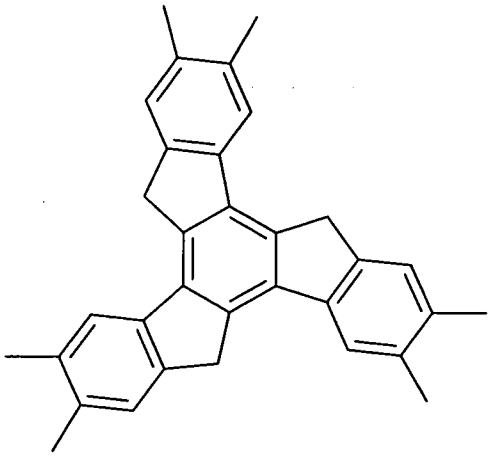
D6



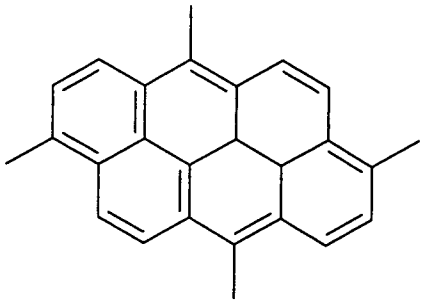
D7



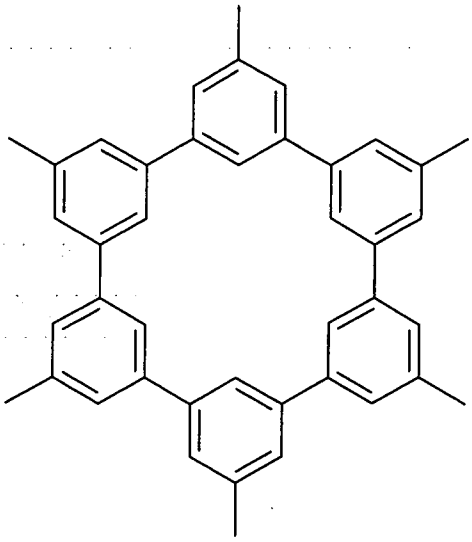
D8



D9

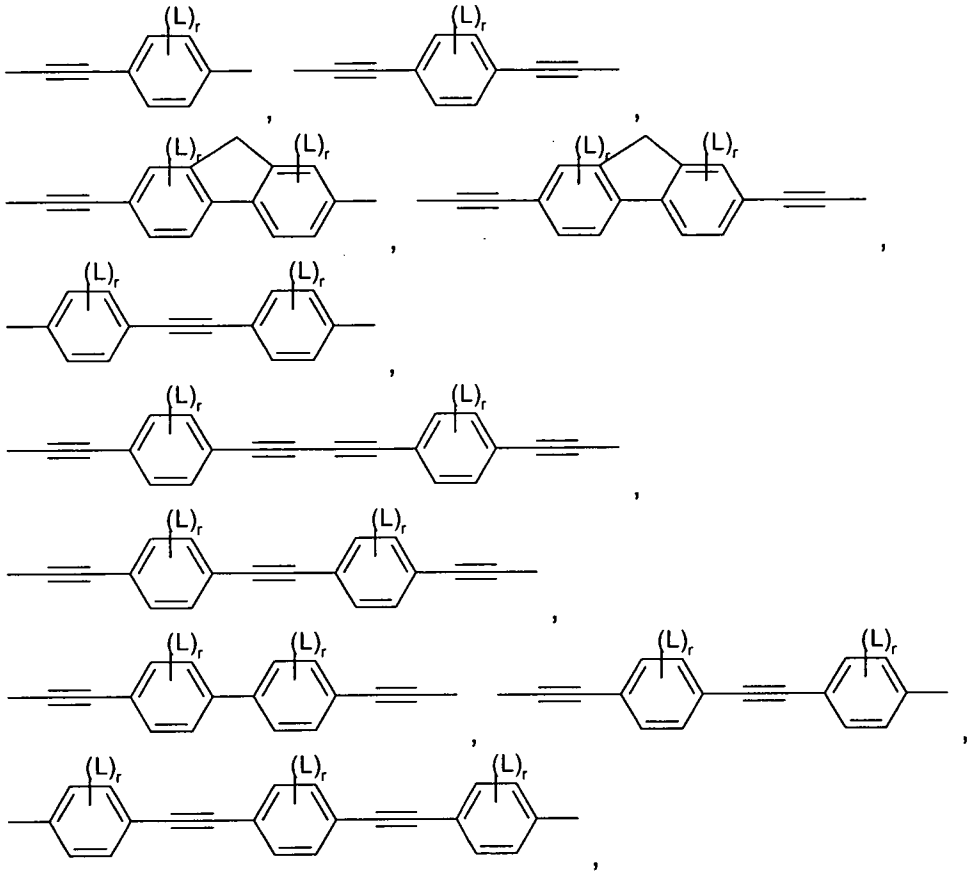


D10



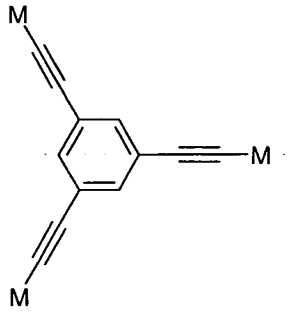
D11

3. Compounds according to claim 1 or 2, characterized in that $-(B)_q-$ is selected from the group consisting of -C≡C-, -C≡C-C≡C-, -C≡C-C≡C-C≡C-, -C≡C-C≡C-C≡C-C≡C-,

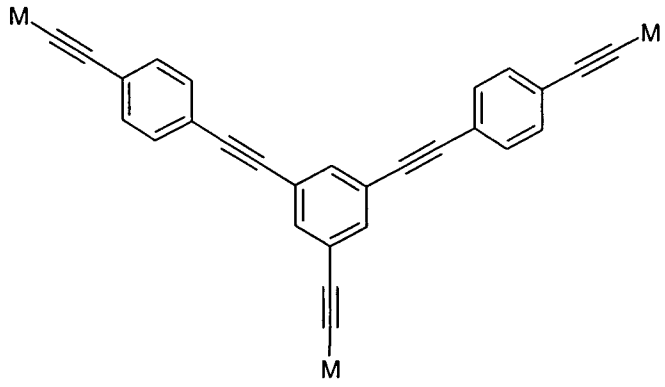


wherein r is 0, 1, 2, 3 or 4 and L is selected from P-Sp-, F, Cl, Br, I, -CN, $-NO_2$, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, -C(=O)X, $-C(=O)OR^0$, $-C(=O)R^0$, $-NR^0R^{00}$, -OH, $-SF_5$, optionally substituted silyl, aryl with 1 to 12 C atoms, and straight chain or branched alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy with 1 to 12 C atoms, wherein one or more H atoms are optionally replaced by F or Cl, wherein R^0 and R^{00} are as defined in claim 1 and X is halogen.

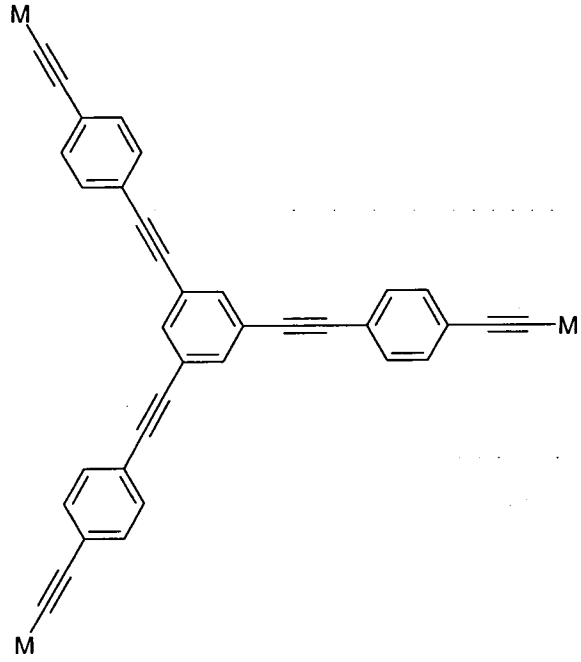
4. Compounds according to one or more of claims 1 to 3, characterized in that they are selected from the group consisting of the following subformulae:



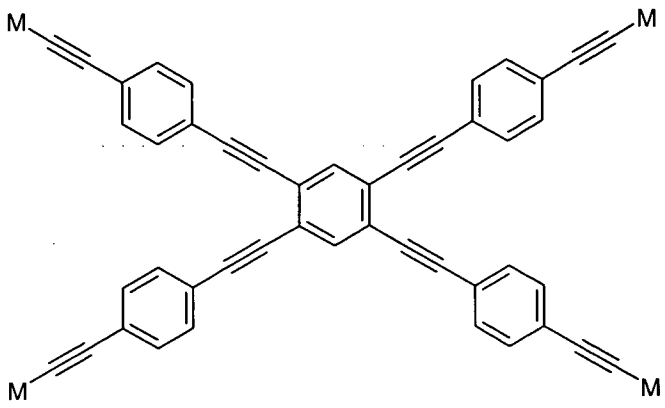
Ia



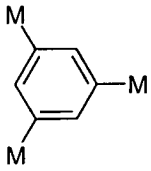
Ib



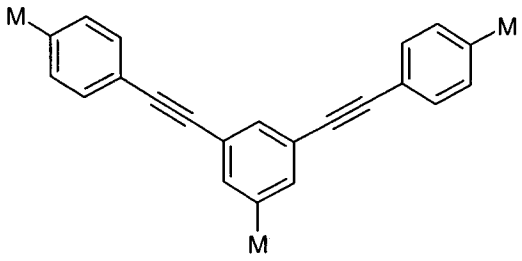
Ic



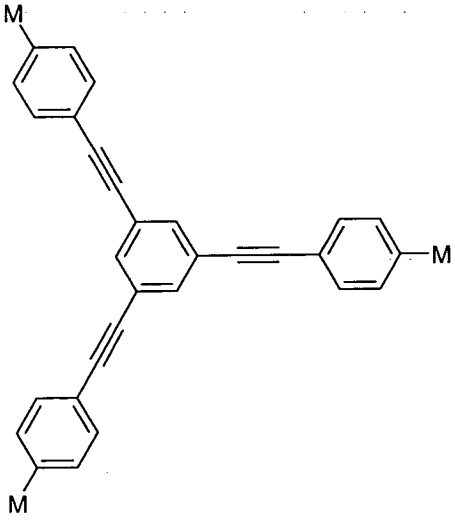
Id



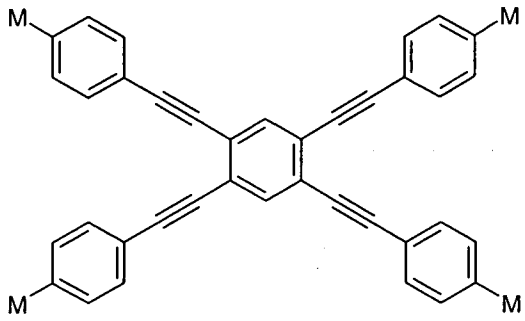
Ie



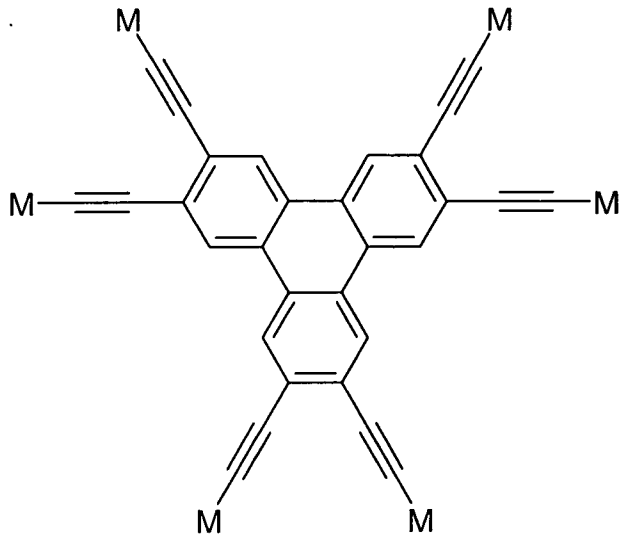
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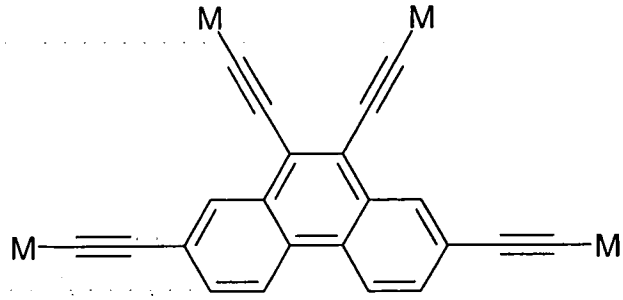
Ig



Ih



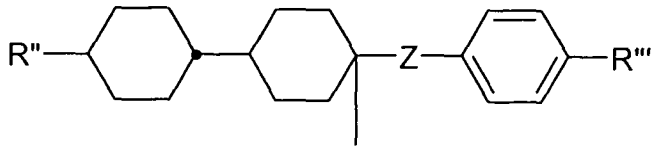
Ii



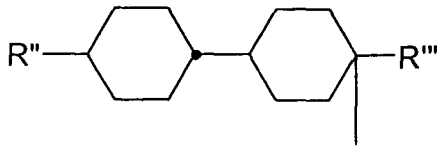
Ik

wherein M is as defined in claim 1, and the phenylene rings are optionally substituted by one or more groups L as defined in claim 3.

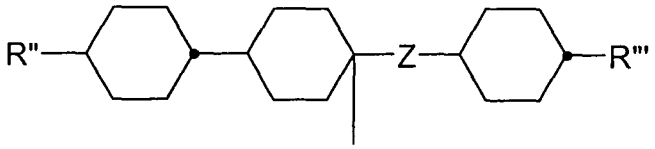
5. Compounds according to one or more of claims 1 to 4, characterized in that the groups M are preferably selected from the group consisting of the following subformulae:



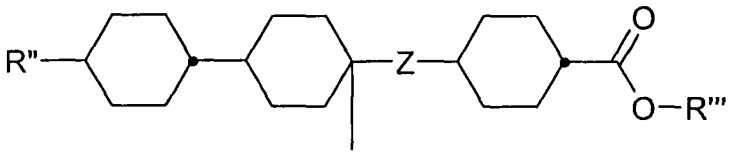
IIa



IIb



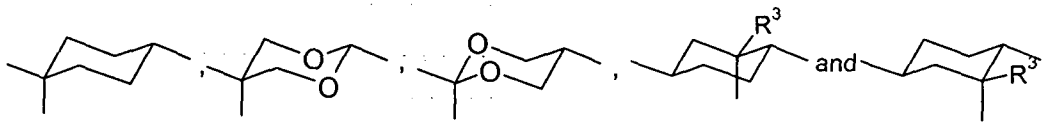
IIc



IId

wherein R" and R''' have independently of each other one of the meanings of R^1 of claim 1, and Z has in each occurrence independently of one another one of the meanings of Z^1 of claim 1.

6. Compounds according to one or more of claims 1 to 5, characterized in that the rings U^1 in formula II are selected from



wherein R^3 is as defined in formula I.

7. Polymerizable LC formulation comprising one or more compounds according to one or more of claims 1 to 6, and one or more further compounds, wherein at least one of the compounds is polymerizable.

8. Birefringent polymer film obtainable by polymerizing a compound or LC formulation according to one or more of claims 1 to 7 in its LC phase in an oriented state in form of a thin film.

9. Birefringent polymer film according to claim 8, characterized in that it has $R_{450}/R_{550} < 1$, wherein R_{450} is the optical on-axis retardation at a wavelength of 450nm and R_{550} is the optical on-axis retardation at a wavelength of 550nm.

10. Use of compounds, LC formulations and polymer films according to one or more of claims 1 to 9 in optical, electronic and electrooptical components and devices, preferably in optical films, retarders or compensators having negative optical dispersion.

11. Optical, electronic or electrooptical component or device, comprising a compound, LC formulation or polymer film according to one or more of claims 1 to 9.

12. Device or component according to claim 11, characterized in that is is selected from electrooptical displays, LCDs, optical films, polarizers, compensators, beam splitters, reflective films, alignment layers, colour filters, holographic elements, hot stamping foils, coloured images, decorative or security markings, LC pigments, adhesives, non-linear optic (NLO) devices, optical information storage devices, electronic devices, organic semiconductors, organic field effect transistors (OFET), integrated circuits (IC), thin film transistors (TFT), Radio Frequency Identification (RFID) tags, organic light emitting diodes (OLED), organic light emitting transistors (OLET), electroluminescent displays, organic photovoltaic (OPV) devices, organic solar cells (O-SC), organic laser diodes (O-laser), organic integrated circuits (O-IC), lighting devices, sensor devices, electrode materials, photoconductors, photodetectors, electrophotographic recording devices, capacitors, charge injection layers, Schottky diodes, planarising layers, antistatic films, conducting substrates, conducting patterns, photoconductors, electrophotographic applications, electrophotographic recording,

organic memory devices, biosensors, biochips, optoelectronic devices requiring similar phase shift at multiple wavelengths, combined CD/DVD/HD-DVD/Blu-Rays, reading, writing re-writing data storage systems, or cameras.

13. Optical component according to claim 11, characterized in that it is an optically uniaxial film selected from an A-plate, C-plate, negative C-plate or O-plate, a twisted optical retarder, a twisted quarter wave foil (QWF), an optically biaxial film, an achromatic retarder, an achromatic QWF or half wave foil (HWF), a film having a cholesteric, smectic, nematic or blue phase, a film having homeotropic, splayed, tilted, planar or blue-phase alignment, which is uniformly oriented or exhibits a pattern of different orientations.

14. Optical component according to claim 11, characterized in that it is an optical compensation film for viewing angle enhancement of LCD's, a component in a brightness enhancement films, or an achromatic element in reflective or transflective LCD's.

15. Method for preparing a compound according to one or more of claims 1 to 6, comprising the steps of

a) reacting a suitably substituted acetylene with an optionally substituted cyclohexanone in the presence of butyllithium,

b) separating the isomers thereby formed,

c) esterification the tertiary alcohol of the isolated isomer of step b) with a suitable aromatic or aliphatic carboxylic acid,

d) coupling the resulting compound via its axial acetylenic substituent to an aromatic ring.

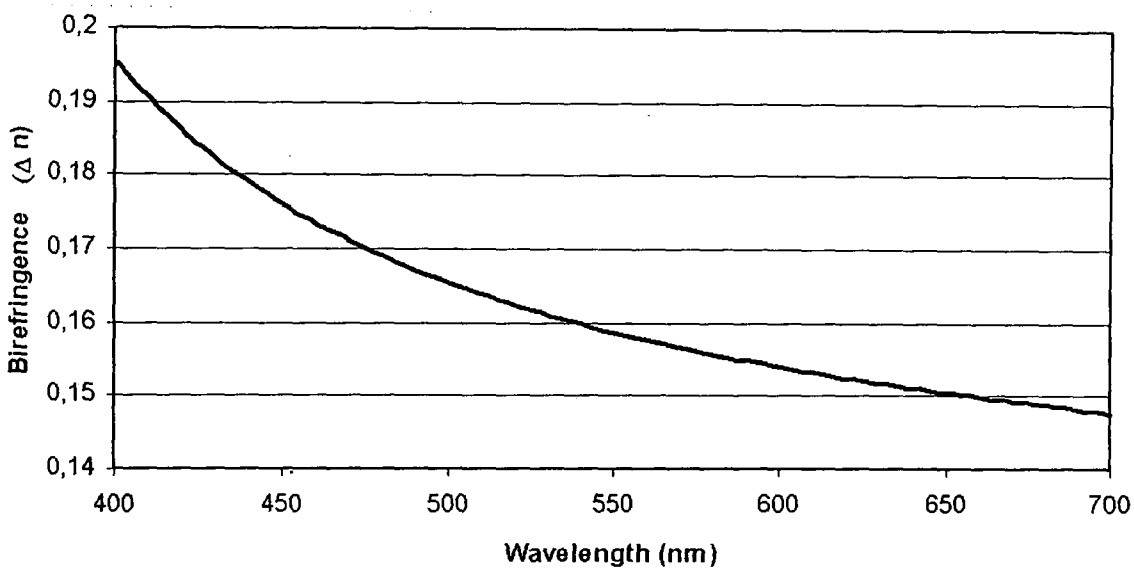


Figure 1

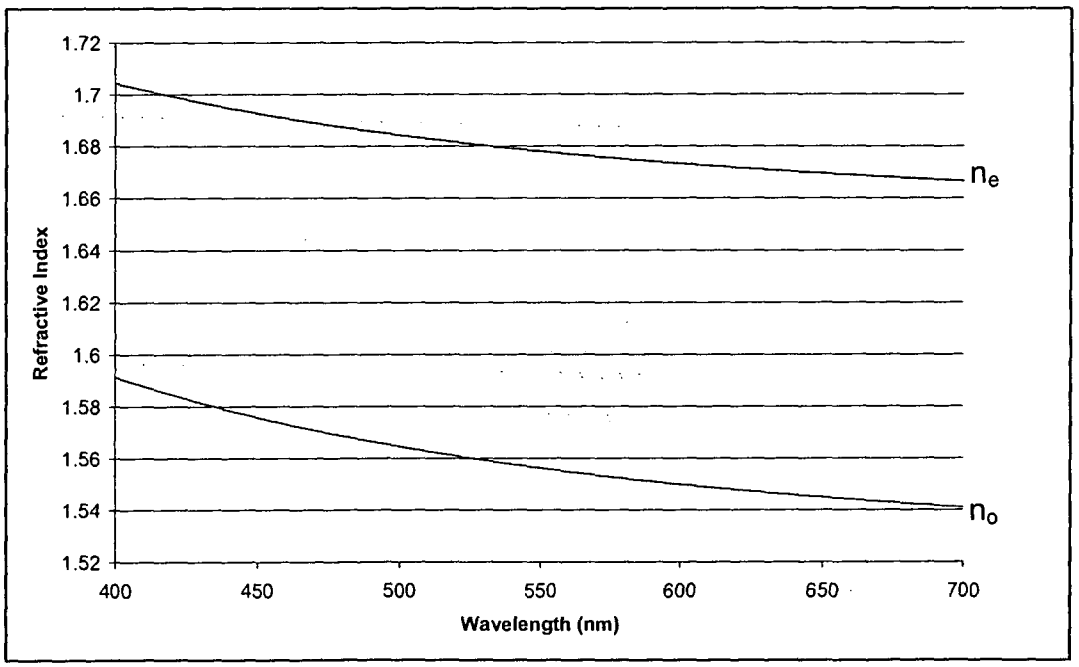


Figure 2

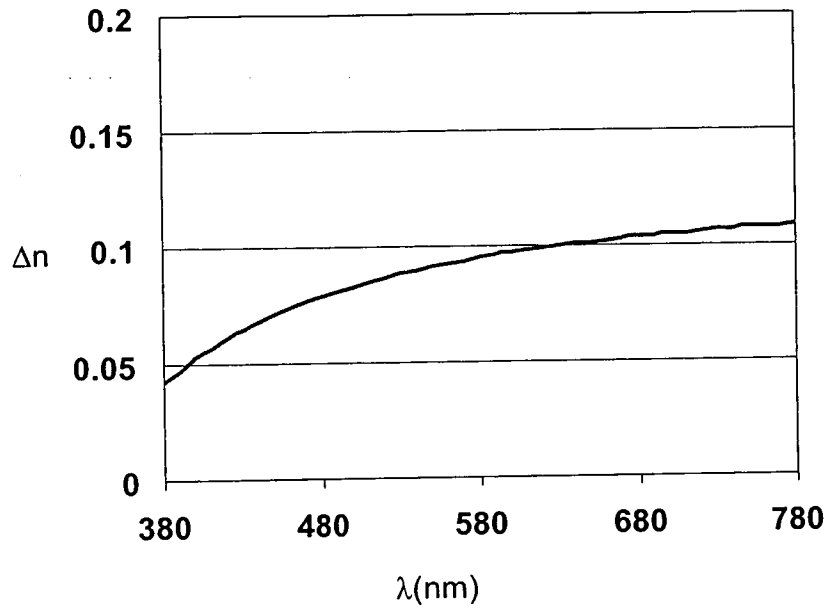


Figure 3a

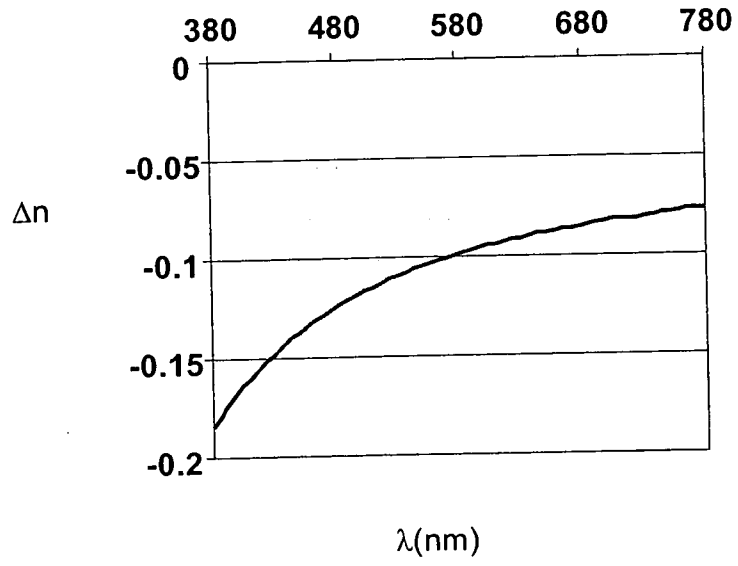


Figure 3b

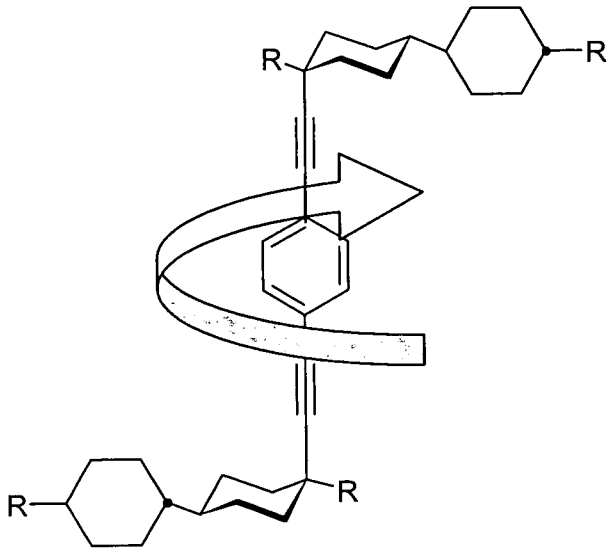


Figure 4

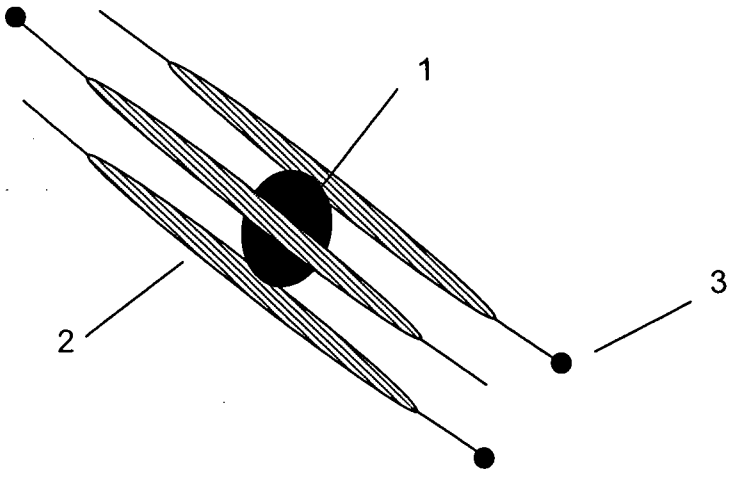


Figure 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/005171

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K19/30 C09K19/40 C09K19/32

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 practical, 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.
P,X	WO 2008/119427 A (MERCK PATENT GMBH [DE]; PARRI OWAIN LLYR [GB]; SKJONNEMAND KARL [GB];) 9 October 2008 (2008-10-09) pages 36-38; compounds I19-I24 pages 40-50; compounds claims; compounds I19-I24 example 17	1,6-15
P,X	WO 2008/119426 A (MERCK PATENT GMBH [DE]; PARRI OWAIN LLYR [GB]; ADLEM KEVIN [GB]; SKJON) 9 October 2008 (2008-10-09) pages 33-35; compounds I19-I24 pages 39-49; compounds claims; compounds I19-I24	1,6-15

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 October 2009	16/10/2009

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

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/005171

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 2007/298191 A1 (YAMAHARA MOTOHIRO [JP] ET AL) 27 December 2007 (2007-12-27) cited in the application paragraphs [0098] - [0103] claims; examples; compounds	1-15
A	& WO 2006/052001 A (SUMITOMO CHEMICAL CO [JP]; YAMAHARA MOTOHIRO [JP]; HASEGAWA HIKARU [JP) 18 May 2006 (2006-05-18) cited in the application	1-15
A	US 6 139 771 A (WALBA DAVID M [US] ET AL) 31 October 2000 (2000-10-31) cited in the application claims; examples; compound VII	1-15
A	US 6 203 724 B1 (REIFFENRATH VOLKER [DE] ET AL) 20 March 2001 (2001-03-20) cited in the application examples 89-94,185-190,219-221,231-238 claims	1-15

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Information on patent family members

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