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(54) **PHOTOCHROMIC COMPOUNDS AND COMPOSITIONS**

PHOTOCHROMISCHE VERBINDUNGEN UND ZUSAMMENSETZUNGEN
COMPOSÉS ET COMPOSITIONS PHOTOCHROMIQUES

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Description

CROSS-REFERENCE TO RELATED APPLICATIONS

5 **[0001]** This application is a continuation-in-part of U.S. Patent Application Serial Number 12/329,092 filed on December 5, 2008, which is a continuation-in-part of U.S. Patent Application Serial Number 10/846,629, filed May 17, 2004, now U.S. Patent 7,342,112, and which in turn claims the benefit of U.S. Provisional Application Serial Number 60/484, 100, filed July 1, 2003.

10 BACKGROUND

[0002] The present invention relates generally to photochromic compounds and to elements made using the photochromic compounds disclosed herein.

15 **[0003]** Conventional photochromic compounds have at least two states, a first state having a first absorption spectrum and a second state having a second absorption spectrum that differs from the first absorption spectrum, and are capable of switching between the two states in response to at least actinic radiation. Further, conventional photochromic compounds can be thermally reversible. That is, conventional photochromic compounds are capable of switching between a first state and a second state in response to at least actinic radiation and reverting back to the first state in response to thermal energy. As used herein "actinic radiation" means electromagnetic radiation, such as but not limited to ultraviolet and visible radiation that is capable of causing a response. More specifically, conventional photochromic compounds can undergo a transformation in response to actinic radiation from one isomer to another, with each isomer having a characteristic absorption spectrum, and can further revert back to the first isomer in response to thermal energy (i.e., be thermally reversible). For example, conventional thermally reversible photochromic compounds are generally capable of switching from a first state, for example a "clear state," to a second state, for example a "colored state," in response to actinic radiation and reverting back to the "clear" state in response to thermal energy.

20 **[0004]** Dichroic compounds are compounds that are capable of absorbing one of two orthogonal plane polarized components of transmitted radiation more strongly than the other. Thus, dichroic compounds are capable of linearly polarizing transmitted radiation. As used herein, "linearly polarize" means to confine the vibrations of the electric vector of light waves to one direction or plane. However, although dichroic materials are capable of preferentially absorbing one of two orthogonal plane polarized components of transmitted radiation, if the molecules of the dichroic compound are not suitably positioned or arranged, no net linear polarization of transmitted radiation will be achieved. That is, due to the random positioning of the molecules of the dichroic compound, selective absorption by the individual molecules will cancel each other such that no net or overall linear polarizing effect is achieved. Thus, it is generally necessary to suitably position or arrange the molecules of the dichroic compound within another material in order to form a conventional linear polarizing element, such as a linearly polarizing filter or lens for sunglasses.

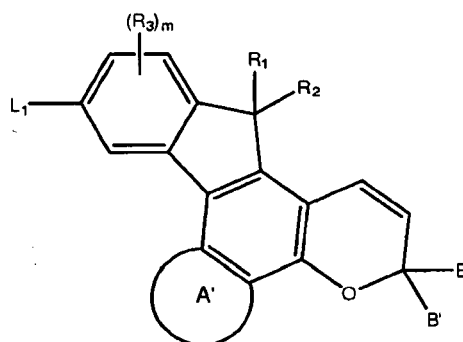
25 **[0005]** In contrast to the dichroic compounds, it is generally not necessary to position or arrange the molecules of conventional photochromic compounds to form a conventional photochromic element. Thus, for example, conventional photochromic elements, such as lenses for photochromic eyewear, can be formed, for example, by spin coating a solution containing a conventional photochromic compound and a "host" material onto the surface of the lens, and suitably curing the resultant coating or layer without arranging the photochromic compound in any particular orientation. Further, even if the molecules of the conventional photochromic compound were suitably positioned or arranged as discussed above with respect to the dichroic compounds, because conventional photochromic compounds do not strongly demonstrate dichroism, elements made therefrom are generally not strongly linearly polarizing.

30 **[0006]** It would be advantageous to provide photochromic compounds, such as but not limited to thermally reversible photochromic compounds, that can exhibit useful photochromic and/or dichroic properties in at least one state, and that can be used in a variety of applications to impart photochromic and/or dichroic properties.

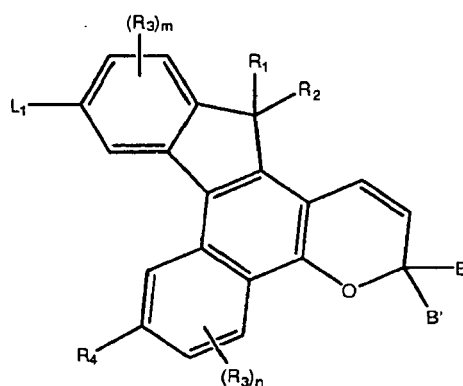
BRIEF SUMMARY OF THE DISCLOSURE

35 **[0007]** Described herein are compounds represented by the following graphic Formulas I and IA:

55



Formula I



Formula IA

30 wherein:

A' is selected from optionally substituted aryl and optionally substituted heteroaryl; wherein A' is optionally substituted with L₂;

35 R₁ and R₂ are each independently selected from hydrogen, hydroxy and chiral or achiral groups selected from optionally substituted heteroalkyl, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, halogen, optionally substituted amino, carboxy, alkylcarbonyl, alkoxy carbonyl, optionally substituted alkoxy, and aminocarbonyl, or R₁ and R₂ may be taken together with any intervening atoms to form a group selected from oxo, optionally substituted cycloalkyl, and optionally substituted heterocycloalkyl; and

40 R₃ for each occurrence, is independently selected from chiral or achiral groups selected from formyl, alkylcarbonyl, alkoxy carbonyl, aminocarbonyl, arylcarbonyl, aryloxy carbonyl, aminocarbonyloxy, alkoxy carbonylamino, aryloxy carbonylamino, boronic acid, boronic acid esters, cycloalkoxy carbonylamino, heterocycloalkyloxy carbonylamino, heteroaryloxy carbonylamino, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, halogen, optionally substituted cycloalkyl, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted alkoxy, optionally substituted heteroalkyl, optionally substituted heterocycloalkyl, and optionally substituted amino;

R₄ is selected from hydrogen, R₃ and L₂;

m and n are each independently an integer selected from 0 to 3;

45 B and B' are each independently selected from L₃, hydrogen, halogen, and chiral or achiral groups selected from metallocenyl, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted heterocycloalkyl, and optionally substituted cycloalkyl, or wherein B and B' are taken together with any intervening atoms to form a group selected from optionally substituted cycloalkyl and optionally substituted heterocycloalkyl; and

50 L₁, L₂, and L₃ for each occurrence, are independently selected from a chiral or achiral lengthening group represented by:

-[S₁]_c-[Q₁-[S₂]_d]_{d'}-[Q₂-[S₃]_e]_{e'}-[Q₃-[S₄]_f]_{f'}-S₅-P wherein:

(a) Q₁, Q₂, and Q₃ for each occurrence, are independently selected from a divalent group selected from optionally substituted aryl, optionally substituted heteroaryl, optionally substituted cycloalkyl, and optionally substituted heterocycloalkyl;

wherein substituents are independently selected from P, liquid crystal mesogens, halogen, poly(C₁-C₁₈alkoxy), C₁-C₁₈alkoxycarbonyl, C₁-C₁₈alkylcarbonyl, C₁-C₁₈alkoxycarbonyloxy, aryloxy carbonyloxy, perfluoro(C₁-C₁₈)alkoxy, perfluoro(C₁-C₁₈)alkoxycarbonyl, perfluoro(C₁-C₁₈)alkylcarbonyl, perfluoro(C₁-C₁₈)alkylamino, di-(perfluoro(C₁-C₁₈)alkyl)amino, perfluoro(C₁-C₁₈)alkylthio, C₁-C₁₈alkylthio, C₁-C₁₈acetyl, C₃-C₁₀cycloalkyl, C₃-C₁₀cycloalkoxy, straight-chain C₁-C₁₈alkyl, and branched C₁-C₁₈alkyl; wherein said straight-chain C₁-C₁₈alkyl and branched C₁-C₁₈alkyl are mono-substituted with a group selected from cyano, halogen, and C₁-C₁₈alkoxy; or

wherein said straight-chain C₁-C₁₈alkyl and branched C₁-C₁₈alkyl are poly-substituted with at least two groups independently selected from halogen, -M(T)_(t-1) and -M(OT)_(t-1); wherein M is chosen from aluminum, antimony, tantalum, titanium, zirconium and silicon, T is chosen from organofunctional radicals, organofunctional hydrocarbon radicals, aliphatic hydrocarbon radicals and aromatic hydrocarbon radicals, and t is the valence of M;

(b) c, d, e, and f are each independently chosen from an integer from 1 to 20; and each S₁, S₂, S₃, S₄, and S₅ is independently chosen for each occurrence from a spacer unit selected from:

(i) optionally substituted alkylene, optionally substituted haloalkylene, -Si(CH₂)_g-, and -(Si[(CH₃)₂O])_h-, wherein g for each occurrence is independently chosen from an integer from 1 to 20; h for each occurrence is independently chosen from an integer from 1 to 16; and said substituents for the alkylene and haloalkylene are independently selected from C₁-C₁₈alkyl, C₃-C₁₀cycloalkyl and aryl;

(ii) -N(Z)-, -C(Z)=C(Z)-, -C(Z)=N-, -C(Z')₂-C(Z')₂-, and a single bond, wherein Z for each occurrence is independently selected from hydrogen, C₁-C₁₈alkyl, C₃-C₁₀cycloalkyl and aryl, and Z' for each occurrence is independently selected from C₁-C₁₈alkyl, C₃-C₁₀cycloalkyl and aryl; and

(iii) -O-, -C(=O)-, -C≡C-, -N=N-, -S-, -S(=O)-, -(O=)S(=O)-, -(O=)S(=O)O-, -O(O=)S(=O)O- and straight-chain or branched C₁-C₂₄alkylene residue, said C₁-C₂₄alkylene residue being unsubstituted, mono-substituted by cyano or halogen, or poly-substituted by halogen,

provided that when two spacer units comprising heteroatoms are linked together the spacer units are linked so that heteroatoms are not directly linked to each other, each bond between S₁ and the compound represented by graphic Formula I and/or IA is free of two heteroatoms linked together, and the bond between S₅ and P is free of two heteroatoms linked to each other;

(c) P for each occurrence is independently selected from hydroxy, amino, C₂-C₁₈alkenyl, C₂-C₁₈alkynyl, azido, silyl, siloxy, silylhydride, (tetrahydro-2H-pyran-2-yl)oxy, thio, isocyanato, thioisocyanato, acryloyloxy, methacryloyloxy, 2-(acryloyloxy)ethylcarbonyl, 2-(methacryloyloxy)ethylcarbonyl, aziridinyl, allyloxy carbonyloxy, epoxy, carboxylic acid, carboxylic ester, acryloylamino, methacryloylamino, aminocarbonyl, C₁-C₁₈alkyl aminocarbonyl, aminocarbonyl(C₁-C₁₈)alkyl, C₁-C₁₈alkyloxy carbonyloxy, halocarbonyl, hydrogen, aryl, hydroxy(C₁-C₁₈)alkyl, C₁-C₁₈alkyl, C₁-C₁₈alkoxy, amino(C₁-C₁₈)alkyl, C₁-C₁₈alkylamino, di-(C₁-C₁₈)alkylamino, C₁-C₁₈alkyl(C₁-C₁₈)alkoxy, C₁-C₁₈alkoxy(C₁-C₁₈)alkoxy, nitro, poly(C₁-C₁₈)alkyl ether, (C₁-C₁₈)alkyl(C₁-C₁₈)alkoxy(C₁-C₁₈)alkyl, polyethyleneoxy, polypropyleneoxy, ethylene, acryloyl, acryloyloxy(C₁-C₁₈)alkyl, methacryloyl, methacryloyloxy(C₁-C₁₈)alkyl, 2-chloroacryloyl, 2-phenylacryloyl, acryloyloxyphenyl, 2-chloroacryloylamino, 2-phenylacryloylaminocarbonyl, oxetanyl, glycidyl, cyano, isocyanato(C₁-C₁₈)alkyl, itaconic acid ester, vinyl ether, vinyl ester, a styrene derivative, main-chain and side-chain liquid crystal polymers, siloxane derivatives, ethyleneimine derivatives, maleic acid derivatives, maleimide derivatives; fumaric acid derivatives, unsubstituted cinnamic acid derivatives, cinnamic acid derivatives that are substituted with at least one of methyl, methoxy, cyano and halogen, and substituted or unsubstituted chiral or non-chiral monovalent or divalent groups chosen from steroid radicals, terpenoid radicals, alkaloid radicals and mixtures thereof, wherein the substituents are independently chosen from C₁-C₁₈alkyl, C₁-C₁₈alkoxy, amino, C₃-C₁₀cycloalkyl, C₁-C₁₈alkyl(C₁-C₁₈)alkoxy, fluoro(C₁-C₁₈)alkyl, cyano, cyano(C₁-C₁₈)alkyl, cyano(C₁-C₁₈)alkoxy or mixtures thereof, or P is a structure having from 2 to 4 reactive groups or P is an unsubstituted or substituted ring opening metathesis polymerization precursor or P is a substituted or unsubstituted photochromic compound; and

(d) d', e' and f are each independently chosen from 0, 1, 2, 3, and 4, provided that a sum of d' + e' + f is at least 2.

[0008] Also provided herein are photochromic compositions and photochromic articles comprising at least one compound of Formulas I and IA.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING(S)

[0009] Various non-limiting embodiments of the present disclosure will be better understood when read in conjunction with the drawings, in which:

5 **[0010]** Fig. 1 shows two average difference absorption spectra obtained for a photochromic compound according to various non-limiting embodiments disclosed herein using the CELL METHOD.

DETAILED DESCRIPTION

10 **[0011]** As used in the present specification, the following words, phrases and symbols are generally intended to have the meanings as set forth below, except to the extent that the context in which they are used indicates otherwise. The following abbreviations and terms have the indicated meanings throughout:

[0012] A dash ("-") that is not between two letters or symbols is used to indicate a point of attachment for a substituent. For example, $-\text{CONH}_2$ is attached through the carbon atom.

15 **[0013]** "Alkyl" by itself or as part of another substituent refers to a saturated or unsaturated, branched, or straight-chain monovalent hydrocarbon radical derived by the removal of one hydrogen atom from a single carbon atom of a parent alkane, alkene, or alkyne. Examples of alkyl groups include, but are not limited to, methyl; ethyls such as ethanyl, ethenyl, and ethynyl; propyls such as propan-1-yl, propan-2-yl, prop-1-en-1-yl, prop-1-en-2-yl, prop-2-en-1-yl (allyl), prop-1-yn-1-yl, prop-2-yn-1-yl, *etc.*; butyls such as butan-1-yl, butan-2-yl, 2-methyl-propan-1-yl, 2-methyl-propan-2-yl, but-1-en-1-yl, but-1-en-2-yl, 2-methyl-prop-1-en-1-yl, but-2-en-1-yl, but-2-en-2-yl, buta-1,3-dien-1-yl, buta-1,3-dien-2-yl, but-1-yn-1-yl, but-1-yn-3-yl, but-3-yn-1-yl, *etc.*

20 **[0014]** The term "alkyl" is specifically intended to include groups having any degree or level of saturation, *i.e.*, groups having exclusively single carbon-carbon bonds, groups having one or more double carbon-carbon bonds, groups having one or more triple carbon-carbon bonds, and groups having mixtures of single, double, and triple carbon-carbon bonds. Where a specific level of saturation is intended, the terms "alkanyl," "alkenyl," and "alkynyl" are used. In certain embodiments, an alkyl group comprises from 1 to 20 carbon atoms, in certain embodiments, from 1 to 10 carbon atoms, in certain embodiments, from 1 to 8 or 1 to 6 carbon atoms, and in certain embodiments from 1 to 3 carbon atoms.

25 **[0015]** "Acyl" by itself or as part of another substituent refers to a radical $-\text{C}(\text{O})\text{R}^{30}$, where R^{30} is hydrogen, alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, cycloalkylalkyl, heterocycloalkylalkyl, aryl, heteroaryl, arylalkyl, or heteroarylalkyl, which can be substituted, as defined herein. Examples of acyl groups include, but are not limited to, formyl, acetyl, cyclohexylcarbonyl, cyclohexylmethylcarbonyl, benzoyl, benzylcarbonyl.

30 **[0016]** "Alkoxy" by itself or as part of another substituent refers to a radical $-\text{OR}^{31}$ where R^{31} is alkyl, cycloalkyl, cycloalkylalkyl, aryl, or arylalkyl, which can be substituted, as defined herein. In some embodiments, alkoxy groups have from 1 to 18 carbon atoms. Examples of alkoxy groups include, but are not limited to, methoxy, ethoxy, propoxy, butoxy, cyclohexyloxy.

35 **[0017]** "Alkoxy carbonyl" by itself or as part of another substituent refers to a radical $-\text{C}(\text{O})\text{OR}^{31}$ where R^{31} is alkyl, cycloalkyl, cycloalkylalkyl, aryl, or arylalkyl, which can be substituted, as defined herein.

[0018] "Amino" refers to the radical $-\text{NH}_2$.

40 **[0019]** "Aminocarbonyl" by itself or as part of another substituent refers to radical of the formula $-\text{N}(\text{R}^{60})\text{C}(\text{O})\text{R}^{60}$ where each R^{60} is independently selected from hydrogen, alkyl, substituted alkyl, alkoxy, substituted alkoxy, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, arylalkyl, substituted arylalkyl, heteroarylalkyl

45 **[0020]** "Aryl" by itself or as part of another substituent refers to a monovalent aromatic hydrocarbon radical derived by the removal of one hydrogen atom from a single carbon atom of a parent aromatic ring system. Aryl encompasses 5- and 6-membered carbocyclic aromatic rings, for example, benzene; bicyclic ring systems wherein at least one ring is carbocyclic and aromatic, for example, naphthalene, indane, and tetralin; and tricyclic ring systems wherein at least one ring is carbocyclic and aromatic, for example, fluorene. Aryl encompasses multiple ring systems having at least one carbocyclic aromatic ring fused to at least one carbocyclic aromatic ring, cycloalkyl ring, or heterocycloalkyl ring. For example, aryl includes 5- and 6-membered carbocyclic aromatic rings fused to a 5- to 7-membered heterocycloalkyl ring containing one or more heteroatoms chosen from N, O, and S. For such fused, bicyclic ring systems wherein only one of the rings is a carbocyclic aromatic ring, the point of attachment may be at the carbocyclic aromatic ring or the heterocycloalkyl ring. Examples of aryl groups include, but are not limited to, groups derived from aceanthrylene, acenaphthylene, acephenanthrylene, anthracene, azulene, benzene, chrysene, coronene, fluoranthene, fluorene, hexacene, hexaphene, hexalene, as-indacene, s-indacene, indane, indene, naphthalene, octacene, octaphene, octalene, ovalene, penta-2,4-diene, pentacene, pentalene, pentaphene, perylene, phenalene, phenanthrene, picene, pleiadene, pyrene, pyranthrene, rubicene, triphenylene, trinaphthalene. In certain embodiments, an aryl group can comprise from 5 to 20 carbon atoms, and in certain embodiments, from 5 to 12 carbon atoms. Aryl, however, does not encompass or overlap in any way with heteroaryl, separately defined herein. Hence, a multiple ring system in which one or more carbocyclic

aromatic rings is fused to a heterocycloalkyl aromatic ring, is heteroaryl, not aryl, as defined herein.

[0021] "Arylalkyl" by itself or as part of another substituent refers to an acyclic alkyl radical in which one of the hydrogen atoms bonded to a carbon atom, typically a terminal or sp^3 carbon atom, is replaced with an aryl group. Examples of arylalkyl groups include, but are not limited to, benzyl, 2-phenylethan-1-yl, 2-phenylethen-1-yl, naphthylmethyl, 2-naphthylethan-1-yl, 2-naphthylethen-1-yl, naphthobenzyl, 2-naphthophenylethan-1-yl. Where specific alkyl moieties are intended, the nomenclature arylalkanyl, arylalkenyl, or arylalkynyl is used. In certain embodiments, an arylalkyl group is C_{7-30} arylalkyl, e.g., the alkanyl, alkenyl, or alkynyl moiety of the arylalkyl group is C_{1-10} and the aryl moiety is C_{6-20} , and in certain embodiments, an arylalkyl group is C_{7-20} arylalkyl, e.g., the alkanyl, alkenyl, or alkynyl moiety of the arylalkyl group is C_{1-8} and the aryl moiety is C_{6-12} .

[0022] "Carboxamidyl" by itself or as part of another substituent refers to a radical of the formula $-C(O)NR^{60}R^{61}$ where each R^{60} and R^{61} are independently hydrogen, alkyl, substituted alkyl, alkoxy, substituted alkoxy, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, arylalkyl, substituted arylalkyl, heteroarylalkyl, or substituted heteroarylalkyl, or R^{60} and R^{61} together with the nitrogen atom to which they are bonded form a heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, or substituted heteroaryl ring.

[0023] "Compounds" refers to compounds encompassed by structural Formulas I and IA herein and includes any specific compounds within these formulae whose structure is disclosed herein. Compounds may be identified either by their chemical structure and/or chemical name. When the chemical structure and chemical name conflict, the chemical structure is determinative of the identity of the compound. The compounds described herein may contain one or more chiral centers and/or double bonds and therefore may exist as stereoisomers such as double-bond isomers (*i.e.*, geometric isomers), enantiomers, or diastereomers. Accordingly, any chemical structures within the scope of the specification depicted, in whole or in part, with a relative configuration encompass all possible enantiomers and stereoisomers of the illustrated compounds including the stereoisomerically pure form (e.g., geometrically pure, enantiomerically pure, or diastereomerically pure) and enantiomeric and stereoisomeric mixtures. Enantiomeric and stereoisomeric mixtures can be resolved into their component enantiomers or stereoisomers using separation techniques or chiral synthesis techniques well known to the skilled artisan.

[0024] For the purposes of the present disclosure, "chiral compounds" are compounds having at least one center of chirality (*i.e.* at least one asymmetric atom, in particular at least one asymmetric C atom), having an axis of chirality, a plane of chirality or a screw structure. "Achiral compounds" are compounds which are not chiral.

[0025] Compounds of Formulas I and IA include, but are not limited to, optical isomers of compounds of Formulas I and IA, racemates thereof, and other mixtures thereof. In such embodiments, the single enantiomers or diastereomers, *i.e.*, optically active forms, can be obtained by asymmetric synthesis or by resolution of the racemates. Resolution of the racemates can be accomplished, for example, by conventional methods such as crystallization in the presence of a resolving agent, or chromatography, using, for example a chiral highpressure liquid chromatography (HPLC) column. However, unless otherwise stated, it should be assumed that Formulas I and IA cover all asymmetric variants of the compounds described herein, including isomers, racemates, enantiomers, diastereomers, and other mixtures thereof. In addition, compounds of Formulas I and IA include Z- and E-forms (e.g., cis- and trans-forms) of compounds with double bonds. In embodiments in which compounds of Formulas I and IA exist in various tautomeric forms, compounds provided by the present disclosure include all tautomeric forms of the compound.

[0026] The compounds of Formulas I and IA may also exist in several tautomeric forms including the enol form, the keto form, and mixtures thereof. Accordingly, the chemical structures depicted herein encompass all possible tautomeric forms of the illustrated compounds. Compounds may exist in unsolvated forms as well as solvated forms, including hydrated forms and as N-oxides. In general, compounds may be hydrated, solvated, or N-oxides. Certain compounds may exist in single or multiple crystalline or amorphous forms. In general, all physical forms are equivalent for the uses contemplated herein and are intended to be within the scope provided by the present disclosure. Further, when partial structures of the compounds are illustrated, an asterisk (*) indicates the point of attachment of the partial structure to the rest of the molecule.

[0027] "Cycloalkyl" by itself or as part of another substituent refers to a saturated or unsaturated cyclic alkyl radical. Where a specific level of saturation is intended, the nomenclature "cycloalkanyl" or "cycloalkenyl" is used. Examples of cycloalkyl groups include, but are not limited to, groups derived from cyclopropane, cyclobutane, cyclopentane, cyclohexane. In certain embodiments, a cycloalkyl group is C_{3-15} cycloalkyl, and in certain embodiments, C_{3-12} cycloalkyl or C_{5-12} cycloalkyl.

[0028] "Cycloalkylalkyl" by itself or as part of another substituent refers to an acyclic alkyl radical in which one of the hydrogen atoms bonded to a carbon atom, typically a terminal or sp^3 carbon atom, is replaced with a cycloalkyl group. Where specific alkyl moieties are intended, the nomenclature cycloalkylalkanyl, cycloalkylalkenyl, or cycloalkylalkynyl is used. In certain embodiments, a cycloalkylalkyl group is C_{7-30} cycloalkylalkyl, e.g., the alkanyl, alkenyl, or alkynyl moiety of the cycloalkylalkyl group is C_{1-10} and the cycloalkyl moiety is C_{6-20} , and in certain embodiments, a cycloalkylalkyl group is C_{7-20} cycloalkylalkyl, e.g., the alkanyl, alkenyl, or alkynyl moiety of the cycloalkylalkyl group is C_{1-8} and the cycloalkyl moiety is C_{4-20} or C_{6-12} .

[0029] "Halogen" refers to a fluoro, chloro, bromo, or iodo group.

[0030] "Heteroalkyl" by itself or as part of another substituent refers to an alkyl group in which one or more of the carbon atoms (and any associated hydrogen atoms) are independently replaced with the same or different heteroatomic groups. In some embodiments, heteroalkyl groups have from 1 to 8 carbon atoms. Examples of heteroatomic groups include, but are not limited to, -O-, -S-, -S-S-, -NR³⁸-, =N-N=, -N=N-, -N=N-NR³⁹R⁴⁰-, -PR⁴¹-, -P(O)₂-, -POR⁴²-, -O-P(O)₂-, -SO-, -SO₂-, -SnR⁴³R⁴⁴-, where R³⁸, R³⁹, R⁴⁰, R⁴¹, R⁴², R⁴³, and R⁴⁴ are independently hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, arylalkyl, substituted arylalkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, heteroalkyl, substituted heteroalkyl, heteroaryl, substituted heteroaryl, heteroarylalkyl, or substituted heteroarylalkyl. Where a specific level of saturation is intended, the nomenclature "heteroalkanyl," "heteroalkenyl," or "heteroalkynyl" is used. In certain embodiments, R³⁸, R³⁹, R⁴⁰, R⁴¹, R⁴², R⁴³, and R⁴⁴ are independently chosen from hydrogen and C₁₋₃ alkyl.

[0031] "Heteroaryl" by itself or as part of another substituent refers to a monovalent heteroaromatic radical derived by the removal of one hydrogen atom from a single atom of a parent heteroaromatic ring system. Heteroaryl encompasses multiple ring systems having at least one aromatic ring fused to at least one other ring, which can be aromatic or non-aromatic in which at least one ring atom is a heteroatom. Heteroaryl encompasses 5- to 12-membered aromatic, such as 5- to 7-membered, monocyclic rings containing one or more, for example, from 1 to 4, or in certain embodiments, from 1 to 3, heteroatoms chosen from N, O, and S, with the remaining ring atoms being carbon; and bicyclic heterocycloalkyl rings containing one or more, for example, from 1 to 4, or in certain embodiments, from 1 to 3, heteroatoms chosen from N, O, and S, with the remaining ring atoms being carbon and wherein at least one heteroatom is present in an aromatic ring. For example, heteroaryl includes a 5- to 7-membered heterocycloalkyl, aromatic ring fused to a 5- to 7-membered cycloalkyl ring. For such fused, bicyclic heteroaryl ring systems wherein only one of the rings contains one or more heteroatoms, the point of attachment may be at the heteroaromatic ring or the cycloalkyl ring. In certain embodiments, when the total number of N, S, and O atoms in the heteroaryl group exceeds one, the heteroatoms are not adjacent to one another. In certain embodiments, the total number of N, S, and O atoms in the heteroaryl group is not more than two. In certain embodiments, the total number of N, S, and O atoms in the aromatic heterocycle is not more than one. Heteroaryl does not encompass or overlap with aryl as defined herein.

[0032] Examples of heteroaryl groups include, but are not limited to, groups derived from acridine, arsinole, carbazole, β-carboline, chromane, chromene, cinnoline, furan, imidazole, indazole, indole, indoline, indolizine, isobenzofuran, isochromene, isoindole, isoindoline, isoquinoline, isothiazole, isoxazole, naphthyridine, oxadiazole, oxazole, perimidine, phenanthridine, phenanthroline, phenazine, phthalazine, pteridine, purine, pyran, pyrazine, pyrazole, pyridazine, pyridine, pyrimidine, pyrrole, pyrrolizine, quinazoline, quinoline, quinolizine, quinoxaline, tetrazole, thiadiazole, thiazole, thiophene, triazole, xanthene. In certain embodiments, a heteroaryl group is from 5- to 20-membered heteroaryl, and in certain embodiments from 5- to 12-membered heteroaryl or from 5- to 10-membered heteroaryl. In certain embodiments heteroaryl groups are those derived from thiophene, pyrrole, benzothiophene, benzofuran, indole, pyridine, quinoline, imidazole, oxazole, and pyrazine.

[0033] "Heteroarylalkyl" by itself or as part of another substituent refers to an acyclic alkyl radical in which one of the hydrogen atoms bonded to a carbon atom, typically a terminal or sp³ carbon atom, is replaced with a heteroaryl group. Where specific alkyl moieties are intended, the nomenclature heteroarylalkanyl, heteroarylalkenyl, or heteroarylalkynyl is used. In certain embodiments, a heteroarylalkyl group is a 6- to 30-membered heteroarylalkyl, e.g., the alkanyl, alkenyl, or alkynyl moiety of the heteroarylalkyl is 1- to 10-membered and the heteroaryl moiety is a 5- to 20-membered heteroaryl, and in certain embodiments, 6- to 20-membered heteroarylalkyl, e.g., the alkanyl, alkenyl, or alkynyl moiety of the heteroarylalkyl is 1- to 8-membered and the heteroaryl moiety is a 5- to 12-membered heteroaryl.

[0034] "Heterocycloalkyl" by itself or as part of another substituent refers to a partially saturated or unsaturated cyclic alkyl radical in which one or more carbon atoms (and any associated hydrogen atoms) are independently replaced with the same or different heteroatom. Examples of heteroatoms to replace the carbon atom(s) include, but are not limited to, N, P, O, S, Si, etc. Where a specific level of saturation is intended, the nomenclature "heterocycloalkanyl" or "heterocycloalkenyl" is used. Examples of heterocycloalkyl groups include, but are not limited to, groups derived from epoxides, azirines, thiiranes, imidazolidine, morpholine, piperazine, piperidine, pyrazolidine, pyrrolidine, quinuclidine.

[0035] "Heterocycloalkylalkyl" by itself or as part of another substituent refers to an acyclic alkyl radical in which one of the hydrogen atoms bonded to a carbon atom, typically a terminal or sp³ carbon atom, is replaced with a heterocycloalkyl group. Where specific alkyl moieties are intended, the nomenclature heterocycloalkylalkanyl, heterocycloalkylalkenyl, or heterocycloalkylalkynyl is used. In certain embodiments, a heterocycloalkylalkyl group is a 6- to 30-membered heterocycloalkylalkyl, e.g., the alkanyl, alkenyl, or alkynyl moiety of the heterocycloalkylalkyl is 1- to 10-membered and the heterocycloalkyl moiety is a 5- to 20-membered heterocycloalkyl, and in certain embodiments, 6- to 20-membered heterocycloalkylalkyl, e.g., the alkanyl, alkenyl, or alkynyl moiety of the heterocycloalkylalkyl is 1- to 8-membered and the heterocycloalkyl moiety is a 5- to 1,2-membered heterocycloalkyl.

[0036] "Leaving group" refers to an atom or a group capable of being displaced by a nucleophile and includes halogen, such as chloro, bromo, fluoro, and iodo, alkoxy carbonyl (e.g., acetoxy), aryloxy carbonyl, mesyloxy, tosyloxy, trifluor-

omethanesulfonyloxy, aryloxy (e.g., 2,4-dinitrophenoxy), methoxy, N,O-dimethylhydroxylamino.

[0037] "Parent aromatic ring system" refers to an unsaturated cyclic or polycyclic ring system having a conjugated π (pi) electron system. Included within the definition of "parent aromatic ring system" are fused ring systems in which one or more of the rings are aromatic and one or more of the rings are saturated or unsaturated, such as, for example, fluorene, indane, indene, phenalene, etc. Examples of parent aromatic ring systems include, but are not limited to, aceanthrylene, acenaphthylene, acephenanthrylene, anthracene, azulene, benzene, chrysene, coronene, fluoranthene, fluorene, hexacene, hexaphene, hexalene, *as*-indacene, *s*-indacene, indane, indene, naphthalene, octacene, octaphene, octalene, ovalene, penta-2,4-diene, pentacene, pentalene, pentaphene, perylene, phenalene, phenanthrene, picene, pleiadene, pyrene, pyranthrene, rubicene, triphenylene, trinaphthalene.

[0038] "Parent heteroaromatic ring system" refers to a parent aromatic ring system in which one or more carbon atoms (and any associated hydrogen atoms) are independently replaced with the same or different heteroatom. Examples of heteroatoms to replace the carbon atoms include, but are not limited to, N, P, O, S, Si, etc. Specifically included within the definition of "parent heteroaromatic ring systems" are fused ring systems in which one or more of the rings are aromatic and one or more of the rings are saturated or unsaturated, such as, for example, arsindole, benzodioxan, benzofuran, chromane, chromene, indole, indoline, xanthene, etc. Examples of parent heteroaromatic ring systems include, but are not limited to, arsindole, carbazole, β -carboline, chromane, chromene, cinnoline, furan, imidazole, indazole, indole, indoline, indolizine, isobenzofuran, isochromene, isoindole, isoindoline, isoquinoline, isothiazole, isoxazole, naphthyridine, oxadiazole, oxazole, perimidine, phenanthridine, phenanthroline, phenazine, phthalazine, pteridine, purine, pyran, pyrazine, pyrazole, pyridazine, pyridine, pyrimidine, pyrrole, pyrrolizine, quinazoline, quinoline, quinolizine, quinoxaline, tetrazole, thiadiazole, thiazole, thiophene, triazole, xanthene.

[0039] "Perhaloalkyl" is a subset of substituted alkyl wherein each hydrogen atom is replaced with the same or different halogen atom. Examples of perhaloalkyl includes, but is not limited to, $-\text{CF}_3$, $-\text{CF}_2\text{CF}_3$, and $-\text{C}(\text{CF}_3)_3$.

[0040] "Perhaloalkoxy" is a subset of substituted alkoxy wherein each hydrogen atom of R^{31} is replaced with the same or different halogen atom. Examples of perhaloalkoxy includes, but is not limited to, $-\text{OCF}_3$, $-\text{OCF}_2\text{CF}_3$, and $-\text{OC}(\text{CF}_3)_3$.

[0041] "Protecting group" refers to a grouping of atoms, which when attached to a reactive group in a molecule masks, reduces, or prevents that reactivity. Examples of protecting groups can be found in Wuts and Greene, "Protective Groups in Organic Synthesis," John Wiley & Sons, 4th ed. 2006; Harrison et al., "Compendium of Organic Synthetic Methods," Vols. 1-11, John Wiley & Sons 1971-2003; Larock "Comprehensive Organic Transformations," John Wiley & Sons, 2nd ed. 2000; and Paquette, "Encyclopedia of Reagents for Organic Synthesis," John Wiley & Sons, 11th ed. 2003. Examples of amino protecting groups include, but are not limited to, formyl, acetyl, trifluoroacetyl, benzyl, benzyloxycarbonyl (CBZ), *tert*-butoxycarbonyl (Boc), trimethylsilyl (TMS), 2-trimethylsilyl-ethanesulfonyl (SES), trityl and substituted trityl groups, allyloxycarbonyl, 9-fluorenylmethyloxycarbonyl (Fmoc), nitro-veratryloxycarbonyl (NVOC), and the like. Examples of hydroxy protecting groups include, but are not limited to, those in which the hydroxy group is either acylated or alkylated such as benzyl, and trityl ethers as well as alkyl ethers, tetrahydropyranyl ethers, trialkylsilyl ethers, and allyl ethers.

[0042] "Silyl" by itself or as part of another substituent refers to a radical of the formula $-\text{SiR}^{30}\text{R}^{31}\text{R}^{31}$ where each of R^{30} , R^{31} , and R^{31} is independently selected from alkyl, alkoxy, and phenyl, which can each be substituted, as defined herein.

[0043] "Siloxy" by itself or as part of another substituent refers to a radical of the formula $-\text{OSiR}^{30}\text{R}^{31}\text{R}^{31}$ where each of R^{30} , R^{31} , and R^{31} is independently selected from alkyl, alkoxy, and phenyl, which can each be substituted, as defined herein.

[0044] "Substituted" refers to a group in which one or more hydrogen atoms are independently replaced with the same or different substituent(s). Examples of substituents include, but are not limited to, $-\text{R}^{64}$, $-\text{R}^{60}$, $-\text{O}^-$, $(-\text{OH})$, $=\text{O}$, $-\text{OR}^{60}$, $-\text{SR}^{60}$, $-\text{S}^-$, $=\text{S}$, $-\text{NR}^{60}\text{R}^{61}$, $=\text{NR}^{60}$, $-\text{CX}_3$, $-\text{CN}$, $-\text{CF}_3$, $-\text{OCN}$, $-\text{SCN}$, $-\text{NO}$, $-\text{NO}_2$, $=\text{N}_2$, $-\text{N}_3$, $-\text{S}(\text{O})_2\text{O}^-$, $-\text{S}(\text{O})_2\text{OH}$, $-\text{S}(\text{O})_2\text{R}^{60}$, $-\text{OS}(\text{O})_2\text{O}^-$, $-\text{OS}(\text{O})_2\text{R}^{60}$, $-\text{P}(\text{O})(\text{O}^-)_2$, $-\text{P}(\text{O})(\text{OR}^{60})(\text{O}^-)$, $-\text{OP}(\text{O})(\text{OR}^{60})(\text{OR}^{61})$, $-\text{C}(\text{O})\text{R}^{60}$, $-\text{C}(\text{S})\text{R}^{60}$, $-\text{C}(\text{O})\text{OR}^{60}$, $-\text{C}(\text{O})\text{NR}^{60}\text{R}^{61}$, $-\text{C}(\text{O})\text{O}^-$, $-\text{C}(\text{S})\text{OR}^{60}$, $-\text{NR}^{62}\text{C}(\text{O})\text{NR}^{60}\text{R}^{61}$, $-\text{NR}^{62}\text{C}(\text{S})\text{NR}^{60}\text{R}^{61}$, $-\text{NR}^{62}\text{C}(\text{NR}^{63})\text{NR}^{60}\text{R}^{61}$, $-\text{C}(\text{NR}^{62})\text{NR}^{60}\text{R}^{61}$, $-\text{S}(\text{O})_2$, $\text{NR}^{60}\text{R}^{61}$, $-\text{NR}^{63}(\text{O})_2\text{R}^{60}$, $-\text{NR}^{62}\text{C}(\text{O})\text{R}^{60}$, and $-\text{S}(\text{O})\text{R}^{60}$ where each $-\text{R}^{64}$ is independently a halogen; each R^{60} and R^{61} are independently hydrogen, alkyl, substituted alkyl, alkoxy, substituted alkoxy, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, arylalkyl, substituted arylalkyl, heteroarylalkyl, or substituted heteroarylalkyl, or R^{60} and R^{61} together with the nitrogen atom to which they are bonded form a heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, or substituted heteroaryl ring, and R^{62} and R^{63} are independently hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, arylalkyl, substituted arylalkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, substituted heteroaryl, heteroarylalkyl, or substituted heteroarylalkyl, or R^{62} and R^{63} together with the atom to which they are bonded form one or more heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, or substituted heteroaryl rings. In certain embodiments, a tertiary amine or aromatic nitrogen may be substituted with one or more oxygen atoms to form the corresponding nitrogen oxide.

[0045] "Sulfonate" by itself or as part of another substituent refers to a sulfur radical of the formula $-\text{S}(\text{O})_2\text{O}^-$.

[0046] "Sulfonyl" by itself or as part of another substituent refers to a sulfur radical of the formula $-\text{S}(\text{O})_2\text{R}^{60}$ where

R⁶⁰ may be selected from hydrogen, alkyl, substituted alkyl, alkoxy, substituted alkoxy, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, arylalkyl, substituted arylalkyl, heteroarylalkyl, and substituted heteroarylalkyl.

[0047] In certain embodiments, substituted aryl and substituted heteroaryl include one or more of the following substitute groups: F, Cl, Br, I, C₁₋₃ alkyl, substituted alkyl, C₁₋₃ alkoxy, -S(O)₂NR⁵⁰R⁵¹, -NR⁵⁰R⁵¹, -CF₃, -OCF₃, -CN, -NR⁵⁰S(O)₂R⁵¹, -NR⁵⁰C(O)R⁵¹, C₅₋₁₀ aryl, substituted C₅₋₁₀ aryl, C₅₋₁₀ heteroaryl, substituted C₅₋₁₀ heteroaryl, -C(O)OR⁵⁰, -NO₂, -C(O)R⁵⁰, -C(O)NR⁵⁰R⁵¹, -OCHF₂, C₁₋₃ acyl, -SR⁵⁰, -S(O)₂OH, -S(O)₂R⁵⁰, -S(O)R⁵⁰, -G(S)R⁵⁰, -C(O)O⁻, -C(S)OR⁵⁰, -NR⁵⁰C(O)NR⁵¹R⁵², -NR⁵⁰C(S)NR⁵¹R⁵², and -C(NR⁵⁰)NR⁵¹R⁵², C₃₋₈cycloalkyl, and substituted C₃₋₈cycloalkyl, wherein R⁵⁰, R⁵¹, and R⁵² are each independently selected from hydrogen and C₁-C₄alkyl.

[0048] As used in this specification and the appended claims, the articles "a," "an," and "the" include plural referents unless expressly and unequivocally limited to one referent.

[0049] Unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and other properties or parameters used in the specification are to be understood as being modified in all instances by the term "about." Accordingly, unless otherwise indicated, it should be understood that the numerical parameters set forth in the following specification and attached claims are approximations. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, numerical parameters should be read in light of the number of reported significant digits and the application of ordinary rounding techniques.

[0050] All numerical ranges herein include all numerical values and ranges of all numerical values within the recited range of numerical values. Further, while the numerical ranges and parameters setting forth the broad scope of the disclosure are approximations as discussed above, the numerical values set forth in the Examples section are reported as precisely as possible. It should be understood, however, that such numerical values inherently contain certain errors resulting from the measurement equipment and/or measurement technique.

[0051] As used herein the term "liquid crystal cell" refers to a structure containing a liquid crystal material that is capable of being ordered. Active liquid crystal cells are cells wherein the liquid crystal material is capable of being switched between ordered and disordered states or between two ordered states by the application of an external force, such as electric or magnetic fields. Passive liquid crystal cells are cells wherein the liquid crystal material maintains an ordered state. One non-limiting example of an active liquid crystal cell element, or device is a liquid crystal display.

[0052] The phrase "an at least partial coating" means an amount of coating covering from a portion to the complete surface of the substrate. The phrase "an at least partially cured coating" refers to a coating in which the curable or crosslinkable components are at least partially cured, crosslinked and/or reacted. In alternate non-limiting embodiments, the degree of reacted components, can vary widely, e.g., from 5% to 100% of all the possible curable, crosslinkable and/or reactable components.

[0053] The phrase "an at least partially abrasion resistant coating or film" refers to a coating or film that demonstrates a Bayer Abrasion Resistance Index of from at least 1.3 to 10.0 in ASTM F-735 Standard Test Method for Abrasion Resistance of Transparent Plastics and Coatings Using the Oscillating Sand Method. The phrase "an at least partially antireflective coating" is a coating that at least partially improves the antireflective nature of the surface to which it is applied by increasing the percent transmittance as compared to an uncoated surface. The improvement in percent transmittance can range from 1 to 9 percent above the untreated surface. Put another way, the percent transmittance of the treated surface can range from a percentage greater than the untreated surface up to 99.9.

[0054] Various non-limiting embodiments of the disclosure will now be described. One non-limiting embodiment provides a thermally reversible, photochromic compound comprising a Lengthening group L also described hereinafter. Another non-limiting embodiment provides a photochromic compound adapted to have at least a first state and a second state, wherein the thermally reversible, photochromic compound has an average absorption ratio greater than 1.5 in at least one state as determined according to the CELL METHOD, which is described in detail below. Further, according to various non-limiting embodiments, the thermally reversible, photochromic compound has an average absorption ratio greater than 1.5 in an activated state as determined according to the CELL METHOD. As used herein with respect to photochromic compounds, the term "activated state" refers to the photochromic compound when exposed to sufficient actinic radiation to cause the at least a portion of the photochromic compound to switch states.

[0055] Generally speaking, the CELL METHOD of measuring average absorption ratio of a photochromic compound involves obtaining an absorption spectrum for the photochromic compound, in an activated or unactivated state, in each of two orthogonal polarization directions while the photochromic compound is at least partially aligned in an aligned liquid crystal medium that is contained within a cell assembly. More specifically, the cell assembly comprises two opposing glass substrates that are spaced apart by 20 microns +/- 1 micron. The substrates are sealed along two opposite edges to form the cell. The inner surface of each of the glass substrates is coated with a polyimide coating, the surface of which has been at least partially ordered by rubbing. Alignment of the photochromic compound is achieved by introducing the photochromic compound and a liquid crystal medium into the cell assembly and allowing the liquid crystal medium to align with the rubbed polyimide surface. Because the photochromic compound is contained within the liquid crystal medium, alignment of the liquid crystal medium causes the photochromic compound to be aligned. It will be appreciated

by those skilled in the art that the choice of the liquid crystal medium and the temperature used during testing can affect the measured absorption ratio. Accordingly, as set forth in more detail in the Examples, for purposes of the CELL METHOD, absorption ratio measurements are taken at room temperature (73°F +/- 0.5°F or better) and the liquid crystal medium is Licristal® E7 (which is reported to be a mixture of cyanobiphenyl and cyanoterphenyl liquid crystal compounds).

[0056] Once the liquid crystal medium and the photochromic compound are aligned, the cell assembly is placed on an optical bench (which is described in more detail in the Examples). To obtain the average absorption ratio in the activated state, activation of the photochromic compound is achieved by exposing the photochromic compound to UV radiation for a time sufficient to reach a saturated or near saturated state (that is, a state wherein the absorption properties of the photochromic compound do not substantially change over the interval of time during which the measurements are made). Absorption measurements are taken over a period of time (typically 10 to 300 seconds) at 3 second intervals for light that is linearly polarized in a plane perpendicular to the optical bench (referred to as the 0° polarization plane or direction) and light that is linearly polarized in a plane that is parallel to the optical bench (referred to as the 90° polarization plane or direction) in the following sequence: 0°, 90°, 90°, 0° etc. The absorbance of the linearly polarized light by the cell is measured at each time interval for all of the wavelengths tested and the unactivated absorbance (i.e., the absorbance of the cell with the liquid crystal material and the unactivated photochromic compound) over the same range of wavelengths is subtracted to obtain absorption spectra for the photochromic compound in each of the 0° and 90° polarization planes to obtain an average difference absorption spectrum in each polarization plane for the photochromic compound in the saturated or near-saturated state.

[0057] For example, with reference to Fig. 1, there is shown the average difference absorption spectrum (generally indicated **10**) in one polarization plane that was obtained for a photochromic compound according to one non-limiting embodiment disclosed herein. The average absorption spectrum (generally indicated **11**) is the average difference absorption spectrum obtained for the same photochromic compound in the orthogonal polarization plane.

[0058] Based on the average difference absorption spectra obtained for the photochromic compound, the average absorption ratio for the photochromic compound is obtained as follows. The absorption ratio of the photochromic compound at each wavelength in a predetermined range of wavelengths corresponding to $\lambda_{\text{max-vis}} \pm 5$ nanometers (generally indicated as **14** in Fig. 1), wherein $A_{\text{max-vis}}$ is the wavelength at which the photochromic compound had the highest average absorbance in any plane, is calculated according to the following equation:

$$AR_{\lambda_i} = Ab_{\lambda_i}^1 / Ab_{\lambda_i}^2 \quad \text{Eq. 1}$$

wherein, AR_{λ_i} is the absorption ratio at wavelength λ_i , $Ab_{\lambda_i}^1$ is the average absorption at wavelength λ_i in the polarization direction (i.e., 0° or 90°) having the higher absorbance, and $Ab_{\lambda_i}^2$ is the average absorption at wavelength λ_i in the remaining polarization direction. As previously discussed, the "absorption ratio" refers to the ratio of the absorbance of radiation linearly polarized in a first plane to the absorbance of the same wavelength radiation linearly polarized in a plane orthogonal to the first plane, wherein the first plane is taken as the plane with the highest absorbance.

[0059] The average absorption ratio ("AR") for the photochromic compound is then calculated by averaging the individual absorption ratios obtained for the wavelengths within the predetermined range of wavelengths (i.e., $\lambda_{\text{max-vis}} \pm 5$ nanometers) according to the following equation:

$$AR = (\sum AR_{\lambda_i}) / n_i \quad \text{Eq. 2}$$

wherein, AR is average absorption ratio for the photochromic compound, AR_{λ_i} are the individual absorption ratios (as determined above in Eq. 1) for each wavelength within the predetermined the range of wavelengths (i.e., $\lambda_{\text{max-vis}} \pm 5$ nanometers), and n_i is the number of individual absorption ratios averaged.

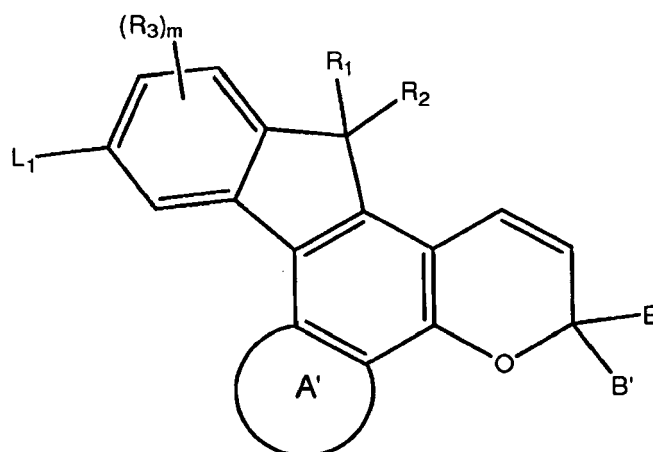
[0060] As previously discussed, conventional thermally reversible photochromic compounds are adapted to switch from a first state to a second state in response to actinic radiation, and to revert back to the first state in response to thermal energy. More specifically, conventional thermally reversible, photochromic compounds are capable of transforming from one isomeric form (for example and without limitation, a closed form) to another isomeric form (for example and without limitation, an open form) in response to actinic radiation, and reverting back to the closed form when exposed to thermal energy. However, as previously discussed, generally conventional thermally reversible photochromic compounds do not strongly demonstrate dichroism.

[0061] As discussed above, non-limiting embodiments disclosed herein provide a thermally reversible photochromic compound having an average absorption ratio greater than 1.5 in at least one state as determined according to CELL METHOD and/or a thermally reversible photochromic compound that can be used as an intermediate in the preparation of a photochromic compound having an absorption ratio greater than 1.5. Thus, the thermally reversible photochromic

compound according to this non-limiting embodiment can display useful photochromic properties and/or useful photochromic and dichroic properties. That is, the thermally reversible, photochromic compound can be a thermally reversible, photochromic and/or photochromic-dichroic compound. As used herein with respect to the photochromic compounds described herein, the term "photochromic-dichroic" means displaying both photochromic and dichroic properties under certain conditions, which properties are at least detectable by instrumentation.

[0062] According to other non-limiting embodiments, the thermally reversible photochromic compounds can be thermally reversible photochromic-dichroic compounds having an average absorption ratio ranging from 4 to 20, from 3 to 30, or from 2.0 to 50 in at least one state as determined according to CELL METHOD. It will be appreciated by those skilled in the art that the higher the average absorption ratio of the photochromic compound the more linearly polarizing the photochromic compound will be. Therefore, according to various non-limiting embodiments, the thermally reversible photochromic compounds can have any average absorption ratio required to achieve a desired level of linear polarization.

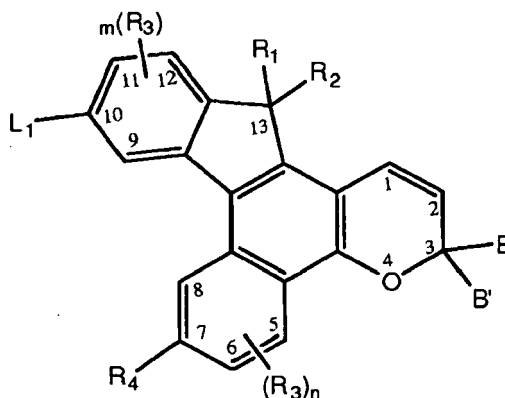
[0063] In some embodiments, the compounds described herein may be photochromic and/or dichroic compounds, and may be represented by the following graphic Formula I, wherein the definitions of the substituents have the same meaning as described herein unless otherwise stated:



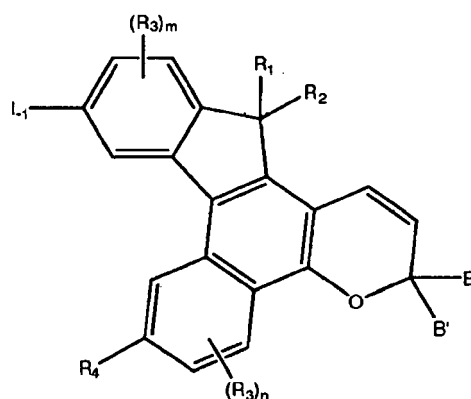
Formula I

wherein A' represents an optionally substituted aryl or optionally substituted heteroaryl. With reference to Formula I, A' may comprise any of the "aryl" or "heteroaryl" groups previously defined above, including monocyclic and multicyclic groups. Further, A' may be unsubstituted, monosubstituted, or multisubstituted, wherein each substituent is independently selected from the groups as previously defined above for the term "substituted." Also, the optional substituents may be independently selected from the groups defined below for R₃ and R₄ in Formula IA. Additionally, A' may be substituted with 0-10 groups, for example, A' may be substituted with 0-8 groups, or A' may be substituted with 0-6 groups, or A' may be substituted with 0-4 groups or A' may be substituted with 0-3 groups.

[0064] The compounds described herein may be represented by the following graphic formula, in which the numbers represent the numbers of the ring atoms of the naphthopyran and in the definitions of the substituents have the same meaning described herein unless stated otherwise:



[0065] More specifically, the compounds described herein are represented by the following graphic Formula IA:



Formula IA

wherein:

R₁ and R₂ are each independently selected from hydrogen, hydroxy and chiral or achiral groups selected from optionally substituted heteroalkyl, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, halogen, optionally substituted amino, carboxy, alkylcarbonyl, alkoxy carbonyl, optionally substituted alkoxy, and aminocarbonyl, or R₁ and R₂ may be taken together with any intervening atoms to form a group selected from oxo, optionally substituted cycloalkyl, and optionally substituted heterocycloalkyl;

R₃ for each occurrence, is independently selected from chiral or achiral groups selected from formyl, alkylcarbonyl, alkoxy carbonyl, aminocarbonyl, arylcarbonyl, aryloxy carbonyl, aminocarbonyloxy, alkoxy carbonylamino, aryloxy carbonylamino, boronic acid, boronic acid esters, cycloalkoxy carbonylamino, heterocycloalkyloxy carbonylamino, heteroaryloxy carbonylamino, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, halogen, optionally substituted cycloalkyl, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted alkoxy, optionally substituted heteroalkyl, optionally substituted heterocycloalkyl, and optionally substituted amino;

R₄ is selected from hydrogen, R₃ and L₂;

m and n are each independently an integer selected from 0 to 3;

B and B' are each independently selected from L₃, hydrogen, halogen, and chiral or achiral groups selected from metallocenyl, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted heterocycloalkyl, and optionally substituted cycloalkyl, or wherein B and B' are taken together with any intervening atoms to form a group selected from optionally substituted cycloalkyl and optionally substituted heterocycloalkyl; and

L₁, L₂, and L₃ for each occurrence, are independently selected from a chiral or achiral lengthening group represented by:

-[S₁]_c-[Q₁ -[S₂]_d]_{d'} -[Q₂ -[S₃]_e]_{e'} -[Q₃ -[4]_f]_{f'} -S₅-P wherein:

(a) Q_1 , Q_2 , and Q_3 for each occurrence, are independently selected from a divalent group selected from optionally substituted aryl, optionally substituted heteroaryl, optionally substituted cycloalkyl, and optionally substituted heterocycloalkyl;

wherein substituents are independently selected from P, liquid crystal mesogens, halogen, poly(C_1 - C_{18} alkoxy), C_1 - C_{18} alkoxycarbonyl, C_1 - C_{18} alkylcarbonyl, C_1 - C_{18} alkoxycarbonyloxy, aryloxy carbonyloxy, perfluoro(C_1 - C_{18})alkoxy, perfluoro(C_1 - C_{18})alkoxycarbonyl, perfluoro(C_1 - C_{18})alkylcarbonyl, perfluoro(C_1 - C_{18})alkylamino, di-(perfluoro(C_1 - C_{18})alkyl)amino, perfluoro(C_1 - C_{18})alkylthio, C_1 - C_{18} alkylthio, C_1 - C_{18} acetyl, C_3 - C_{10} cycloalkyl, C_3 - C_{10} cycloalkoxy, straight-chain C_1 - C_{18} alkyl, and branched C_1 - C_{18} alkyl;

wherein said straight-chain C_1 - C_{18} alkyl and branched C_1 - C_{18} alkyl are mono-substituted with a group selected from cyano, halogen, and C_1 - C_{18} alkoxy; or

wherein said straight-chain C_1 - C_{18} alkyl and branched C_1 - C_{18} alkyl are poly-substituted with at least two groups independently selected from halogen, $-M(T)_{(t-1)}$ and $-M(OT)_{(t-1)}$, wherein M is chosen from aluminum, antimony, tantalum, titanium, zirconium and silicon, T is chosen from organofunctional radicals, organofunctional hydrocarbon radicals, aliphatic hydrocarbon radicals and aromatic hydrocarbon radicals, and t is the valence of M;

(b) c, d, e, and f are each independently chosen from an integer from 1 to 20; and each S_1 , S_2 , S_3 , S_4 , and S_5 is independently chosen for each occurrence from a spacer unit selected from:

(i) optionally substituted alkylene, optionally substituted haloalkylene, $-\text{Si}(\text{CH}_2)_g-$, and $-\text{Si}[(\text{CH}_3)_2\text{O}]_h-$, wherein g for each occurrence is independently chosen from an integer from 1 to 20; h for each occurrence is independently chosen from an integer from 1 to 16; and said substituents for the alkylene and haloalkylene are independently selected from C_1 - C_{18} alkyl, C_3 - C_{10} cycloalkyl and aryl;

(ii) $-\text{N}(\text{Z})-$, $-\text{C}(\text{Z})=\text{C}(\text{Z})-$, $-\text{C}(\text{Z})=\text{N}-$, $-\text{C}(\text{Z}')_2-\text{C}(\text{Z}')_2-$, and a single bond, wherein Z for each occurrence is independently selected from hydrogen, C_1 - C_{18} alkyl, C_3 - C_{10} cycloalkyl and aryl, and Z' for each occurrence is independently selected from C_1 - C_{18} alkyl, C_3 - C_{10} cycloalkyl and aryl; and

(iii) $-\text{O}-$, $-\text{C}(=\text{O})-$, $-\text{C}\equiv\text{C}-$, $-\text{N}=\text{N}-$, $-\text{S}-$, $-\text{S}(=\text{O})-$, $-\text{O}(=\text{S})(=\text{O})-$, $-\text{O}(=\text{S})(=\text{O})\text{O}-$, $-\text{O}(=\text{S})(=\text{O})\text{O}-$ and straight-chain or branched C_1 - C_{24} alkylene residue, said C_1 - C_{24} alkylene residue being unsubstituted, mono-substituted by cyano or halogen, or poly-substituted by halogen,

provided that when two spacer units comprising heteroatoms are linked together the spacer units are linked so that heteroatoms of the first spacer unit are not directly linked to the heteroatoms of the second spacer unit, and

provided that when S_1 and S_5 are linked to Formula I and P, respectively, they are linked so that two heteroatoms are not directly linked to each other;

(c) P for each occurrence is independently selected from hydroxy, amino, C_2 - C_{18} alkenyl, C_2 - C_{18} alkynyl, azido, silyl, siloxy, silylhydride, (tetrahydro-2H-pyran-2-yl)oxy, thio, isocyanato, thioisocyanato, acryloyloxy, methacryloyloxy, 2-(acryloyloxy)ethylcarbonyl, 2-(methacryloyloxy)ethylcarbonyl, aziridinyl, allyloxy carbonyloxy, epoxy, carboxylic acid, carboxylic ester, acryloylamino, methacryloylamino, aminocarbonyl, C_1 - C_{18} alkyl aminocarbonyl, aminocarbonyl(C_1 - C_{18})alkyl, C_1 - C_{18} alkylalkoxy carbonyloxy, halocarbonyl, hydrogen, aryl, hydroxy(C_1 - C_{18})alkyl, C_1 - C_{18} alkyl, C_1 - C_{18} alkoxy, amino(C_1 - C_{18})alkyl, C_1 - C_{18} alkylamino, di-(C_1 - C_{18})alkylamino, C_1 - C_{18} alkyl(C_1 - C_{18})alkoxy, C_1 - C_{18} alkoxy(C_1 - C_{18})alkoxy, nitro, poly(C_1 - C_{18})alkyl ether, (C_1 - C_{18})alkyl(C_1 - C_{18})alkoxy(C_1 - C_{18})alkyl, polyethyleneoxy, polypropyleneoxy, ethylene, acryloyl, acryloyloxy(C_1 - C_{18})alkyl, methacryloyl, methacryloyloxy(C_1 - C_{18})alkyl, 2-chloroacryloyl, 2-phenylacryloyl, acryloyloxyphenyl, 2-chloroacryloylamino, 2-phenylacryloylamino, oxetanyl, glycidyl, cyano, isocyanato(C_1 - C_{18})alkyl, itaconic acid ester, vinyl ether, vinyl ester, a styrene derivative, main-chain and side-chain liquid crystal polymers, siloxane derivatives, ethyleneimine derivatives, maleic acid derivatives, maleimide derivatives, fumaric acid derivatives, unsubstituted cinnamic acid derivatives, cinnamic acid derivatives that are substituted with at least one of methyl, methoxy, cyano and halogen, and substituted or unsubstituted chiral or non-chiral monovalent or divalent groups chosen from steroid radicals, terpenoid radicals, alkaloid radicals and mixtures thereof, wherein the substituents are independently chosen from C_1 - C_{18} alkyl, C_1 - C_{18} alkoxy, amino, C_3 - C_{10} cycloalkyl, C_1 - C_{18} alkyl(C_1 - C_{18})alkoxy, fluoro(C_1 - C_{18})alkyl, cyano, cyano(C_1 - C_{18})alkyl, cyano(C_1 - C_{18})alkoxy or mixtures thereof, or P is a structure having from 2 to 4 reactive groups or P is an unsubstituted or substituted ring opening metathesis polymerization precursor or P is a substituted or unsubstituted photochromic compound; and

(d) d', e' and f are each independently chosen from 0, 1, 2, 3, and 4, provided that a sum of d' + e' + f is at least 2.

[0066] With referene to Formula IA, R_1 and R_2 each independently can be selected from hydrogen, hydroxy, and chiral and achiral groups selected from optionally substituted heteroalkyl, optionally substituted alkyl, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted cycloalkyl/halogen, optionally substituted amino, carboxy,

alkylcarbonyl, alkoxy carbonyl, optionally substituted alkoxy, and aminocarbonyl or R_1 and R_2 may be taken together with any intervening atoms to form a group selected from oxo, optionally substituted cycloalkyl and optionally substituted heterocycloalkyl;

R_3 for each occurrence, independently can be selected from formyl, alkylcarbonyl, alkoxy carbonyl, aminocarbonyl, arylcarbonyl, aryloxy carbonyl, optionally substituted alkyl, boronic acid ester, halogen, optionally substituted cycloalkyl, optionally substituted aryl, optionally substituted alkoxy, optionally substituted heteroalkyl, optionally substituted heterocycloalkyl and optionally substituted amino;

m and n each independently can be an integer selected from 0 to 2;

B and B' each independently can be selected from L_3 , hydrogen, halogen, chiral or achiral groups selected from optionally substituted alkyl, optionally substituted alkenyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted aryl, optionally substituted heteroaryl, and optionally substituted cycloalkyl, or wherein B and B' are taken together with any intervening atoms to form a group selected from optionally substituted cycloalkyl and optionally substituted heterocycloalkyl;

L_1 , L_2 , and L_3 for each occurrence, independently can be selected from a chiral or achiral lengthening group represented by:

$-[S_1]_c-[Q_1-[S_2]_d]_{d'}-[Q_2-[S_3]_e]_e'-[Q_3-[S_4]_f]_f'-S_5-P$ wherein:

(a) Q_1 , Q_2 , and Q_3 for each occurrence, are independently selected from a divalent group selected from optionally substituted aryl and optionally substituted heteroaryl, optionally substituted cycloalkyl and optionally substituted heterocycloalkyl;

wherein substituents are independently selected from P, liquid crystal mesogens, halogen, poly(C_1-C_{12} alkoxy), C_1-C_{12} alkoxy carbonyl, C_1-C_{12} alkylcarbonyl, perfluoro(C_1-C_{12})alkoxy, perfluoro(C_1-C_{12})alkoxy carbonyl, perfluoro(C_1-C_{12})alkylcarbonyl, C_1-C_{18} acetyl, C_3-C_7 cycloalkyl, C_3-C_7 cycloalkoxy, straight-chain C_1-C_{12} alkyl, and branched C_1-C_{12} alkyl,

wherein said straight-chain C_1-C_{12} alkyl and branched C_1-C_{12} alkyl are mono-substituted with a group selected from, halogen, C_1-C_{12} alkoxy, or

wherein said straight-chain C_1-C_{12} alkyl and branched C_1-C_{12} alkyl are poly-substituted with at least two groups independently selected from halogen;

(b) c, d, e, and f are each independently chosen from an integer from 1 to 10; and each S_1 , S_2 , S_3 , S_4 , and S_5 is independently chosen for each occurrence from a spacer unit selected from:

(i) substituted or unsubstituted alkylene, substituted or unsubstituted haloalkylene, $-Si(CH_2)_g-$, and $-(Si[(CH_3)_2]O)_h-$, wherein g for each occurrence is independently chosen from an integer from 1 to 10; h for each occurrence is independently chosen from an integer from 1 to 8; and said substitutes for the alkylene and haloalkylene are independently selected from C_1-C_{12} alkyl, C_3-C_7 cycloalkyl and phenyl;

(ii) $-N(Z)-$, $-C(Z)=C(Z)-$, and a single bond, wherein Z for each occurrence is independently selected from hydrogen, C_1-C_{12} alkyl, C_3-C_7 cycloalkyl and phenyl; and

(iii) $-O-$, $-C(=O)-$, $-C\equiv C-$, $-N=N-$, $-S-$, and $-S(=O)-$,

provided that when two spacer units comprising heteroatoms are linked together the spacer units are linked so that heteroatoms of the first spacer unit are not directly linked to the heteroatoms of the second spacer unit, and provided that when S_1 and S_5 are linked to Formula I and P, respectively, they are linked so that two heteroatoms are not directly linked to each other;

(c) P for each occurrence is independently selected from hydroxy, amino, C_2-C_{12} alkenyl, C_2-C_{12} alkenyl, silyl, siloxy, (tetrahydro-2H-pyran-2-yl)oxy, isocyanato, acryloyloxy, methacryloyloxy, epoxy, carboxylic acid, carboxylic ester, C_1-C_{12} alkyloxy carbonyloxy, halocarbonyl, hydrogen, aryl, hydroxy(C_1-C_{12})alkyl, C_1-C_{12} alkyl, C_1-C_{12} alkoxy, ethylene, acryloyl, acryloyloxy(C_1-C_{12})alkyl, methacryloyl, methacryloyloxy(C_1-C_{12})alkyl, oxetanyl, glycidyl, vinyl ether, siloxane derivatives, unsubstituted cinnamic acid derivatives, cinnamic acid derivatives that are substituted with at least one of methyl, methoxy, cyano and halogen, and substituted or unsubstituted chiral or non-chiral monovalent or divalent groups chosen from steroid radicals, wherein each substituent is independently chosen from C_1-C_{12} alkyl, C_1-C_{12} alkoxy, amino, C_3-C_7 cycloalkyl, C_1-C_{12} alkyl(C_1-C_{12})alkoxy, or fluoro(C_1-C_{12})alkyl, or P is a structure having from 2 to 4 reactive groups; and

(d) d', e' and f' are each independently chosen from 0, 1, 2, 3, and 4, provided that a sum of d' + e' + f' is at least 2.

[0067] Additionally, R_1 and R_2 are each independently can be selected from hydrogen, hydroxy, and chiral groups selected from optionally substituted heteroalkyl, optionally substituted alkyl, optionally substituted aryl, optionally substituted cycloalkyl, halogen, carboxy, alkylcarbonyl, alkoxy carbonyl, optionally substituted alkoxy, and aminocarbonyl or R_1 and R_2 may be taken together with any intervening atoms to form a group selected from oxo and optionally

substituted cycloalkyl;

R₃ for each occurrence, independently can be selected from alkylcarbonyl, alkoxy carbonyl, aminocarbonyl, optionally substituted alkyl, boronic acid ester, halogen, optionally substituted cycloalkyl, optionally substituted aryl, optionally substituted alkoxy, optionally substituted heterocycloalkyl and optionally substituted amino;

where m and n are each independently an integer selected from 0 to 2;

B and B' are each independently selected from L₃, hydrogen, chiral groups selected from optionally substituted alkyl, optionally substituted alkenyl, optionally substituted aryl, optionally substituted heteroaryl, and optionally substituted cycloalkyl, or wherein B and B' are taken together with any intervening atoms to form a group selected from optionally substituted cycloalkyl;

L₁, L₂, and L₃ for each occurrence, are independently selected from a chiral or achiral lengthening group represented by:

- [S₁]_c-[Q₁-[S₂]_d]_{d'}-[Q₂-[S₃]_e]_{e'}-[Q₃-[S₄]_f]_{f'}-S₅-P wherein:

(a) Q₁, Q₂, and Q₃ for each occurrence, are independently selected from a divalent group selected from optionally substituted aryl and optionally substituted heteroaryl, optionally substituted cycloalkyl and optionally substituted heterocycloalkyl;

wherein substituents are independently selected from P, C₁-C₆ alkoxy carbonyl, perfluoro(C₁-C₆)alkoxy, C₃-C₇ cycloalkyl, C₃-C₇ cycloalkoxy, straight-chain C₁-C₆ alkyl, and branched C₁-C₆ alkyl,

wherein said straight-chain C₁-C₆ alkyl and branched C₁-C₆ alkyl are mono-substituted with a group selected from halogen and C₁-C₁₂ alkoxy, or

wherein said straight-chain C₁-C₆ alkyl and branched C₁-C₆ alkyl are poly-substituted with at least two groups independently selected from halogen;

(b) c, d, e, and f are each independently chosen from an integer from 1 to 10; and each S₁, S₂, S₃, S₄, and S₅ is independently chosen for each occurrence from a spacer unit selected from:

(i) substituted or unsubstituted alkylene;

(ii) -N(Z)-, -C(Z)=C(Z)-, and a single bond, wherein Z for each occurrence is independently selected from hydrogen and C₁-C₆ alkyl; and

(iii) -O-, -C(=O)-, -C≡C-, and -N=N-, -S-;

provided that when two spacer units comprising heteroatoms are linked together the spacer units are linked so that heteroatoms of the first spacer unit are not directly linked to the heteroatoms of the second spacer unit, and

provided that when S₁ and S₅ are linked to Formula I and P, respectively, they are linked so that two heteroatoms are not directly linked to each other;

(c) P for each occurrence is independently selected from hydroxy, amino, C₂-C₆ alkenyl, C₂-C₆ alkenyl, siloxy, (tetrahydro-2H-pyran-2-yl)oxy, isocyanato, acryloyloxy, methacryloyloxy, epoxy, carboxylic acid, carboxylic ester, C₁-C₆ alkoxy carbonyloxy, hydrogen, aryl, hydroxy(C₁-C₆)alkyl, C₁-C₆ alkyl, ethylene, acryloyl, acryloyloxy(C₁-C₁₂)alkyl, oxetanyl, glycidyl, vinyl ether, siloxane derivatives, and substituted or unsubstituted chiral or non-chiral monovalent or divalent groups chosen from steroid radicals, wherein each substituent is independently chosen from C₁-C₆ alkyl, C₁-C₆ alkoxy, amino, C₃-C₇ cycloalkyl.

[0068] More specifically, R₁ and R₂ are each independently can be selected from methyl, ethyl, propyl and butyl; R₃ and R₄ for each occurrence are independently can be selected from methyl, ethyl, bromo, chloro, fluoro, iodo, methoxy, ethoxy and CF₃; B and B' are each independently selected from phenyl substituted with one or more groups independently selected from aryl, heteroaryl, heterocycloalkyl, alkyl, alkenyl, alkynyl, alkoxy, halogen, amino, alkylcarbonyl, carboxy, and alkoxy carbonyl; and for L₁: Q₁ is unsubstituted aryl; e' is 1 or 2; e each occurrence is 1; S₃ for each occurrence is a single bond; Q₂ for each occurrence is independently selected from optionally substituted aryl; f' is 1; f is 1; S₄ is a single bond; and Q₃ is optionally substituted cycloalkyl; S₅ is -(CH₂)_g-, wherein g is an integer from 1 to 20; and P is hydrogen.

[0069] Typically, R₁ and R₂ are methyl; R₃ and R₄ for each occurrence are independently selected from methyl, bromo, chloro, fluoro, methoxy, and CF₃; B and B' are each independently selected from phenyl substituted with one group selected from C₁-C₄ alkoxy, fluoro, CF₃, piperidinyl, and morpholino; and for L₁: Q₁ is unsubstituted phenyl; Q₂ for each occurrence is unsubstituted phenyl; Q₃ is unsubstituted cyclohexyl; and g is 5.

[0070] In the compounds of the present invention, L₁ can be selected from:

4-[4-(4-butyl-cyclohexyl)-phenyl]-cyclohexyloxy;

4"-butyl-[1,1',4',1"]tercyclohexan-4-yloxy;

4-[4-(4-butyl-phenyl)-cyclohexyloxycarbonyl]-phenoxy;
 4'-(4-butyl-benzoyloxy)-biphenyl-4-carbonyloxy;
 4-(4-pentyl-phenylazo)-phenylcarbamoyle;
 4-(4-dimethylamino-phenylazo)-phenylcarbamoyle;
 5 4-[5-(4-propyl-benzoyloxy)-pyrimidin-2-yl]-phenyl
 4-[2-(4'-methyl-biphenyl-4-carbonyloxy)-1,2-diphenyl-ethoxycarbonyl]-phenyl;
 4-(1,2-diphenyl-2-{3-[4-(4-propyl-benzoyloxy)-phenyl]-acryloyloxy}-ethoxycarbonyl)-phenyl;
 4-[4-(4-[4-[3-(6-{4-[4-(4-nonyl-benzoyloxy)-phenoxy-carbonyl]-phenoxy}-hexyloxycarbonyl)propionylloxy]-benzoyloxy]-benzoyloxy)-phenyl]-piperazin-1-yl;
 10 4-[4-(4-[4-[4-(4-nonyl-benzoyloxy)-benzoyloxy]-benzoyloxy]-benzoyloxy)-phenyl]-piperazin-1-yl;
 4-(4'-propyl-biphenyl-4-ylethynyl)-phenyl;
 4-(4-fluoro-phenoxy-carbonyloxy)-piperidin-1-yl;
 2-[17-(1,5-dimethyl-hexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxy]-indan-5-yl;;
 15 4-[17-(1,5-dimethyl-hexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxy-carbonyloxy]-piperidin-1-yl;
 4-(biphenyl-4-carbonyloxy)-piperidin-1-yl;
 4-(naphthalene-2-carbonyloxy)-piperidin-1-yl;
 4-(4-phenylcarbamoyle-phenylcarbamoyle)-piperidin-1-yl;
 20 4-(4-(4-phenylpiperidin-1-yl)-benzoyloxy)-piperidin-1-yl;
 4-butyl-[1,1';4',1'']terphenyl-4-yl;
 4-(4-pentadecafluoroheptyloxy-phenylcarbamoyle)-benzoyloxy;
 4-(3-piperidin-4-yl-propyl)-piperidin-1-yl;
 4-(4-[4-[17-(1,5-dimethyl-hexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxy-carbonyloxy]-benzoyloxy]-phenoxy-carbonyl)phenoxy-methyl;
 25 4-[4-(4-cyclohexyl-phenylcarbamoyle)-benzoyloxy]-piperidin-1-yl;
 4-[4-(4-cyclohexyl-phenylcarbamoyle)-benzoyloxy]-piperidin-1-yl;
 N-{4-[(4-pentyl-benzylidene)-amino]-phenyl}-acetamidyl;
 4-(3-piperidin-4-yl-propyl)-piperidin-1-yl;
 30 4-(4-hexyloxy-benzoyloxy)-piperidin-1-yl;
 4-(4'-hexyloxy-biphenyl-4-carbonyloxy)-piperidin-1-yl;
 4-(4-butyl-phenylcarbamoyle)-piperidin-1-yl;
 4-[4-[4-[4-piperidinyl-4-oxy]-phenyl]phenoxy]piperidin-4-yl;
 4-(4-(9-(4-butylphenyl)-2,4,8,10-tetraoxaspiro[5.5]undec-3-yl)phenyl)piperazin-1-yl;
 35 4-(6-(4-butylphenyl)carbonyloxy-(4,8-dioxabicyclo[3:3:0]oct-2-yl)oxycarbonyl)phenyl;
 1-{4-[5-(4-butyl-phenyl)-[1,3]dioxan-2-yl]-phenyl}-4-methyl-piperazin-1-yl;
 4-(7-(4-propylphenylcarbonyloxy)bicyclo[3.3.0]oct-2-yl)oxycarbonyl)phenyl;
 4-[17-(1,5-dimethyl-hexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxy-carbonyloxy;
 40 (4-trans-(4-pentylcyclohexyl)benzamido)phenyl;
 (4-(4-trans-(4-pentylcyclohexyl)phenoxy)carbonyl)phenyl;
 4-(4-(4-trans-(4-pentylcyclohexyl)phenyl)benzamido)phenyl;
 4-((trans-(4'-pentyl-[1,1'-bi(cyclohexan)]-4-yl)oxy)carbonyl)phenyl;
 4-(4'-(4-pentylcyclohexyl)-[1,1'-biphenyl]-4-ylcarboxamido)phenyl;
 45 4-((4'-(4-pentylcyclohexyl)-[1,1'-biphenyl]-4-carbonyl)oxy)benzamido;
 4-(4'-(4-pentylcyclohexyl)-[1,1'-biphenyl]-4-carbonyl)piperazin-1-yl;
 4-(4-(4-trans-(4-pentylcyclohexyl)phenyl)benzamido)-2-(trifluoromethyl)phenyl;
 2-methyl-4-trans-(4-((4'-trans-(4-pentylcyclohexyl)biphenyl-4-yloxy)carbonyl)cyclohexanecarboxamido)phenyl;
 4'-(4'-pentylbi(cyclohexane-4-)carbonyloxy)biphenylcarbonyloxy;
 50 4-(((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxy)carbonyl)piperazin-1-yl; and
 4-((S)-2-methylbutoxy)phenyl)-10-(4-(((3R,3aS,6S,6aS)-6-(4'-trans-(4-pentylcyclohexyl)biphenylcarbonyloxy)hexahydrofuro[3,2-b]furan-3-yloxy)carbonyl)phenyl.

[0071] More specifically, the compounds described herein can be chosen from:

3,3-Bis(4-methoxyphenyl)-10-[4-(4-(trans-4-pentylcyclohexyl)benzamido)phenyl]-13,13-dimethyl-12-bromo-3,13-

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dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3,3-Bis(4-methoxyphenyl)-10-[4-((4-(trans-4-pentylcyclohexyl)phenoxy)carbonyl) phenyl]-6,13,13-trimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

5

3-(4-Fluorophenyl)-3-(4-piperidinophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-11,13,13-trimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

10

3,3-Bis(4-methoxyphenyl)-10-[4-(4-(trans-4-pentylcyclohexyl)benzamido)phenyl]-5,7-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-(4-Methoxyphenyl)-3-(4-piperidinophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-5,7-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

15

3-(4-Methoxyphenyl)-3-(4-morpholinophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-5,7-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

20

3-(4-Fluorophenyl)-3-(4-piperidinophenyl)-10-[4-((4-(trans-4-pentylcyclohexyl)phenoxy)carbonyl)phenyl]-12-bromo-5,7-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-Phenyl-3-(4-piperidinophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-12-bromo-5,7-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

25

3-Phenyl-3-(4-piperidinophenyl)-10-[4-((4-(trans-4-pentylcyclohexyl)phenoxy)carbonyl)phenyl]-12-bromo-5,7-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-(4-Fluorophenyl)-3-(4-piperidinophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-12-bromo-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

30

3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-12-bromo-6,7-dimethoxy-11,13,13-trimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido) phenyl]-6-trifluoromethyl-12-bromo-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

35

3,3-Bis(4-methoxyphenyl)-10,12-bis[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl) benzamido)phenyl]-5,7-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

40

3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido) phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

45

3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl) benzamido)phenyl]-5,7-difluoro-12-bromo-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-(4-Fluorophenyl)-3-(4-morpholinophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl) phenyl)benzamido)phenyl]-6-trifluoromethyl-13-methyl-13-butyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

50

3-(4-Fluorophenyl)-3-(4-morpholinophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl) phenyl)benzamido)phenyl]-5,7-difluoro-12-bromo-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-Phenyl-3-(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl) phenyl)benzamido)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

55

3-Phenyl-3-(4-morpholinophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl) phenyl)benzamido)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

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3,3-Bis(4-fluorophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-12-bromo-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

5 3,3-Bis(4-fluorophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-(4-Methoxyphenyl)-3-(4-butoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl) phenyl)benzamido)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

10 3-(4-Fluorophenyl)-13,13-dimethyl-3-(4-morpholinophenyl)-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-ylcarboxamido)phenyl)-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-(4-Butoxyphenyl)-3-(4-fluorophenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-ylcarboxamido)phenyl)-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

15 3-(4-(4-(4-Methoxyphenyl)piperazin-1-yl)phenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-ylcarboxamido)phenyl)-3-phenyl-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

20 3-(4-Butoxyphenyl)-3-(4-fluorophenyl)-13,13-dimethyl-10-(4-(((trans,trans-4'-pentyl-[1,1'-bi(cyclohexan)]-4-yl)oxy)carbonyl)phenyl)-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-(4-Fluorophenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-ylcarboxamido)phenyl)-3-(4-butoxyphenyl)-6-(trifluoromethyl)-3,13-dihydro indeno[2',3':3,4]naphtho[1,2-b]pyran;

25 3-(4-Methoxyphenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-ylcarboxamido)phenyl)-3-(4-(trifluoromethoxy)phenyl)-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3,3-Bis(4-hydroxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido) phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

30 12-Bromo-3-(4-butoxyphenyl)-3-(4-fluorophenyl)-13,13-dimethyl-10-(4-((4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-carbonyl)oxy)benzamido)-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

35 3-(4-Butoxyphenyl)-5,7-dichloro-11-methoxy-3-(4-methoxyphenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-ylcarboxamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-(4-Butoxyphenyl)-3-(4-fluorophenyl)-13,13-dimethyl-10-(4-((4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-carbonyl)oxy)benzamido)-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

40 5,7-Dichloro-3,3-bis(4-hydroxyphenyl)-11-methoxy-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-ylcarboxamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

6,8-Dichloro-3,3-bis(4-hydroxyphenyl)-11-methoxy-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-ylcarboxamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

45 3-(4-Butoxyphenyl)-5,8-difluoro-3-(4-fluorophenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-ylcarboxamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

50 3-(4-Butoxyphenyl)-3-(4-fluorophenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-carbonyl)piperazin-1-yl)-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-(4-Morpholinophenyl)-3-(4-methoxyphenyl)-10,7-bis[4-(4-(4-(trans-4-pentylcyclohexyl) phenyl)benzamido)phenyl]-5-fluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

55 3-(4-Morpholinophenyl)-3-(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl) phenyl)benzamido)-2-(trifluoromethyl)phenyl]-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)-2-(trifluoromethyl)phenyl]-

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13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-(4-Morpholinophenyl)-3-(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl) phenyl)benzamido)-2-(trifluoromethyl)phenyl]-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3,3-Bis(4-methoxyphenyl)-13,13-dimethyl-10-(2-methyl-4-(trans-4-(4'-(trans-4-pentylcyclohexyl)biphenyl-4-yloxy)carbonyl)cyclohexanecarboxamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-(4-(4-(4-Butylphenyl)piperazin-1-yl)phenyl)-3-(4-methoxyphenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)biphenyl-4-ylcarboxamido)-2-(trifluoromethyl)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-(4-(4-(4-Butylphenyl)piperazin-1-yl)phenyl)-3-(4-methoxyphenyl)-13,13-dimethyl-10-(2-methyl-4-(4'-(trans-4-pentylcyclohexyl)biphenyl-4-ylcarboxamido)phenyl)-7-(4-(4-(trans-4-pentylcyclohexyl)benzamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-(4-Methoxyphenyl)-13,13-dimethyl-7,10-bis(4-(4'-(trans-4-pentylcyclohexyl)biphenyl-4-ylcarboxamido)phenyl)-3-phenyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-p-Tolyl-3-(4-methoxyphenyl)-6-methoxy-13,13-dimethyl-7-(4'-(trans,trans-4'-pentylbi(cyclohexane-4-)carbonyloxy)biphenylcarbonyloxy)-10-(4-(4'-(trans-4-pentylcyclohexyl)biphenyl-4-ylcarboxamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

10-(4-(((3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxy)carbonyl)piperazin-1-yl)-3-(4-methoxyphenyl)-13,13-dimethyl-3-(4-morpholinophenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

6-Methoxy-3-(4-methoxyphenyl)-13,13-dimethyl-3-(4-((S)-2-methylbutoxy)phenyl)-10-(4-(4'-(trans-4-pentylcyclohexyl)biphenyl-4-ylcarboxamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

6-Methoxy-3-(4-methoxyphenyl)-13,13-dimethyl-3-(4-((S)-2-methylbutoxy)phenyl)-7-(4'-(trans,trans-4'-pentylbi(cyclohexane-4-)carbonyloxy)biphenylcarbonyloxy)-10-(4-(4'-(trans-4-pentylcyclohexyl)biphenyl-4-ylcarboxamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran; and

6-Methoxy-3-(4-methoxyphenyl)-13,13-dimethyl-3-(4-((S)-2-methylbutoxy)phenyl)-10-(4-(((3R,3aS,6S,6aS)-6-(4'-(trans-4-pentylcyclohexyl)biphenylcarbonyloxy)hexahydrofuro[3,2-b]furan-3-yloxy)carbonyl)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

[0072] In all of the foregoing examples, the compounds described may be useful alone, as mixtures, or in combination with other compounds, compositions, and/or materials.

[0073] Methods for obtaining the novel compounds described herein will be apparent to those of ordinary skill in the art, suitable procedures being described, for example, in the reaction schemes and examples below, and in the references cited herein.

[0074] In the schemes and examples below, the following abbreviations have the following meanings. If an abbreviation is not defined, it has its generally accepted meaning.

BINAP	= 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
Bi(OTf) ₃	= bismuth triflate
CuI	= copper iodide
DHP	= 3,4-dihydro-2H-pyran
DCC	= dicyclohexylcarbodiimide
DCM	= dichloromethane
DBSA	= dodecylbenzenesulfonic acid
DIBAL	= diisobutylaluminium hydride
DMAP	= 4-dimethylaminopyridine
DME	= dimethyl ether

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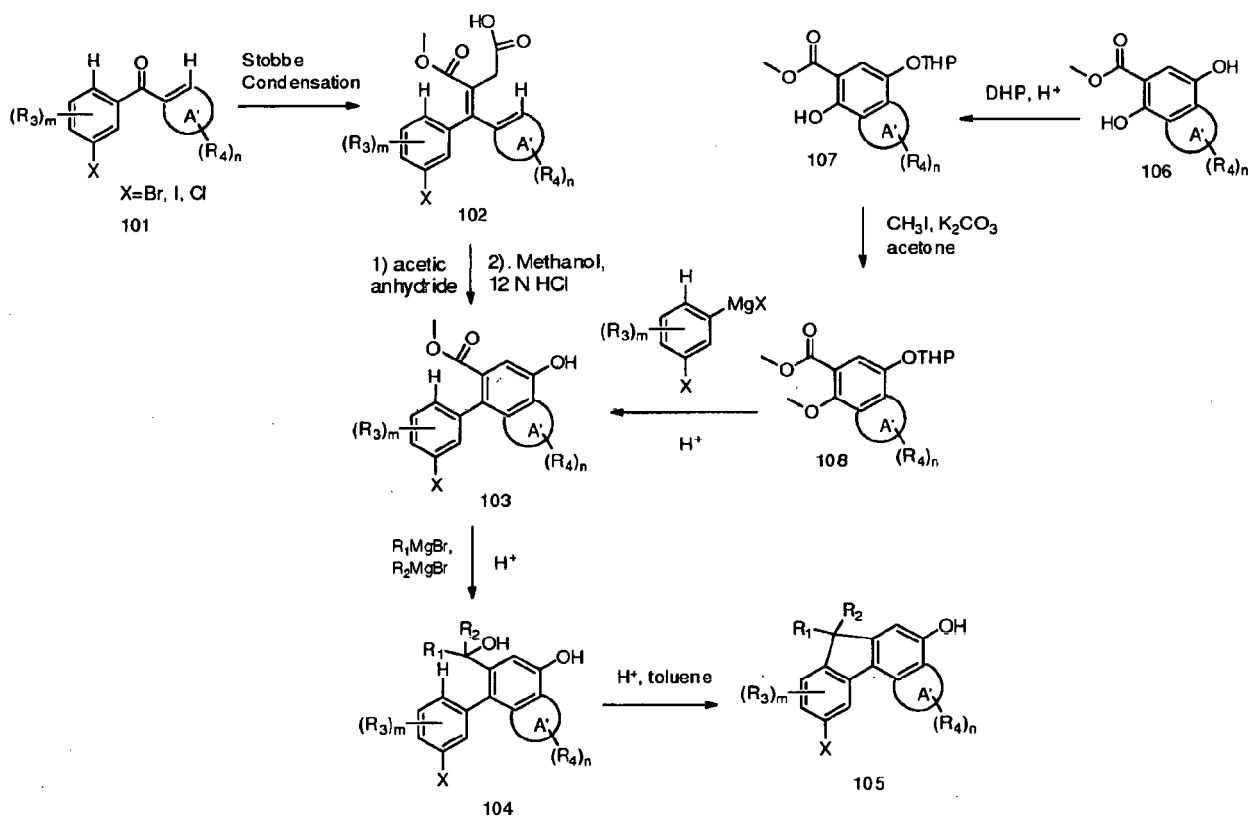
(continued)

	DMF	= N,N-dimethylformamide
	DMSO	= "dimethylsulfoxide
5	Dppf	= 1,1'-bis(diphenylphosphino)ferrocene
	EtMgBr	= ethyl magnesium bromide
	Et ₂ O	= diethylether
	g	= gram
	h	= hour
10	HPLC	= high-performance liquid chromatography
	(iPr) ₂ NH	= diisopropyl amine
	HOAc	= acetic acid
	LDA	= lithium diisopropylamide
15	KMnO ₄	= potassium permanganate
	M	= molar (molarity)
	mCPBA	= meta-Chloroperoxybenzoic acid
	MeLi	= methyl lithium
20	mg	= milligram
	min	= minutes
	mL	= milliliter
	mmol	= millimoles
	mM	= millimolar
25	NatOBu	= sodium <i>tert</i> -butoxide
	N	= normal (normality)
	ng	= nanogram
	nm	= nanometer
	nM	= nanomolar
30	NMP	= <i>N</i> -methyl pyrrolidone
	NMR	= nuclear magnetic resonance
	Pd(OAc) ₂	= palladium acetate
	Pd ₂ (dba) ₃	= tris(dibenzylideneacetone)dipalladium(0)
35	PPh ₃	= triphenyl phosphine
	PPTS	= pyridine <i>p</i> -toluenesulfonate
	<i>p</i> TSA	= <i>p</i> -toluenesulfonic acid
	PdCl ₂ (PPh ₃) ₂	= bis(triphenylphosphine)palladium(II) chloride
40	PBS	= phosphate buffered saline
	TBAF	= Tetra- <i>n</i> -butylammonium fluoride
	THF	= tetrahyrdofuran
	TLC	= thin layer chromatography
	<i>t</i> -BuOH	= <i>t</i> -butanol
45	(Tf) ₂ O	= trifluoromethanesulfonic acid anhydride
	μL	= microliter
	μM	= micromolar
	Zn(OAc) ₂	= zinc acetate
50	Zn(CN) ₂	= Zinc cyanide

[0075] As discussed in the schemes outlined further below, compound **105** represents one intermediate that may serve as the basis for preparing the photochromic dichroic dyes described herein. For example, it can be prepared as shown in Scheme **1**, **2**, **3**, **4** and **5**. Once prepared, the hydroxy functionality of compound **105** can be used for pyran formation as observed in Scheme **6**. The halogen of **105** can be either converted into a lengthening group via Suzuki Reaction or converted into other functional group **Q** as illustrated in Scheme **6**. Chemistries that can be used for functional group conversion can be observed in Scheme **7**, **8** and **9**. The new functional group **Q** can either be a lengthening group or be converted to lengthening group.

[0076] In all schemes, X may be selected from halogen, e.g., F, Br, Cl and I. Each m and n is an integer chosen from 0 to the total number of available positions. From Scheme 1 to Scheme 9, R₃ for each occurrence, may be independently selected from hydrogen, halogen and optionally substituted chiral or achiral groups selected from alkyl, perfluoroalkyl, alkenyl, alkynyl, cycloalkyl, aryl, heteroaryl, alkoxy, perfluoroalkoxy, heteroalkyl, heterocycloalkyl, alkylthiol, arylthiol, amino aminocarbonyl, aryloxy carbonyl, alkyloxy carbonyl, aminocarbonyloxy, alkoxy carbonylamino, aryloxy carbonylamino, cycloalkoxy carbonylamino, heterocycloalkoxy carbonylamino and heteroaryloxy carbonylamino. R₄ is selected from R₃.

Scheme 1



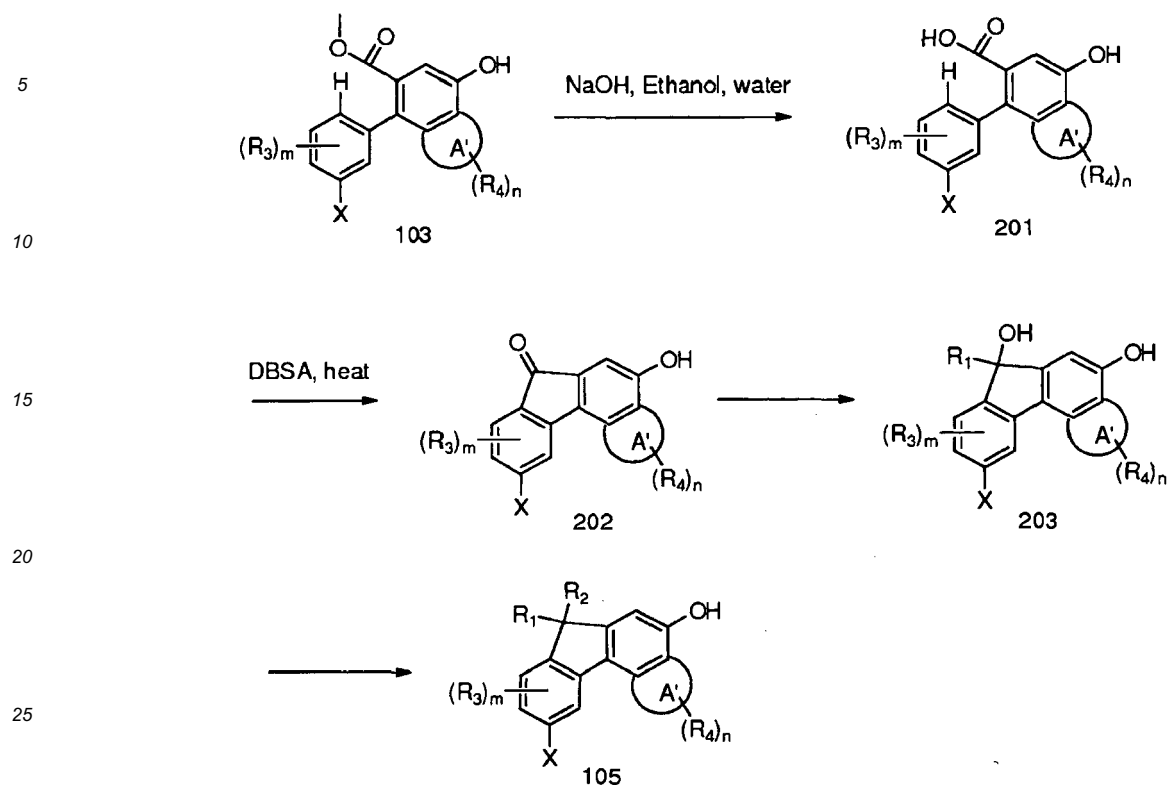
[0077] Scheme 1 shows one way of preparing compound **105**. R₁ and R₂ may be selected from optionally substituted chiral or achiral groups such as heteroalkyl, alkyl, perfluoroalkyl, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl, and heterocycloalkyl.

[0078] The aryl ketone **101** can either be purchased or prepared by Friedel-Crafts methods or Grignard or Cuperate methods known in the art. For example, see the publication Friedel-Crafts and Related Reactions, George A. Olah, Interscience Publishers, 1964, Vol. 3, Chapter XXXI (Aromatic Ketone Synthesis); "Regioselective Friedel-Crafts Acylation of 1,2,3,4-Tetrahydroquinoline and Related Nitrogen Heterocycles: Effect on NH Protective Groups and Ring Size" by Ishihara, Yugi et al, J. Chem. Soc., Perkin Trans. 1, pages 3401 to 3406, 1992; "Addition of Grignard Reagents to Aryl Acid Chlorides: An efficient synthesis of aryl ketones" by Wang, Xiao-jun et al, Organic Letters, Vol. 7, No. 25, 5593-5595, 2005, and references cited therein. A Stobbe reaction of aryl ketone **101** with dimethyl succinate in the presence of potassium t-butoxide provides the condensed product of compound **102**, which undergoes a ring closure reaction in acetic anhydride followed by methanolysis to form the product of compound **103**.

[0079] Compound **103** can also be prepared from an ester-mediated nucleophilic aromatic substitution reaction starting from compound **106** by methods known to those skilled in the art, for example, as further described in Synthesis, January 1995, pages 41-43; The Journal of Chemistry Society Perkin Transaction 1, 1995, pages 235-241 and U.S. Patent No. 7,557,208 B2.

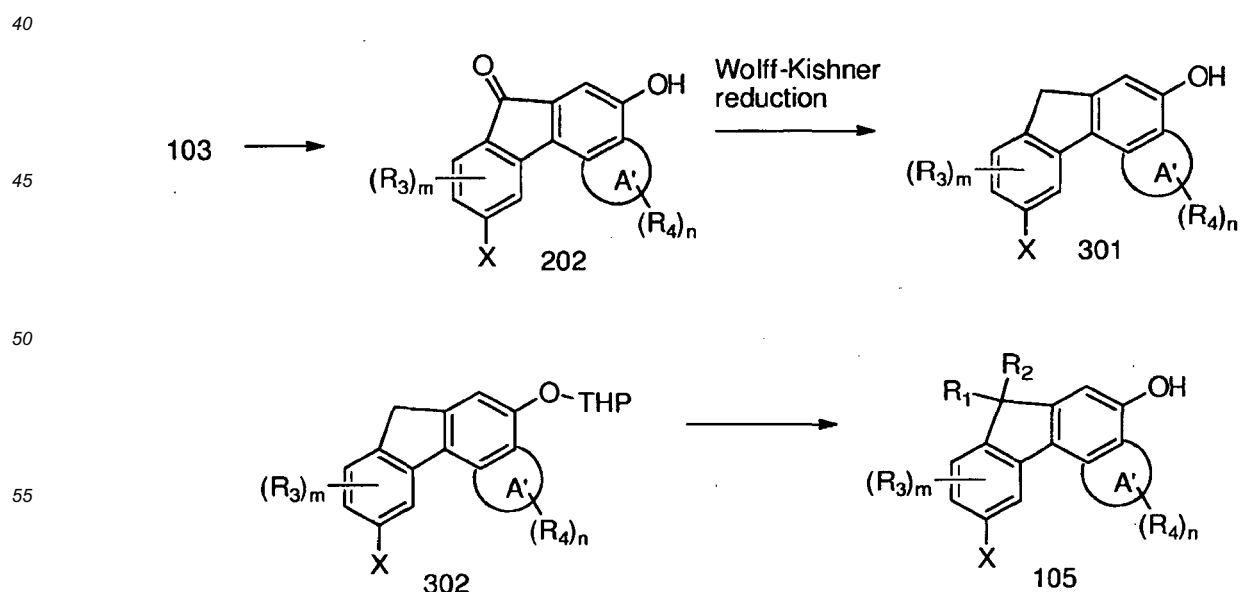
[0080] Once prepared, compound **103** can be further converted to indeno-fused product of compound **105** with various substitutions on the bridge carbon via various multistep reactions that can be found in U.S. Pat. Nos. 5,645,767; 5,869,658; 5,698,141; 5,723,072; 5,961,892; 6,113,814; 5,955,520; 6,555,028; 6,296,785; 6,555,028; 6,683,709; 6,660,727; 6,736,998; 7,008,568; 7,166,357; 7,262,295; 7,320,826 and 7,557,208. What is shown in Scheme 1 illustrates that compound **103** reacts with Grignard reagent followed by a ring closure reaction to provide compound **105**.

Scheme 2



[0081] Scheme 2 illustrates a second way of converting compound **103** to compound **105**. After hydrolysis of compound **103** followed by a ring closure reaction, compound **202** was obtained. The carbonyl of compound **202** can react with a nucleophile, like Grignard reagent, Organo lithium reagent, or perfluoroalkyl trimethylsilane to form compound **203**. R_1 may be selected from optionally substituted chiral or achiral groups such as heteroalkyl, alkyl, perfluoroalkyl, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl and heterocycloalkyl. The hydroxyl group of compound **203** can be easily converted into R_2 , which may be selected from halogen and optionally substituted chiral or achiral groups such as alkoxy, silanoxy, heteroaryloxy and aryloxy.

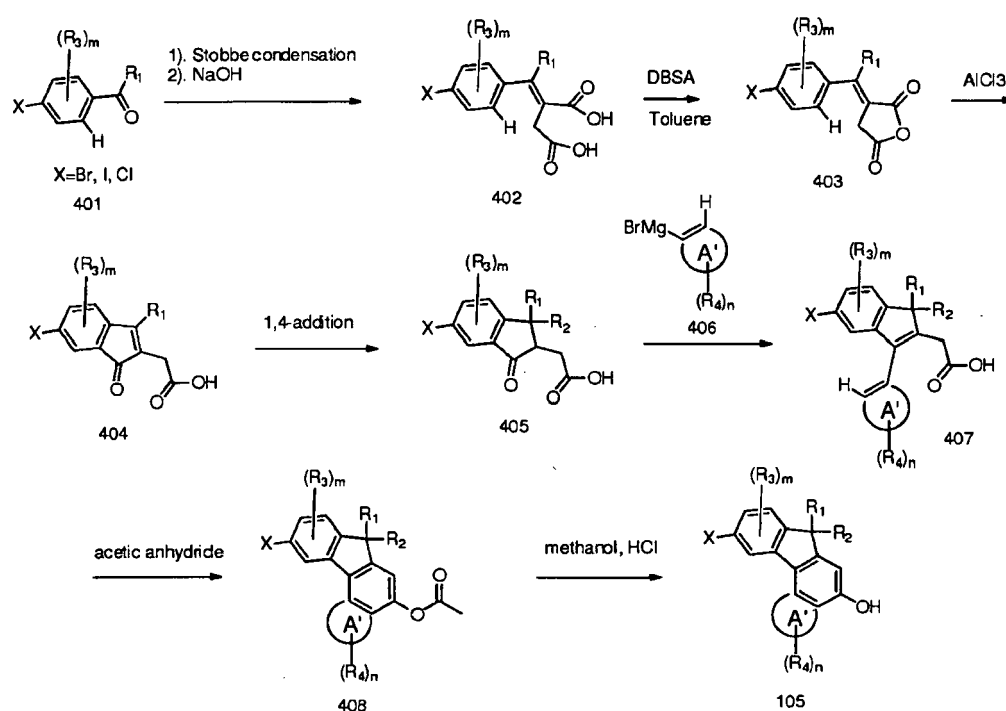
Scheme 3



[0082] Scheme 3 illustrates a third way of converting compound **103** to compound **105**. Compound **202** from Scheme 2 can be reduced to **301** using a Wolff-Kishner reduction or its modified version. Examples can be found in "Practical procedures for the preparation of N-tert-butylidimethylsilylhydrozones and their use in modified Wolff-Kishner reductions and in the synthesis of vinyl halides and gem-dihalides" by Furrow, M.E., et al, J Am Chem Soc: 126(17): 5436-45, May 5 2004, and references therein. After hydroxy protection, compound **302** has a very nucleophilic gem-carbon once deprotonated by base like LDA or methyl Grignard reagent. By those skilled in the art, the deprotonated compound **302** can be converted to R_1 and R_2 by reacting it with electrophiles such as alkyl halides, carbon dioxide, acid chlorides, nitriles and chloroformate derivatives. As a result, compound **105** can be prepared with R_1 and R_2 selected from hydrogen, optionally substituted chiral or achiral groups selected from heteroalkyl, alkyl, cycloalkyl, carboxy, alkylcarbonyl, alkoxy-carbonyl, alkylcarbonyl, alkoxy-carbonyl, aminocarbonyl, arylcarbonyl, aryloxy-carbonyl, or R_1 and R_2 may be taken together with any intervening atoms to form a group selected from oxo, optionally substituted cycloalkyl, and optionally substituted heterocycloalkyl.

[0083] Schemes 4 and 5 summarize two novel methods of preparing compound **105**, which are not believed to have been previously described.

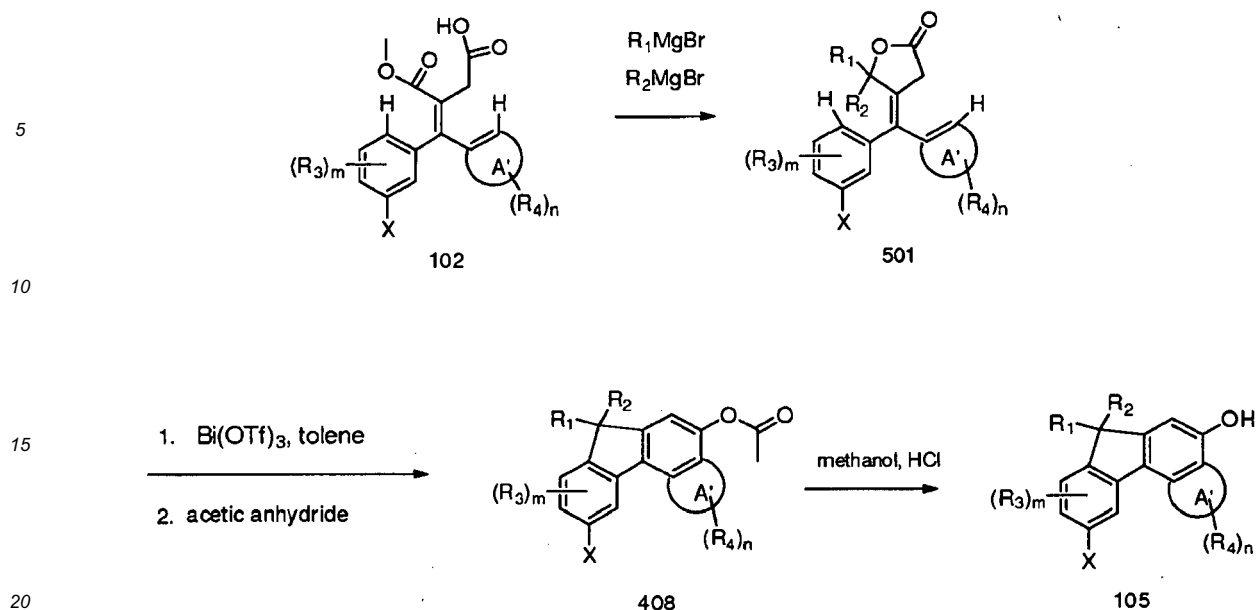
Scheme 4



[0084] Scheme 4 starts from aryl ketone **401**. R_1 may be selected from hydrogen, optionally substituted chiral or achiral groups such as heteroalkyl, alkyl, perfluoroalkyl, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl and heterocycloalkyl.

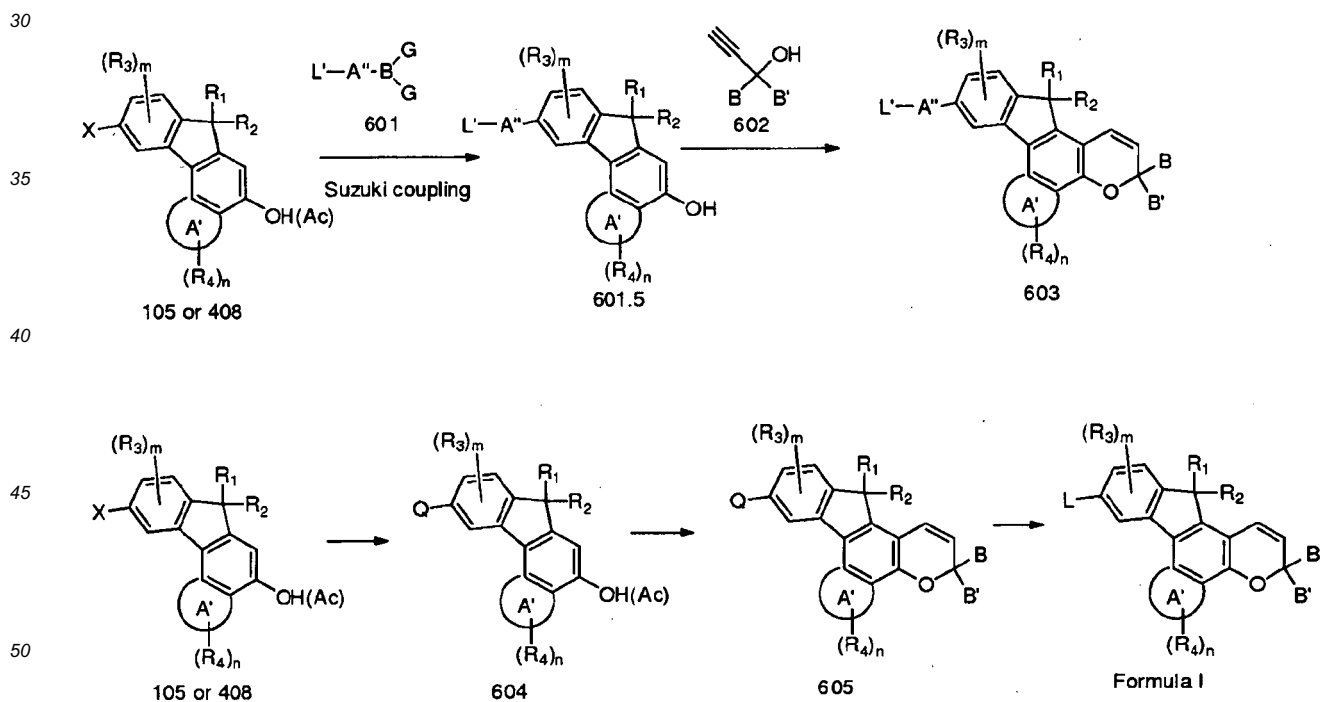
[0085] After a Stobbe reaction with dimethyl succinate, compound **402** is converted to an anhydride **403**. This anhydride can be transformed into an indenoic acid **404** with the use of aluminum chloride. A 1,4-addition reaction can be done with the use of nucleophiles like organometallic reagent, amine, alcohol and thiol. The reaction provides indenoic acid **405**. R_2 may be selected from hydrogen, optionally substituted chiral or achiral groups such as heteroalkyl, alkyl, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl, heterocycloalkyl, amino, alkoxy, and thiol. Compound **405** can react with a Grignard reagent **406** to form compound **407** after acidic workup. Compound **407** undergoes a ring closure reaction in acetic anhydride followed by methanolysis to form product **408**, which can be either used directly in Scheme 6 or converted to compound **105** by hydrolysis.

Scheme 5



[0086] Scheme 5 starts from Stobbe product **102**, which reacts with Grignard reagents to provide compound **501**. R_1 and R_2 may be selected from optionally substituted chiral or achiral groups such as heteroalkyl, alkyl, perfluoroalkyl, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl and heterocycloalkyl. After treating with bismuth triflate in toluene and then acetic anhydride, two ring closure reactions occur in the same pot sequentially. The efficient reaction results in compound **408**, which can be converted into compound **105**.

Scheme 6



[0087] Scheme 6 illustrates methods of converting compounds **105** and **408** into photochromic dichroic dyes. When Suzuki reaction is applied, the lengthening group is added with the use of a boronic derivative **601**, the synthesis of which can be found from "Palladium(0)-Catalyzed Cross-Coupling Reaction of Alkoxydiboron with Haloarenes: A Direct Procedure for Arylboronic Esters, J. Org. Chem. 60, page 7508-7519, 1995" by Miyaura, Norio et al. and references therein. The pyran ring of compound **603** is formed with the coupling with a propargyl alcohol **602**. Compound **603** may

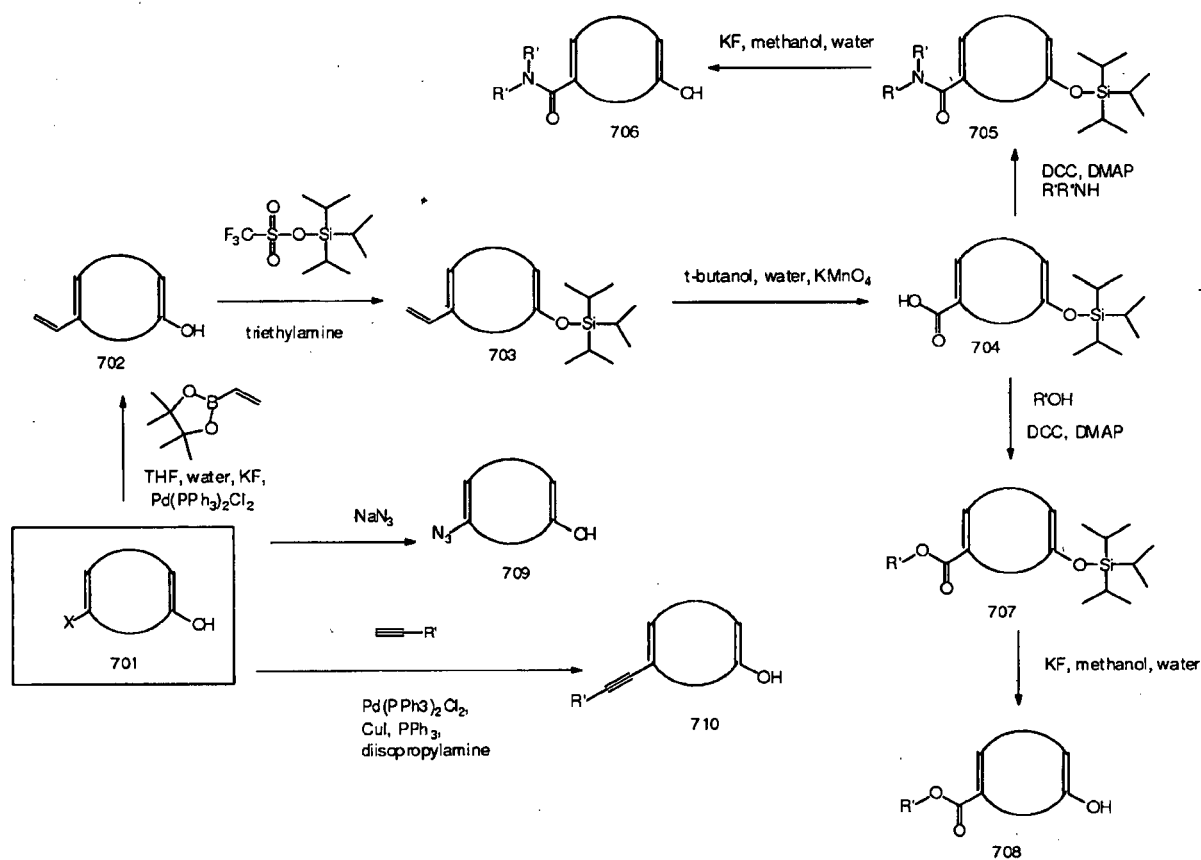
also be obtained when the sequence of the two reactions are changed. As described herein, G may be -OH or -O-Alkyl; A" may be selected from aryl, alkenyl, alkynyl and heteroaryl; A" and L' together form the L₁, L₂ or L₃ group; and B and B' may be each independently selected from L₃, hydrogen, halogen, and optionally substituted chiral or achiral groups such as metallocenyl, alkyl or perfluoroalkyl, alkenyl, alkynyl, heteroalkyl, alkoxy, perfluoroalkoxy, aryl, heteroaryl, heterocycloalkyl, and cycloalkyl, or wherein B and B' are taken together with any intervening atoms to form a group such as optionally substituted cycloalkyl and optionally substituted heterocycloalkyl.

[0088] Also shown in Scheme 6 as alternative ways of incorporating lengthening groups, halogen X can be converted to other functional group Q with the formation of compound **604**. Compound **604** can react with a propargyl alcohol to form pyran dye **605**, which can be a photochromic dichroic dye itself or can be converted to photochromic dichroic dye **Formula I**. These new functional groups Q may include:

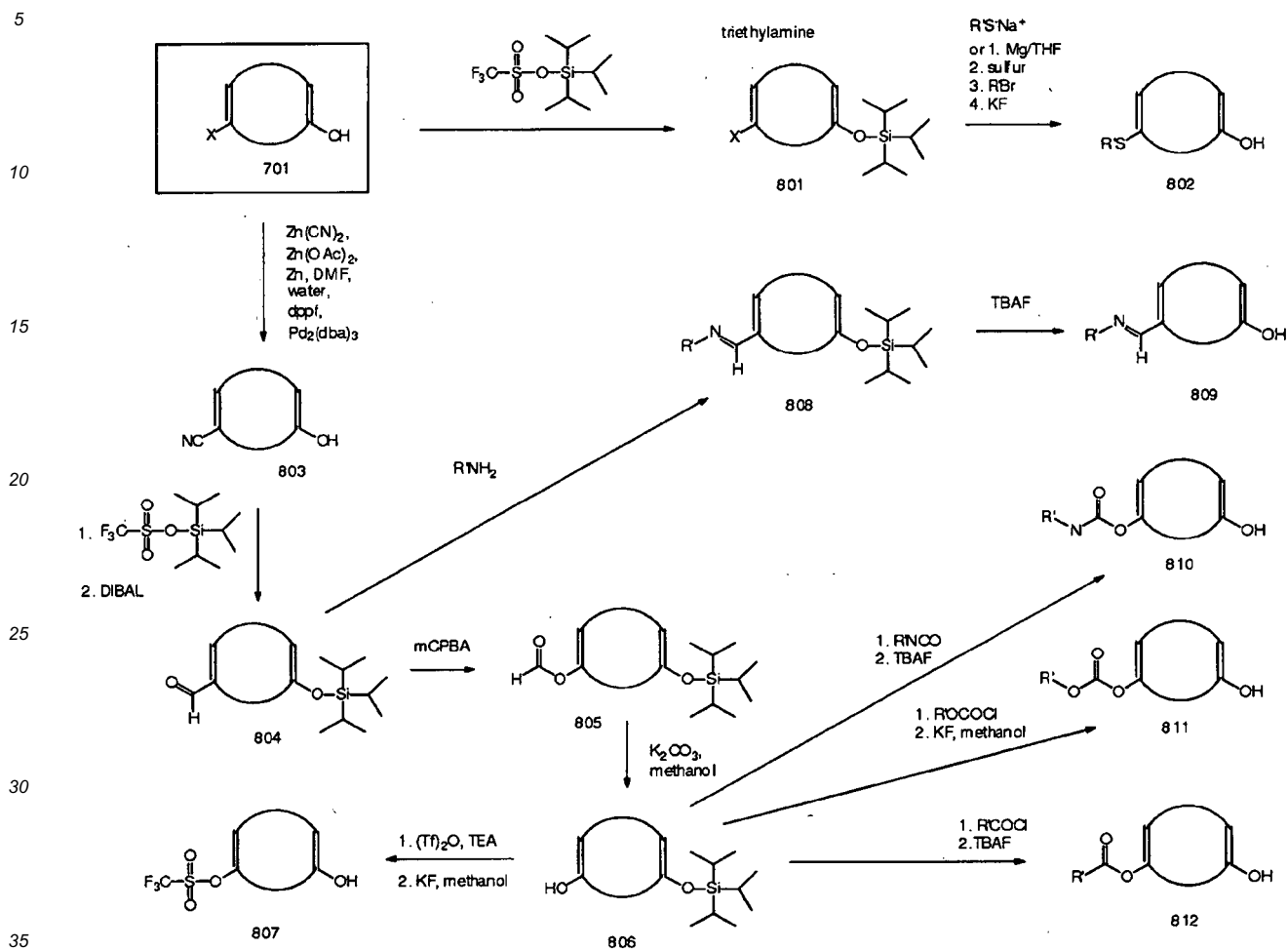
-N₃, -CN; -COOR', -CCR', -CHCHR', -OCOR', -OCOOR', -SR', -OSO₂R', -OR', -OTf, -CHO, -OCHO, -OCONR', -NR'R', -NR'CONR', -NR'COR', -NR'COOR', -CHNR', and -CONR'R', wherein R' may be independently chosen from hydrogen, L, an unsubstituted or substituted alkyl group having from 1 to 18 carbon atoms, an unsubstituted or substituted aryl group, an unsubstituted or substituted alkene or alkyne group having from 2 to 18 carbon atoms, -CF₃ and a perfluorinated alkyl group having from 2 to 18 carbon atoms or two R' can come together with -N and form a heterocycloalkyl such as piperaziny.

[0089] Schemes 7, 8 and 9 illustrate details of converting halogen to other functional groups that can be either further converted to lengthening groups or are lengthening groups themselves. The chemistries are done at hydroxy stage starting from compound **105**, which is simplified as compound **701** in Schemes 7 and 8. Each of the hydroxy products of compounds **702**, **706**, **708**, **709**, **710**, **802**, **803**, **807**, **809**, **810**, **811**, **812**, **901**, **903**, **904** and **906** can be converted to pyran photochromic compounds using the propargyl alcohol chemistry shown in Scheme 6.

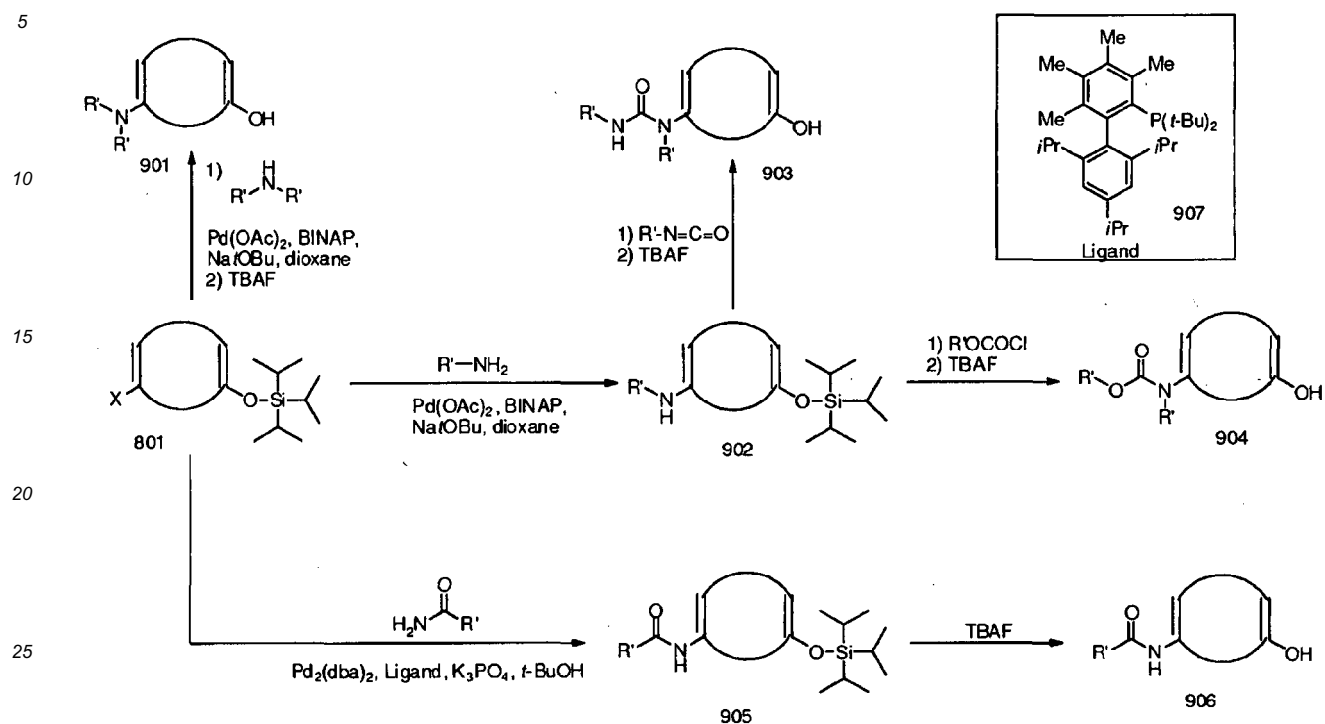
Scheme 7



Scheme 8

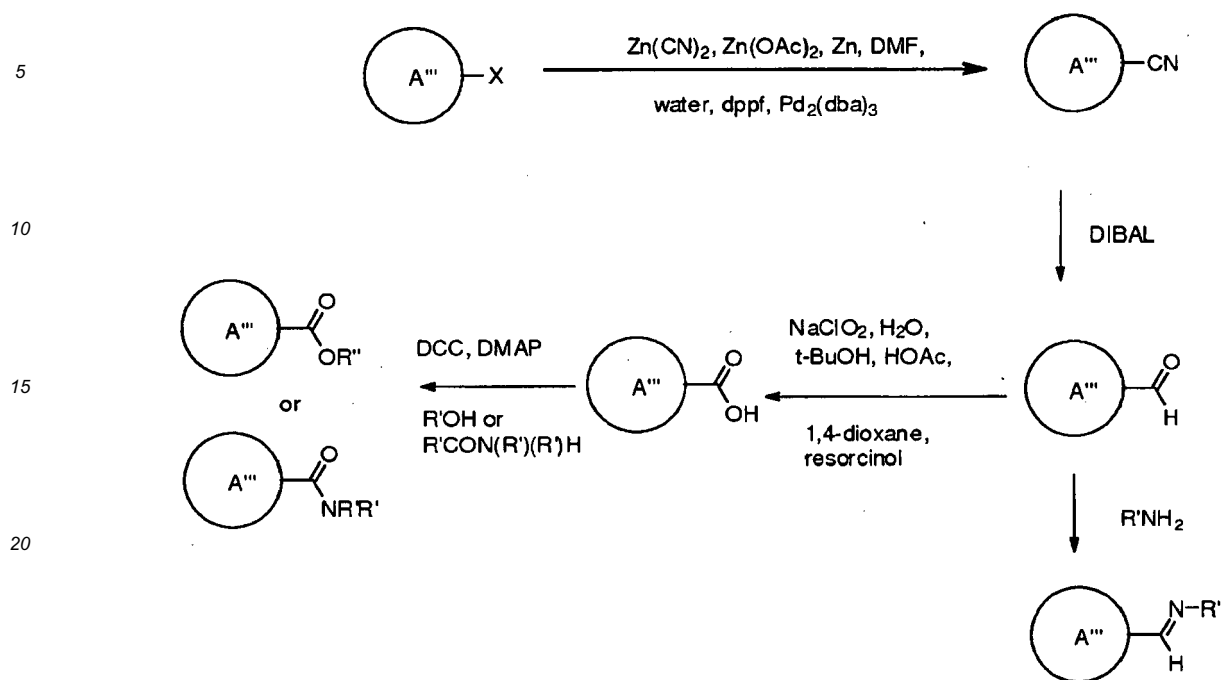


Scheme 9



[0090] Scheme 10 shows chemistries that can be done on the photochromic dichroic dye. A''' is a simplified version of Formula I with one of R_3 or R_4 selected from halogen X. X is located at one of the positions where R_3 and R_4 would be located. This Scheme compliments what can be done from Scheme 1 to 9 for R_3 and R_4 and install groups like cyano, aldehyde, carboxylic acid, and optionally substituted chiral or achiral groups selected from imine, alkoxy carbonyl, aminocarbonyl and aryloxy carbonyl as R_3 and R_4 . The cyanation and oxidation methods have been described in U.S. Patent Pub. No. 2009/0309076A1.

Scheme 10



[0091] The compounds described herein may be useful as thermally reversible photochromic compounds and/or compositions according to various non-limiting embodiments disclosed herein. Such compounds may be useful in a variety of applications to provide photochromic and/or photochromic-dichroic properties.

[0092] The photochromic compositions of the present invention may comprise at least one of the compounds described herein, and optionally at least one other photochromic compound. The photochromic composition can be chosen from a variety of materials. Examples of such materials may be selected from:

- (a) a single photochromic compound;
- (b) a mixture of photochromic compounds;
- (c) a material comprising at least one photochromic compound such as a polymeric resin or an organic monomer solution;
- (d) a material such as a monomer or polymer to which at least one photochromic compound is chemically bonded;
- (e) material (c) or (d) further comprising a coating to substantially prevent contact of the at least one photochromic compound with external materials;
- (f) a photochromic polymer; or
- (g) mixtures thereof.

[0093] The present invention further provides a photochromic article comprising an organic material and a photochromic compound/composition of the present disclosure connected to at least a portion of the organic host material. As used herein the term "connected to" means in direct contact with an object or indirect contact with an object through one or more other structures or materials, at least one of which is in direct contact with the object. Further, the photochromic compound can be connected to at least a portion of the host by incorporation into the host material or by application onto the host material, for example, as part of a coating or layer. In addition to the photochromic compound, the photochromic composition may further comprise at least one additive chosen from dyes, alignment promoters, antioxidants, kinetic enhancing additives, photoinitiators, thermal initiators, polymerization inhibitors, solvents, light stabilizers, e.g., ultraviolet light absorbers and hindered amines stabilizers, heat stabilizers, mold release agents, rheology control agents, leveling agents, free radical scavengers, gelators and adhesion promoters.

[0094] Examples of dyes that can be present in the at least partial coating according to various embodiments disclosed herein include organic dyes that are capable of imparting a desired color or other optical property to the at least partial coating.

[0095] As used herein, the term "alignment promoter" means an additive that can facilitate at least one of the rate and uniformity of the alignment of a material to which it is added. Examples of alignment promoters that can be present in the at least partial coatings according to various embodiments disclosed herein include those described in U.S. Patent

6,338,808 and U.S. Patent Publication No. 2002/0039627.

[0096] Antioxidants, e.g., polyphenolic antioxidants, are organic compounds used to retard oxidation. Examples of antioxidants are described in U.S. Pat. Nos. 4,720,356, 5,391,327 and 5,770,115.

[0097] Examples of kinetic enhancing additives that can be present in the at least partial coating according to various embodiments disclosed herein include epoxy-containing compounds, organic polyols, and/or plasticizers. More specific examples of such kinetic enhancing additives are disclosed in U.S. Patent 6,433,043 and U.S. Patent Publication No. 2003/0045612.

[0098] Examples of photoinitiators that can be present in the at least partial coating according to various embodiments disclosed herein include cleavage-type photoinitiators and abstraction-type photoinitiators. Examples of cleavage-type photoinitiators include acetophenones, α -aminoalkylphenones, benzoin ethers, benzoyl oximes, acylphosphine oxides and bisacylphosphine oxides or mixtures of such initiators. A commercial example of such a photoinitiator is DAROCURE® 4265, which is available from Ciba Chemicals, Inc. Examples of abstraction-type photoinitiators include benzophenone, Michler's ketone, thioxanthone, anthraquinone, camphorquinone, fluorone, ketocoumarin or mixtures of such initiators.

[0099] Another Example of a photoinitiator that can be present in according to various embodiments disclosed herein is a visible light photoinitiator. Examples of suitable visible light photoinitiators are set forth at column 12, line 11 to column 13, line 21 of U.S. Patent 6,602,603.

[0100] Examples of thermal initiators include organic peroxy compounds and azobis(organonitrile) compounds. Specific examples of organic peroxy compounds that are useful as thermal initiators include peroxydicarbonate esters, such as tertiarybutylperoxy isopropyl carbonate; peroxydicarbonate esters, such as di(2-ethylhexyl) peroxydicarbonate, di(secondary butyl) peroxydicarbonate and diisopropylperoxydicarbonate; diacyperoxides, such as 2,4-dichlorobenzoyl peroxide, isobutyryl peroxide, decanoyl peroxide, lauroyl peroxide, propionyl peroxide, acetyl peroxide, benzoyl peroxide and *p*-chlorobenzoyl peroxide; peroxyesters such as *t*-butylperoxy pivalate, *t*-butylperoxy octylate and *t*-butylperoxyisobutyrate; methylethylketone peroxide, and acetylcyclohexane sulfonyl peroxide. In one embodiment the thermal initiators used are those that do not discolor the resulting polymerizate. Examples of azobis(organonitrile) compounds that can be used as thermal initiators include azobis(isobutyronitrile), azobis(2,4-dimethylvaleronitrile) or a mixture thereof.

[0101] Examples of polymerization inhibitors include: nitrobenzene, 1,3,5-trinitrobenzene, *p*-benzoquinone, chloranil, DPPH, FeCl₃, CuCl₂, oxygen, sulfur, aniline, phenol, *p*-dihydroxybenzene, 1,2,3-trihydroxybenzene, and 2,4,6-trimethylphenol.

[0102] Examples of solvents that can be present in the LC compositions according to various embodiments disclosed herein include those that will dissolve solid components of the LC compositions, that are compatible with the LC compositions and the elements and substrates, and/or can ensure uniform coverage of a surface(s) to which the LC composition is applied. Potential solvents include the following: propylene glycol monomethyl ether acetate and their derivatives (sold as DOWANOL® industrial solvents), acetone, amyl propionate, anisole, benzene, butyl acetate, cyclohexane, dialkyl ethers of ethylene glycol, e.g., diethylene glycol dimethyl ether and their derivatives (sold as CELLOSOLVE® industrial solvents), diethylene glycol dibenzoate, dimethyl sulfoxide, dimethyl formamide, dimethoxybenzene, ethyl acetate, isopropyl alcohol, methyl cyclohexanone, cyclopentanone, methyl ethyl ketone, methyl isobutyl ketone, methyl propionate, propylene carbonate, tetrahydrofuran, toluene, xylene, 2-methoxyethyl ether, 3-propylene glycol methyl ether, and mixtures thereof.

[0103] Examples of thermal stabilizers may include a basic nitrogen-containing compound for example, biurea, allantoin or a metal salt thereof, a carboxylic acid hydrazide, e.g., an aliphatic or aromatic carboxylic acid hydrazide, a metal salt of an organic carboxylic acid, an alkali or alkaline earth metal compound, a hydrotalcite, a zeolite and an acidic compound (e.g., a boric acid compound, a nitrogen-containing cyclic compound having a hydroxyl group, a carboxyl group-containing compound, a (poly)phenol, butylated hydroxytoluene, and an aminocarboxylic acid) or mixtures thereof.

[0104] Examples of mold release agents include esters of long-chain aliphatic acids and alcohols such as pentaerythritol, guerbet alcohols, long-chain ketones, siloxanes, α -olefin polymers, long-chain alkanes and hydrocarbons having 15 to 600 carbon atoms.

[0105] Rheology control agents are thickeners that are typically powders that may be inorganic, such as silica, organic such as microcrystalline cellulose or particulate polymeric materials. Gelators or gelling agents are often organic materials that can also affect the thixotropy of the material in which they are added. Examples of suitable gelators or gelling agents include natural gums, starches, pectins, agar-agar, and gelatins. Gelators or gelling agents may often be based on polysaccharides or proteins.

[0106] In certain embodiments, one or more surfactants may be used. Surfactants include materials otherwise known as wetting agents, anti-foaming agents, emulsifiers, dispersing agents, leveling agents etc. Surfactants can be anionic, cationic and nonionic, and many surfactants of each type are available commercially. Examples of nonionic surfactants that may be used include ethoxylated alkyl phenols, such as the IGEPAL® DM surfactants or octylphenoxypolyethoxyethanol sold as TRITON® X-100, an acetylenic diol such as 2,4,7,9-tetramethyl-5-decyne-4,7-diol sold as SURFYNOL® 104, ethoxylated acetylenic diols, such as the SURFYNOL® 400 surfactant series, fluoro-surfactants, such as the FLUO-

RAD[®] fluorochemical surfactant series, and capped nonionics such as the benzyl capped octyl phenol ethoxylates sold as TRITON[®] CF87, the propylene oxide capped alkyl ethoxylates, which are available as the PLURAFAC[®] RA series of surfactants, octylphenoxyhexadecylethoxy benzyl ether, polyether modified dimethylpolysiloxane copolymer in solvent sold as BYK[®]-306 additive by Byk Chemie and mixtures of such recited surfactants.

[0107] Free radical scavengers include synthetic pseudopeptides resistant to hydrolysis such as Carcine hydrochloride; lipoamino acids such as L-lysine lauroylmethionine; plant extracts containing multi-enzymes; natural tocopherol and related compounds as well as compounds containing an active hydrogen such as -OH, -SH, or -NRH group. Further examples of free radical scavengers are chosen from the group of sterically hindered amines (HALS=hindered amine light stabilizer) which, unlike customary light protection agents, are not based on the absorption of the irradiated light or on the quenching of the absorbed light, but essentially on the ability to scavenge or to replace free radicals and hydroperoxides formed during the photodegradation of polymeric materials and antioxidants.

[0108] Adhesion promoters include adhesion promoting organo-silane materials, such as aminoorganosilane materials, silane coupling agents, organic titanate coupling agents and organic zirconate coupling agents described in U.S. Patent Application Publication 2004/0207809 at paragraphs [0033] to [0042]. Further examples of adhesion promoters include zircon-aluminate adhesion promoting compounds that are commercially available from Rhone-Poulenc. Preparation of aluminum-zirconium complexes is described in the U.S. Patent Nos. 4,539,048 and 4,539,049. These patents describe zircon-aluminate complex reaction products corresponding to the empirical formula: $(Al)_2(OR_1O)_aA_bB_c)_x(OC(R_2)O)_y(ZrA_dB_e)_z$ wherein X, Y, and Z are at least 1, R₂ is an alkyl, alkenyl, aminoalkyl, carboxyalkyl, mercaptoalkyl, or epoxyalkyl group, having from 2 to 17 carbon atoms, and the ratio of X:Z is from about 2:1 to about 5:1. Additional zircon-aluminate complexes are described in U.S. Patent No. 4,650,526.

[0109] Non-limiting examples of organic host materials that may be used in conjunction with various non-limiting embodiments disclosed herein include liquid crystal materials and polymeric materials. Liquid crystal materials may be chosen from liquid crystal polymers, liquid crystal pre-polymers and liquid crystal monomers. As used herein the term "pre-polymer" means partially polymerized materials. Liquid crystal polymers ("LCPs") are polymers capable of forming regions of highly ordered structure while in a liquid phase. As used herein, the term "liquid crystal monomer" means a monomeric compound that may display liquid crystal properties in the monomeric state and/or in the polymeric state. That is, the liquid crystal monomer may display liquid crystal properties by itself and/or after it has been incorporated into a polymer or copolymer to form a liquid crystal polymer (LCP). The LCPs may display at least one of a nematic phase, a smectic phase, a chiral nematic phase (i.e., a cholesteric phase), a discotic phase (including chiral discotic), a discontinuous cubic phase, a hexagonal phase, a bicontinuous cubic phase, a lamellar phase, a reverse hexagonal columnar phase, or an inverse cubic phase. In addition, in certain LCPs of the present disclosure, the LC monomers or residues thereof may transition from one phase to another, for example, in response to thermal energy or actinic radiation.

[0110] Examples of polymeric materials include homopolymers and copolymers, prepared from the monomers and mixtures of monomers disclosed in U.S. Patent 5,962,617 and in U.S. Patent 5,658,501 from column 15, line 28 to column 16, line 17, an oligomeric material, a monomeric material or a mixture or combination thereof. Polymeric materials can be thermoplastic or thermoset polymeric materials, can be transparent or optically clear, and can have any refractive index required. Non-limiting examples of such disclosed monomers and polymers include: polyol(allyl carbonate) monomers, e.g., allyl diglycol carbonates such as diethylene glycol bis(allyl carbonate), which monomer is sold under the trademark CR-39 by PPG Industries, Inc.; polyurea-polyurethane (polyurea-urethane) polymers, which are prepared, for example, by the reaction of a polyurethane prepolymer and a diamine curing agent, a composition for one such polymer being sold under the trademark TRIVEX by PPG Industries, Inc.; polyol(meth)acryloyl terminated carbonate monomer; diethylene glycol dimethacrylate monomers; ethoxylated phenol methacrylate monomers; diisopropenyl benzene monomers; ethoxylated trimethylol propane triacrylate monomers; ethylene glycol bismethacrylate monomers; poly(ethylene glycol) bismethacrylate monomers; urethane acrylate monomers; poly(ethoxylated bisphenol A dimethacrylate); poly(vinyl acetate); poly(vinyl alcohol); poly(vinyl chloride); poly(vinylidene chloride); polyethylene; polypropylene; polyurethanes; polythiourethanes; thermoplastic polycarbonates, such as the carbonate-linked resin derived from bisphenol A and phosgene, one such material being sold under the trademark LEXAN; polyesters, such as the material sold under the trademark MYLAR; poly(ethylene terephthalate); polyvinyl butyral; poly(methyl methacrylate), such as the material sold under the trademark PLEXIGLAS, and polymers prepared by reacting polyfunctional isocyanates with polythiols or polyepisulfide monomers, either homopolymerized or co-and/or terpolymerized with polythiols, polyisocyanates, polyisothiocyanates and optionally ethylenically unsaturated monomers or halogenated aromatic-containing vinyl monomers. Also contemplated are copolymers of such monomers and blends of the described polymers and copolymers with other polymers, for example, to form block copolymers or interpenetrating network products. Polymeric materials can also be self-assembled materials.

[0111] In specific embodiments, the polymer may be a block or non-block copolymer. In certain embodiments, the block copolymer may comprise hard blocks and soft blocks. In other embodiments, the polymer may be a non-block copolymer (i.e., a copolymer that does not have large blocks of specific monomer residues), such as a random copolymer, an alternating copolymer, periodic copolymers, and statistical copolymers. The present disclosure is also intended to

cover copolymers of more than two different types of co-monomer residues.

[0112] According to one specific non-limiting embodiment, the organic host material is chosen from polyacrylates, polymethacrylates, poly(C₁-C₁₂) alkyl methacrylates, polyoxy(alkylene methacrylates), poly (alkoxylated phenol methacrylates), cellulose acetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate, poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl chloride), poly(vinylidene chloride), poly(vinylpyrrolidone), poly((meth)acrylamide), poly(dimethyl acrylamide), poly(hydroxyethyl methacrylate), poly((meth)acrylic acid), thermoplastic polycarbonates, polyesters, polyurethanes, polythiourethanes, poly(ethylene terephthalate), polystyrene, poly(alpha methylstyrene), copoly(styrene-methylmethacrylate), copoly(styrene-acrylonitrile), polyvinylbutyral and polymers of members of the group consisting of polyol(allyl carbonate)monomers, mono-functional acrylate monomers, mono-functional methacrylate monomers, polyfunctional acrylate monomers, polyfunctional methacrylate monomers, diethylene glycol dimethacrylate monomers, diisopropenyl benzene monomers, alkoxylated polyhydric alcohol monomers and diallylidene pentaerythritol monomers.

[0113] According to another specific non-limiting embodiment, the organic host material is a homopolymer or copolymer of monomer(s) chosen from acrylates, methacrylates, methyl methacrylate, ethylene glycol bis methacrylate, ethoxylated bisphenol A dimethacrylate, vinyl acetate, vinylbutyral, urethane, thiourethane, diethylene glycol bis(allyl carbonate), diethylene glycol dimethacrylate, diisopropenyl benzene, and ethoxylated trimethylol propane triacrylate. The polymeric material most often comprises liquid crystal materials, self-assembling materials, polycarbonate, polyamide, polyimide, poly(meth)acrylate, polycyclic alkene, polyurethane, poly(urea)urethane, polythiourethane, polythio(urea)urethane, polyol(allyl carbonate), cellulose acetate, cellulose diacetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate, polyalkene, polyalkylene-vinyl acetate, poly(vinylacetate), poly(vinyl alcohol), poly(vinyl chloride), poly(vinylformal), poly(vinylacetal), poly(vinylidene chloride), poly(ethylene terephthalate), polyester, polysulfone, polyolefin, copolymers thereof, and/or mixtures thereof.

[0114] Further, according to various non-limiting embodiments disclosed herein, the organic host material can form an optical element or portion thereof. Non-limiting examples of optical elements include ophthalmic elements, display elements, windows, and mirrors. As used herein the term "optical" means pertaining to or associated with light and/or vision. For example, although not limiting herein, according to various non-limiting embodiments, the optical element or device can be chosen from ophthalmic elements and devices, display elements and devices, windows, mirrors, packaging material such as shrinkwrap, and active and passive liquid crystal cell elements and devices.

[0115] As used herein the term "ophthalmic" means pertaining to or associated with the eye and vision. Non-limiting examples of ophthalmic elements include corrective and non-corrective lenses, including single vision or multi-vision lenses, which may be either segmented or non-segmented multi-vision lenses (such as, but not limited to, bifocal lenses, trifocal lenses and progressive lenses), as well as other elements used to correct, protect, or enhance (cosmetically or otherwise) vision, including without limitation, contact lenses, intra-ocular lenses, magnifying lenses, and protective lenses or visors. As used herein the term "display" means the visible or machine-readable representation of information in words, numbers, symbols, designs or drawings. Non-limiting examples of display elements and devices include screens, monitors, and security elements, including without limitation, security marks and authentication marks. As used herein the term "window" means an aperture adapted to permit the transmission of radiation therethrough. Non-limiting examples of windows include automotive and aircraft transparencies, filters, shutters, and optical switches. As used herein the term "mirror" means a surface that specularly reflects a large fraction of incident light.

[0116] For example, the organic host material can be an ophthalmic element, and more particularly, an ophthalmic lens.

[0117] Further, it is contemplated that the photochromic compounds disclosed herein can be used alone or in conjunction with at least one other complementary organic photochromic compound having at least one activated absorption maxima within the range of 300 nm to 1000 nm, inclusive (or substances containing the same). For example, the photochromic compound disclosed herein can be combined with at least one other conventional organic photochromic compound such that the combination of photochromic compound, when activated, exhibits a desired hue. Non-limiting examples of suitable conventional organic photochromic compounds include the pyrans, oxazines, fulgides and fulgimides described hereinafter.

[0118] Non-limiting examples of thermally reversible complementary photochromic pyrans include benzopyrans, naphthopyrans, e.g., naphtho[1,2-b]pyrans, naphtho[2,1-b]pyrans, indenofused naphthopyrans, such as those disclosed in U.S. Patent 5,645,767, and heterocyclic-fused naphthopyrans, such as those disclosed in U.S. Patent Nos. 5,723,072, 5,698,141, 6,153,126, and 6,022,497; spiro-9-fluoreno[1,2-b]pyrans; phenanthropyrans; quinopyrans; fluoroanthropyrans; spiropyrans, e.g., spiro(benzindoline)naphthopyrans, spiro(indoline)benzopyrans, spiro(indoline)naphthopyrans, spiro(indoline)quinopyrans and spiro(indoline)pyrans. More specific examples of naphthopyrans and the complementary organic photochromic substances are described in U.S. Patent 5,658,501. Spiro(indoline)pyrans are also described in the text, Techniques in Chemistry, Volume III, "Photochromism", Chapter 3, Glenn H. Brown, Editor, John Wiley and Sons, Inc., New York, 1971.

[0119] Non-limiting examples of thermally reversible complementary photochromic oxazines include benzoxazines, naphthoxazines, and spiro-oxazines, e.g., spiro(indoline)naphthoxazines, spiro(indoline)pyridobenzoxazines, spiro(ben-

zindoline)pyridobenzoxazines, spiro(benzindoline)naphthoxazines, spiro(indoline)benzoxazines, spiro(indoline)fluoranthenoxazine, and spiro(indoline)quinoxazine.

5 [0120] More non-limiting examples of thermally reversible complementary photochromic fulgides include: fulgimides, and the 3-furyl and 3-thienyl fulgides and fulgimides, which are disclosed in U.S. Patent 4,931,220 and mixtures of any of the aforementioned photochromic materials/compounds.

10 [0121] For example, it is contemplated that the photochromic compounds disclosed herein can be used alone or in conjunction with another conventional organic photochromic compound (as discussed above), in amounts or ratios such that the organic host material into which the photochromic compounds are incorporated, or onto which the organic host materials are applied, can exhibit a desired color or colors, either in an activated or a "bleached" state. Thus the amount of the photochromic compounds used is not critical provided that a sufficient amount is present to produce a desired photochromic effect. As used herein, the term "photochromic amount" refers to the amount of the photochromic compound necessary to produce the desired photochromic effect.

15 [0122] The present invention also provides a photochromic article comprising a substrate, and an at least partial coating of a coating composition having a photochromic amount of a photochromic compound of the present disclosure connected to at least a portion of at least one surface thereof of the substrate. Further, although not limiting herein, at least a portion of the at least partial coating can be at least partially set. As used herein the term "set" means to fix in a desired orientation.

20 [0123] For example, according to the above-mentioned non-limiting embodiment, the coating composition can be chosen from, without limitation, polymeric coating compositions, paints, and inks. Further, in addition to the photochromic compounds disclosed herein, the coating compositions according to various non-limiting embodiments can further comprise at least one other conventional organic photochromic compounds having at least one activated absorption maxima within the range of 300 nm to 1000 nm, inclusive.

25 [0124] Non-limiting examples of suitable substrates to which the coating composition comprising the photochromic amount of the photochromic compounds can be applied include glass, masonry, textiles, ceramics, metals, wood, paper and polymeric organic materials. Non-limiting examples of suitable polymeric organic materials are set forth above.

30 [0125] Further provided are optical elements comprising a substrate and an at least partial coating comprising at least one photochromic compound of the present disclosure connected to at least a portion of the substrate. Non-limiting examples of optical elements include, ophthalmic elements, display elements, windows, and mirrors. For example, the optical element can be an ophthalmic element, and the substrate can be an ophthalmic substrate chosen from corrective and non-corrective lenses, partially formed lenses, and lens blanks.

[0126] Although not limiting herein, the optical elements can comprise any amount of the photochromic compound necessary to achieve the desired optical properties, such as but not limited to, photochromic properties and dichroic properties.

35 [0127] Other non-limiting examples of substrates that are suitable for use in conjunction with the foregoing non-limiting embodiment include untinted substrates, tinted substrates, photochromic substrates, tinted-photochromic substrates, linearly polarizing substrates, circularly polarizing substrates, elliptically polarizing substrates, reflective substrates, and wave plates or retarder substrates, e.g., quarter wave plate and half wave plate. As used herein with reference to substrates the term "untinted" means substrates that are essentially free of coloring agent additions (such as, but not limited to, conventional dyes) and have an absorption spectrum for visible radiation that does not vary significantly in response to actinic radiation. Further, with reference to substrates the term "tinted" means substrates that have a coloring agent addition (such as, but not limited to, conventional dyes) and an absorption spectrum for visible radiation that does not vary significantly in response to actinic radiation.

40 [0128] As used herein the term "linearly polarizing" with reference to substrates refers to substrates that are adapted to linearly polarize radiation (i.e., confine the vibrations of the electric vector of light waves to one direction). As used herein the term "circularly polarizing" with reference to substrates refers to substrates that are adapted to circularly polarize radiation. As used herein the term "elliptically polarizing" with reference to substrates refers to substrates that are adapted to elliptically polarize radiation. As used herein with the term "photochromic" with reference to substrates refers to substrates having an absorption spectrum for visible radiation that varies in response to at least actinic radiation and is thermally reversible. Further, as used herein with reference to substrates, the term "tinted-photochromic" means substrates containing a coloring agent addition as well as a photochromic compound, and having an absorption spectrum for visible radiation that varies in response to at least actinic radiation and is thermally reversible. Thus for example, the tinted-photochromic substrate can have a first color characteristic of the coloring agent and a second color characteristic of the combination of the coloring agent and the photochromic compound when exposed to actinic radiation.

45 [0129] The present invention also is directed to an optical element comprising a substrate and an at least partial coating comprising at least one photochromic compound of the present disclosure connected to at least a portion of the substrate. Further, the at least one thermally reversible photochromic compound can be a photochromic-dichroic compound having an average absorption ratio greater than 1.5 in an activated state as determined according to CELL METHOD.

50 [0130] As discussed above, the optical elements according to the present invention can be display elements, such

as, but not limited to screens, monitors, and security elements. For example, the optical element can be a display element comprising a first substrate having a first surface, a second substrate having a second surface, wherein the second surface of the second substrate is opposite and spaced apart from the first surface of the first substrate so as to define a gap; and a fluid material comprising at least one photochromic compound of the present disclosure positioned within the gap defined by the first surface of the first substrate and the second surface of the second substrate. Further, the at least one photochromic compound can be a photochromic-dichroic compound having an average absorption ratio greater than 1.5 in an activated state as determined according to CELL METHOD.

[0131] Further, according to this non-limiting embodiment, the first and second substrates can be independently chosen from untinted substrates, tinted substrates, photochromic substrates, tinted-photochromic substrates, linearly polarizing substrates, circularly polarizing substrates, elliptically polarizing substrates and reflective substrates and retarder substrates.

[0132] The present invention also provides a security element comprising a substrate and at least one photochromic compound of the present disclosure connected to at least a portion of the substrate. Non-limiting examples of security elements include security marks and authentication marks that are connected to at least a portion of a substrate, such as and without limitation: access cards and passes, e.g., tickets, badges, identification or membership cards, debit cards etc.; negotiable instruments and non-negotiable instruments e.g., drafts, checks, bonds, notes, certificates of deposit, stock certificates, etc.; government documents, e.g., currency, licenses, identification cards, benefit cards, visas, passports, official certificates, deeds etc.; consumer goods, e.g., software, compact discs ("CDs"), digital-video discs ("DVDs"), appliances, consumer electronics, sporting goods, cars, etc.; credit cards; and merchandise tags, labels and packaging.

[0133] Although not limiting herein, the security element can be connected to at least a portion of a substrate chosen from a transparent substrate and a reflective substrate. Alternatively, wherein a reflective substrate is required, if the substrate is not reflective or sufficiently reflective for the intended application, a reflective material can be first applied to at least a portion of the substrate before the security mark is applied thereto. For example, a reflective aluminum coating can be applied to the at least a portion of the substrate prior to forming the security element thereon. Still further, security element can be connected to at least a portion of a substrate chosen from untinted substrates, tinted substrates, photochromic substrates, tinted-photochromic substrates, linearly polarizing, circularly polarizing substrates, and elliptically polarizing substrates.

[0134] Additionally, the at least one photochromic compound can be a thermally reversible photochromic-dichroic compound having an average absorption ratio greater than 1.5 in the activated state as determined according to CELL METHOD.

[0135] Furthermore, the aforementioned security element can further comprise one or more other coatings or sheets to form a multi-layer reflective security element with viewing angle dependent characteristics as described in U.S. Patent No. 6,641,874.

[0136] The photochromic articles and optical elements described above can be formed by methods known in the art. Although not limiting herein, it is contemplated that the photochromic compounds disclosed herein can be connected to a substrate or host by incorporation into the host material or application onto the host or substrate, such as in the form of a coating.

[0137] For example, the photochromic-dichroic compound can be incorporated into an organic host material by dissolving or dispersing the photochromic compound within the host material, e.g., casting it in place by adding the photochromic compound to the monomeric host material prior to polymerization, imbibition of the photochromic compound into the host material by immersion of the host material in a hot solution of the photochromic compound or by thermal transfer. As used herein the term "imbibition" includes permeation of the photochromic compound alone into the host material, solvent assisted transfer of the photochromic compound into a porous polymer, vapor phase transfer, and other such transfer methods.

[0138] Additionally, the photochromic compound disclosed herein can be applied to the organic host material or other substrate as part of a coating composition (as discussed above) or a sheet comprising the photochromic compound. As used herein the term "coating" means a supported film derived from a flowable composition, which may or may not have a uniform thickness. As used herein the term "sheet" means a pre-formed film having a generally uniform thickness and capable of self-support. In such cases ultraviolet light absorbers can be admixed with the photochromic materials before their addition to the coating or sheet or such absorbers can be superposed, e.g., superimposed, as a coating or film between the photochromic article and the incident light.

[0139] Non-limiting methods of applying coating compositions comprising the photochromic compounds disclosed herein include those methods known in the art for applying coatings, such as, spin coating, spray coating, spray and spin coating, curtain coating, flow coating, dip coating, injection molding, casting, roll coating, wire coating, and overmolding. the coating comprising the photochromic compound can be applied to a mold and the substrate can be formed on top of the coating (i.e., overmolding). Additionally or alternatively, a coating composition without the photochromic compound can be first applied to the substrate or organic host material using any of the aforementioned techniques and thereafter imbibed with the photochromic compound as described above.

[0140] Non-limiting examples of coating compositions of film forming polymers that can include photochromic materials are as follows: photochromic/dichroic liquid crystal coatings, such as those described in U.S. Patent No. 7,256,921 at column 2, line 60 to column 94, line 23; photochromic polyurethane coatings, such as those described in U.S. Patent No. 6,187,444 at column 3, line 4 to column 12, line 15; photochromic aminoplast resin coatings, such as those described in U.S. Patent Nos. 6,432,544 at column 2, line 52 to column 14, line 5 and 6,506,488 at column 2, line 43 to column 12, line 23; photochromic polysiloxane coatings, such as those described in U.S. Patent No. 4,556,605 at column 2, line 15 to column 7, line 27; photochromic poly(meth)acrylate coatings, such as those described in U.S. Patent Nos. 6,602,603 at column 3, line 15 to column 7, line 50, 6,150,430 at column 8, lines 15-38, and 6,025,026 at column 8, line 66 to column 10, line 32; polyanhydride photochromic coatings, such as those described in U.S. Patent No. 6,436,525 at column 2, line 52 to column 11, line 60; photochromic polyacrylamide coatings such as those described in U.S. Patent No. 6,060,001 at column 2, line 6 to column 5, line 40; photochromic epoxy resin coatings, such as those described in U.S. Patent Nos. 6,268,055 at column 2, line 63 to column 15, line 12; and photochromic poly(urea-urethane) coatings, such as those described in U.S. Patent No. 6,531,076 at column 2, line 60 to column 10, line 49.

[0141] Non-limiting methods of applying sheets comprising the photochromic compound disclosed herein to a substrate include, for example, at least one of: laminating, fusing, in-mold casting, and adhesively bonding the polymeric sheet to the at least a portion of the substrate. As used herein, the in-mold casting includes a variety of casting techniques, such as but not limited to: overmolding, wherein the sheet is placed in a mold and the substrate is formed (for example by casting) over at least a portion of the substrate; and injection molding, wherein the substrate is formed around the sheet. Further, it is contemplated that the photochromic compound can be applied to the sheet as a coating, incorporated into the sheet by imbibition or by other suitable methods, either prior to applying the sheet to the substrate or thereafter.

[0142] The polymeric sheet can comprise a polymeric composition of any of a wide variety of polymers, including both thermosetting polymers and thermoplastic polymers. As used herein, the term "polymer," is intended to include both polymers and oligomers, as well as both homopolymers and copolymers. Such polymers can include, for example, acrylic polymers, polyester polymers, polyurethane polymers, poly(urea)urethane polymers, polyamine polymers, polyepoxide polymers, polyamide polymers, polyether polymers, polysiloxane polymers, polysulfide polymers, copolymers thereof, and mixtures thereof. Generally these polymers can be any polymers of these types made by any method known to those skilled in the art.

[0143] The polymers used to form the polymeric sheet also may comprise functional groups including, but not limited to, carboxylic acid groups, amine groups, epoxide groups, hydroxyl groups, thiol groups, carbamate groups, amide groups, urea groups, isocyanate groups (including blocked isocyanate groups) mercaptan groups, groups having ethylenic unsaturation e.g., acrylate groups), vinyl groups, and combinations thereof. Appropriate mixtures of film-forming resins may also be used in the preparation of the coating compositions. If the polymer composition from which the polymeric sheet is formed comprises functional group-containing polymers (such as any of the previously mentioned functional group-containing polymers), the polymer composition can further comprise a material having functional groups reactive with those of said polymer. Reaction may be facilitated, for example, by thermal, photoinitiated, oxidative, and/or radiative curing techniques. Also contemplated are mixtures of any of the foregoing polymers.

[0144] Further non-limiting examples of polymers suitable for use in forming the polymeric sheet of the present invention are the thermoplastic block copolymers of polyalkyl(meth)acrylate and polyamide described in Published U.S. Patent Application 2004/0068071 A1 at paragraphs [0020] - [0042]; and U.S. Patent No. 6,096,375 at column 18, line 8 to column 19, line 5.

[0145] In a particular embodiment of the present invention, the polymeric sheet comprises an elastomeric polymer, for example thermoplastic elastomeric polymers. As used herein, by "elastomeric polymer" is meant a polymer that has a high degree of resiliency and elasticity such that it is capable of at least partially reversible deformation or elongation. In some instances, when stretched, the molecules of an elastomer are aligned and can take on aspects of a crystalline arrangement; and upon release, the elastomer can, to some extent, return to its natural disordered state. For purposes of the present invention, elastomeric polymers can include thermoplastic, thermoplastic elastomeric polymers, and thermosetting polymers provided such polymers fall within the description provided above for "elastomeric polymer".

[0146] The elastomeric polymer can comprise any of wide variety of art recognized elastomers including but not limited to copolymers of any of the previously mentioned polymers. In an embodiment of the present invention, the elastomeric polymer can comprise a block copolymer having ether and/or ester linkages in the polymer backbone. Examples of suitable block copolymers can include, but are not limited to, poly(amide-ether) block copolymers, poly(ester-ether) block copolymers, poly(ether-urethane) block copolymers, poly(ester-urethane) block copolymers, and/or poly(ether-urea) block copolymers. Suitable specific examples of such elastomeric polymers can include, but are not limited to, those commercially available under the tradenames DESMOPAN[®] and TEXIN[®] from Bayer Material Science; ARNITEL[®] from Royal DSM; and PEBAX[®] from Atofina Chemicals or Cordis Corporation.

[0147] Moreover, as discussed above, the photochromic compounds disclosed herein can be incorporated or applied alone, or in combination with at least one other conventional organic photochromic compound, which can also be applied or incorporated into the host materials and substrates as described above. Additional coatings may be applied to the

photochromic article including other photochromic coatings, anti-reflective coatings, linearly polarizing coatings, transitional coatings, primer coatings, adhesive coatings, mirrored coatings and protective coatings including antifogging coatings, oxygen barrier coatings and ultraviolet light absorbing coatings.

[0148] The embodiments described herein are further illustrated by the following non-limiting examples.

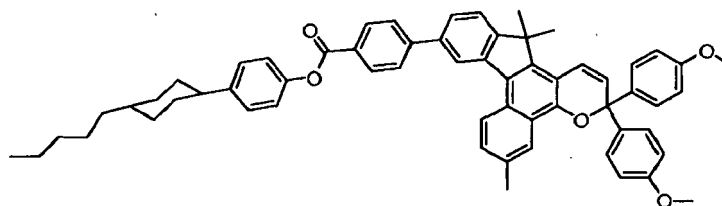
EXAMPLES

[0149] Part 1 describes the preparation of Examples 1-34. Part 2 describes the testing of the photochromic properties of the Examples. Part 3 describes the testing of the dichroic properties of the Examples.

Part 1 - Preparation of Examples 1-34

Example 1

[0150]



Step 1

[0151] 3-Bromo-4'-methylbenzophenone (50 g), dimethyl succinate (34.5 g) and toluene (1 liter (L)) were added to a reaction flask equipped with a mechanical stirrer, a solid addition funnel and a nitrogen blanket. The mixture was stirred at room temperature until the solids were dissolved. Solid potassium t-butoxide (22.4 g) was added through the solid addition funnel and the mixture was stirred at room temperature for 4 hours. The resulting reaction mixture was poured into 1 L of water and the aqueous layer, which contained the product, was collected. The toluene layer was extracted with 200 mL water. The combined water solution was washed with toluene. HCl (2 N, 20 mL) was added to the water solution. A yellow oil precipitated. The resulting mixture was extracted with ethyl acetate, dried over magnesium sulfate, concentrated and dried in a vacuum. A yellow glassy oil (55 g) was obtained as product. It was used directly in the next step.

Step 2

[0152] A mixture of the Stobbe acid products from Step 1 (55 g) and acetic anhydride (300 mL) was mixed and refluxed in a reaction flask equipped with a condenser. After one hour, the acetic anhydride was removed by vacuum evaporation and 55 grams of oil was obtained as the product. It was used directly in the next step.

Step 3

[0153] To a reaction flask containing the 55 grams of oil obtained from Step 2 were added methanol (300 mL) of and HCl (12 N, 1 ml). The mixture was refluxed for four hours. The methanol was removed by vacuum evaporation. The recovered oil was dissolved in methylene chloride, washed with sodium bicarbonate saturated water, dried over magnesium sulfate, concentrated and dried in vacuum. The resulting oil (51 g) was used directly in the next step.

Step 4

[0154] The product (51 g) from Step 3 was dissolved in 500 ml of anhydrous THF in an oven dried flask equipped with a dropping funnel and a magnetic stir bar. The mixture was stirred mixture at room temperature, and 1.6 M toluene/THF (1:1) solution of methyl magnesium bromide was added dropwise. After the addition, the mixture was stirred at room temperature for about 16 hours. The reaction mixture was then poured into 2 L of ice water. The pH value of the mixture was adjusted to ~2 using HCl (12 N). Ethyl acetate (500 mL) was added. The resulting organic layer was separated, dried over magnesium sulfate, concentrated and dried in vacuum. The recovered product (50 g of oil) was used directly in the next step.

Step 5

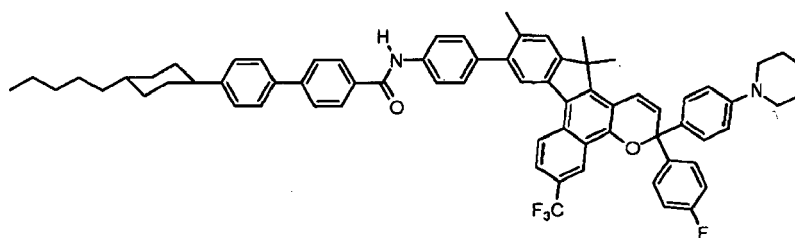
[0155] The product from Step 4 (50 g) and xylene (300 mL) were added to a reaction flask equipped with a magnetic stir bar. p-Toluenesulfonic acid (1 g) was added and the resulting mixture was refluxed for eight hours. Xylene was removed by vacuum evaporation and the resulting oily product was dissolved in ethyl acetate, washed with water, dried over magnesium sulfate and concentrated. A small portion of the product (50 g of oil) contained four naphthol isomers. The product (1.8 g) was purified using a CombiFlash® Rf from Teledyne ISCO. After separation, four grouped fractions were obtained. NMR analysis showed the products to have structures consistent with: 8-bromo-3,7,7-trimethyl-7H-benzo[c]fluoren-8-ol (0.32 g); 4-bromo-7,7,9-trimethyl-7H-benzo[c]fluoren-5-ol (0.08 g); and a mixture (0.36 g) of 10-bromo-3,7,7-trimethyl-7H-benzo[c]fluoren-5-ol (the desired isomer, being 55 weight % of the mixture) and 2-bromo-7,7,9-trimethyl-7H-benzo[c]fluoren-5-ol (the undesired isomer being 45 weight % of the mixture).

Step 6

[0156] The mixture of naphthols from Step 5, (0.36 g) of 10-bromo-3,7,7-trimethyl-7H-benzo[c]fluoren-5-ol and 2-bromo-7,7,9-trimethyl-7H-benzo[c]fluoren-5-ol was placed in a reaction flask. To the flask were added 0.27 grams of 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol, a few crystals of p-toluenesulfonic acid and methylene chloride (10 ml). The mixture was stirred at room temperature for 18 hours. The formation of a blue dye and a purple dye was observed from TLC. The product was purified using a CombiFlash® Rf. A product (0.5 g) with two isomers was obtained. It was used directly in the next step.

Step 7

[0157] The dye mixture from Step 6 (0.5 g) was placed in a reaction flask and the following were added: 4-(4-trans-pentylcyclohexyl)phenyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (0.39 g, prepared following the procedure from Step 2 of Example 3 except that 4-(trans-4-pentylcyclohexyl)phenol and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid was used in place of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline and 4-(trans-4-pentylcyclohexyl)benzoic acid); potassium fluoride (0.19 g); dichlorobis(triphenylphosphine)palladium (II) (0.012 g); THF (20 mL) and water (20 mL). The mixture was degassed, protected by nitrogen and heated to reflux. After 18 hours, TLC showed the formation of a grey dye and a purple dye. The mixture was extracted using methylene chloride and water. The organic layer was recovered, isolated, dried over magnesium sulfate and concentrated. The resulting product was purified using CombiFlash®Rf. The grey dye was obtained as a green solid (0.25 g, less polar). The purple dye was obtained as an off-white solid (0.18 g, more polar). NMR analysis showed the more polar purple dye to have a structure consistent with 3,3-bis(4-methoxyphenyl)-10-[4-((4-(trans-4-pentylcyclohexyl)phenoxy)carbonyl)phenyl]-6,13,13-trimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 2**[0158]**Step 1

[0159] Magnesium (3.2 g) and THF (50 ml) was placed in a dry flask equipped with a dropping funnel which contained a mixture of 1-bromo-4-(trifluoromethyl) benzene (30 g) and THF (200 ml). 20 ml of the solution in the dropping funnel was added to the flask. A few drops of dibromoethane were also added to the flask to help initiate the reaction. Few minutes later, solvent in the reaction flask started to boil. Rest of the solution in the dropping funnel was added drop wise. Ice water was used occasionally to cool the reaction mixture. After the addition, the mixture was stirred at room temperature for two hours. 3-bromo-4-methylbenzonitrile (26 g) was then added to the reaction mixture. Mixture was stirred at room temperature over night. 3 N HCl (200 ml) was added. The mixture was stirred for 4 hours. Organic layer

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was collected by a separatory funnel and then concentrated. A silica gel plug column separation was used to clean up the product with the use of mixture solvent 90/10 Hexanes/ethyl acetate. The type of silica gel used in this step and others was Grade 60, 230-400 mesh. White crystals (19 g) were obtained as the product. NMR showed that the product had a structure consistent with 3-bromo-4-methyl-4'-trifluoromethylbenzophenone.

Step 2

[0160] A suspension of 1-bromo-4-(trans-4-pentylcyclohexyl)benzene (96 g), 4-(methoxycarbonyl)phenylboronic acid (56 g), K_2CO_3 (17 g), $Pd(PPh_3)_4$ (1.5 g), 1,4-dioxane (400 mL) and water (12 mL) was placed in a reaction flask and stirred at 105 °C for 10 hours. After the reaction, the mixture was poured into water (1 L) under stirring. Grey solid was obtained after filtration. The solid was washed with water, dissolved in CH_2Cl_2 (400 mL), dried over $MgSO_4$ and filtered through celite. The filtrate was concentrated and poured into methanol (600 mL) under stirring. The precipitate was collected by filtration, washed with methanol and dried. White solid was obtained (80.4 g) as product. NMR showed that the product had a structure consistent with methyl 4'-(4-pentylcyclohexyl)biphenyl-4-carboxylate.

Step 3

[0161] Product from Step 2 (20 g) was mixed with sodium hydroxide (6.57 g) and ethanol (500 mL) in a reaction flask. The mixture was heated to reflux for 4 hours, cooled to room temperature and acidified using conc. HCl. The precipitate was collected by filtration, washed with water and dried. White solid was obtained (18.2 g) as product. NMR showed that the product had a structure consistent with 4'-(4-pentylcyclohexyl)biphenyl-4-carboxylic acid.

Step 4

[0162] Product from Step 3 (18.2 g) was mixed with $SOCl_2$ (300 mL) and DMF (three drops) in a reaction flask and heated to reflux for 8 hours. The solution was concentrated under atmospheric pressure and the resulting residue was poured into 200 mL hexane under stirring. The precipitated white solid was collected by filtration, washed with hexane and dried. White solid (17.53 g) was obtained as product. NMR showed that the product had a structure consistent with 4'-(4-pentylcyclohexyl)biphenyl-4-carbonyl chloride.

Step 5

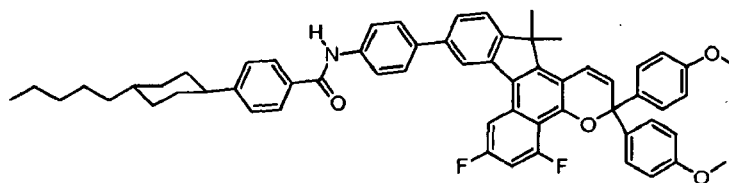
[0163] Product from Step 4 (10 g) in methylene chloride (30 ml) was dropped into a solution of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (5.94 g) and TEA (4.13 g) in CH_2Cl_2 (60 ml) under stirring. After addition, the solution was kept stirring for 24 hours. The solution was then washed with water (50 mL) three times, dried over $MgSO_4$, concentrated under reduced pressure and then poured into methanol (200 ml) under stirring. The precipitate was filtered, washed with methanol and dried. White solid (12.24 g) was obtained as product. NMR showed that the product had a structure consistent with 4'-(4-pentylcyclohexyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)biphenyl-4-carboxamide.

Step 6

[0164] The procedures from Step 1 to Step 7 of Example 1 were followed except that 3-bromo-4-methyl-4'-trifluoromethylbenzophenone from step 1 of this example was used in place of 3-bromo-4'-methylbenzophenone in Step 1 of Example 1, 1-(4-fluorophenyl)-1-(4-(piperidin-1-yl)phenyl)prop-2-yn-1-ol was used in place of 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol in Step 6 of Example 1 and 4'-(4-trans-pentylcyclohexyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-[1,1'-biphenyl]-4-carboxamide from step 5 of this example was used in place of 4-(4-trans-pentylcyclohexyl)phenyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate in Step 7 of Example 1. Blue solid was obtained as the product. NMR showed that the product had a structure consistent with 3-(4-fluorophenyl)-3-(4-piperidinophenyl)-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-11,13,13-trimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 3

[0165]



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Step 1

10 **[0166]** Magnesium (5.26 g) and THF (50 ml) was placed in a dry flask equipped with a dropping funnel, which contained THF (400ml) solution of 1-bromo-3,5-difluorobenzene (44 g). One tenth of the solution in the dropping funnel was added to the flask. A few drops of dibromoethane were also added to the flask to help initiate the reaction. Few minutes later, solvent in the reaction flask started to boil. Ice bath was applied. The rest of the solution in the dropping funnel was added drop wise at 0 °C in half an hour. Half an hour after the addition, most Mg disappeared. Mixture was let stir at room temperature for 2 more hours. All Mg went into solution. At 0 °C, bis[2-(N,N-dimethylamino)ethyl]ether (35 g) was added. Stir for 15 minutes. Then 3-bromobenzoyl chloride (50 g) was added in one portion. The mixture was stirred for 2 hours at 0°C. Water (500 mL) was added to the mixture. 12N HCl was used to adjust pH to ~2. DCM was added to the mixture (500 ml). Organic layer was collected, washed with water once, washed with sodium bicarbonate once, dried over magnesium sulfate and concentrated. A viscous oil (57 g) was obtained. The oil was used directly in the next step.

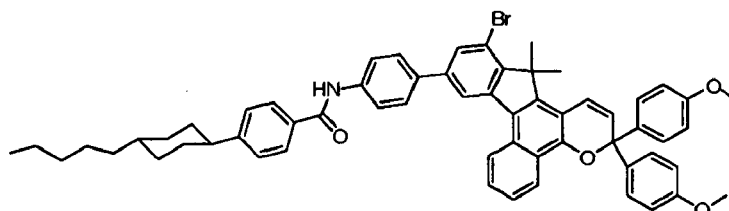
20 NMR showed that 3-bromo-3',5'-difluorobenzophenone was the major component in the oil.

Step 2

25 **[0167]** A mixture of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (52 g), 4-(trans-4-pentylcyclohexyl)benzoic acid (65 g), DCC (64.4 g), DMAP (3 g) and methylene chloride (500 ml) was placed in a reaction flask and stirred for 24 hours. Solid was filtered off. The filtrate was concentrated. Methanol (1 L) was added. The formed crystals were collected by filtration and dried. White crystals (91 g) were obtained as the product. NMR showed that the product had a structure consistent with 4-(4-trans-pentylcyclohexyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)benzamide.

Step 3

30 **[0168]** The procedures from Step 1 to Step 7 of Example 1 were followed except that 3-bromo-3',5'-difluorobenzophenone from Step 1 of this example was used in place of 3-bromo-4'-methylbenzophenone in Step 1 of Example 1, and 4-(4-trans-pentylcyclohexyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)benzamide from Step 2 of this example was used in place of 4-(4-trans-pentylcyclohexyl)phenyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate in Step 7 of Example 1. Grey solid was obtained as the product. NMR showed that the product had a structure consistent with 3,3-bis(4-methoxyphenyl)-10-(4-(4-(4-trans-pentylcyclohexyl)benzamido)phenyl)-5,7-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 4**[0169]**

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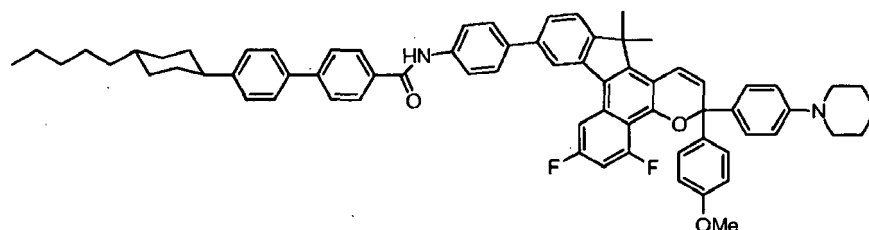
55 **[0170]** The procedures from Example 3 were followed except that in Step 1, tribromobenzene was used in place of 1-bromo-3,5-difluorobenzene and benzoyl chloride was used in place of 3-bromobenzoyl chloride. Black solid was obtained as the product. NMR analysis showed that the product had a structure consistent with 3,3-bis(4-methoxyphenyl)-10-[4-(4-(4-trans-pentylcyclohexyl)benzamido)phenyl]-13,13-dimethyl-12-bromo-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 5

[0171]

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[0172] The procedures from Example 1 were followed except that 3-bromo-3',5'-difluorobenzophenone from Step 1 of Example 3 was used in place of 3-bromo-4'-methylbenzophenone in Step 1, 1-(4-methoxyphenyl)-1-(4-(N-piperidino)phenyl)prop-2-yn-1-ol was used in place of 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol in step 6 and 4'-(4-trans-pentylcyclohexyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-[1,1'-biphenyl]-4-carboxamide was used in place of 4-(4-trans-pentylcyclohexyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)benzamide in step 7. NMR analysis showed that the product had a structure consistent with 3-(4-methoxyphenyl)-3-(4-(N-piperidino)phenyl)-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-5,7-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

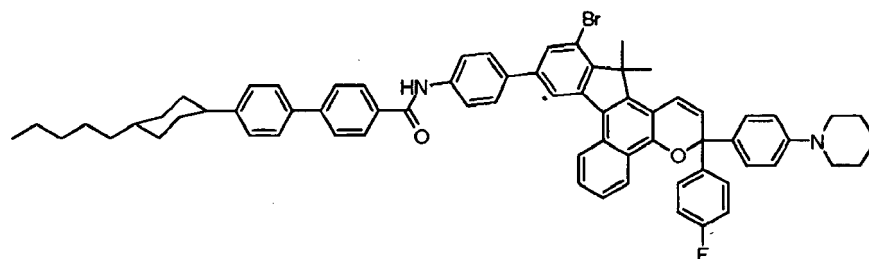
Example 6

[0173]

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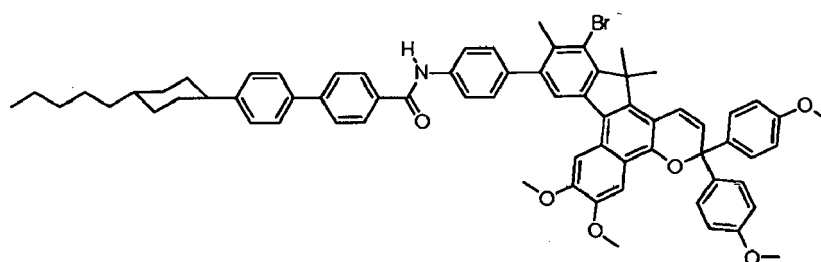
[0174] The procedures from Step 1 and Step 3 of Example 3 were followed except that: in Step 1, tribromobenzene was used in place of 1-bromo-3,5-difluorobenzene and benzoyl chloride was used in place of 3-bromobenzoyl chloride; in Step 3, 1-(4-fluorophenyl)-1-(4-(N-piperidino)phenyl)prop-2-yn-1-ol was used in place of 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol; 4'-(4-trans-pentylcyclohexyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-[1,1'-biphenyl]-4-carboxamide was used in place of 4-(4-trans-pentylcyclohexyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)benzamide. NMR analysis showed that the product had a structure consistent with 3-(4-fluorophenyl)-3-(4-(N-piperidino)phenyl)-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-12-bromo-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 7

[0175]

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Step 5

[0182] A mixture of manganese chloride (7.46 g) and lithium chloride (5 g) was dried at 200 °C in a vacuum oven for an hour. Under the protection of nitrogen, THF was added (200 ml). The dissolution took about 30 minutes. To the solution, copper (I) chloride (0.59 g) and 2-(6-bromo-3-methyl-1-oxo-1H-inden-2-yl)acetic acid (19.4 g) from Step 4 were added. The mixture was stirred to clear and then cooled to 0°C. To the mixture, 2M THF solution of butylmagnesium bromide (99 ml) was added dropwise. The reaction mixture turned black eventually with the addition of more BuMgBr. The addition was finished in 2 hours. After the-addition, the mixture was stirred at 0°C for 2 more hours and then quenched using water (200 ml). The pH of the mixture was adjusted to ~2 using 12 N HCl. Ethyl acetate (200 ml) was added. The organic portion was collected by a separatory funnel, dried, and concentrated. The product was purified by CombiFlash®.Rf Oil (4 g) was obtained as the product. NMR analysis showed that the product had a structure consistent with 2-(5-bromo-1-butyl-1-methyl-3-oxo-2,3-dihydro-1H-inden-2-yl)acetic acid.

Step 6

[0183] Solid magnesium (1.5 g) was placed in a reaction flask equipped with a dropping funnel and dried in an oven. THF (60 ml) and 1-bromo-4-trifluoromethylbenzene (15.3 g) was added. With the initiation of one drop of 1,2-dibromoethane, Grignard started to form. Ice bath was used occasionally to control the rate of the reaction. Two hours later, all magnesium was consumed. In the dropping funnel, 2-(5-bromo-1-butyl-1-methyl-3-oxo-2,3-dihydro-1H-inden-2-yl)acetic acid (4.2 g) from Step 5 was mixed with anhydrous THF (20 ml) and dropped into the Grignard solution. The addition was completed in 10 minutes. After the addition, the mixture was stirred at room temperature for 2 hours. The reaction was stopped by the addition of water (100 ml). The pH was adjusted to 2 using 12 N HCl. Ethyl acetate was added (100 ml). The organic phase was collected by a separatory funnel, washed with NaCl/water, dried over magnesium sulfate and concentrated. The obtained oil was re-dissolved in toluene (100 ml) in a reaction flask. Acetic anhydride (10 grams) and bismuth triflate (0.5 g) was added. The mixture was refluxed for 1 hour and cooled to room temperature. Methanol (100 ml) and 12 N HCl (1 ml) were added. The mixture was refluxed for 12 hours. All the solvent was removed. A silica gel plug column separation was applied to the product. Oil (3 g) was obtained as the product. NMR analysis supported that the product had a structure consistent with 10-bromo-7-butyl-7-methyl-3-(trifluoromethyl)-7H-benzo[c]fluoren-5-ol.

Step 7

[0184] The 10-bromo-7-butyl-7-methyl-3-(trifluoromethyl)-7H-benzo[c]fluoren-5-ol (3 g) from Step 6 was placed in a reaction flask. To the flask, 1-(4-fluorophenyl)-1-(4-(N-morpholino)phenyl)prop-2-yn-1-ol (2.1 g), 1,2-dichloroethane (30 ml) and p-toluenesulfonic acid (70 mg) were added. The mixture was refluxed for 4 hours. All solvent was removed. A silica gel plug column was used to purify the product. A brownish oil (2 grams) was obtained as the product. NMR analysis showed that the product had a structure consistent with 3-(4-fluorophenyl)-3-(4-(N-morpholino)phenyl)-10-bromo-6-trifluoromethyl-13-methyl-13-butyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Step 8

[0185] A mixture of 3-(4-fluorophenyl)-3-(4-(N-morpholino)phenyl)-10-bromo-6-trifluoromethyl-13-methyl-13-butyl-indeno[2',3':3,4]naphtho[1,2-b]pyran (1.4 g) from Step 7, 4'-(4-trans-pentylcyclohexyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-[1,1'-biphenyl]-4-carboxamide (1.5 g), palladium acetate (24 mg), triphenyl phosphine (112 mg), sodium carbonate (0.8 g), THF (20 ml) and water (10 ml) was degassed and refluxed for 4 hours. The reaction mixture was passed through CELITE® filtering aid elite to get rid of the insoluble solid in the mixture. The product was washed off using methylene chloride. After extraction with water, organic layer was collected and concentrated. The product was purified by CombiFlash® Rf. Blue solid (0.7 g) was obtained as the product. NMR showed that the product had a structure consistent with 3-(4-fluorophenyl)-3-(4-(N-morpholino)phenyl)-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamide)phenyl]-6-trifluoromethyl-13-methyl-13-butyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 9**[0186]**

EP 2 652 552 B9

Step 3

[0191] Solid anhydrous lanthanum (III) chloride (100 g) was ground to a very fine powder and then mixed with lithium chloride (52 g) and dry THF (1 liter) in a 5 liter three-neck flask equipped with a mechanical stir and a dropping funnel. The mixture was refluxed for few hours until it dissolved. Solid (E)-4-(3,5-dibromophenyl)-3-(methoxycarbonyl)-4-(4-(trifluoromethyl)phenyl)but-3-enoic acid (106 g) from Step 2 was dissolved in the mixture. The mixture was then cooled to -15 °C. A solution of 3M methyl magnesium chloride (238 ml) was placed in the dropping funnel. The first 30% of the Grignard was added slowly to the mixture. Generation of gas bubbles was observed. After the temperature returned to -15 °C, the remainder of the Grignard was added to the mixture in 2 minutes. After 30 minutes, water (1 L) was added slowly to the mixture and the pH was adjusted to acidic using acetic acid. The mixture turned clear with formation of two layers. The water layer was drained off. The organic layer was washed with NaCl/water four times and then concentrated to dry. A light yellowish solid was recovered and dissolved in toluene. The solution was filtered using a silica gel plug column and the recovered clear solution was concentrated to dryness. White solid product was obtained and used in the next Step without further purification. A portion of the product was recrystallized from methanol and NMR analysis showed that the purified crystals had a structure consistent with (E)-4-((3,5-dibromophenyl)(4-(trifluoromethyl)phenyl)methylene)-5,5-dimethyldihydrofuran-2(3H)-one.

Step 4

[0192] Into a reaction flask were added the product from Step 3, toluene (500 ml), bismuth triflate (20 g) and acetic acid (0.24 g). The resulting mixture was stirred at reflux for 1 hour. After it cooled to room temperature, acetic anhydride (100 ml) was added. The mixture was heated to reflux again and after one hour, the mixture was cooled to room temperature and filtered through a silica gel plug column. The recovered clear solution was concentrated to dryness. Acetone (50 ml) was added to the obtained solid to form a slurry and methanol (250 ml) was subsequently added. The resulting mixture was cooled to form crystals. The recovered white crystals (58 g) were analyzed by NMR which showed that the product had a structure consistent with 8,10-dibromo-7,7-dimethyl-3-(trifluoromethyl)-7H-benzo[c]fluoren-5-yl acetate.

Step 5

[0193] To a flask containing 8,10-dibromo-7,7-dimethyl-3-(trifluoromethyl)-7H benzo[c]fluoren-5-yl acetate (2.42 g) from Step 4 were added methanol (20 mL) and tetrahydrofuran (10 mL). Concentrated hydrochloric acid (1 mL) was added and the solution was heated to reflux for 4 h. The solvent was removed under vacuum and the residue was purified by filtration through a plug of silica gel, using 4:1 hexane/ethyl acetate mixture as the eluent. Fractions containing the desired material were grouped and concentrated to provide a cream colored solid (1.63 g). NMR analysis of the cream colored solid indicated a structure that was consistent with 8,10-dibromo-7,7-dimethyl-3-(trifluoromethyl)-7H-benzo[c]fluoren-5-ol.

Step 6

[0194] Into a reaction flask containing a chloroform solution (50 mL) of the product from Step 6, 8,10-dibromo-7,7-dimethyl-3-(trifluoromethyl)-7H-benzo[c]fluoren-5-ol (1.63 g) were added 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (1.08 g), triisopropylorthoformate (0.90 mL) and pyridinium p-toluenesulfonate (0.10 g). The solution was heated to reflux for 2 h. The reaction mixture was concentrated under reduced pressure to provide an oily residue. Diethyl ether was added to the residue to provide a cream colored precipitate. The cream colored precipitate was collected by vacuum filtration (2.30 g) and used directly in the next Step. NMR analysis of the cream colored precipitate indicated a structure that was consistent with 3,3-bis(4-methoxyphenyl)-10,12-dibromo-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

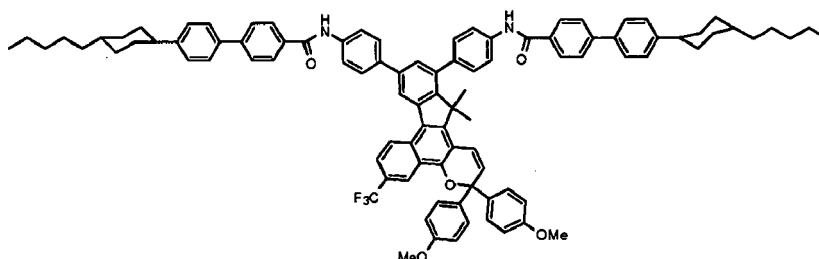
Step 7

[0195] Into a reaction flask containing the product from Step 6 (2.30 g) and 4'-(4-trans-pentylcyclohexyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-[1,1'-biphenyl]-4-carboxamide (1.72 g) in a 1:1 mixture of THF (40 mL) and water (40 mL) was added potassium fluoride (1.81 g, 30.68 mmol). The solution was degassed by bubbling with nitrogen for 10 min. To the resulting solution, bis(triphenylphosphine) palladium(II) chloride (0.22 g, 0.31 mmol) was added. The solution was heated to reflux for 16 h. The reaction mixture was cooled to room temperature and diluted with ethyl acetate. The mixture was filtered through a bed of CELITE® filtering aid and the filtrate was partitioned with ethyl acetate and water. The ethyl acetate extract was collected, dried with anhydrous sodium sulfate and concentrated to provide

an oily residue. The residue was purified by column chromatography using 4:1 hexane and ethyl acetate mixture as the eluent. Fractions that contained the desired product were grouped and concentrated in vacuo to provide an oily residue. The oil was dissolved in a minimum amount of dichloromethane and added drop-wise to a vigorously stirred solution of methanol. The resulting precipitate was collected by vacuum filtration and dried to yield a purple solid (0.90 g). NMR analysis of the purple solid indicated a structure that was consistent with 3,3-bis(4-methoxyphenyl)-10-[4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-12-bromo-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 11

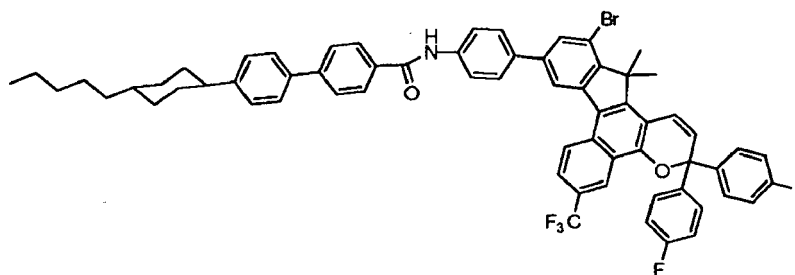
[0196]



[0197] The product of Example 10 was fractionated using column chromatography by increasing the polarity of the hexane and ethyl acetate (1:1) eluent to provide polar fractions. The fractions were grouped and concentrated in vacuo to yield an oily residue. The oil was dissolved in a minimum amount of dichloromethane and added drop-wise to vigorously stirred solution of methanol. The resulting precipitate was collected by vacuum filtration and dried to provide blue-purple solid (0.30g). NMR analysis of the purple solid indicated a structure that was consistent with 3,3-bis(4-methoxyphenyl)-10,12-bis[4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 12

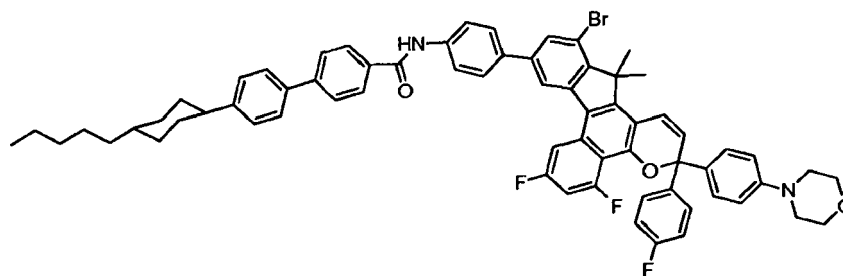
[0198]



[0199] The procedures of Example 10 were followed except that 1,1-bis(4-fluorophenyl)prop-2-yn-1-ol was used in place of 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol in Step 6. NMR analysis showed that the final product had a structure consistent with 3,3-bis(4-fluorophenyl)-10-[4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-12-bromo-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 13

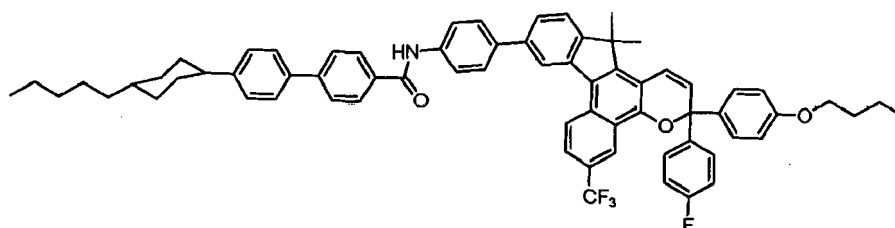
[0200]



[0201] The procedures of Example 10 were followed except for the following: in Step 1, 3,5-difluorobenzoyl chloride was used in place of 4-trifluoromethylbenzoyl chloride; in Step 4, the product was used without purification in the next Step; in Step 5, the desired 8,10-dibromo-2,4-difluoro-7,7-dimethyl-7H-benzo[c]fluoren-5-ol was recrystallized using ethyl acetate as solvent; in Step 6, 1-(4-fluorophenyl)-1-(4-(N-morpholino)phenyl)prop-2-yn-1-ol was used in place of 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol; in Step 7, a different catalysis system of palladium acetate / triphenylphosphine / sodium carbonate / dimethoxymethane / ethanol was used in place of bis(triphenylphosphine)palladium(II) chloride / potassium fluoride / THF / water. NMR analysis showed that the final product had a structure consistent with 3-(4-fluorophenyl)-3-(4-morpholinophenyl)-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-5,7-difluoro-12-bromo-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 14

[0202]



Step 1 to Step 4

[0203] Procedures from Step 1 to Step 4 of Example 10 were followed.

Step 5

[0204] 8,10-Dibromo-7,7-dimethyl-3-(trifluoromethyl)-7H-benzo[c]fluoren-5-yl acetate (53.88 g) from Step 4 and 4'-(4-trans-pentylcyclohexyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-[1,1'-biphenyl]-4-carboxamide (56.27 g) were added to reaction flask and dissolved in a 1:1 mixture of toluene (1000 mL) and ethanol (1000 mL). Potassium carbonate (42.26 g) and triphenylphosphine (8.02 g) were added to the solution which was degassed by bubbling nitrogen for 20 min. To the resulting solution, palladium acetate (2.29 g) was added and the mixture was heated to reflux for 3 h. The reaction mixture was cooled to room temperature and a degassed suspension of bis(triphenylphosphine)palladium(II) chloride (7.15 g) in toluene (100 mL) and ethanol (100 mL) was added. The reaction mixture was heated to reflux for 16 h. The reaction mixture was cooled to room temperature and diluted with ethyl acetate (500 mL). The mixture was filtered through CELITE® filtering aid and the filtrate was collected and concentrated in vacuo to provide a residue. The residue was purified by column chromatography using 19:1 toluene and ethyl acetate mixture as the eluent. Fractions that contained the desired product were grouped and concentrated in vacuo to provide a cream colored residue. Toluene was added to the residue to precipitate the product. The resulting precipitate was collected by vacuum filtration and dried to provide a cream colored solid (32 g). NMR analysis of the cream colored solid indicated a structure that was consistent 7,7-dimethyl-3-trifluoromethyl-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-7H benzo[c]fluoren-5-ol.

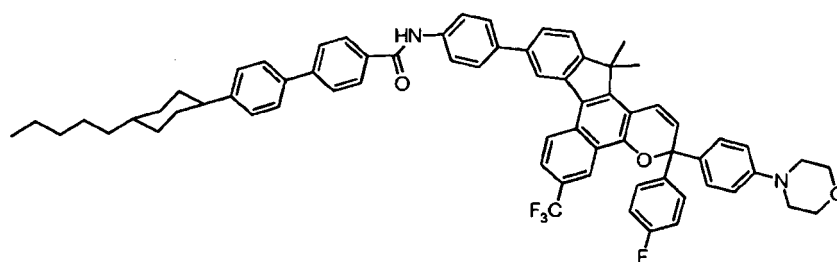
Step 6

[0205] 7,7-Dimethyl-3-trifluoromethyl-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl) benzamido)phenyl]-7H ben-

zo[c]fluoren-5-yl from Step 5 (18.00 g) was added to a reaction flask and dissolved in tetrahydrofuran (200 mL). 4-Dodecylbenzenesulfonic acid (0.54 g) was added as a solution in toluene (20 mL). 1-(4-Butoxyphenyl)-1-(4-fluorophenyl)prop-2-yn-1-ol (14.52 g) was added in 5 portions as a solution in toluene (20 mL) and the mixture was heated to reflux for 6 h. The reaction mixture was cooled to room temperature and the solvent was removed in vacuo to provide a residue. The residue was purified by column chromatography using 1:1 hexane and toluene mixture as the eluent. Fractions containing the desired product were grouped and concentrated in vacuo to provide an oily residue. The oil was dissolved in a minimum amount of dichloromethane and added drop-wise to a vigorously stirred solution of methanol. The resulting precipitate was collected by vacuum filtration and dried to provide purple solid (9.97 g). NMR analysis of the purple solid indicated a structure that was consistent with 3-(4-fluorophenyl)-3-(4-butoxyphenyl)-10-[4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 15

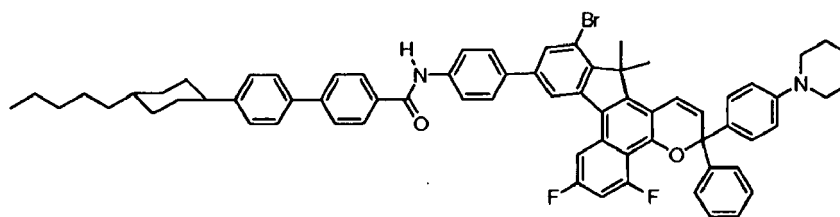
[0206]



[0207] The procedures from Example 14 were followed except that 1-(4-fluorophenyl)-1-(4-(N-morpholino)phenyl)prop-2-yn-1-ol was used in place of 1-(4-butoxyphenyl)-1-(4-fluorophenyl)prop-2-yn-1-ol in Step 6. NMR analysis showed that the structure was consistent with 3-(4-fluorophenyl)-3-(4-(N-morpholino)phenyl)-10-[4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 16

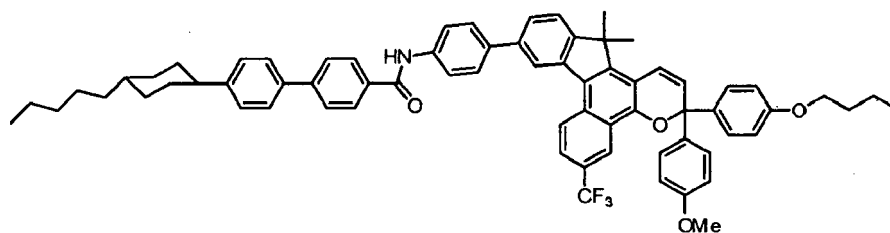
[0208]



[0209] The procedures from Example 13 were followed except that 1-phenyl-1-(4-piperidinophenyl)prop-2-yn-1-ol was used in place of 1-(4-N-morpholinophenyl)-1-(4-fluorophenyl)prop-2-yn-1-ol. NMR analysis showed that the structure was consistent with 3-phenyl-3-(4-piperidinophenyl)-10-[4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-5,7-difluoro-12-bromo-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 17

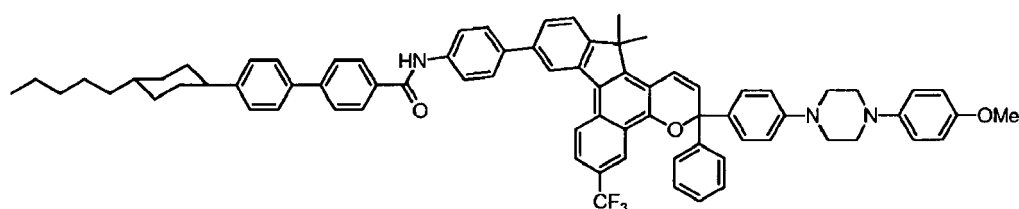
[0210]



[0211] The procedures from Example 14 were followed except that 1-(4-butoxyphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol was used in place of 1-(4-butoxyphenyl)-1-(4-fluorophenyl)prop-2-yn-1-ol. NMR analysis showed that the product had a structure consistent with 3-(4-methoxyphenyl)-3-(4-butoxyphenyl)-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

15 **Example 18**

[0212]

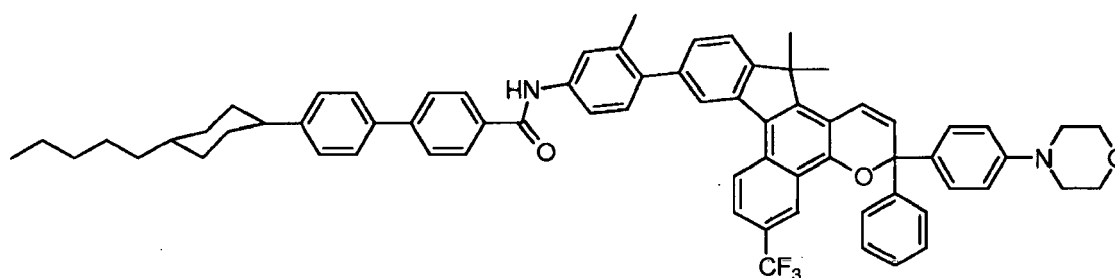


[0213] The procedures from Example 14 were followed except that 1-(4-(4-(4-methoxyphenyl)piperazin-1-yl)phenyl)-l-phenylprop-2-yn-1-ol was used in place of 1-(4-butoxyphenyl)-1-(4-fluorophenyl)prop-2-yn-1-ol. NMR analysis showed that the product had a structure consistent with 3-(4-(4-(4-methoxyphenyl)piperazin-1-yl)phenyl)-3-phenyl-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

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Example 19

[0214]

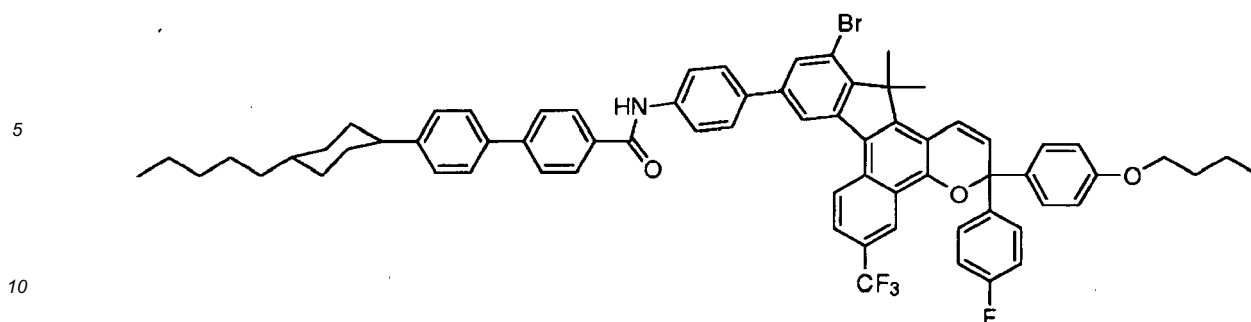


[0215] The procedures from Example 14 were followed except that 1-phenyl-1-(4-(N-morpholino)phenyl)prop-2-yn-1-ol was used in place of 1-(4-butoxyphenyl)-1-(4-fluorophenyl)prop-2-yn-1-ol and N-(3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-4'-(4-pentylcyclohexyl)-[1,1'-biphenyl]-4-carboxamide was used in place of 4'-(4-trans-pentylcyclohexyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-[1,1'-biphenyl]-4-carboxamide. NMR indicated that the structure was consistent with 3-phenyl-3-(4-(N-morpholino)phenyl)-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)-2-methylphenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

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55 **Example 20**

[0216]



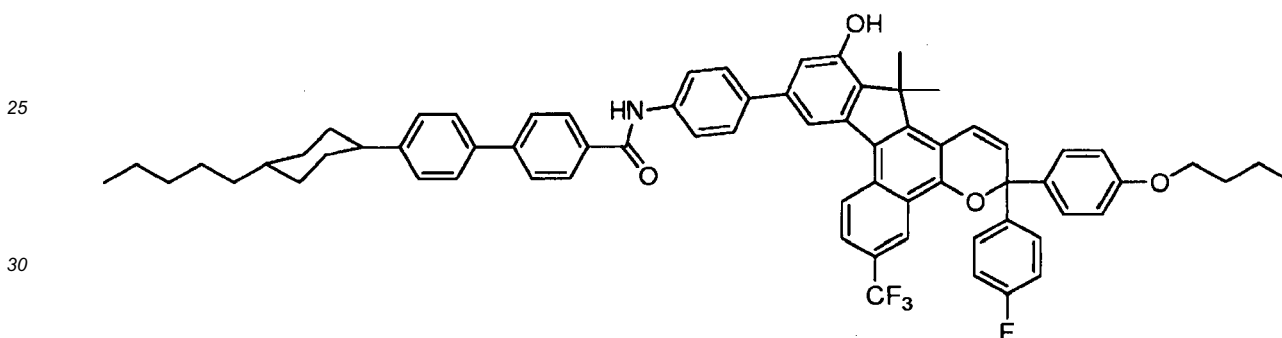
[0217] The procedures of Example 10 were followed except that in Step 6, 1-(4-fluorophenyl)-1-(4-butoxyphenyl)prop-2-yn-1-ol was used in place of 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol. NMR analysis showed that the final product had a structure consistent with 3-(4-fluorophenyl)-3-(4-butoxyphenyl)-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-12-bromo-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4] naphtho[1,2-b]pyran.

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Example 21

[0218]

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[0219] Product from Example 20, 3-(4-fluorophenyl)-3-(4-butoxyphenyl)-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-12-bromo-13,13-dimethyl-indeno[2',3':3,4]naphtho[1,2-b]pyran (3.77 g), was added to a reaction flask and dissolved in tetrahydrofuran (10 mL) and cooled to -78°C. n-Butyl lithium (6 mL, 2.5 M in hexanes) was added and stirred for 30 min. Brine was added to the reaction mixture and it was warmed to room temperature. The aqueous layer was extracted with ethyl acetate. The recovered organic layer was dried with anhydrous sodium sulfate, filtered and concentrated to provide an oily residue. Two photochromic compounds were present in the oily residue. They were separated by column chromatography using 9:1 hexane and ethyl acetate mixture as the eluent. Fractions containing the more polar compound were grouped and concentrated to provide an oil. The oil was dissolved in a minimum amount of dichloromethane and added drop-wise to vigorously stirred methanol. The resulting precipitate was collected by vacuum filtration and dried to a purple solid (0.3 g). NMR analysis of the purple solid indicated a structure that was consistent with 3-(4-butoxyphenyl)-3-(4-fluorophenyl)-12-hydroxyl-10-[4-(4-(4-(4-trans-pentylcyclohexyl) phenyl)benzamido)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

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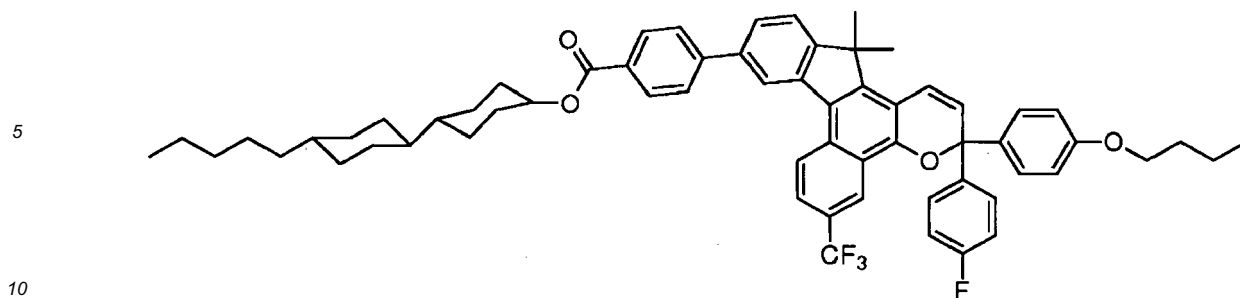
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Example 22

[0220]

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55



Step 1

15 **[0221]** The procedure from Step 2 of Example 3 was followed except that 4'-pentyl-[(trans, trans)-1,1'-bi(cyclohexan)]-4-ol was used in place of 4-(trans-4-pentylcyclohexyl)benzoic acid. NMR showed that the product had a structure consistent with (trans, trans)-4'-pentyl-[1,1'-bi(cyclohexan)]-4-yl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate.

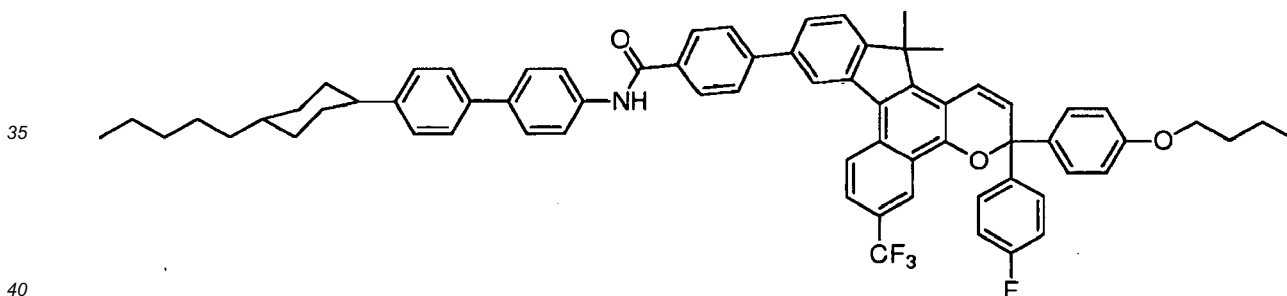
Step 2

20 **[0222]** The procedures from Example 14 were followed except that in Step 5 (trans, trans)-4'-pentyl-[1,1'-bi(cyclohexan)]-4-yl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate was used in place of 4'-(4-trans-pentylcyclohexyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-[1,1'-biphenyl]-4-carboxamide. NMR analysis showed that the product had a structure consistent with 3-(4-butoxyphenyl)-3-(4-fluorophenyl)-10-[4-((trans,trans)-4'-pentyl-[1,1'-bi(cyclohexan)]-4-oxycarbonyl)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

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Example 23

[0223]



Step 1

45 **[0224]** To a degassed solution of 1-bromo-4-(4-pentylcyclohexyl)benzene (300 g) in 1,4-dioxane (2 L) in a reaction flask was added Pd(PPh₃)₄ (10.7 g). After stirring for 10 min at room temperature, a solution of aqueous 1 M K₂CO₃ (485 mL, 4.85 mmol) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (274.5 g, 0.97 mol) were added. The reaction mixture was refluxed for 36 h. The solvent was evaporated and the residue was recrystallized using CH₂Cl₂-MeOH (400 mL-1500 mL). White crystals (256 g) were obtained as the product. NMR showed that the product had a structure consistent with 4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-amine.

50

Step 2

55 **[0225]** A mixture of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (82.6 g 0.35 mol), 1,1'-carbonyldiimidazole (56.6 g, 0.35 mol) and 500 mL of THF (500 ml) were stirred in a reaction flask at room temperature for 5 h. To the reaction mixture, the product of Step 1, 4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-amine (102 g) was added. The mixture was stirred at room temperature for 24 hours. The solvent was evaporated and the residue was recrystallized with CH₂Cl₂-MeOH (150 mL- 400 mL). White crystals (156 g) were obtained as the product. NMR showed that the product had a structure consistent with N-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-yl)-4-(4,4,5,5-tetramethyl-

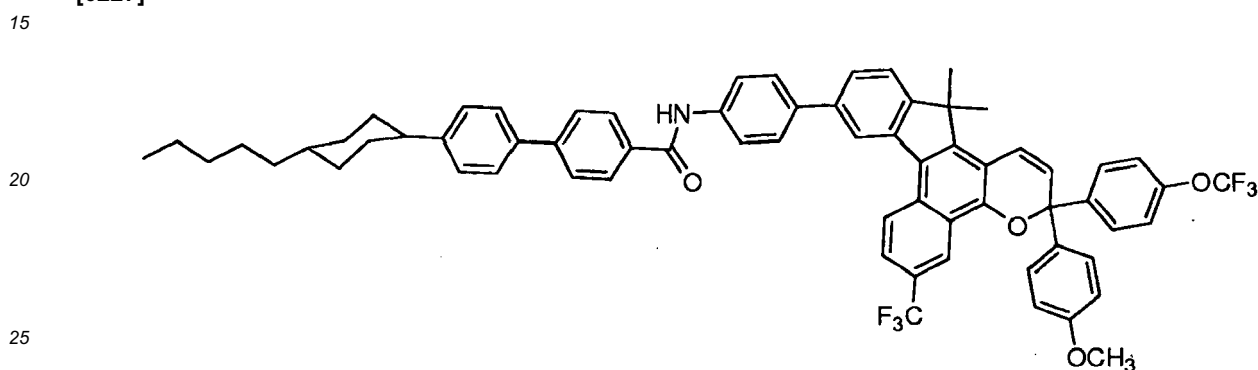
1,3,2-dioxaborolan-2-yl)benzamide.

Step 3

5 **[0226]** The procedures from Example 14 were followed except that in Step 5, N-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide was used in place of 4'-(4-trans-pentylcyclohexyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-[1,1'-biphenyl]-4-carboxamide. NMR analysis showed that the product had a structure consistent with 3-(4-methoxyphenyl)-3-(4-butoxyphenyl)-10-[4-((4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-yl)carbamoyl)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 24

[0227]



Step 1

30 **[0228]** 4-Trifluoromethoxy benzoylchloride (1.00 g) and anisole (0.60 g) were dissolved in chloroform (20 mL) in a reaction flask and cooled to 0-5°C by an ice bath. Aluminum chloride (0.90 g) was added and stirred for 15 min at 0-5°C. The ice bath was removed and the reaction was warmed to room temperature and stirred for 48 h and poured into water (100 mL) and stirred for 15 min. The aqueous layer was extracted with ethyl acetate (300 mL). The organic layer was recovered, washed with saturated sodium bicarbonate, brine, dried with anhydrous sodium sulfate and concentrated in vacuo to provide a residue. The residue was purified by column chromatography using 9:1 hexane and ethyl acetate mixture as the eluent. Fractions containing the desired material were grouped and concentrated to provide a solid. Hexanes were added and the solids were collected by vacuum filtration (0.55 g). NMR of the solid indicated a structure that was consistent with (4-methoxyphenyl)(4-(trifluoromethoxy)phenyl)methanone.

Step 2

40 **[0229]** (4-Methoxyphenyl)(4-(trifluoromethoxy)phenyl)methanone (0.55 g) was added to a reaction flask and dissolved in dimethylformamide (10 mL) saturated with acetylene. Sodium acetylide (0.1 g) was added and the reaction mixture was stirred at room temperature for 30 min. The reaction mixture was carefully poured into ice-cold water (100 mL) and stirred for 15 min. The aqueous layer was extracted with ethyl acetate. The organic layers were recovered and combined. The resulting product was dried with anhydrous sodium sulfate and concentrated to provide an oil (0.55 g). NMR analysis of the oil indicated a structure that was consistent with 1-(4-methoxyphenyl)-1-(4-(trifluoromethoxy)phenyl)prop-2-yn-1-ol.

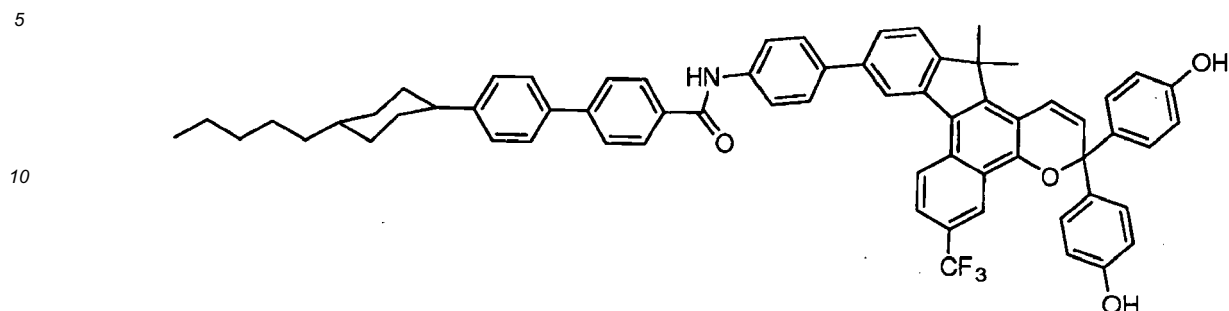
Step 3

50 **[0230]** The procedures from Example 14 were followed except that 1-(4-methoxyphenyl)-1-(4-(trifluoromethoxy)phenyl)prop-2-yn-1-ol from Step 2 above was used in place of 1-(4-butoxyphenyl)-1-(4-fluorophenyl)prop-2-yn-1-ol in Step 6 of Example 14. NMR analysis showed that the product had a structure consistent with 3-(4-methoxyphenyl)-3-(4-trifluoromethoxyphenyl)-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

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Example 25

[0231]

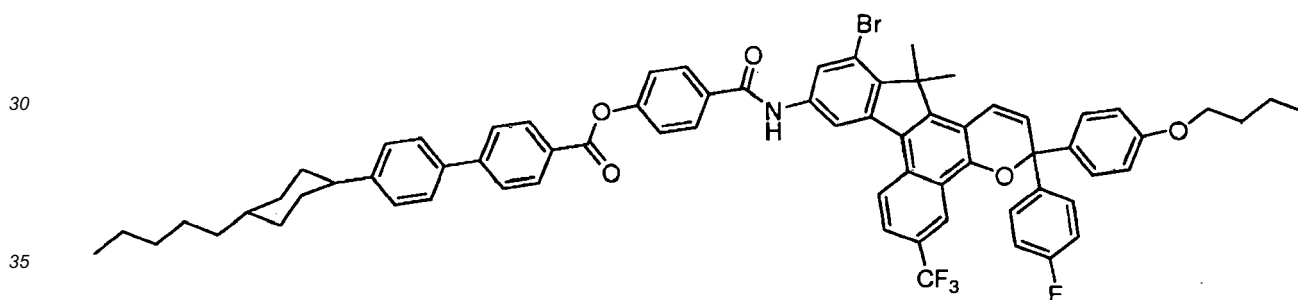


20

[0232] The procedures from Example 14 were followed except that 1,1-bis(4-((tetrahydro-2H-pyran-2-yl)oxy)phenyl)prop-2-yn-1-ol was used in place of 1-(4-butoxyphenyl)-1-(4-fluorophenyl)prop-2-yn-1-ol in Step 6. Also in Step 6 after the reaction and before the column separation, the residue was taken up in tetrahydrofuran and methanol with the addition of p-toluenesulfonic acid, refluxed for 1 h and concentrated. NMR analysis of the obtained solid indicated a structure that was consistent with 3-bis(4-hydroxyphenyl)-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 26

[0233]



Step 1

40

[0234] To a three neck round bottom flask (100 mL) were added bis(dibenzylideneacetone)platinum(0) (0.55 g), 2-di-tert-butylphosphino-3,4,5,6-tetramethyl-2',4',6'-triisopropyl-1,1'-biphenyl (1.14 g), crushed potassium phosphate (8.72 g), 8,10-dibromo-7,7-dimethyl-3-(trifluoromethyl)-7H-benzo[c]fluoren-5-yl acetate (5.00 g) from Step 4 of Example 10 and 4-hydroxybenzamide (2.15 g). The flask was evacuated and filled with nitrogen. Degassed tert-butanol (30 mL) was added and the mixture was heated to reflux for 6 h. The reaction mixture was cooled to room temperature and diluted with EtOAc. The solution was filtered through Celite and the filtrate was collected, concentrated and the residue was purified by column chromatography using 4:1 ethyl acetate and hexanes mixture as the eluent. Fractions containing the desired material were grouped and concentrated to provide an oil. The oil was dissolved in a minimum amount of ethyl acetate and hexanes were added to crystallize the product. The crystals were collected by vacuum filtration and dried to provide a white colored solid (4.27g). NMR analysis of the white colored solid indicated a structure that was consistent with N-(8-bromo-5-hydroxy-7,7-dimethyl-3-(trifluoromethyl)-7H-benzo[c]fluoren-10-yl)-4-hydroxybenzamide.

50

Step 2

55

[0235] To a chloroform solution (20 mL) in a reaction flask, of the product from Step 5 (1.69 g) were added 1-(4-butoxyphenyl)-1-(4-fluorophenyl)prop-2-yn-1-ol (1.12 g) and 4-dodecylbenzenesulfonic acid (0.10 g). The reaction mixture was stirred at room temperature for 18 h. The reaction mixture was concentrated under reduced pressure to provide an oily residue. The residue was purified by column chromatography using 1:1 hexane and toluene mixture as the eluent. Fractions containing the desired product were grouped and concentrated in vacuo to provide an oily residue. The oily

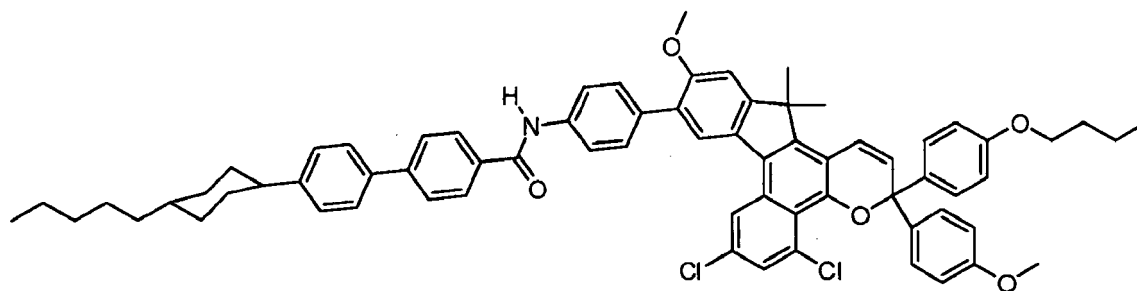
residue was re-crystallized from methanol. The resulting solid was collected by vacuum filtration and dried to provide a cream colored solid (0.88 g). NMR analysis of the cream colored solid indicated a structure that was consistent with 12-bromo-3-(4-butoxyphenyl)-3-(4-fluorophenyl)-10-[4-hydroxybenzamido]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Step 3

[0236] Product from Step 2 (1.15 g) was dissolved in chloroform (20 mL) in a reaction flask. Triethylamine (0.6 mL) was added followed by 4'-(4-pentylcyclohexyl)biphenyl-4-carbonyl chloride from Step 4 of Example 2 (0.80 g). The reaction mixture was stirred at room temperature for 30 min. The solvent was removed in vacuo and the residue was purified by column chromatography using 9:1 hexanes and ethyl acetate mixtures as the eluent. Fractions containing the desired material were grouped and concentrated. The residue was dissolved in a minimum amount of dichloromethane and added drop-wise to a vigorously stirred solution of methanol. The resulting precipitate was collected by vacuum filtration and dried to a purple solid (1.30 g). NMR analysis of the purple solid indicated a structure that was consistent with 12-bromo-3-(4-butoxyphenyl)-3-(4-fluorophenyl)-10-[4-(4'-(4-trans-pentylcyclohexyl)-[1,1'-biphenyl]-4-carboxyloxy)benzamido]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 27

[0237]



Step 1 to Step 4

[0238] Procedures from Step 1 to Step 4 of Example 10 were followed except that in Step 1, 3,5-dichlorobromobenzene and 4-methoxybenzoyl chloride were used in place of tribromobenzene and 4-trifluoromethylbenzoyl chloride. An off-white solid was obtained as the product. NMR indicated that the product had a structure consistent with 2,4-dichloro-9-methoxy-7,7-dimethyl-7H-benzo[c]fluoren-5-yl acetate.

Step 5

[0239] A mixture of 2,4-dichloro-9-methoxy-7,7-dimethyl-7H-benzo[c]fluoren-5-yl acetate from Step 4 (5 g), NBS (2.7 g) and DMF (100 ml) was stirred in a reaction flask and heated to 90°C. Two hours later, the resulting reaction mixture was poured into water (400 ml) and extracted with 1/1 ethyl acetate/THF (200 ml). The organic layer was collected, washed with sodium bisulfite water solution three times, dried and concentrated. To the recovered product, methanol (100 ml) was added. After filtration, an off white solid (4.4 g) was obtained as the product. NMR indicated that the product had a structure consistent with 10-bromo-2,4-dichloro-9-methoxy-7,7-dimethyl-7H-benzo[c]fluoren-5-yl acetate.

Step 6

[0240] A mixture of 10-bromo-2,4-dichloro-9-methoxy-7,7-dimethyl-7H-benzo[c]fluoren-5-yl acetate from Step 5 (4.3 g), 4'-(4-trans-pentylcyclohexyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-[1,1'-biphenyl]-4-carboxamide (4.94 g), sodium carbonate (4 g), THF (200 ml), water (20 ml) and tetrakis(triphenylphosphine)palladium(0) (1 g) was placed in a reaction flask and degassed by bubbling nitrogen through the mixture for 10 minutes. The mixture was heated to reflux for 17 hours and potassium carbonate (5 g) and ethanol (50 ml) was added. After reflux for another 8 hours, extraction was applied using THF and sodium chloride saturated water. The resulting organic layer was collected, washed with 100 ml 1 N HCl three times, washed with 100 ml 1 N sodium sulfite water solution once, washed with sodium chloride saturated water once, dried over magnesium sulfate and concentrated. The obtained residue was

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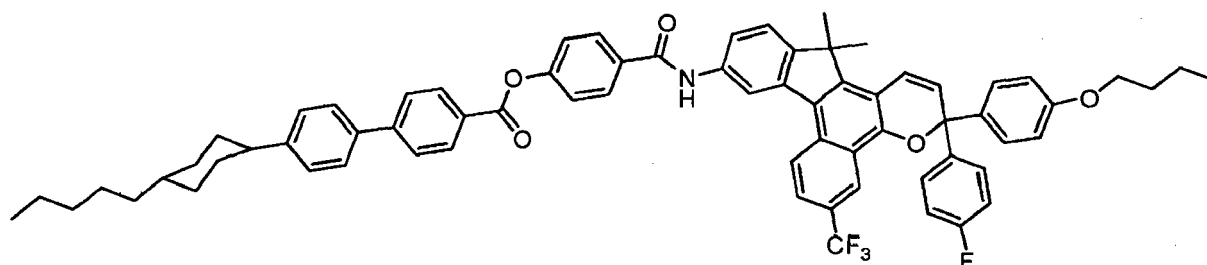
dissolved in 10/1 toluene/THF (200 ml) and then passed through a silica gel plug column. The recovered clear solution was concentrated added to methanol and stirred for half an hour. The resulting solid was collected and dried. An off-white solid (7.5 g) was obtained as the product. NMR indicated that the product had a structure consistent with N-(4-(2,4-dichloro-5-hydroxy-9-methoxy-7,7-dimethyl-7H-benzo[c]fluoren-10-yl)phenyl)-4'-(4-trans-pentylcyclohexyl)-[1,1'-biphenyl]-4-carboxamide.

Step 7

[0241] N-(4-(2,4-dichloro-5-hydroxy-9-methoxy-7,7-dimethyl-7H-benzo[c]fluoren-10-yl)phenyl)-4'-(4-pentylcyclohexyl)-[1,1'-biphenyl]-4-carboxamide from Step 6 (3 g), 1-(4-butoxyphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (1.8 g), p-toluenesulfonic acid (73 mg) and 1,2-dichloroethane (50 ml) were added to a reaction flask. The mixture was stirred and refluxed for 4 hours. After the solvent was removed, the product was purified by CombiFlash. A black solid (2 g) was obtained as the product. NMR indicated that the structure was consistent with 3-(4-butoxyphenyl)-3-(4-methoxyphenyl)-10-[4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido]phenyl]-5,7-dichloro-11-methoxy-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 28

[0242]



Step 1

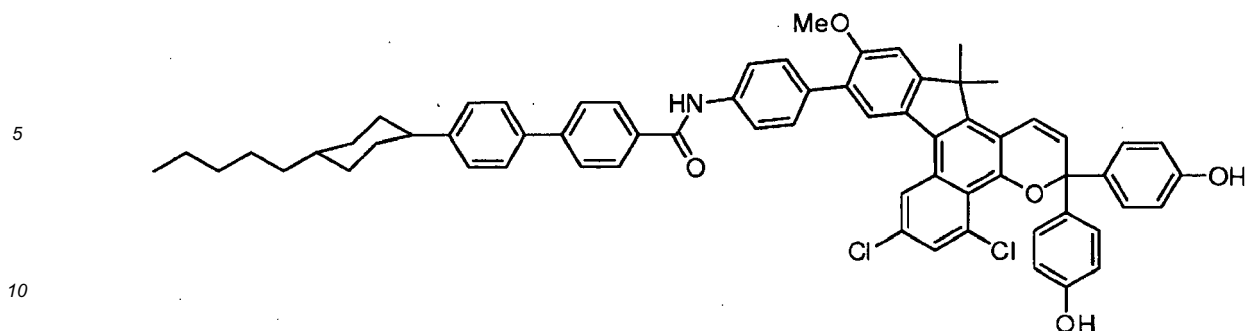
[0243] N-(8-bromo-5-hydroxy-7,7-dimethyl-3-(trifluoromethyl)-7H-benzo[c]fluoren-10-yl)-4-hydroxybenzamide (5.00 g) from Step 1 of Example 26, potassium carbonate (5.10 g), 2-butanol (50 mL) and methanol (50 mL) were added to a round bottom flask and degassed for 10 min. Tetrakis(triphenyl)phosphine palladium (0) (0.55 g) was added and heated to reflux under nitrogen for 2 h. The reaction mixture was cooled to room temperature and filtered through CELITE® filtering aid. The filtrate was concentrated and the residue was purified by column chromatography using 4:1 ethyl acetate and hexanes mixtures as the eluent. Fractions containing the desired material were grouped and concentrated to provide a foam (4.00 g). NMR analysis of the foam indicated a structure that was consistent with 4-hydroxy-N-(5-hydroxy-7,7-dimethyl-3-(trifluoromethyl)-7H-benzo[c]fluoren-10-yl)benzamide.

Step 2

[0244] The procedure of Steps 2 and 3 of Example 26 was followed except that in Step 2, the product of Step 1 above was used in place of N-(8-bromo-5-hydroxy-7,7-dimethyl-3-(trifluoromethyl)-7H-benzo[c]fluoren-10-yl)-4-hydroxybenzamide. NMR indicated that the structure was consistent with 3-(4-butoxyphenyl)-3-(4-fluorophenyl)-10-[4-(4-(4-trans-pentylcyclohexyl)-[1,1'-biphenyl]-4-carboxamide)benzamido]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 29

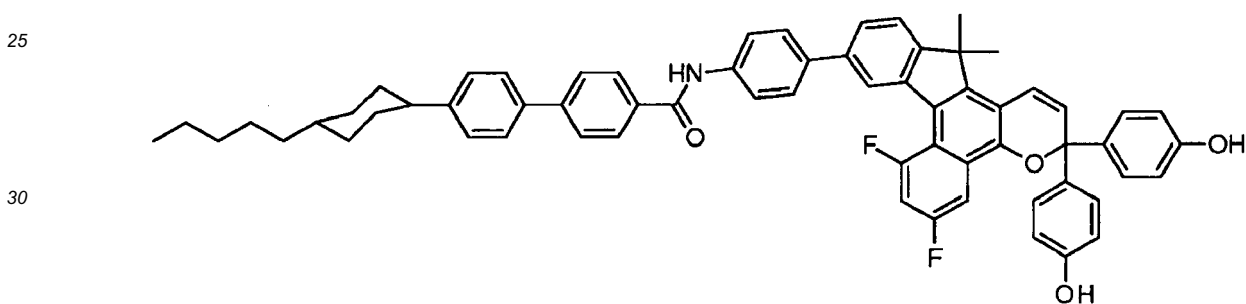
[0245]



15 **[0246]** Procedures from Example 27 were followed except for the following in Step 7: 1,1-bis(4-((tetrahydro-2H-pyran-2-yl)oxy)phenyl)prop-2-yn-1-ol was used in place of 1-(4-butoxyphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol and before being subjected to CombiFlash, the product was dissolved in a solvent mixture of THF and methanol with pTSA (1 g) and refluxed for an hour and concentrated. NMR indicated that the product had a structure consistent with 3-bis(4-hydroxyphenyl)-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-5,7-dichloro-11-methoxy-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

20 **Example 30**

25 **[0247]**

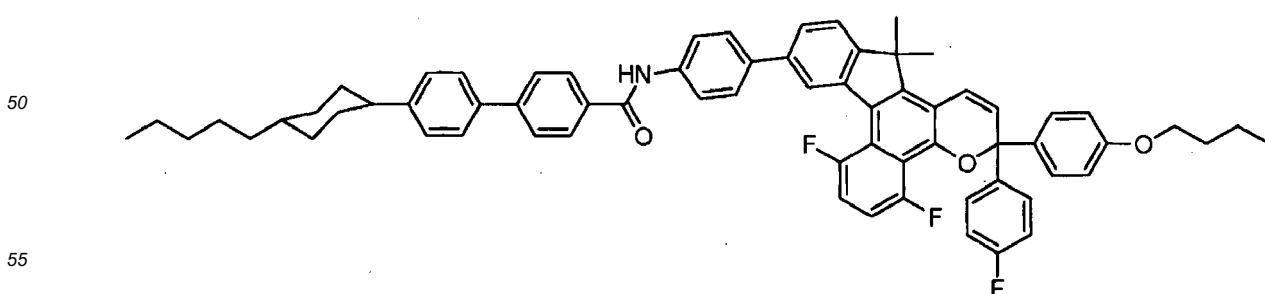


35 **[0248]** The procedures from Example 14 were followed except that in Step 1, 2,4-difluorobenzoyl chloride was used in place of 4-trifluoromethylbenzoyl chloride and in Step 6, 1,1-bis(4-((tetrahydro-2H-pyran-2-yl)oxy)phenyl)prop-2-yn-1-ol was used in place of 1-(4-butoxyphenyl)-1-(4-fluorophenyl)prop-2-yn-1-ol and after the reaction and before the column separation, the residue was dissolved in tetrahydrofuran and methanol with the addition of p-toluenesulfonic acid, refluxed for 1 h and concentrated. NMR analysis of the obtained light blue solid indicated a structure that was

40 consistent with 3-bis(4-hydroxyphenyl)-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-6,8-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

45 **Example 31**

50 **[0249]**

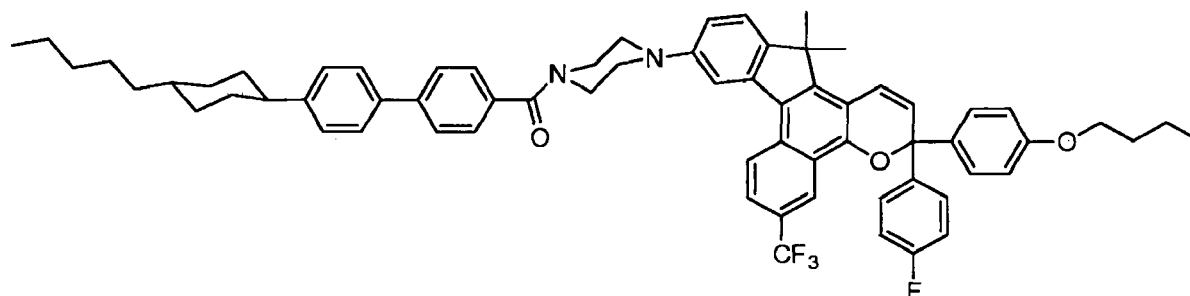


[0250] The procedures from Example 14 were followed except that in Step 1, 2,5-difluorobenzoyl chloride was used

in place of 4-trifluoromethylbenzoyl chloride. NMR analysis of the obtained solid indicated a structure that was consistent with 3-(4-fluorophenyl)-3-(4-butoxyphenyl)-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-5,8-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 32

[0251]



Step 1

[0252] Procedures from Step 1 to Step 5 of Example 10 were followed.

Step 2

[0253] To degassed dioxane (100 mL) and toluene (100 mL) in a reaction flask was added 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (1.20 g), palladium (II) acetate (0.30 g) and 8,10-dibromo-7,7-dimethyl-3-(trifluoromethyl)-7H-benzo[c]fluoren-5-yl acetate (5.10 g) from Step 5 of Example 10, followed by the addition of 1-formylpiperazine (2.80 g) under a stream of nitrogen. Sodium *tert*-butoxide (2.80 g) was added and the solution was heated to reflux for 22 h. The reaction mixture was cooled to room temperature and diluted with tetrahydrofuran. The solution was filtered through CELITE® filtering aid and the filtrate was concentrated under vacuum. The residue was purified by column chromatography using 1:4 methylene chloride and ethyl acetate mixtures as the eluent. Fractions containing the desired material were grouped and concentrated. The residue (1.25 g) was used directly in the next step. NMR analysis of the residue indicated a structure that was consistent with 4-(8-bromo-5-hydroxy-7,7-dimethyl-3-(trifluoromethyl)-7H-benzo[c]fluoren-10-yl)piperazine-1-carbaldehyde.

Step 3

[0254] 4-(8-Bromo-5-hydroxy-7,7-dimethyl-3-(trifluoromethyl)-7H-benzo[c]fluoren-10-yl)piperazine-1-carbaldehyde from Step 2 (0.69 g) and 1-(4-butoxyphenyl)-1-(4-fluorophenyl)prop-2-yn-1-ol (0.60 g) were dissolved in 1,2-dichloroethane (20 mL) in a reaction flask. *p*-Toluenesulfonic acid (0.1 g) was added and the solution was heated to reflux for 18 h. The reaction mixture was cooled to room temperature and the solvent was removed in vacuo. The residue was purified by column chromatography using 1:1 hexanes and dichloromethane mixtures as the eluent. Fractions containing the desired material were grouped and concentrated. The residue (0.75 g) was used directly in the next step.

Step 4

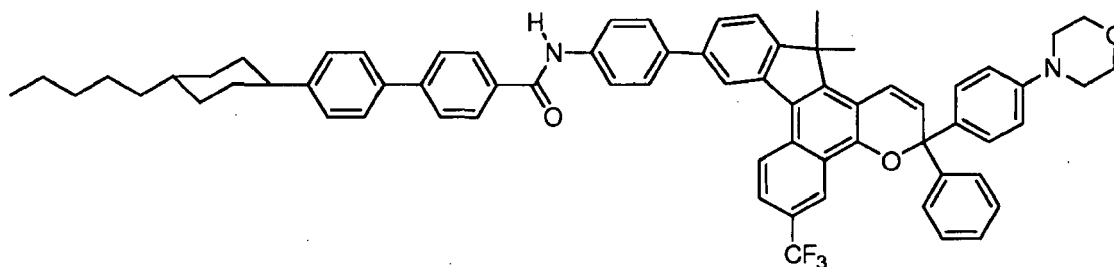
[0255] The product of Step 3, 4-(12-Bromo-3-(4-butoxyphenyl)-3-(4-fluorophenyl)-13,13-dimethyl-6-(trifluoromethyl)-3,13-dihydrobenzo[h]indeno[2,1-f]chromen-10-yl)piperazine-1-carbaldehyde (2.00 g) was dissolved in dioxane (30 mL) in a reaction flask. 10% HCl aq (5 mL) was added and the solution was heated to reflux for 2 h. The reaction mixture was cooled to room temperature and carefully poured into saturated aqueous sodium bicarbonate solution (300 mL). The resulting aqueous layer was extracted with ethyl acetate (300 mL). The ethyl acetate solution was dried with anhydrous sodium sulfate, filtered and concentrated to provide a residue. The residue was purified by column chromatography using 1:1 ethyl acetate and methanol mixture as the eluent. Fractions containing the desired material were grouped and concentrated. The residue (1.00 g) was used directly in the next step.

Step 5

[0256] The procedure from Step 3 of Example 26 was followed using the residue of Step 4 above in place of 12-bromo-3-(4-butoxyphenyl)-3-(4-fluorophenyl)-10-[4-hydroxybenzamido]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran. NMR indicated that the structure was consistent with 3-(4-fluorophenyl)-3-(4-butoxyphenyl)-10-[(4-(4'-(4-trans-pentylcyclohexyl)-[1,1'-biphenyl]-4-yl)carbonyl)piperazin-1-yl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 33

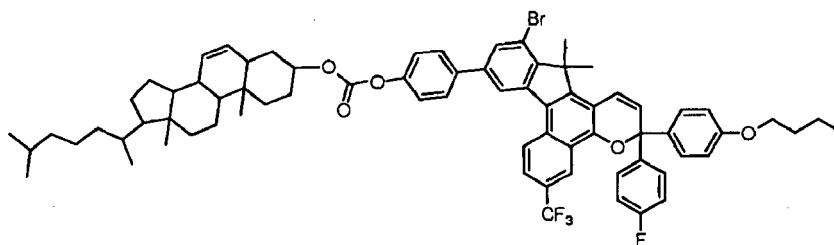
[0257]



[0258] The procedures from Example 14 were followed except that in Step 6, 1-(4-N-morpholinophenyl)-1-(4-phenyl)prop-2-yn-1-ol was used in place of 1-(4-butoxyphenyl)-1-(4-fluorophenyl)prop-2-yn-1-ol. NMR analysis indicated that the product had a structure consistent with 3-(4-(N-morpholino)phenyl)-3-phenyl-10-[4-(4-(4-(4-trans-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 34

[0259]

Step 1

[0260] The procedures from Example 10 were followed except that in Step 6, 1-(4-butoxyphenyl)-1-(4-fluorophenyl)prop-2-yn-1-ol was used in place of 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol and in Step 7, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol was used in place of 4'-(4-trans-pentylcyclohexyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-[1,1'-biphenyl]-4-carboxamide. NMR analysis of the product indicated a structure that was consistent with 3-(4-butoxyphenyl)-3-(4-fluorophenyl)-10-(4-hydroxyphenyl)-6-trifluoromethyl-12-bromo-13,13-dimethyl-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Step 2

[0261] The product from Step 1, 3-(4-butoxyphenyl)-3-(4-fluorophenyl)-10-(4-hydroxyphenyl)-6-trifluoromethyl-12-bromo-13,13-dimethyl-indeno[2',3':3,4]naphtho[1,2-b]pyran (1.00 g), was added to a reaction flask and dissolved in dichloromethane (20 mL). Triethylamine (0.2 mL) was added followed by cholesteryl chloroformate (0.90 g) and the reaction mixture was stirred for 30 min. The solvent was removed in vacuo and the residue was purified by column chromatography using 19:1 hexanes and ethyl acetate mixture as the eluent. Fractions containing the desired material were grouped and concentrated. The residue was dissolved in a minimum amount of dichloromethane and added drop-

wise to vigorously stirred methanol. The precipitate was collected by vacuum filtration and dried to provide a purple solid. NMR analysis of the purple solid indicated structure that was consistent with 3-(4-butoxyphenyl)-3-(4-fluorophenyl)-10-[4-[17-(1,5-dimethyl-hexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxy]phenyl]-6-trifluoromethyl-12-bromo-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Part 2- Photochromic Property Testing

Part 2A - Test Square Preparation

[0262] Testing was done with the compounds described in Examples 1-3, 5, 7, and 10-34 in the following manner. A quantity of compound calculated to yield a 1.5×10^{-3} molal solution was added to a flask containing 50 grams of a monomer blend of 4 parts ethoxylated bisphenol A dimethacrylate (BPA 2EO DMA), 1 part poly(ethylene glycol) 600 dimethacrylate, and 0.033 weight percent 2,2'-azobis(2-methyl propionitrile) (AIBN). Each compound was dissolved into the monomer blend by stirring and gentle heating, if necessary. After a clear solution was obtained, the sample was degassed in a vacuum oven for 5-10 minutes at 25 torr. Using a syringe, the sample was poured into a flat sheet mold having an interior dimension of 2.2 mm +/- 0.3 mm x 6 inch (15.24 cm) x 6 inch (15.24 cm). The mold was sealed and placed in a horizontal airflow, programmable oven to ramp from 40° C. to 95° C. over a 5 hour interval, the temperature was held at 95° C. for 3 hours, ramp down to 60° C. over a 2 hour interval and then held at 60° C. for 16 hours. After curing, the mold was opened, and the polymer sheet was cut into 2 inch (5.1 cm) test squares using a diamond blade saw.

Part 2B - Response Testing

[0263] Prior to response testing on an optical bench, the test squares from Part 2A were conditioned by exposing them to 365 nm ultraviolet light for 10 minutes at a distance of about 14 cm from the source in order to pre-activate the photochromic compounds in samples. The UVA irradiance at the sample surface was measured with a Licor Model Li-1800 spectroradiometer and found to be 22.2 Watts per square meter. The samples were then placed under a halogen lamp (500 W, 120V) for about 10 minutes at a distance of about 36 cm from the lamp in order to bleach, or inactivate, the photochromic compounds in the samples. The illuminance at the sample was measured with the Licor spectroradiometer and found to be 21.9 Klux. The samples were then kept in a dark environment for at least 1 hour prior to testing in order to cool and continue to fade back to a ground state.

[0264] The optical bench was fitted with an Newport Model #67005 300-watt Xenon arc lamp, and Model 69911 power supply, Vincent Associates (model VS25S2ZM0R3 with VMM-D4 controller) high-speed computer controlled shutter, a Schott 3 mm KG-2 band-pass filter, which removed short wavelength radiation, neutral density filter(s) to attenuate light from the xenon lamp, a fused silica condensing lens for beam collimation, and a fused silica water cell/sample holder for maintaining sample temperature in which the test sample to be tested was inserted. The temperature in the water cell was controlled with a pumped water circulation system in which the water passed through copper coils that were placed in the reservoir of a chiller unit. The water cell used to hold test samples contained fused silica sheets on the front and back facings in order to eliminate spectral change of the activation or monitoring light beams. The filtered water passing through the water cell was maintained at 72° F. ± 2° for photochromic response testing. A Newport Model 689456 Digital Exposure Timer was used to control the intensity of the xenon arc lamp during activation of the sample.

[0265] A broadband light source for monitoring response measurements was positioned in a perpendicular manner to a surface of the cell assembly. Increased signal of shorter visible wavelengths was obtained by collecting and combining separately filtered light from a 100-Watt tungsten halogen lamp (controlled by a Lambda UP60-14 constant voltage powder supply) with a split-end, bifurcated fiber optical cable. Light from one side of the tungsten halogen lamp was filtered with a Schott KG1 filter to absorb heat and a Hoya B-440 filter to allow passage of the shorter wavelengths. The other side of the light was either filtered with a Schott KG1 filter or unfiltered. The light was collected by focusing light from each side of the lamp onto a separate end of the split-end, bifurcated fiber optic cable, and subsequently combined into one light source emerging from the single end of the cable. A 10.16 cm (4") light pipe was attached to the single end of the cable to insure proper mixing. After passing through the sample, the light was refocused into a 5.08 cm (2-inch) integrating sphere and fed to an Ocean Optics S2000 spectrophotometer by fiber optic cables. Ocean Optics SpectraSuite and PPG proprietary software were used to measure response and control the operation of the optical bench.

[0266] Irradiance for response testing of the samples on the optical bench was established at the sample surface using an International Light Research Radiometer, Model IL-1700 with a detector system comprising a Model SED033 detector, B Filter and diffuser. The output display of the radiometer was corrected (factor values set) against a Licor 1800-02 Optical Calibration Calibrator in order to display values representing Watts per square meter UVA. The irradiance at the sample point for initial response testing was set at to 3.0 Watts per square meter UVA and approximately 8.6 Klux illuminance. During sample response testing, if a sample darkened beyond an acceptable detection capability limit, the

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irradiance was lowered to 1.0 Watts per square meter UVA or the sample was remade at a one-half concentration in the copolymer. Adjusting the output of the filtered xenon arc lamp was accomplished by increasing or decreasing the current to the lamp through the controller and/or by adding or removing neutral density filters in the light path. The test samples were exposed to the activation light at 31° normal to its surface while being perpendicular to the monitoring light.

[0267] Samples were activated in the 73° F(22.8°C) controlled water cell for 30 minutes, then allowed to fade under room light conditions until the change in optical density of the activated sample faded to ¼ of its highest dark (saturated) state or for a maximum of 30 minutes of fade.

[0268] Change in optical density (ΔOD) from the bleached state to the darkened state was determined by establishing the initial transmittance, opening the shutter from the Xenon lamp to provide ultraviolet radiation to change the test lens from the bleached state to an activated (i.e., darkened) state. Data was collected at selected intervals of time, measuring the transmittance in the activated state, and calculating the change in optical density according to the formula: $\Delta OD = \log(\% Tb / \% Ta)$, where % Tb is the percent transmittance in the bleached state, % Ta is the percent transmittance in the activated state and the logarithm is to the base 10.

[0269] The $\lambda_{\max\text{-vis}}$ in the visible light range is the wavelength in the visible spectrum at which the maximum absorption of the activated form of the photochromic compound occurs. The $\lambda_{\max\text{-vis}}$ was determined by testing the photochromic test square in a Varian Cary 4000 UV-Visible spectrophotometer or comparable equipment.

[0270] The $\Delta OD/\text{Min}$, which represents the sensitivity of the photochromic compound's response to UV light, was measured over the first five (5) seconds of UV exposure, then expressed on a per minute basis. The saturation optical density (ΔOD at saturation) was taken under identical conditions except UV exposure was continued for a total of 30 minutes. The fade half life is the time interval in seconds for the ΔOD of the activated form of the photochromic compound in the test squares to reach one half the ΔOD measured after thirty minutes, or after saturation or near-saturation was achieved, at room temperature after removal of the source of activating light, e.g., by closing the shutter. Results are listed in Table I.

TABLE 1 - Photochromic Performance Test Results

Example #	$\lambda_{\max\text{-vis}}$ (nm)	Sensitivity ($\Delta OD/\text{Min}$)	ΔOD at saturation	T ½ (sec)
1	592	0.56	0.71	122
2	629	0.45	0.34	44
3	556	0.65	0.62	62
5	602	0.45	0.35	47
7	456	0.48	0.85	168
10	568	0.30	0.13	19
11	577	0.35	0.16	23
12	538	0.49	0.36	46
13	576	0.44	0.37	51
14	572	0.53	0.41	49
15	610	0.42	0.30	43
16	607	0.46	0.43	65
17	573	0.41	0.25	33
18	616	0.47	0.45	62
19	610	0.48	0.44	60
20	558	0.40	0.21	27
21	564	0.52	0.45	54
22	560	0.50	0.36	42
23	563	0.45	0.34	45
24	562	0.52	0.53	74
25	584	0.46	0.20	18

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(continued)

Example #	$\lambda_{\text{max-vis}}$ (nm)	Sensitivity ($\Delta\text{OD}/\text{Min}$)	ΔOD at saturation	T $\frac{1}{2}$ (sec)
26	552	0.44	0.21	22
27	580	0.77	0.70	82
28	564	0.52	0.39	45
29	587	1.06	0.77	61
30	588	0.48	0.22	22
31	547	0.75	0.85	96
32	577	0.55	0.44	53
33*	605	0.46	0.44	60
34	555	0.39	0.19	21

(*) Indicates that Example 33 was tested after an exposure level of 2.0 rather than 6.7 W/m² in order to obtain a measurable reading.

Part 3 - Dichroic Property Testing

Part 3A - Liquid Crystal Cell Preparation

[0271] The average absorption ratio of each of the compounds of Examples 1-8, 10-30, and 33 was determined according to the CELL METHOD described as follows.

[0272] A cell assembly having the following configuration was obtained from Design Concepts, Inc. Each of the cell assemblies was formed from two opposing glass substrates that are spaced apart with a glass bead spacer having a diameter of 20 microns +/-1 micron. The inner surfaces of each of the glass substrates had oriented polyimide coating thereon to provide for the alignment of a liquid crystal material as discussed below. Two opposing edges of the glass substrates were sealed with an epoxy sealant, leaving the remaining two edges open for filling.

[0273] The gap between the two glass substrates of the cell assembly was filled with a liquid crystal solution containing the one of the compounds of Examples 1-33. The liquid crystal solution was formed by mixing the following components in the weight percents listed below with heating, if necessary, to dissolve the test material.

<u>Material</u>	<u>Weight Percent</u>
Licristal™ E7	97-99.5
Example Compound	0.5-3

Part 3B - Liquid Crystal Cell Testing

[0274] An optical bench was used to measure the optical properties of the cell and derive the absorption ratios for each of the Test Materials. The filled cell assembly was placed on the optical bench with an activating light source (an Oriel Model 66011 300-Watt Xenon arc lamp fitted with a Vincent Associates (model VS25S2ZM0R3 with VMM-D4 controller) high-speed computer controlled shutter that momentarily closed during data collection so that stray light would not interfere with the data collection process, a Schott 3 mm KG-1 band-pass filter, which removed short wavelength radiation, neutral density filter(s) for intensity attenuation and a condensing lens for beam collimation) positioned at a 30° to 35° angle of incidence a surface of the cell assembly.

[0275] A broadband light source for monitoring response measurements was positioned in a perpendicular manner to a surface of the cell assembly. Increased signal of shorter visible wavelengths was obtained by collecting and combining separately filtered light from a 100-Watt tungsten halogen lamp (controlled by a Lambda UP60-14 constant voltage powder supply) with a split-end, bifurcated fiber optical cable. Light from one side of the tungsten halogen lamp was filtered with a Schott KG1 filter to absorb heat and a Hoya B-440 filter to allow passage of the shorter wavelengths. The other side of the light was either filtered with a Schott KG1 filter or unfiltered. The light was collected by focusing light

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from each side of the lamp onto a separate end of the split-end, bifurcated fiber optic cable, and subsequently combined into one light source emerging from the single end of the cable. A 10.16 cm (4") light pipe was attached to the single end of the cable to insure proper mixing.

[0276] Polarization of the light source was achieved by passing the light from the single end of the cable through a Moxtek, Proflux Polarizer held in a computer driven, motorized rotation stage (Model M-061-PD from Polytech, PI). The monitoring beam was set so that the one polarization plane (0°) was perpendicular to the plane of the optical bench table and the second polarization plane (90°) was parallel to the plane of the optical bench table. The samples were run in air, at room temperature (73° F ± 0.3° F or better (22.8° C ± 0.1°)) maintained by the lab air conditioning system or a temperature controlled air cell.

[0277] To conduct the measurements, the cell assembly and the coating stack were exposed to 6.7 W/m² of UVA from the activating light source for 5 to 15 minutes to activate the Test Material. This was done for all of the Examples except Example 33, when tested in the coating stack, it was exposed to 2.0 W/m² of UVA. The lower exposure level was needed to obtain measurable results. An International Light Research Radiometer (Model IL-1700) with a detector system (Model SED033 detector, B Filter, and diffuser) was used to verify exposure prior to each test. Light from the monitoring source that was polarized to the 0° polarization plane was then passed through the coated sample and focused on a 1" integrating sphere, which was connected to an Ocean Optics S2000 spectrophotometer using a single function fiber optic cable. The spectral information, after passing through the sample, was collected using Ocean Optics SpectraSuite and PPG propriety software. While the photochromic-dichroic material was activated, the position of the polarizer was rotated back and forth to polarize the light from the monitoring light source to the 90° polarization plane and back. Data was collected for approximately 10 to 300 seconds at 5-second intervals during activation. For each test, rotation of the polarizers was adjusted to collect data in the following sequence of polarization planes: 0°, 90°, 90°, 0°, etc.

[0278] Absorption spectra were obtained and analyzed for each cell assembly using the Igor Pro software (available from WaveMetrics). The change in the absorbance in each polarization direction for each cell assembly was calculated by subtracting out the 0 time (i.e., unactivated) absorption measurement for the cell assembly at each wavelength tested. Average absorbance values were obtained in the region of the activation profile where the response of the Examples 1-33 was saturated or nearly saturated (i.e., the regions where the measured absorbance did not increase or did not increase significantly over time) for each cell assembly by averaging absorbance at each time interval in this region. The average absorbance values in a predetermined range of wavelengths corresponding $\lambda_{\text{max-vis}} \pm 5$ nm were extracted for the 0° and 90° polarizations, and the absorption ratio for each wavelength in this range was calculated by dividing the larger average absorbance by the small average absorbance. For each wavelength extracted, 5 to 100 data points were averaged. The average absorption ratio for the Test Material was then calculated by averaging these individual absorption ratios.

[0279] For the Examples listed in Table 2 the above-described procedure was run at least twice. The tabled value for the Average Absorption Ratio represents an average of the results obtained from the runs measured at the wavelength indicated. The results of these tests are present in Table 2 below.

TABLE 2 - Absorption Ratio (AR) Test Data

Example # (nm)	Wavelength	Absorption Ratio
1	592	6.56
2	629	8.04
3	555	6.86
4	556	4.75
5	601	6.96
6	601	5.98
7	456	8.68
8	600	7.51
10	565	6.15
11	572	3.80
12	536	6.85
13	579	6.84

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(continued)

Example # (nm)	Wavelength	Absorption Ratio
14	565	6.89
15	605	7.36
16	606	5.49
17	571	6.23
18	610	8.71
19	605	7.11
20	555	6.60
21	562	5.03
22	560	5.58
23	560	6.84
24	561	7.25
25	579	8.16
26	557	5.71
27	584	7.06
28	567	5.07
29	587	8.49
30	587	7.24
33*	606	7.80

(* Indicates that Example 33 (of Table 2) was tested after an exposure level of 2.0 rather than 6.7 W/m² in order to obtain a measurable reading.

Part 3C - Preparation of Coatings for Aligned Liquid Crystal Coated Substrates

Part 3C-1 - Preparation of Primer

[0280] Into a 250 mL amber glass bottle equipped with a magnetic stir-bar following materials were added in the order and amounts indicated:

Polyacrylate polyol (15.2334 g) (Composition D of Example 1 in U.S. Patent 6,187,444);
 Polyalkylenecarbonate diol (40.0000 g) T-5652 from Asahi Kasei Chemicals;
 DESMODUR® PL 340 (33.7615 g) from Bayer Material Science;
 TRIXENE® BI 7960 (24.0734 g) from Baxenden);
 Polyether modified polydimethylsiloxane (0.0658 g) BYK®-333 from BYK-Chemie GmbH);
 Urethane catalyst (0.8777 g) KKAT® 348 from King Industries;
 γ-Glycidoxypropyltrimethoxysilane (3.5109 g) A-187 from Momentive Performance Materials;
 Light stabilizer (7.8994 g) TINUVIN® 928 from Ciba Specialty Chemicals; and
 1-Methyl-2-pyrrolidinone (74.8250 g) from Sigma-Aldrich).

[0281] The mixture was stirred at room temperature for 2 hrs to yield a solution having 50 weight % final solids based on the total weight of the solution.

Part 3C-2 - Preparation of Photo-Alignment Coating Component

[0282] Staralign 2200CP10 purchased from Ventico was diluted to 2% solution with cyclopentanone solvent.

Part 3C-3- Liquid Crystal Coating Components and Formulations

[0283] Liquid crystal monomers (LCM) used for monomer solution include the following:

- 5 LCM-1 is 1-(6-(6-(6-(6-(6-(6-(6-(8-(4-(4-(4-(8-acryloyloxyhexylloxy)benzoyloxy) phenoxy)oc-
tyloxy)-6-oxohexyloxy)-6-oxohexyloxy)-6-oxohexyloxy)-6-oxohexyloxy)-6-oxohexyloxy)-6-oxohexyloxy)-6-oxohex-
10 yloxy)-6-oxohexan-1-ol which was prepared according to the procedures described in Example 17 of U.S. Patent
Publication 2009/0323011.
LCM-2 is commercially available RM257 reported to be 4-(3-acryloyloxypropyloxy)-benzoic acid 2-methyl-1,4-phe-
nylene ester, available from EMD Chemicals, Inc., having the molecular formula of $C_{33}H_{32}O_{10}$.
LCM-3 is commercially available RM105 reported to be 4-methoxy-3-methylphenyl 4-(6-(acryloyloxy)hexyloxy)ben-
zoate, available from EMD Chemicals, Inc., having the molecular formula of $C_{23}H_{26}O_6$.
LCM-4 is commercially available RM82 reported to be 2-methyl-1,4-phenylene bis(4-(6-(acryloyloxy)hexyloxy)ben-
zoate), available from EMD Chemicals, Inc., having the molecular formula of $C_{39}H_{44}O_{10}$.

15 **[0284]** Liquid crystal coating formulation (LCCF) was prepared as follows: to a suitable flask containing a mixture of
anisole (3.4667 g) and BYK[®]-346 additive (0.0347 g, reported to be a polyether modified poly-dimethyl-siloxane available
from BYK Chemie, USA), was added LCM-1 (1.3 g), LCM-2 (1.3 g), LCM-3 (1.3 g), LCM-4 (1.3 g), 4-methoxyphenol
(0.0078 g), and IRGACURE[®] 819 (0.078 g, a photoinitiator available from Ciba-Geigy Corporation) and the Example
20 compounds listed in Table 3 in a concentration of 6.3 mmol per 100 g of LCCF. The resulting mixture was stirred for 2
hours at 80°C and cooled to about 26°C.

Part 3C-4: Transitional Layer Coating Formulation (TLCF)

25 **[0285]** The TLCF was prepared as follows:

In a 50 mL amber glass bottle equipped with a magnetic stir-bar following materials were added:

- 30 Hydroxy methacrylate (1.242 g) from Sigma-Aldrich;
Neopentyl glycol diacrylate (13.7175 g) SR247 from Sartomer;
Trimethylolpropane trimethacrylate (2.5825 g) SR350 from Sartomer;
DESMODUR[®] PL 340 (5.02 g) from Bayer Material Science;
IRGACURE[®]-819 (0.0628 g) from Ciba Speciality Chemicals;
DAROCUR[®] TPO (0.0628 g; from Ciba Speciality Chemicals,
35 Polybutyl acrylate (0.125 g),
3-Aminopropylpropyltrimethoxysilane (1.4570 g) A-1100 from Momentive Performance Materials; and
200 proof absolute anhydrous Ethanol (1.4570 g) from Pharmaco-Aaper.

40 **[0286]** The mixture was stirred at room temperature for 2 hrs.

Part 3C-5: Protective Coating Formulation (PCF)

[0287] The PCF (Hard Coat) was prepared as follows: Charge 1 was added to a clean dry beaker and placed in an
ice bath at 5C with stirring. Charge 2 was added and an exotherm raised the temperature of the reaction mixture to 50C.
45 The temperature of the resulting reaction mixture was cooled to 20-25C and Charge 3 was added with stirring. Charge
4 was added to adjust the pH from about 3 to about 5.5. Charge 5 was added and the solution was mixed for half an
hour. The resulting solution was filtered through a nominal 0.45 micron capsule filter and stored at 4°C until use.

	<u>Charge 1</u>	
50	glycidoxypropyltrimethoxysilane	32.4 grams
	methyltrimethoxysilane	345.5 grams
	<u>Charge 2</u>	
	Solution of deionized water (DI) with nitric	292 grams
55	acid (nitric acid 1g/7000g)	
	<u>Charge 3</u>	
	DOWANOL [®] PM solvent	228 grams

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(continued)

Charge 4

TMAOH (25% tetramethylammonium hydroxide in methanol) 0.45 grams

Charge 5

BYK®-306 surfactant 2.0 grams

Part 3C-6 - Procedures Used for Preparing Coating Stacks Reported in Table 3

Part 3C-6A - Substrate Preparation

[0288] Square substrates measuring 5.08 cm by 5.08 cm by 0.318 cm (2 inches (in.) by 2 in. by 0.125 in.) prepared from CR-39® monomer were obtained from Homalite, Inc. Each substrate prepared from CR-39® monomer was cleaned by wiping with a tissue soaked with acetone and dried with a stream of air.

[0289] Each of the aforementioned substrates was corona treated by passing on a conveyor belt in Tantec EST Systems Serial No. 020270 Power Generator HV 2000 series corona treatment equipment with a high voltage transformer. The substrates were exposed to corona generated by 53.99 KV, 500 Watts while traveling on a conveyor at a belt speed 3 ft/min.

Part 3C-6B - Coating Procedure for Primer

[0290] The primer solution was applied to the test substrates by spin-coating on a portion of the surface of the test substrate by dispensing approximately 1.5 mL of the solution and spinning the substrates at 500 revolutions per minute (rpm) for 3 seconds, followed by 1,500 rpm for 7 seconds, followed by 2,500 rpm for 4 seconds. A spin processor from Laurell Technologies Corp. (WS-400B-6NPP/LITE) was used for spin coating. Afterwards, the coated substrates were placed in an oven maintained at 125° C for 60 minutes. The coated substrates were cooled to about 26° C. The substrate was corona treated by passing on a conveyor belt in Tantec EST Systems Serial No. 020270 Power Generator HV 2000 series corona treatment equipment with a high voltage transformer. The dried primer layer were exposed to corona generated by 53.00 KV, 500 Watts while traveling on a conveyor at a belt speed 3 ft/min.

Part 3C-6C - Coating Procedure for Photo-Alignment Materials

[0291] The 2wt% Staralign 2200 solutions prepared in Part 3C-2 was applied to the test substrates by spin-coating on a portion of the surface of the test substrate by dispensing approximately 1.0 mL of the solution and spinning the substrates at 800 revolutions per minute (rpm) for 3 seconds, followed by 1,000 rpm for 7 seconds, followed by 4,000 rpm for 4 seconds. A spin processor from Laurell Technologies Corp. (WS-400B-6NPP/LITE) was used for spin coating. Afterwards, the coated substrates were placed in an oven maintained at 120° C for 30 minutes. The coated substrates were cooled to about 26° C.

[0292] The dried photo alignment layer on each of the substrates was at least partially ordered by exposure to linearly polarized ultraviolet radiation using a DYMAX® UVC-6 UV/conveyor system by DYMAX® Corp. having a 400 Watt power supply. The light source was oriented such that the radiation was linearly polarized in a plane perpendicular to the surface of the substrate. The amount of ultraviolet radiation that each photoalignment layer was exposed to was measured using a UV Power Puck™ High energy radiometer from EIT Inc (Serial No. 2066) and was as follows: UVA 0.121W/cm² and 5.857 J/cm²; UVB 0.013 W/cm² and 0.072 J/cm²; UVC 0 W/cm² and 0 J/cm²; and UVV 0.041 W/cm² and 1.978 J/cm². After ordering at least a portion of the photo-orientable polymer network, the substrates were cooled to about 26° C and kept covered.

Part 3C-6D - Coating Procedure for Liquid Crystal Coating Formulations

[0293] The Liquid Crystal Coating Formulations ("LCCF") described in Part 3C-3 were each spin coated at a rate of 300 revolutions per minute (rpm) for 6 seconds, followed by 800rpm for 6 seconds onto the at least partially ordered photoalignment materials of Part 6C on the test substrates. Each coated square substrate was placed in an oven at 50°C for 20 minutes and each coated lens was placed in an oven at 50°C for 30 minutes. Afterwards substrates were cured under an ultraviolet lamp in the Irradiation Chamber BS-03 from Dr. Gröbel UV-Elektronik GmbH in a nitrogen atmosphere for 30 minutes at a peak intensity of 11-16 Watts/m² of UVA. Post curing of the coated substrates was completed at 105°C for 3 hours.

Part 3C-6E - Coating Procedure for Transitional Layer

5 [0294] The Transitional layer solution prepared in Part 3C-4 was spin coated at a rate of 1,400 revolutions per minute (rpm) for 7 seconds onto the cured LCCF coated substrates. Afterwards, the lenses were cured under an ultraviolet lamp in the Irradiation Chamber BS-03 from Dr. Dr. Gröbel UV-Elektronik GmbH in a nitrogen atmosphere for 30 minutes at a peak intensity of 11-16 Watts/m² of UVA. Post curing of the coated substrates was completed at 105°C for 3 hours.

Part 3C-6F - Coating Procedure for the Protective Coating (Hard Coat)

10 [0295] The hard coat solution prepared in Part 3C-5 was spin coated at a rate of 2,000 revolutions per minute (rpm) for 10 seconds onto the cured tie layer coated substrates. Post curing of the coated substrates was completed at 105°C for 3 hours.

Table 3 - Absorption Ratio Results for Different Coating Stacks

Example #	Primer	Alignment Layer	LCCF	Tie Layer	Hard Coat	AR
8		x	x			6.18
13		x	x			6.61
12		x	x			5.38
17		x	x			5.49
18		x	x			7.14
8		x	x	x		5.96
17		x	x	x		5.32
18		x	x	x		7.05
13		x	x		x	6.53
33	x	x	x	x		7.12
12	x	x	x	x		5.24
17	x	x	x	x		5.13
33	x	x	x			7.62
33	x	x	x	x	x	7.13
12	x	x	x	x	x	4.77

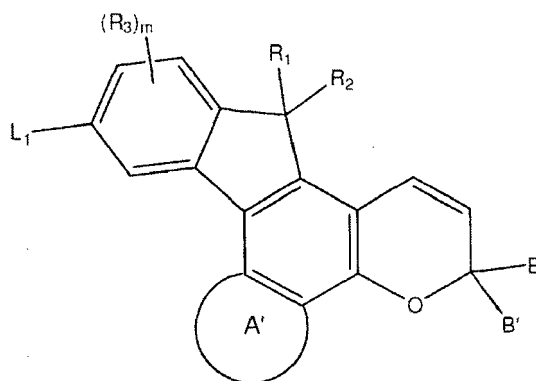
40 [0296] The present invention has been described with reference to specific details of particular embodiments thereof. It is not intended that such details be regarded as limitations upon the scope of the invention except insofar as to the extent that they are included in the accompanying claims.

45 **Claims**

1. A compound represented by the following graphic Formula I :

50

55



Formula I

wherein:

A' is selected from optionally substituted heteroaryl and optionally substituted aryl wherein A' is optionally substituted with L₂;

R₁ and R₂ are each independently selected from hydrogen, hydroxy and chiral or achiral groups selected from optionally substituted heteroalkyl, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, halogen, optionally substituted amino, carboxy, alkylcarbonyl, alkoxy carbonyl, optionally substituted alkoxy, and aminocarbonyl, or R₁ and R₂ may be taken together with any intervening atoms to form a group selected from oxo, optionally substituted cycloalkyl, and optionally substituted heterocycloalkyl; and

R₃ for each occurrence, is independently selected from chiral or achiral groups selected from formyl, alkylcarbonyl, alkoxy carbonyl, aminocarbonyl, arylcarbonyl, aryloxy carbonyl, aminocarbonyloxy, alkoxy carbonylamino, aryloxy carbonylamino, boronic acid, boronic acid esters, cycloalkoxy carbonylamino, heterocycloalkoxy carbonylamino, heteroaryloxy carbonylamino, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, halogen, optionally substituted cycloalkyl, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted alkoxy, optionally substituted heteroalkyl, optionally substituted heterocycloalkyl, and optionally substituted amino;

m is an integer selected from 0 to 3;

B and B' are each independently selected from L₃, hydrogen, halogen, and chiral or achiral groups selected from metallocenyl, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted heterocycloalkyl, and optionally substituted cycloalkyl, or wherein B and B' are taken together with any intervening atoms to form a group selected from optionally substituted cycloalkyl and optionally substituted heterocycloalkyl; and

L₁, L₂, and L₃ for each occurrence, are independently selected from a chiral or achiral lengthening group represented by:

- [S₁]_c-[Q₁-[S₂]_d]_{d'}-[Q₂-[S₃]_e]_{e'}-[Q₃-[S₄]_f]_{f'}-S₅-P wherein:

(a) Q₁, Q₂, and Q₃ for each occurrence, are independently selected from a divalent group selected from optionally substituted aryl, optionally substituted heteroaryl, optionally substituted cycloalkyl, and optionally substituted heterocycloalkyl;

wherein substituents are independently selected from P, liquid crystal mesogens, halogen, poly(C₁-C₁₈ alkoxy), C₁-C₁₈ alkoxy carbonyl, C₁-C₁₈ alkyl carbonyl, C₁-C₁₈ alkoxy carbonyloxy, aryloxy carbonyloxy, perfluoro(C₁-C₁₈)alkoxy, perfluoro(C₁-C₁₈)alkoxy carbonyl, perfluoro(C₁-C₁₈)alkyl carbonyl, perfluoro(C₁-C₁₈)alkyl amino, di-(perfluoro(C₁-C₁₈)alkyl)amino, perfluoro(C₁-C₁₈)alkyl thio, C₁-C₁₈ alkyl thio, C₁-C₁₈ acetyl, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkoxy, straight-chain C₁-C₁₈ alkyl, and branched C₁-C₁₈ alkyl;

wherein said straight-chain C₁-C₁₈ alkyl and branched C₁-C₁₈ alkyl are mono-substituted with a group

selected from cyano, halogen, and C₁-C₁₈ alkoxy; or
 wherein said straight-chain C₁-C₁₈ alkyl and branched C₁-C₁₈ alkyl are poly-substituted with at least two groups independently selected from halogen, -M(T)_(t-1) and -M(OT)_(t-1), wherein M is chosen from aluminum, antimony, tantalum, titanium, zirconium and silicon, T is chosen from organofunctional radicals, organofunctional hydrocarbon radicals, aliphatic hydrocarbon radicals and aromatic hydrocarbon radicals, and t is the valence of M;

(b) c, d, e, and f are each independently chosen from an integer from 1 to 20; and each S₁, S₂, S₃, S₄, and S₅ is independently chosen for each occurrence from a spacer unit selected from:

(i) optionally substituted alkylene, optionally substituted haloalkylene, -Si(CH₂)_g-, and -(Si[(CH₃)₂]O)_h-, wherein g for each occurrence is independently chosen from an integer from 1 to 20; h for each occurrence is independently chosen from an integer from 1 to 16; and said substituents for the alkylene and haloalkylene are independently selected from C₁-C₁₈ alkyl, C₃-C₁₀ cycloalkyl and aryl;

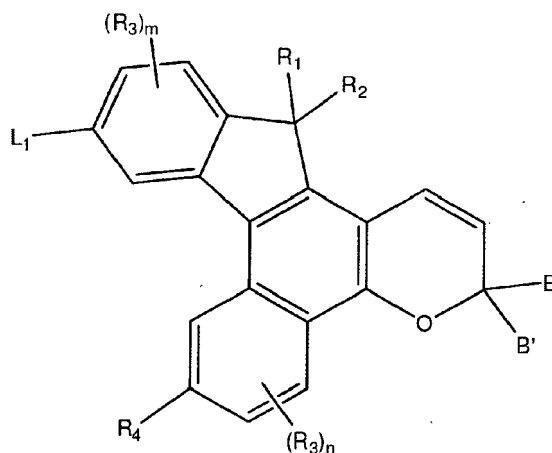
(ii) -N(Z)-, -C(Z)=C(Z)-, -C(Z)=N-, -C(Z')₂-C(Z')₂-, and a single bond, wherein Z for each occurrence is independently selected from hydrogen, C₁-C₁₈ alkyl, C₃-C₁₀ cycloalkyl and aryl, and Z' for each occurrence is independently selected from C₁-C₁₈ alkyl, C₃-C₁₀ cycloalkyl and aryl; and

(iii) -O-, -C(=O)-, -C≡C-, -N=N-, -S-, -S(=O)-, -(O=)S(=O)-, -(O=)S(=O)O-, -O(O=)S(=O)O- and straight-chain or branched C₁-C₂₄ alkylene residue, said C₁-C₂₄ alkylene residue being unsubstituted, mono-substituted by cyano or halogen, or poly-substituted by halogen, provided that when two spacer units comprising heteroatoms are linked together the spacer units are linked so that heteroatoms are not directly linked to each other, each bond between S₁ and the compound represented by graphic Formula I is free of two heteroatoms linked together, and the bond between S₅ and P is free of two heteroatoms linked to each other;

(c) P for each occurrence is independently selected from hydroxy, amino, C₂-C₁₈ alkenyl, C₂-C₁₈ alkynyl, azido, silyl, siloxy, silylhydride, (tetrahydro-2H-pyran-2-yl)oxy, thio, isocyanato, thioisocyanato, acryloyloxy, methacryloyloxy, 2-(acryloyloxy)ethylcarbonyl, 2-(methacryloyloxy)ethylcarbonyl, aziridinyl, allyloxycarbonyloxy, epoxy, carboxylic acid, carboxylic ester, acryloylamino, methacryloylamino, aminocarbonyl, C₁-C₁₈ alkyl aminocarbonyl, aminocarbonyl(C₁-C₁₈)alkyl, C₁-C₁₈ alkyloxycarbonyloxy, halocarbonyl, hydrogen, aryl, hydroxy(C₁-C₁₈)alkyl, C₁-C₁₈ alkyl, C₁-C₁₈ alkoxy, amino(C₁-C₁₈)alkyl, C₁-C₁₈ alkylamino, di-(C₁-C₁₈)alkyl-amino, C₁-C₁₈ alkyl(C₁-C₁₈)alkoxy, C₁-C₁₈ alkoxy(C₁-C₁₈)alkoxy, nitro, poly(C₁-C₁₈)alkyl ether, (C₁-C₁₈)alkyl(C₁-C₁₈)alkoxy(C₁-C₁₈)alkyl, polyethyleneoxy, polypropyleneoxy, ethylene, acryloyl, acryloyloxy(C₁-C₁₈)alkyl, methacryloyl, methacryloyloxy(C₁-C₁₈)alkyl, 2-chloroacryloyl, 2-phenylacryloyl, acryloyloxyphenyl, 2-chloro-acryloylamino, 2-phenylacryloylaminocarbonyl, oxetanyl, glycidyl, cyano, isocyanato(C₁-C₁₈)alkyl, itaconic acid ester, vinyl ether, vinyl ester, a styrene derivative, main-chain and side-chain liquid crystal polymers, siloxane derivatives, ethyleneimine derivatives, maleic acid derivatives, maleimide derivatives, fumaric acid derivatives, unsubstituted cinnamic acid derivatives, cinnamic acid derivatives that are substituted with at least one of methyl, methoxy, cyano and halogen, and substituted or unsubstituted chiral or non-chiral monovalent or divalent groups chosen from steroid radicals, terpenoid radicals, alkaloid radicals and mixtures thereof, wherein the substituents are independently chosen from C₁-C₁₈ alkyl, C₁-C₁₈ alkoxy, amino, C₃-C₁₀ cycloalkyl, C₁-C₁₈ alkyl(C₁-C₁₈)alkoxy, fluoro(C₁-C₁₈)alkyl, cyano, cyano(C₁-C₁₈)alkyl, cyano(C₁-C₁₈)alkoxy or mixtures thereof, or P is a structure having from 2 to 4 reactive groups or P is an unsubstituted or substituted ring opening metathesis polymerization precursor or P is a substituted or unsubstituted photochromic compound; and

(d) d', e' and f' are each independently chosen from 0, 1, 2, 3, and 4, provided that a sum of d' + e' + f' is at least 2.

2. The compound of claim 1 represented by graphic Formula IA:



Formula IA

wherein

R_4 is selected from hydrogen, R_3 and L_2 ; and

n is an integer selected from 0 to 3,

preferably wherein

R_1 and R_2 are each independently selected from hydrogen, hydroxy, and chiral and achiral groups selected from optionally substituted heteroalkyl, optionally substituted alkyl, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted cycloalkyl, halogen, optionally substituted amino, carboxy, alkylcarbonyl, alkoxy-carbonyl, optionally substituted alkoxy, and aminocarbonyl or R_1 and R_2 may be taken together with any intervening atoms to form a group selected from oxo, optionally substituted cycloalkyl and optionally substituted heterocycloalkyl; R_3 for each occurrence, is independently selected from formyl, alkylcarbonyl, alkoxy-carbonyl, aminocarbonyl, aryl-carbonyl, aryloxy-carbonyl, optionally substituted alkyl, boronic acid ester, halogen, optionally substituted cycloalkyl, optionally substituted aryl, optionally substituted alkoxy, optionally substituted heteroalkyl, optionally substituted heterocycloalkyl and optionally substituted amino;

m and n are each independently an integer selected from 0 to 2;

B and B' are each independently selected from L_3 , hydrogen, halogen, chiral or achiral groups selected from optionally substituted alkyl, optionally substituted alkenyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted aryl, optionally substituted heteroaryl, and optionally substituted cycloalkyl, or wherein B and B' are taken together with any intervening atoms to form a group selected from optionally substituted cycloalkyl and optionally substituted heterocycloalkyl; and

L_1 , L_2 , and L_3 for each occurrence, are independently selected from a chiral or achiral lengthening group represented by:



(a) Q_1 , Q_2 , and Q_3 for each occurrence, are independently selected from a divalent group selected from optionally substituted aryl and optionally substituted heteroaryl, optionally substituted cycloalkyl and optionally substituted heterocycloalkyl;

wherein substituents are independently selected from P, liquid crystal mesogens, halogen, poly(C_1 - C_{12} alkoxy), C_1 - C_{12} alkoxy-carbonyl, C_1 - C_{12} alkylcarbonyl, perfluoro(C_1 - C_{12})alkoxy, perfluoro(C_1 - C_{12})alkoxy-carbonyl, perfluoro(C_1 - C_{12})alkylcarbonyl, C_1 - C_{18} acetyl, C_3 - C_7 cycloalkyl, C_3 - C_7 cycloalkoxy, straight-chain C_1 - C_{12} alkyl, and branched C_1 - C_{12} alkyl, wherein said straight-chain C_1 - C_{12} alkyl and branched C_1 - C_{12} alkyl are mono-substituted with a group selected from, halogen, and C_1 - C_{12} alkoxy, or wherein said straight-chain C_1 - C_{12} alkyl and branched C_1 - C_{12} alkyl are poly-substituted with at least two groups independently selected from halogen;

(b) c , d , e , and f are each independently chosen from an integer from 1 to 10; and each S_1 , S_2 , S_3 , S_4 , and S_5 is independently chosen for each occurrence from a spacer unit selected from:

(i) substituted or unsubstituted alkylene, substituted or unsubstituted haloalkylene, $-\text{Si}(\text{CH}_2)_g-$, and

$-(\text{Si}[(\text{CH}_3)_2\text{O}]_g)_n-$, wherein g for each occurrence is independently chosen from an integer from 1 to 10; h for each occurrence is independently chosen from an integer from 1 to 8; and said substituents for the alkylene and haloalkylene are independently selected from C₁-C₁₂ alkyl, C₃-C₇ cycloalkyl and phenyl;

(ii) -N(Z)-, -C(Z)=C(Z)-, and a single bond, wherein Z for each occurrence is independently selected from hydrogen, C₁-C₁₂ alkyl, C₃-C₇ cycloalkyl and phenyl, and

(iii) -O-, -C(=O)-, -C≡C-, -N=N-, -S-, and -S(=O)-,

provided that when two spacer units comprising heteroatoms are linked together the spacer units are linked so that heteroatoms are not directly linked to each other, each bond between S₁ and the compound represented by graphic Formula IA is free of two heteroatoms linked together, and the bond between S₅ and P is free of two heteroatoms linked to each other;

(c) P for each occurrence is selected from hydroxy, amino, C₂-C₁₂ alkenyl, silyl, siloxy, (tetrahydro-2H-pyran-2-yl)oxy, isocyanato, acryloyloxy, methacryloyloxy, epoxy, carboxylic acid, carboxylic ester, C₁-C₁₂ alkyloxycarbonyloxy, halocarbonyl, hydrogen, aryl, hydroxy(C₁-C₁₂)alkyl, C₁-C₁₂ alkyl, C₁-C₁₂ alkoxy, ethylene, acryloyl, acryloyloxy(C₁-C₁₂)alkyl, methacryloyl, methacryloyloxy(C₁-C₁₂)alkyl, oxetanyl, glycidyl, vinyl ether, siloxane derivatives, unsubstituted cinnamic acid derivatives, cinnamic acid derivatives that are substituted with at least one of methyl, methoxy, cyano and halogen, and substituted or unsubstituted chiral or non-chiral monovalent or divalent groups chosen from steroid radicals, wherein each substituent is independently chosen from C₁-C₁₂ alkyl, C₁-C₁₂ alkoxy, amino, C₃-C₇ cycloalkyl, C₁-C₁₂ alkyl(C₁-C₁₂)alkoxy, or fluoro(C₁-C₁₂)alkyl, or P is a structure having from 2 to 4 reactive groups; and

(d) d', e' and f' are each independently chosen from 0, 1, 2, 3, and 4, provided that a sum of d' + e' + f' is at least 2,

more preferably wherein:

R₁ and R₂ are each independently selected from hydrogen, hydroxy, and chiral groups selected from optionally substituted heteroalkyl, optionally substituted alkyl, optionally substituted aryl, optionally substituted cycloalkyl, halogen, carboxy, alkylcarbonyl, alkoxy, optionally substituted alkoxy, and aminocarbonyl or R₁ and R₂ may be taken together with any intervening atoms to form a group selected from oxo and optionally substituted cycloalkyl; and

R₃ for each occurrence, is independently selected from alkylcarbonyl, alkoxy, aminocarbonyl, optionally substituted alkyl, boronic acid ester, halogen, optionally substituted cycloalkyl, optionally substituted aryl, optionally substituted alkoxy, optionally substituted heterocycloalkyl and optionally substituted amino;

m and n are each independently an integer selected from 0 to 2;

B and B' are each independently selected from L₃, hydrogen, chiral groups selected from optionally substituted alkyl, optionally substituted alkenyl, optionally substituted aryl, optionally substituted heteroaryl, and optionally substituted cycloalkyl, or wherein B and B' are taken together with any intervening atoms to form a group selected from optionally substituted cycloalkyl;

L₁, L₂, and L₃ for each occurrence, are independently selected from a chiral or achiral lengthening group represented by:

$-[\text{S}_1]_c-[\text{Q}_1-[\text{S}_2]_d]_d-[\text{Q}_2-[\text{S}_3]_e]_e-[\text{Q}_3-[\text{S}_4]_f]_f-\text{S}_5-\text{P}$ wherein:

(a) Q₁, Q₂, and Q₃ for each occurrence, are independently selected from a divalent group selected from optionally substituted aryl and optionally substituted heteroaryl, optionally substituted cycloalkyl and optionally substituted heterocycloalkyl;

wherein substituents are independently selected from P, C₁-C₆ alkoxy, perfluoro(C₁-C₆)alkoxy, C₃-C₇ cycloalkyl, C₃-C₇ cycloalkoxy, straight-chain C₁-C₆ alkyl, and branched C₁-C₆ alkyl, wherein said straight-chain C₁-C₆ alkyl and branched C₁-C₆ alkyl are mono-substituted with a group selected from halogen and C₁-C₁₂ alkoxy, or

wherein said straight-chain C₁-C₆ alkyl and branched C₁-C₆ alkyl are poly-substituted with at least two groups independently selected from halogen;

(b) c, d, e, and f are each independently chosen from an integer from 1 to 10; and each S₁, S₂, S₃, S₄, and S₅ is independently chosen for each occurrence from a spacer unit selected from:

(i) substituted or unsubstituted alkylene;

(ii) -N(Z)-, -C(Z)=C(Z)-, and a single bond, wherein Z for each occurrence is independently selected from hydrogen and C₁-C₆ alkyl; and

(iii) -O-, -C(=O)-, -C≡C-, and -N=N-, -S-;

provided that when two spacer units comprising heteroatoms are linked together the spacer units are linked so that heteroatoms of the first spacer unit are not directly linked to the heteroatoms of the second spacer unit, and

provided that when S₁ and S₅ are linked to Formula I and P, respectively, they are linked so that two heteroatoms are not directly linked to each other;

(c) P for each occurrence is independently selected from hydroxy, amino, C₂-C₆ alkenyl, siloxy, (tetrahydro-2H-pyran-2-yl)oxy, isocyanato, acryloyloxy, methacryloyloxy, epoxy, carboxylic acid, carboxylic ester, C₁-C₆ alkoxycarbonyloxy, hydrogen, aryl, hydroxy(C₁-C₆)alkyl, C₁-C₆ alkyl, ethylene, acryloyl, acryloyloxy(C₁-C₁₂)alkyl, oxetanyl, glycidyl, vinyl ether, siloxane derivatives, and substituted or unsubstituted chiral or non-chiral monovalent or divalent groups chosen from steroid radicals, wherein each substituent is independently chosen from C₁-C₆ alkyl, C₁-C₆ alkoxy, amino, and C₃-C₇ cycloalkyl,

and even more preferably wherein: R₁ and R₂ are each independently selected from methyl, ethyl, propyl and butyl; R₃ and R₄ for each occurrence are independently selected from methyl, ethyl, bromo, chloro, fluoro, methoxy, ethoxy and CF₃; B and B' are each independently selected from phenyl substituted with one or more groups independently selected from aryl, heteroaryl, heterocycloalkyl, alkyl, alkenyl, alkynyl, alkoxy, halogen, amino, alkylcarbonyl, carboxy, and alkoxycarbonyl; and for L₁: Q₁ is unsubstituted aryl; e' is 1 or 2; e each occurrence is 1; S₃ for each occurrence is a single bond; Q₂ for each occurrence is independently selected from optionally substituted aryl; f is 1; f is 1; S₄ is a single bond; and Q₃ is optionally substituted cycloalkyl; S₅ is -(CH₂)_g-, wherein g is an integer from 1 to 20; and P is hydrogen.

3. The compound of claim 1 wherein L₁ is selected from:

4-[4-(4-butyl-cyclohexyl)-phenyl]-cyclohexyloxy;
 4"-butyl-[1,1',4',1"]tercyclohexan-4-yloxy;
 4-[4-(4-butyl-phenyl)-cyclohexyloxycarbonyl]-phenoxy;
 4'-(4-butyl-benzoyloxy)-biphenyl-4-carbonyloxy;
 4-(4-pentyl-phenylazo)-phenylcarbamoyle;
 4-(4-dimethylamino-phenylazo)-phenylcarbamoyle;
 4-[5-(4-propyl-benzoyloxy)-pyrimidin-2-yl]-phenyl;
 4-[2-(4'-methyl-biphenyl-4-carbonyloxy)-1,2-diphenyl-ethoxycarbonyl]-phenyl;
 4-(1,2-diphenyl-2-[3-[4-(4-propyl-benzoyloxy)-phenyl]-acryloyloxy]-ethoxycarbonyl)-phenyl;
 4-[4-(4-[4-[3-(6-[4-[4-(4-nonyl-benzoyloxy)-phenoxy]carbonyl]-phenoxy]-hexyloxycarbonyl]propionyloxy]-benzoyloxy)-benzoyloxy)-phenyl]-piperazin-1-yl;
 4-[4-(4-[4-[4-(4-nonyl-benzoyloxy)-benzoyloxy]-benzoyloxy]-benzoyloxy)-phenyl]-piperazin-1-yl;
 4-(4'-propyl-biphenyl-4-ylethynyl)-phenyl;
 4-(4-fluoro-phenoxy)carbonyloxy)-piperidin-1-yl;
 2-[17-(1,5-dimethyl-hexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxy]-indan-5-yl;
 4-[17-(1,5-dimethyl-hexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxycarbonyloxy]-piperidin-1-yl;
 4-(biphenyl-4-carbonyloxy)-piperidin-1-yl;
 4-(naphthalene-2-carbonyloxy)-piperidin-1-yl;
 4-(4-phenylcarbamoyle-phenylcarbamoyle)-piperidin-1-yl;
 4-(4-(4-phenylpiperidin-1-yl)-benzoyloxy)-piperidin-1-yl;
 4-butyl-[1,1';4',1"]terphenyl-4-yl;
 4-(4-pentadecafluoroheptyloxy-phenylcarbamoyle)-benzyloxy;
 4-(3-piperidin-4-yl-propyl)-piperidin-1-yl;
 4-(4-[4-[17-(1,5-dimethyl-hexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxycarbonyloxy]-benzoyloxy]-phenoxy]carbonyl)phenoxy)methyl;
 4-[4-(4-cyclohexyl-phenylcarbamoyle)-benzyloxy]-piperidin-1-yl;
 4-[4-(4-cyclohexyl-phenylcarbamoyle)-benzoyloxy]-piperidin-1-yl;
 N-{4-[4-(4-pentyl-benzylidene)-amino]-phenyl}-acetamidyl;
 4-(3-piperidin-4-yl-propyl)-piperidin-1-yl;
 4-(4-hexyloxy-benzoyloxy)-piperidin-1-yl;
 4-(4'-hexyloxy-biphenyl-4-carbonyloxy)-piperidin-1-yl;

4-(4-butyl-phenylcarbamoyl)-piperidin-1-yl;
 4-[4-[4-[4-piperidinyl-4-oxy]-phenyl]phenoxy]piperidin-4-yl;
 4-(4-(9-(4-butylphenyl)-2,4,8,10-tetraoxaspiro[5.5]undec-3-yl) phenyl)piperazin-1-yl;
 4-(6-(4-butylphenyl)carbonyloxy-(4,8-dioxabicyclo[3.3.0]oct-2-yl)oxycarbonyl)phenyl;
 1-[4-[5-(4-butyl-phenyl)-[1,3]dioxan-2-yl]-phenyl]-4-methyl-piperazin-1-yl;
 4-(7-(4-propylphenylcarbonyloxy)bicyclo[3.3.0]oct-2-yl) oxycarbonyl)phenyl;
 4-[17-(1,5-dimethyl-hexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxy]carbonyloxy;
 (4-trans-(4-pentylcyclohexyl)benzamido)phenyl;
 (4-(4-trans-(4-pentylcyclohexyl)phenoxy)carbonyl)phenyl;
 4-(4-(4-trans-(4-pentylcyclohexyl)phenyl)benzamido)phenyl;
 4-((trans-(4'-pentyl-[1,1'-bi(cyclohexane)]-4-yl)oxy)carbonyl)phenyl;
 4-(4'-(4-pentylcyclohexyl)-[1,1'-biphenyl]-4-ylcarboxamido)phenyl;
 4-((4'-(4-pentylcyclohexyl)-[1,1'-biphenyl]-4-carbonyl)oxy)benzamido;
 4-(4'-(4-pentylcyclohexyl)-[1,1'-biphenyl]-4-carbonyl)piperazin-1-yl;
 4-(4-(4-(4-pentylcyclohexyl)phenyl)benzamido)-2-(trifluoromethyl)phenyl;
 2-methyl-4-trans-(4-((4'-trans-(4-pentylcyclohexyl)biphenyl-4-yloxy)carbonyl)cyclohexanecarboxamido)phenyl;
 4'-((1r,1's,4R,4'R)-4'-pentylbi(cyclohexane-4-)carbonyloxy)biphenyl-carbonyloxy;
 4-(((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1 H-cyclopenta[a]phenanthren-3-yloxy)carbonyl)piperazin-1-yl; and
 4-((S)-2-methylbutoxy)phenyl)-10-(4-(((3R,3aS,6S,6aS)-6-(4'-trans-(4-pentylcyclohexyl)biphenylcarbonyloxy)hexahydrofuro[3,2-b]furan-3-yloxy)carbonyl)phenyl).

4. The compound of claim 1 selected from:

3,3-Bis(4-methoxyphenyl)-10-[4-(4-(trans-4-pentylcyclohexyl)-benzamido)phenyl]-13,13-dimethyl-12-bromo-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-10-[4-((4-(trans-4-pentylcyclohexyl)phenoxy)carbonyl)phenyl]-6,13,13-trimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Fluorophenyl)-3-(4-piperidinophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-11,13,13-trimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-10-[4-(4-(trans-4-pentylcyclohexyl)benzamido)phenyl]-5,7-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Methoxyphenyl)-3-(4-piperidinophenyl)-10-[4-(4-(4-(trans-4-pentyl-cyclohexyl)phenyl)benzamido)phenyl]-5,7-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Methoxyphenyl)-3-(4-morpholinophenyl)-10-[4-(4-(4-(trans-4-pentyl-cyclohexyl)phenyl)benzamido)phenyl]-5,7-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Fluorophenyl)-3-(4-piperidinophenyl)-10-[4-((4-(trans-4-pentylcyclohexyl)phenoxy)carbonyl)phenyl]-12-bromo-5,7-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-Phenyl-3-(4-piperidinophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-12-bromo-5,7-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-Phenyl-3-(4-piperidinophenyl)-10-[4-((4-(trans-4-pentylcyclohexyl)phenoxy)carbonyl)phenyl]-12-bromo-5,7-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Fluorophenyl)-3-(4-piperidinophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-12-bromo-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-12-bromo-6,7-dimethoxy-11,13,13-trimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-12-bromo-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-10,12-bis[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl) benzamido)phenyl]-5,7-difluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl) benzamido)phenyl]-5,7-difluoro-12-

bromo-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Fluorophenyl)-3-(4-morpholinophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-
 6-trifluoromethyl-13-methyl-13-butyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Fluorophenyl)-3-(4-morpholinophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-
 5,7-difluoro-12-bromo-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-Phenyl-3-(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluorome-
 5 thyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-Phenyl-3-(4-morpholinophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluor-
 omethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 10 3,3-Bis(4-fluorophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl) phenyl)benzamido)phenyl]-6-trifluoromethyl-12-
 bromo-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-fluorophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl) phenyl)benzamido)phenyl]-6-trifluoromethyl-
 13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Methoxyphenyl)-3-(4-butoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-
 15 trifluoromethyl-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Fluorophenyl)-13,13-dimethyl-3-(4-morpholinophenyl)-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphe-
 nyl]-4-ylcarboxamido)phenyl)-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Butoxyphenyl)-3-(4-fluorophenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-yl-
 carboxamido)phenyl)-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 20 3-(4-(4-(4-Methoxyphenyl)piperazin-1-yl)phenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-bi-
 phenyl]-4-ylcarboxamido)phenyl)-3-phenyl-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-
 b]pyran;
 3-(4-Butoxyphenyl)-3-(4-fluorophenyl)-13,13-dimethyl-10-(4-(((trans,trans-4'-pentyl-[1,1'-bi(cyclohexan)]-4-
 yl)oxy)carbonyl)phenyl)-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 25 3-(4-Fluorophenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-ylcarboxamido)phe-
 nyl)-3-(4-butoxyphenyl)-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Methoxyphenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-ylcarboxami-
 do)phenyl)-3-(4-(trifluoromethoxy)phenyl)-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-
 b]pyran;
 30 3,3-Bis(4-hydroxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)phenyl]-6-trifluoromethyl-
 13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 12-Bromo-3-(4-butoxyphenyl)-3-(4-fluorophenyl)-13,13-dimethyl-10-(4-((4'-(trans-4-pentylcyclohexyl)-[1,1'-bi-
 phenyl]-4-carbonyl)oxy)benzamido)-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 35 3-(4-Butoxyphenyl)-5,7-dichloro-11-methoxy-3-(4-methoxyphenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcy-
 clohexyl)-[1,1'-biphenyl]-4-ylcarboxamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Butoxyphenyl)-3-(4-fluorophenyl)-13,13-dimethyl-10-(4-((4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-
 carbonyl)oxy)benzamido)-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 5,7-Dichloro-3,3-bis(4-hydroxyphenyl)-11-methoxy-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-
 biphenyl]-4-ylcarboxamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 40 6,8-Dichloro-3,3-bis(4-hydroxyphenyl)-11-methoxy-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-
 biphenyl]-4-ylcarboxamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Butoxyphenyl)-5,8-difluoro-3-(4-fluorophenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-
 biphenyl]-4-ylcarboxamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Butoxyphenyl)-3-(4-fluorophenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-
 45 carbonyl)piperazin-1-yl)-6-(trifluoromethyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Morpholinophenyl)-3-(4-methoxyphenyl)-10,7-bis[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzami-
 do)phenyl]-5-fluoro-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Morpholinophenyl)-3-(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)-2-(trif-
 luoromethyl)phenyl]-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 50 3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)-2-(trifluoromethyl)phe-
 nyl]-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Morpholinophenyl)-3-(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)-2-(trif-
 luoromethyl)phenyl]-13,13-dimethyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-13,13-dimethyl-10-(2-methyl-4-(trans-4-((4'-(trans-4-pentylcyclohexyl)biphenyl-4-
 55 yloxy)carbonyl)cyclohexane-carboxamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-(4-(4-Butylphenyl)piperazin-1-yl)phenyl)-3-(4-methoxyphenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentyl-
 cyclohexyl)biphenyl-4-ylcarboxamido)-2-(trifluoromethyl)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-
 b]pyran;

3-(4-(4-(4-Butylphenyl)piperazin-1-yl)phenyl)-3-(4-methoxyphenyl)-13,13-dimethyl-10-(2-methyl-4-(4'-(trans-4-pentylcyclohexyl)biphenyl-4-ylcarboxamido)phenyl)-7-(4-(4-(trans-4-pentylcyclohexyl)benz-amido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-(4-Methoxyphenyl)-13,13-dimethyl-7,10-bis(4-(4'-(trans-4-pentylcyclohexyl)biphenyl-4-ylcarboxamido)phenyl)-3-phenyl-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

3-p-Tolyl-3-(4-methoxyphenyl)-6-methoxy-13,13-dimethyl-7-(4'-(trans,trans-4'-pentylbi(cyclohexane-4-)carbonyloxy)biphenylcarbonyloxy)-10-(4-(4'-(trans-4-pentylcyclohexyl)biphenyl-4-ylcarboxamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

10-(4-(((3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methyl-heptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxy)carbonyl)piperazin-1-yl)-3-(4-methoxyphenyl)-13,13-dimethyl-3-(4-morpholinophenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

6-Methoxy-3-(4-methoxyphenyl)-13,13-dimethyl-3-(4-((S)-2-methyl-butoxy)phenyl)-10-(4-(4'-(trans-4-pentylcyclohexyl)biphenyl-4-ylcarboxamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran;

6-Methoxy-3-(4-methoxyphenyl)-13,13-dimethyl-3-(4-((S)-2-methylbutoxy)phenyl)-7-(4'-(trans,trans-4'-pentylbi(cyclohexane-4-)carbonyloxy)biphenylcarbonyloxy)-10-(4-(4'-(trans-4-pentylcyclohexyl)biphenyl-4-ylcarboxamido)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran; and

6-Methoxy-3-(4-methoxyphenyl)-13,13-dimethyl-3-(4-((S)-2-methylbutoxy)phenyl)-10-(4-(((3R,3aS,6S,6aS)-6-(4'-(trans-4-pentylcyclohexyl)biphenylcarbonyloxy)hexahydrofuro[3,2-b]furan-3-yloxy)carbonyl)phenyl)-3,13-dihydro-indeno[2',3':3,4]naphtho[1,2-b]pyran.

5. A photochromic composition comprising a photochromic compound of claim 1 and optionally at least one other photochromic compound, wherein said composition comprises:

- (a) a single photochromic compound;
- (b) a mixture of photochromic compounds;
- (c) a material comprising at least one photochromic compound;
- (d) a material to which at least one photochromic compound is chemically bonded;
- (e) material (c) or (d) further comprising a coating to substantially prevent contact of the at least one photochromic compound with external materials;
- (f) a photochromic polymer; or
- (g) mixtures thereof.

6. A photochromic composition comprising at least one photochromic compound of claim 1 incorporated into at least a portion of an organic material, said organic material being a polymeric material, an oligomeric material, a monomeric material or a mixture or combination thereof.

7. The photochromic composition of claim 6 wherein said polymeric material comprises liquid crystal materials, self-assembling materials, polycarbonate, polyamide, polyimide, poly(meth)acrylate, polycyclic alkene, polyurethane, poly(urea)urethane, polythiourethane, polythio(urea)-urethane, polyol(allyl carbonate), cellulose acetate, cellulose diacetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate, polyalkene, polyalkylenevinyl acetate, poly(vinylacetate), poly(vinyl alcohol), poly(vinyl chloride), poly(vinylformal), poly(vinylacetal), poly(vinylidene chloride), poly(ethylene terephthalate), polyester, polysulfone, polyolefin, copolymers thereof, and/or mixtures thereof, or wherein the photochromic composition further comprises at least one additive chosen from dyes, alignment promoters, antioxidants, kinetic enhancing additives, photoinitiators, thermal initiators, polymerization inhibitors, solvents, light stabilizers, heat stabilizers, mold release agents, rheology control agents, leveling agents, free radical scavengers, gelators and adhesion promoters.

8. The photochromic composition of claim 6 comprising a coating composition chosen from liquid crystal materials, self-assembling materials and film forming materials.

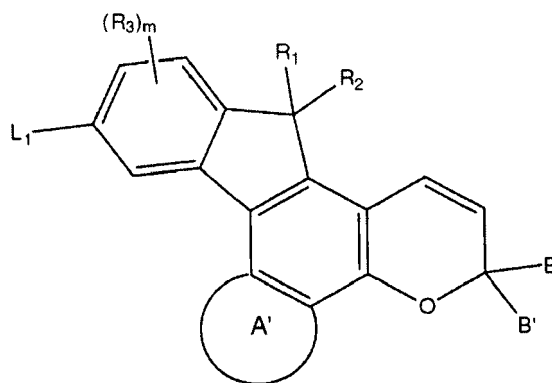
9. A photochromic article comprising a substrate and a photochromic compound according to claim 1 connected to at least a portion of a substrate.

10. The photochromic article of claim 9 comprising an optical element, said optical element being at least one of an ophthalmic element, a display element, a window, a mirror, packaging material and an active or passive liquid crystal cell element, wherein the ophthalmic element preferably comprises corrective lenses, non-corrective lenses, contact lenses, intraocular lenses, magnifying lenses, protective lenses, or visors.

- 5
11. The photochromic article of claim 9 wherein the substrate comprises a polymeric material and the photochromic material is incorporated into at least a portion of the polymeric material, wherein the photochromic material preferably is blended with at least a portion of the polymeric material, bonded to at least a portion of the polymeric material, and/or imbibed into at least a portion of the polymeric material.
12. The photochromic article of claim 9 wherein the photochromic article comprises a coating or film connected to at least a portion of the substrate, said coating or film comprising the photochromic material, wherein said substrate is preferably formed from organic materials, inorganic materials, or combinations thereof.
- 10
13. The photochromic article of claim 9 further comprising at least one additional at least partial coating chosen from photochromic coatings, anti-reflective coatings, linearly polarizing coatings, transitional coatings, primer coatings, adhesive coatings, reflective coatings, antifogging coatings, oxygen barrier coatings, ultraviolet light absorbing coatings, and protective coatings.
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14. A photochromic article comprising
a substrate;
at least a partial coating of one alignment material;
at least one additional at least partial coating of a liquid crystal material; and
at least one photochromic compound of claim 1.
- 20
15. The photochromic article of claim 14 further comprising at least one additive chosen from dichroic dyes, non-dichroic dyes, alignment promoters, antioxidants, kinetic enhancing additives, photoinitiators, thermal initiators, polymerization inhibitors, solvents, light stabilizers, heat stabilizers, mold release agents, rheology control agents, leveling agents, free radical scavengers, gelators and adhesion promoters.
- 25
16. The photochromic article of claim 14, wherein
- the substrate is selected from glass, quartz, and polymeric organic materials,
 - the at least one alignment material comprises a polymer network orientable by exposure to at least one of: a magnetic field, an electric field, linearly polarized infrared radiation, linearly polarized ultraviolet radiation, linearly polarized visible radiation and a shear force, or
 - said liquid crystal material is a liquid crystal polymer.
- 30
17. The photochromic article of claim 14, further comprising at least one primer coating, transitional coating, protective coating or a combination thereof, preferably wherein
- the transitional coating comprises an acrylate polymer,
 - the protective coating comprises at least one siloxane derivative, or
 - the at least one primer coating comprises a polyurethane.
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Patentansprüche

- 45
1. Eine Verbindung, dargestellt durch die nachfolgende grafische Formel I:
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Formel I

wobei:

A' aus wahlweise substituiertem Heteroaryl und wahlweise substituiertem Aryl ausgewählt ist, wobei A' wahlweise mit L₂ substituiert ist;

R₁ und R₂ jeweils unabhängig voneinander aus Wasserstoff, Hydroxy und chiralen oder achiralen Gruppen, die aus wahlweise substituiertem Heteroalkyl, wahlweise substituiertem Alkyl, wahlweise substituiertem Alkenyl, wahlweise substituiertem Alkinyl, wahlweise substituiertem Aryl, wahlweise substituiertem Heteroaryl, wahlweise substituiertem Cycloalkyl, wahlweise substituiertem Heterocycloalkyl, Halogen, wahlweise substituiertem Amino, Carboxy, Alkylcarbonyl, Alkoxy carbonyl, wahlweise substituiertem Alkoxy und Aminocarbonyl ausgewählt sind, oder R₁ und R₂ mit jeglichen dazwischen liegenden Atomen zusammengefasst werden können, um eine Gruppe zu bilden, die aus Oxo, wahlweise substituiertem Cycloalkyl and wahlweise substituiertem Heterocycloalkyl ausgewählt ist, und

R₃ bei jedem Auftreten unabhängig aus chiralen oder achiralen Gruppen, die aus Formyl, Alkylcarbonyl, Alkoxy carbonyl, Aminocarbonyl, Arylcarbonyl, Aryloxycarbonyl, Aminocarbonyloxy, Alkoxy carbonylamino, Aryloxy carbonylamino, Borsäure, Borsäureestern, Cycloalkoxy carbonylamino, Heterocycloalkoxy carbonylamino, Heteroaryloxy carbonylamino, wahlweise substituiertem Alkyl, wahlweise substituiertem Alkenyl, wahlweise substituiertem Alkinyl, Halogen, wahlweise substituiertem Cycloalkyl, wahlweise substituiertem Aryl, wahlweise substituiertem Heteroaryl, wahlweise substituiertem Alkoxy, wahlweise substituiertem Heteroalkyl, wahlweise substituiertem Heterocycloalkyl und wahlweise substituiertem Amino ausgewählt sind, ausgewählt ist; m eine ganze Zahl ist, die von 0 bis 3 ausgewählt ist;

B und B' jeweils unabhängig voneinander aus L₃, Wasserstoff, Halogen und chiralen oder achiralen Gruppen, die aus Metallocenyl, wahlweise substituiertem Alkyl, wahlweise substituiertem Alkenyl, wahlweise substituiertem Alkinyl, wahlweise substituiertem Heteroalkyl, wahlweise substituiertem Alkoxy, wahlweise substituiertem Aryl, wahlweise substituiertem Heteroaryl, wahlweise substituiertem Heterocycloalkyl und wahlweise substituiertem Cycloalkyl ausgewählt ist, ausgewählt sind oder wobei B und B' mit jeglichen dazwischen liegenden Atomen zusammengefasst werden können, um eine Gruppe zu bilden, die aus wahlweise substituiertem Cycloalkyl und wahlweise substituiertem Heterocycloalkyl ausgewählt ist, und

L₁, L₂ und L₃ bei jedem Auftreten unabhängig voneinander aus einer chiralen oder achiralen verlängernden Gruppe ausgewählt sind, die dargestellt ist durch:

- [S₁]_c-[Q₁-[S₂]_d]_d-[Q₂-[S₃]_e]_e-[Q₃-[S₄]_f]_f-S₅-P, wobei:

(a) Q₁, Q₂ und Q₃ bei jedem Auftreten unabhängig voneinander aus einer zweiwertigen Gruppe ausgewählt sind, die aus wahlweise substituiertem Aryl, wahlweise substituiertem Heteroaryl, wahlweise substituiertem Cycloalkyl und wahlweise substituiertem Heterocycloalkyl ausgewählt ist;

wobei die Substituenten unabhängig voneinander aus P, flüssigkristallinen Mesogenen, Halogen, Poly(C₁-C₁₈-alkoxy), C₁-C₁₈-Alkoxy carbonyl, C₁-C₁₈-Alkylcarbonyl, C₁-C₁₈-Alkoxy carbonyloxy, Aryloxy carbonyloxy, Perfluor(C₁-C₁₈)alkoxy, Perfluor(C₁-C₁₈)alkoxy carbonyl, Perfluor(C₁-C₁₈)alkylcarbonyl, Perfluor(C₁-C₁₈)alkylamino, Di(perfluor(C₁-C₁₈)alkyl)amino, Perfluor(C₁-C₁₈)alkylthio, C₁-C₁₈-Alkylthio, C₁-C₁₈-Acetyl, C₃-C₁₀-Cycloalkyl, C₃-C₁₀-Cycloalkoxy, geradkettigem C₁-C₁₈-Alkyl und ver-

zweigtem C₁-C₁₈-Alkyl ausgewählt sind,

wobei dieses geradkettige C₁-C₁₈-Alkyl und verzweigte C₁-C₁₈-Alkyl mit einer Gruppe, die aus Cyano, Halogen und C₁-C₁₈-Alkoxy ausgewählt ist, monosubstituiert sind oder

wobei dieses geradkettige C₁-C₁₈-Alkyl und verzweigte C₁-C₁₈-Alkyl mit mindestens zwei Gruppen, die unabhängig voneinander aus Halogen, -M(T)_(t-1) und -M(OT)_(t-1) ausgewählt sind, mehrfach substituiert sind, wobei M aus Aluminium, Antimon, Tantal, Titan, Zirconium und Silizium ausgewählt ist, T aus organofunktionellen Radikalen, organofunktionellen Kohlenwasserstoffradikalen, aliphatischen Kohlenwasserstoffradikalen und aromatischen Kohlenwasserstoffradikalen ausgewählt ist und t die Valenz von M ist;

(b) c, d, e und f jeweils unabhängig voneinander aus einer ganzen Zahl von 1 bis 20 ausgewählt sind und jedes S₁, S₂, S₃, S₄ und S₅ unabhängig voneinander bei jedem Auftreten aus einer Spacereinheit ausgewählt ist, die ausgewählt ist aus:

(i) wahlweise substituiertem Alkylen, wahlweise substituiertem Halogenalkylen, -Si(CH₂)_g- und -(Si[(CH₃)₂O]_h)-, wobei g bei jedem Auftreten unabhängig aus einer ganzen Zahl von 1 bis 20 ausgewählt ist, h bei jedem Auftreten unabhängig aus einer ganzen Zahl von 1 bis 16 ausgewählt ist, und diese Substituenten für das Alkylen und Halogenalkylen unabhängig voneinander aus C₁-C₁₈-Alkyl, C₃-C₁₀-Cycloalkyl und Aryl ausgewählt sind;

(ii) -N(Z)-, -C(Z)=C(Z)-, -C(Z)=N-, -C(Z')₂-C(Z')₂- und einer Einfachbindung, wobei Z bei jedem Auftreten unabhängig aus Wasserstoff, C₁-C₁₈-Alkyl, C₃-C₁₀-Cycloalkyl und Aryl ausgewählt ist und Z' bei jedem Auftreten unabhängig aus C₁-C₁₈-Alkyl, C₃-C₁₀-Cycloalkyl und Aryl ausgewählt ist, und

(iii) -O-, -C(=O)-, -C≡C-, -N=N-, -S-, -S(=O)-, -(O=)S(=O)-, -(O=)S(=O)O-, -O(O=)S(=O)O- und geradkettigem oder verzweigtem C₁C₂₄-Alkylenrest, wobei dieser C₁-C₂₄-Alkylenrest unsubstituiert, mit Cyano oder Halogen monosubstituiert oder mit Halogen mehrfach substituiert ist, vorausgesetzt, dass, falls zwei Spacereinheiten, die Heteroatome enthalten, miteinander verknüpft sind, die Spacereinheiten so verknüpft sind, dass die Heteroatome nicht direkt miteinander verknüpft sind, jede Bindung zwischen S₁ und der Verbindung, die durch die grafische Formel I dargestellt ist, frei von zwei miteinander verknüpften Heteroatomen ist und die Bindung zwischen S₅ und P frei von zwei Heteroatomen, die miteinander verknüpft sind, ist;

(c) P bei jedem Auftreten unabhängig aus Hydroxy, Amino, C₂-C₁₈-Alkenyl, C₂-C₁₈-Alkynyl, Azido, Silyl, Siloxy, Silylhydrid, (Tetrahydro-2H-pyran-2-yl)oxy, Thio, Isocyanato, Thioisocyanato, Acryloyloxy, Methacryloyloxy, 2-(Acryloyloxy)ethylcarbonyl, 2-(Methacryloyloxy)-ethylcarbonyl, Aziridinyl, Allyloxy-carbonyloxy, Epoxy, Carbonsäure, Carbonsäureester, Acryloylamino, Methacryloylamino, Aminocarbonyl, C₁-C₁₈-Alkylaminocarbonyl, Aminocarbonyl(C₁-C₁₈)alkyl, C₁-C₁₈-Alkyloxycarbonyloxy, Halogencarbonyl, Wasserstoff, Aryl, Hydroxy(C₁-C₁₈)alkyl, C₁-C₁₈-Alkyl, C₁-C₁₈-Alkoxy, Amino(C₁-C₁₈)alkyl, C₁-C₁₈-Alkylamino, Di(C₁-C₁₈)alkylamino, C₁-C₁₈-Alkyl(C₁-C₁₈)alkoxy, C₁-C₁₈-Alkoxy(C₁-C₁₈)alkoxy, Nitro, Poly(C₁-C₁₈)alkylether, (C₁-C₁₈)Alkyl(C₁-C₁₈)alkoxy(C₁-C₁₈)alkyl, Polyethylenoxy, Polypropylenoxy, Ethylen, Acryloyl, Acryloyloxy(C₁-C₁₈)alkyl, Methacryloyl, Methacryloyloxy(C₁-C₁₈)alkyl, 2-Chloracryloyl, 2-Phenylacryloyl, Acryloyloxyphenyl, 2-Chloracryloylamino, 2-Phenylacryloylaminocarbonyl, Oxetanyl, Glycidyl, Cyano, Isocyanato(C₁-C₁₈)alkyl, Itaconsäureester, Vinylether, Vinylester, einem Styrolderivat, Hauptketten- und Seitenketten-Flüssigkristallpolymeren, Siloxanderivaten, Ethyleniminderivaten, Maleinsäurederivaten, Maleinimidderivaten, Fumarsäurederivaten, unsubstituierten Zimtsäurederivaten, Zimtsäurederivaten, die mit mindestens einem von Methyl, Methoxy, Cyano und Halogen substituiert sind und substituierten oder unsubstituierten, chiralen oder nicht chiralen, einwertigen oder zweiwertigen Gruppen, die aus Steroidradikalen, Terpenoidradikalen, Alkaloidradikalen und Mischungen derselben ausgewählt sind, wobei die Substituenten unabhängig voneinander aus C₁-C₁₈-Alkyl, C₁-C₁₈-Alkoxy, Amino, C₃-C₁₀-Cycloalkyl, C₁-C₁₈-Alkyl(C₁-C₁₈)alkoxy, Fluor(C₁-C₁₈)alkyl, Cyano, Cyano(C₁-C₁₈)alkyl, Cyano(C₁-C₁₈)alkoxy oder Mischungen derselben ausgewählt sind oder P eine Struktur mit 2 bis 4 reaktiven Gruppen ist oder P ein unsubstituierter oder substituierter Ringöffnungsmetathesepolymerisationsvorläufer ist oder P eine substituierte oder unsubstituierte photochrome Verbindung ist und

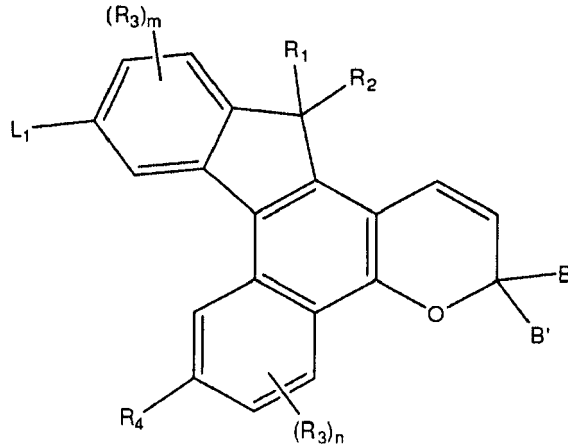
(d) d', e' und f' jeweils unabhängig voneinander aus 0, 1, 2, 3 und 4 ausgewählt sind, vorausgesetzt, dass die Summe von d' + e' + f' mindestens 2 ist.

2. Die Verbindung gemäß Anspruch 1, dargestellt durch die grafische Formel IA:

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Formel IA

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wobei

R_4 aus Wasserstoff, R_3 und L_2 ausgewählt ist und
 n eine ganze Zahl ist, die von 0 bis 3 ausgewählt ist,
 vorzugsweise wobei

25

R_1 und R_2 jeweils unabhängig voneinander aus Wasserstoff, Hydroxy und chiralen oder achiralen Gruppen, die aus
 wahlweise substituiertem Heteroalkyl, wahlweise substituiertem Alkyl, wahlweise substituiertem Aryl, wahlweise
 substituiertem Heteroaryl, wahlweise substituiertem Cycloalkyl, Halogen, wahlweise substituiertem Amino, Carboxy,
 Alkylcarbonyl, Alkoxy carbonyl, wahlweise substituiertem Alkoxy und Aminocarbonyl ausgewählt sind, ausgewählt
 sind oder R_1 und R_2 mit jeglichen dazwischen liegenden Atomen zusammengefasst werden können, um eine Gruppe
 zu bilden, die aus Oxo, wahlweise substituiertem Cycloalkyl und wahlweise substituiertem Heterocycloalkyl ausge-
 wählt ist;

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R_3 bei jedem Auftreten unabhängig aus Formyl, Alkylcarbonyl, Alkoxy carbonyl, Aminocarbonyl, Arylcarbonyl, Aryl-
 loxycarbonyl, wahlweise substituiertem Alkyl, Boronsäuresster, Halogen, wahlweise substituiertem Cycloalkyl, wahl-
 weise substituiertem Aryl, wahlweise substituiertem Alkoxy, wahlweise substituiertem Heteroalkyl, wahlweise sub-
 stituiertem Heterocycloalkyl und wahlweise substituiertem Amino ausgewählt ist;

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m und n jeweils unabhängig voneinander eine ganze Zahl sind, die von 0 bis 2 ausgewählt ist;

B und B' jeweils unabhängig voneinander aus L_3 , Wasserstoff, Halogen, chiralen oder achiralen Gruppen, die aus
 wahlweise substituiertem Alkyl, wahlweise substituiertem Alkenyl, wahlweise substituiertem Heteroalkyl, wahlweise
 substituiertem Alkoxy, wahlweise substituiertem Aryl, wahlweise substituiertem Heteroaryl und wahlweise substi-
 tuiertem Cycloalkyl ausgewählt sind, ausgewählt sind oder wobei B und B' mit jeglichen dazwischen liegenden
 Atomen zusammengefasst sind, um eine Gruppe zu bilden, die aus wahlweise substituiertem Cycloalkyl und wahl-
 weise substituiertem Heterocycloalkyl ausgewählt ist, und

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L_1 , L_2 und L_3 bei jedem Auftreten unabhängig voneinander aus einer chiralen oder achiralen verlängernden Gruppe
 ausgewählt sind, die dargestellt ist durch:

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- $[S_1]_c-[Q_1-[S_2]_d]_d-[Q_2-[S_3]_e]_e-[Q_3-[S_4]_f]_f-S_5-P$, wobei:

(a) Q_1 , Q_2 und Q_3 bei jedem Auftreten unabhängig voneinander aus einer zweiwertigen Gruppe ausgewählt
 sind, die aus wahlweise substituiertem Aryl und wahlweise substituiertem Heteroaryl, wahlweise substitu-
 iertem Cycloalkyl und wahlweise substituiertem Heterocycloalkyl ausgewählt sind;

50

wobei die Substituenten unabhängig voneinander aus P , flüssigkristallinen Mesogenen, Halogen, Poly-
 (C_1-C_{12}) -alkoxy, C_1-C_{12} -Alkoxy carbonyl, C_1-C_{12} -Alkylcarbonyl, Perfluor (C_1-C_{12}) alkoxy, Perfluor-
 (C_1-C_{12}) alkoxy carbonyl, Perfluor (C_1-C_{12}) alkylcarbonyl, C_1-C_{18} -Acetyl, C_3-C_7 -Cycloalkyl, C_3-C_7 -Cyclo-
 alkoxy, geradkettigem C_1-C_{12} -Alkyl und verzweigtem C_1-C_{12} -Alkyl ausgewählt sind,

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wobei dieses geradkettige C_1-C_{12} -Alkyl und verzweigte C_1-C_{12} -Alkyl mit einer Gruppe monosubstituiert
 sind, die aus Halogen und C_1-C_{12} -Alkoxy ausgewählt ist, oder
 wobei dieses geradkettige C_1-C_{12} -Alkyl und verzweigte C_1-C_{12} -Alkyl mit mindestens zwei Gruppen mehr-
 fach substituiert sind, die unabhängig voneinander aus Halogen, ausgewählt sind;

(b) c, d, e und f jeweils unabhängig aus einer ganzen Zahl von 1 bis 10 ausgewählt sind und jedes S₁, S₂, S₃, S₄ und S₅ unabhängig voneinander bei jedem Auftreten aus einer Spacereinheit ausgewählt ist, die ausgewählt ist aus:

(i) substituiertem oder unsubstituiertem Alkylen, substituiertem oder unsubstituiertem Halogenalkylen, -Si(CH₂)_g- und -(Si[(CH₃)₂O])_h-, wobei g bei jedem Auftreten unabhängig aus einer ganzen Zahl von 1 bis 10 ausgewählt ist; h bei jedem Auftreten unabhängig aus einer ganzen Zahl von 1 bis 8 ausgewählt ist und diese Substituenten für das Alkylen und Halogenalkylen unabhängig voneinander aus C₁-C₁₂-Alkyl, C₃-C₇-Cycloalkyl und Phenyl ausgewählt sind;

(ii) -N(Z)-, -C(Z)=C(Z)- und einer Einfachbindung, wobei Z bei jedem Auftreten unabhängig aus Wasserstoff, C₁-C₁₂-Alkyl, C₃-C₇-Cycloalkyl und Phenyl ausgewählt ist, und

(iii) -O-, -C(=O)-, -C≡C-, -N=N-, -S- und -S(=O)-, vorausgesetzt, dass, falls zwei Spacereinheiten, die Heteroatome umfassen, miteinander verknüpft sind, die Spacereinheiten so verknüpft sind, dass die Heteroatome nicht direkt aneinander gebunden sind, jede Bindung zwischen S₁ und der Verbindung, die durch die grafische Formel IA dargestellt ist, frei von zwei aneinander gebundenen Heteroatomen ist und die Bindung zwischen S₅ und P frei von zwei aneinander gebundenen Heteroatomen ist;

(c) P bei jedem Auftreten aus Hydroxy, Amino, C₂-C₁₂-Alkenyl, Silyl, Siloxy, (Tetrahydro-2H-pyran-2-yl)oxy, Isocyanato, Acryloyloxy, Methacryloyloxy, Epoxy, Carbonsäure, Carbonsäureester, C₁-C₁₂-Alkyloxycarboxyloxy, Halogencarbonyl, Wasserstoff, Aryl, Hydroxy-(C₁-C₁₂)Alkyl, C₁-C₁₂-Alkyl, C₁-C₁₂-Alkoxy, Ethylen, Acryloyl, Acryloyloxy(C₁-C₁₂)alkyl, Methacryloyl, Methacryloyloxy(C₁-C₁₂)alkyl, Oxetanyl, Glycidyl, Vinyl-ether, Siloxanderivaten, unsubstituierten Zimtsäurederivaten, Zimtsäurederivaten, die mit mindestens einem von Methyl, Methoxy, Cyano und Halogen substituiert sind und substituierten oder unsubstituierten, chiralen oder nicht chiralen, einwertigen oder zweiwertigen Gruppen, ausgewählt aus Steroidradikalen, ausgewählt ist, wobei jeder Substituent unabhängig aus C₁-C₁₂-Alkyl, C₁-C₁₂-Alkoxy, Amino, C₃-C₇-Cycloalkyl, C₁-C₁₂-Alkyl-(C₁-C₁₂)alkoxy oder Fluor(C₁-C₁₂)alkyl ausgewählt ist oder P eine Struktur mit 2 bis 4 reaktiven Gruppen ist und

(d) d', e' und f' jeweils unabhängig voneinander aus 0, 1, 2, 3 und 4 ausgewählt sind, vorausgesetzt, dass die Summe von d' + e' + f' mindestens 2 ist,

bevorzugter wobei:

R₁ und R₂ jeweils unabhängig aus Wasserstoff, Hydroxyl und chiralen Gruppen, die aus wahlweise substituiertem Heteroalkyl, wahlweise substituiertem Alkyl, wahlweise substituiertem Aryl, wahlweise substituiertem Cycloalkyl, Halogen, Carboxy, Alkylcarbonyl, Alkoxycarbonyl, wahlweise substituiertem Alkoxy und Aminocarbonyl ausgewählt sind, ausgewählt sind oder R₁ und R₂ mit jeglichen dazwischen liegenden Atomen zusammengefasst werden können, um eine Gruppe zu bilden, die aus Oxo und wahlweise substituiertem Cycloalkyl ausgewählt ist; und

R₃ bei jedem Auftreten unabhängig aus Alkylcarbonyl, Alkoxycarbonyl, Aminocarbonyl, wahlweise substituiertem Alkyl, Boronsäureester, Halogen, wahlweise substituiertem Cycloalkyl, wahlweise substituiertem Aryl, wahlweise substituiertem Alkoxy, wahlweise substituiertem Heterocycloalkyl und wahlweise substituiertem Amino ausgewählt ist;

m und n jeweils unabhängig voneinander eine ganze Zahl sind, die von 0 bis 2 ausgewählt ist;

B und B' jeweils unabhängig voneinander aus L₃, Wasserstoff, chiralen Gruppen, die aus wahlweise substituiertem Alkyl, wahlweise substituiertem Alkenyl, wahlweise substituiertem Aryl, wahlweise substituiertem Heteroaryl und wahlweise substituiertem Cycloalkyl ausgewählt sind, oder wobei B und B' mit jeglichen dazwischen liegenden Atomen zusammengefasst sind, um eine Gruppe zu bilden, die aus wahlweise substituiertem Cycloalkyl ausgewählt ist;

L₁, L₂ und L₃ bei jedem Auftreten unabhängig voneinander aus einer chiralen oder achiralen verlängernden Gruppe ausgewählt sind, die dargestellt ist durch:

- [S₁]_c-[Q₁-[S₂]_d]_{d'}-[Q₂-[S₃]_e]_{e'}-[Q₃-[S₄]_f]_{f'}-S₅-P, wobei:

(a) Q₁, Q₂ und Q₃ bei jedem Auftreten unabhängig voneinander aus einer zweiwertigen Gruppe ausgewählt sind, die aus wahlweise substituiertem Aryl und wahlweise substituiertem Heteroaryl, wahlweise substituiertem Cycloalkyl und wahlweise substituiertem Heterocycloalkyl ausgewählt sind;

wobei die Substituenten unabhängig voneinander aus P, C₁-C₆-Alkoxycarbonyl, Perfluor(C₁-C₆)alkoxy, C₃-C₇-Cycloalkyl, C₃-C₇-Cycloalkoxy, geradkettigem C₁-C₆-Alkyl und verzweigtem C₁-C₆-Alkyl aus-

gewählt sind,

wobei dieses geradkettige C₁-C₆-Alkyl und verzweigte C₁-C₆-Alkyl mit einer Gruppe monosubstituiert sind, die aus Halogen und C₁-C₁₂-Alkoxy ausgewählt ist oder

wobei dieses geradkettige C₁-C₆-Alkyl und verzweigte C₁-C₆-Alkyl mit mindestens zwei Gruppen mehrfach substituiert sind, die unabhängig voneinander aus Halogen ausgewählt sind;

(b) c, d, e und f jeweils unabhängig voneinander aus einer ganzen Zahl von 1 bis 10 ausgewählt sind und jedes S₁, S₂, S₃, S₄ und S₅ unabhängig voneinander bei jedem Auftreten aus einer Spacereinheit ausgewählt ist, die ausgewählt ist aus:

(i) substituiertem oder unsubstituiertem Alkylen;

(ii) -N(Z)-, -C(Z)=C(Z)- und eine Einfachbindung, wobei Z bei jedem Auftreten unabhängig aus Wasserstoff und C₁-C₆-Alkyl ausgewählt ist und

(iii) -O-, -C(=O)-, -C≡C- und -N=N-, -S-;

vorausgesetzt, dass, falls zwei Spacereinheiten, die Heteroatome umfassen, miteinander verknüpft sind, die Spacereinheiten so verknüpft sind, dass die Heteroatome der ersten Spacereinheit nicht direkt an die Heteroatome der zweiten Spacereinheit gebunden sind, und

vorausgesetzt, dass, wenn S₁ und S₅ mit Formel I bzw. P verknüpft sind, sie so verknüpft sind, dass zwei Heteroatome nicht direkt aneinander gebunden sind;

(c) P bei jedem Auftreten aus Hydroxy, Amino, C₂-C₆-Alkenyl, Siloxy, (Tetrahydro-2H-pyran-2-yl)oxy, Isocyanato, Acryloyloxy, Methacryloyloxy, Epoxy, Carbonsäure, Carbonsäureester, C₁-C₆-Alkyloxy-carbonyloxy, Wasserstoff, Aryl, Hydroxy(C₁-C₆)alkyl, C₁-C₆-Alkyl, Ethylen, Acryloyl, Acryloyloxy(C₁-C₁₂)alkyl, Oxetanyl, Glycidyl, Vinylether, Siloxanderivaten und substituierten oder unsubstituierten, chiralen oder nicht chiralen, einwertigen oder zweiwertigen Gruppen, die aus Steroidradikalen ausgewählt sind, ausgewählt sind, wobei jeder Substituent unabhängig aus C₁-C₆-Alkyl, C₁-C₆-Alkoxy, Amino und C₃-C₇-Cycloalkyl ausgewählt ist,

und noch bevorzugter, wobei: R₁ und R₂ jeweils unabhängig voneinander aus Methyl, Ethyl, Propyl und Butyl ausgewählt sind; R₃ und R₄ bei jedem Auftreten unabhängig voneinander aus Methyl, Ethyl, Brom, Chlor, Fluor, Methoxy, Ethoxy und CF₃ ausgewählt sind; B und B' jeweils unabhängig voneinander aus Phenyl, welches mit einer oder mehreren Gruppen substituiert ist, die unabhängig voneinander aus Aryl, Heteroaryl, Heterocycloalkyl, Alkyl, Alkenyl, Alkynyl, Alkoxy, Halogen, Amino, Alkylcarbonyl, Carboxy und Alkoxy-carbonyl ausgewählt sind, ausgewählt sind und für L₁: Q₁ ein unsubstituiertes Aryl ist; e' 1 oder 2 ist; e bei jedem Auftreten 1 ist; S₃ bei jedem Auftreten eine Einfachbindung ist; Q₂ bei jedem Auftreten unabhängig aus wahlweise unsubstituiertem Aryl ausgewählt ist; f' 1 ist; f 1 ist; S₄ eine Einfachbindung ist und Q₃ wahlweise substituiertes Cycloalkyl ist; S₅ -(CH₂)_g- ist, wobei g eine ganze Zahl von 1 bis 20 ist und P Wasserstoff ist.

3. Die Verbindung gemäß Anspruch 1, wobei L₁ ausgewählt ist aus:

4-[4-(4-Butylcyclohexyl)phenyl]cyclohexyloxy;

4"-Butyl[1,1',4',1"]tercyclohexan-4-yloxy;

4-[4-(4-Butylphenyl)cyclohexyloxy-carbonyl]phenoxy;

4'-(4-Butylbenzoyloxy)biphenyl-4-carbonyloxy;

4-(4-Pentylphenylazo)phenylcarbamoxy;

4-(4-Dimethylaminophenylazo)phenylcarbamoxy;

4-[5-(4-Propylbenzoyloxy)pyrimidin-2-yl]phenyl;

4-[2-(4'-Methylbiphenyl-4-carbonyloxy)1,2-diphenylethoxycarbonyl]phenyl;

4-(1,2-Diphenyl-2-[3-[4-(4-propylbenzoyloxy)phenyl]acryloyloxy]ethoxycarbonyl)phenyl;

4-[4-(4-[4-[3-(6-[4-(4-Nonylbenzoyloxy)phenoxy-carbonyl]phenoxy)-hexyloxy-carbonyl]propionyloxy]benzoyloxy)benzoyloxy)phenyl]piperazin-1-yl;

4-[4-(4-[4-[4-(4-Nonylbenzoyloxy)benzoyloxy]benzoyloxy]-benzoyloxy)phenyl]-piperazin-1-yl;

4-(4'-Propylbiphenyl-4-ylethynyl)phenyl;

4-(4-Fluorphenoxycarbonyloxy)piperidin-1-yl;

2-[17-(1,5-Dimethylhexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,

17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxy]indan-5-yl;

4-[17-(1,5-Dimethylhexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15, 16,17-tetradecahydro-1 H-cyclopenta[a]phenanthren-3-yloxy-carbonyloxy]-piperidin-1-yl;

4-(Biphenyl-4-carbonyloxy)piperidin-1-yl;

4-(Naphthalin-2-carbonyloxy)piperidin-1-yl;
 4-(4-Phenylcarbamoylephenylcarbamoyle)piperidin-1-yl;
 4-(4-(4-Phenylpiperidin-1-yl)benzoyloxy)piperidin-1-yl;
 4-Butyl[1, 1', 4', 1'']terphenyl-4-yl;
 5 4-(4-Pentadecafluorheptyloxyphenylcarbamoyle)benzoyloxy;
 4-(3-Piperidin-4-yl-propyl)piperidin-1-yl;
 4-(4-[4-(17-(1,5-Dimethylhexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14, 15,16,17-tetradecahydro-1 H-cyclopenta[a]phenanthren-3-yloxy)carbonyloxy]benzoyloxy)-phenoxy)carbonyl)phenoxy)methyl;
 10 4-[4-(4-Cyclohexylphenylcarbamoyle)benzoyloxy]piperidin-1-yl;
 4-[4-(4-Cyclohexylphenylcarbamoyle)benzoyloxy]piperidin-1-yl;
 N-{4-[(4-Pentylbenzyliden)amino]phenyl}acetamidyl;
 4-(3-Piperidin-4-yl-propyl)piperidin-1-yl;
 4-(4-Hexyloxybenzoyloxy)piperidin-1-yl;
 4-(4'-Hexyloxybiphenyl-4-carbonyloxy)piperidin-1-yl;
 15 4-(4-Butylphenylcarbamoyle)piperidin-1-yl;
 4-[4-[4-Piperidinyl-4-oxy]phenyl]phenoxy]piperidin-4-yl;
 4-(4-(9-(4-Butylphenyl)-2,4,8,10-tetraoxaspiro[5.5]undec-3-yl)phenyl)-piperazin-1-yl;
 4-(6-(4-Butylphenyl)carbonyloxy(4,8-dioxabicyclo[3.3.0]oct-2-yl)oxy-carbonyl)phenyl;
 1-4-[5-(4-Butylphenyl)-[1,3]dioxan-2-yl]phenyl]-4-methylpiperazin-1-yl;
 20 4-(7-(4-Propylphenylcarbonyloxy)bicyclo[3.3.0]oct-2-yl)oxycarbonyl)phenyl;
 4-[17-(1,5-Dimethylhexyl)-10, 13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16, 17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxy)carbonyloxy;
 (4-trans-(4-Pentylcyclohexyl)benzamido)phenyl;
 (4-(4-trans-(4-Pentylcyclohexyl)phenoxy)carbonyl)phenyl;
 25 4-(4-(4-trans-(4-Pentylcyclohexyl)phenyl)benzamido)phenyl;
 4-((trans-(4'-Pentyl-[1, 1'-bi(cyclohexan)]-4-yl)oxy)carbonyl)phenyl;
 4-(4'-(4-Pentylcyclohexyl)-[1,1'-biphenyl]-4-yl)carboxamido)phenyl;
 4-((4'-(4-Pentylcyclohexyl)-[1,1'-biphenyl]-4-carbonyl)oxy)benzamido;
 4-(4'-(4-Pentylcyclohexyl)[1,1'-biphenyl]-4-carbonyl)piperazin-1-yl;
 30 4-(4-(4-(4-Pentylcyclohexyl)phenyl)benzamido)-2-(trifluormethyl)phenyl;
 2-Methyl-4-trans-(4-((4'-trans-(4-pentylcyclohexyl)biphenyl-4-yloxy)carbonyl)cyclohexancarboxamido)phenyl;
 4'-((1r,1's,4R,4'R)-4'-Pentylbi(cyclohexan-4-)carbonyloxy)biphenyl-carbonyloxy;
 4-(((3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)- 2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxy)carbonyl)piperazin-1-yl und
 35 4-((S)-2-Methylbutoxy)phenyl)-10-(4-(((3R,3aS,6S,6aS)-6-(4'-trans-(4-pentylcyclohexyl)biphenyl)carbonyloxy)hexahydrofluor[3, 2-b]furan-3-yloxy)carbonyl)phenyl.

4. Die Verbindung gemäß Anspruch 1, ausgewählt aus:

40 3,3-Bis(4-methoxyphenyl)-10-[4-(4-(trans-4-pentylcyclohexyl)benzamido)-phenyl]-13,13-dimethyl-12-brom-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-10-[4-((4-(trans-4-pentylcyclohexyl)phenoxy)-carbonyl)phenyl]-6,13,13-trimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 45 3-(4-Fluorphenyl)-3-(4-piperidinophenyl)-10-[4-(4-(4-(trans-4-pentyl-cyclohexyl)phenyl)benzamido)phenyl]-6-trifluormethyl-11,13,13-trimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-10-[4-(4-(trans-4-pentylcyclohexyl)benzamido)-phenyl]-5,7-difluor-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Methoxyphenyl)-3-(4-piperidinophenyl)-10-[4-(4-(4-(trans-4-pentyl-cyclohexyl)phenyl)benzamido)phenyl]-5,7-difluor-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 50 3-(4-Methoxyphenyl)-3-(4-morpholinophenyl)-10-[4-(4-(4-(trans-4-pentyl-cyclohexyl)phenyl)benzamido)phenyl]-5,7-difluor-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Fluorphenyl)-3-(4-piperidinophenyl)-10-[4-((4-(trans-4-pentyl-cyclohexyl)phenoxy)carbonyl)phenyl]-12-brom-5,7-difluor-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 55 3-Phenyl-3-(4-piperidinophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)-phenyl)benzamido)phenyl]-12-brom-5,7-difluor-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-Phenyl-3-(4-piperidinophenyl)-10-[4-((4-(trans-4-pentylcyclohexyl)-phenoxy)carbonyl)phenyl]-12-brom-5,7-difluor-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;

3-(4-Fluorphenyl)-3-(4-piperidinophenyl)-10-[4-(4-(4-(trans-4-pentyl-cyclohexyl)phenyl)benzamido)phenyl]-
 12-brom-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)-benzamido)phenyl]-12-brom-6,7-di-
 methoxy-11,13,13-trimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 5 3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)-benzamido)phenyl]-6-trifluormethyl-
 12-brom-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-10,12-bis[4-(4-(4-(trans-4-pentylcyclohexyl)-phenyl)benzamido)phenyl]-6-trifluor-
 methyl-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl) benzamido)phenyl]-5,7-difluor-13,13-
 10 dimethyl-3,13-dihydroindeno-[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)-phenyl)benzamido) phenyl]-6-trifluormethyl-
 13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl) benzamido)phenyl]-5,7-difluor-12-
 brom-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 15 3-(4-Fluorphenyl)-3-(4-morpholinophenyl)-10-[4-(4-(4-(trans-4-pentyl-cyclohexyl)phenyl)benzamido)phenyl]-
 6-trifluormethyl-13-methyl-13-butyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Fluorphenyl)-3-(4-morpholinophenyl)-10-[4-(4-(4-(trans-4-pentyl-cyclohexyl)phenyl)benzamido)phenyl]-
 5,7-difluor-12-brom-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-Phenyl-3-(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)-phenyl)benzamido)phenyl]-6-trifluorme-
 20 methyl-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-Phenyl-3-(4-morpholinophenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)-phenyl)benzamido)phenyl]-6-trifluor-
 methyl-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-fluorphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)-benzamido)phenyl]-6-trifluormethyl-12-
 brom-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 25 3,3-Bis(4-fluorphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)-benzamido)phenyl]-6-trifluormethyl-
 13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Methoxyphenyl)-3-(4-butoxyphenyl)-10-[4-(4-(4-(trans-4-pentyl-cyclohexyl)phenyl)benzamido)phenyl]-6-
 trifluormethyl-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Fluorphenyl)-13,13-dimethyl-3-(4-morpholinophenyl)-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-
 30 4-ylcarboxamido)phenyl)-6-(trifluor-methyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Butoxyphenyl)-3-(4-fluorphenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-yl-
 carboxamido)phenyl)-6-(trifluormethyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-(4-(4-Methoxyphenyl)piperazin-1-yl)phenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-bi-
 35 phenyl]-4-ylcarboxamido)phenyl)-3-phenyl-6-(trifluormethyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]py-
 ran;
 3-(4-Butoxyphenyl)-3-(4-fluorphenyl)-13,13-dimethyl-10-(4-(((trans,trans-4'-pentyl-[1,1'-bi(cyclohexan)]-4-
 yl)oxy)carbonyl)phenyl)-6-(trifluormethyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Fluorphenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-ylcarboxamido)phe-
 40 nyl)-3-(4-butoxyphenyl)-6-(trifluormethyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Methoxyphenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-ylcarboxami-
 do)phenyl)-3-(4-(trifluoromethoxy)phenyl)-6-(trifluormethyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-hydroxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)-phenyl)benzamido)phenyl]-6-trifluormethyl-
 13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 12-Brom-3-(4-butoxyphenyl)-3-(4-fluorphenyl)-13,13-dimethyl-10-(4-((4'-(trans-4-pentylcyclohexyl)-[1,1'-bi-
 45 phenyl]-4-carbonyl)oxy)benzamido)-6-(trifluormethyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Butoxyphenyl)-5,7-dichlor-11-methoxy-3-(4-methoxyphenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyc-
 lohexyl)-[1,1'-biphenyl]-4-yl-carboxamido)phenyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Butoxyphenyl)-3-(4-fluorphenyl)-13,13-dimethyl-10-(4-((4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-
 carbonyl)oxy)benzamido)-6-(trifluormethyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 50 5,7-Dichlor-3,3-bis(4-hydroxyphenyl)-11-methoxy-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-bi-
 phenyl]-4-ylcarboxamido)phenyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 6,8-Dichlor-3,3-bis(4-hydroxyphenyl)-11-methoxy-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-bi-
 phenyl]-4-ylcarboxamido)phenyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Butoxyphenyl)-5,8-difluor-3-(4-fluorphenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-bi-
 55 phenyl]-4-ylcarboxamido)phenyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Butoxyphenyl)-3-(4-fluorphenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphenyl]-4-
 carbonyl)piperazin-1-yl)-6-(trifluormethyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Morpholinophenyl)-3-(4-methoxyphenyl)-10,7-bis[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzami-

do)phenyl]-5-fluor-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Morpholinophenyl)-3-(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)-
 2-(trifluormethyl)phenyl]-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)-2-(trifluormethyl)phenyl]-
 13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Morpholinophenyl)-3-(4-methoxyphenyl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phenyl)benzamido)-
 2-(trifluormethyl)phenyl]-13,13-dimethyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3,3-Bis(4-methoxyphenyl)-13,13-dimethyl-10-(2-methyl-4-(trans-4-((4'-((trans-4-pentylcyclohexyl)biphenyl-4-
 yloxy)carbonyl)cyclohexan-carboxamido)phenyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-(4-(4-Butylphenyl)piperazin-1-yl)phenyl)-3-(4-methoxyphenyl)-13,13-dimethyl-10-(4-(4'-(trans-4-pentyl-
 cyclohexyl)biphenyl-4-ylcarboxamido)-2-(trifluormethyl)phenyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-
 b]pyran;
 3-(4-(4-(4-Butylphenyl)piperazin-1-yl)phenyl)-3-(4-methoxyphenyl)-13,13-dimethyl-10-(2-methyl-4-(4'-(trans-
 4-pentylcyclohexyl)biphenyl-4-yl-carboxamido)phenyl)-7-(4-(4-(trans-4-pentylcyclohexyl)benzamido)phenyl)-
 3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-(4-Methoxyphenyl)-13,13-dimethyl-7,10-bis(4-(4'-(trans-4-pentylcyclohexyl)biphenyl-4-ylcarboxamido)phe-
 nyl)-3-phenyl-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 3-p-Tolyl-3-(4-methoxyphenyl)-6-methoxy-13,13-dimethyl-7-(4'-(trans, trans-4'-pentylbi(cyclohexan-4-)carbo-
 nyloxy)biphenylcarbonyloxy)-10-(4-(4'-(trans-4-pentylcyclohexyl)biphenyl-4-ylcarboxamido)phenyl)-3,13-dihy-
 droindeno[2',3':3,4]naphtho[1,2-b]pyran;
 10-(4-(((3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-
 2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxy)carbonyl)pipera-
 zin-1-yl)-3-(4-methoxyphenyl)-13,13-dimethyl-3-(4-morpholinophenyl)-3,13-dihydroindeno[2',3':3,4]naph-
 tho[1,2-b]pyran;
 6-Methoxy-3-(4-methoxyphenyl)-13,13-dimethyl-3-(4-((S)-2-methyl-butoxy)phenyl)-10-(4-(4'-(trans-4-pentyl-
 cyclohexyl)biphenyl-4-ylcarbox-amido)phenyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran;
 6-Methoxy-3-(4-methoxyphenyl)-13,13-dimethyl-3-(4-((S)-2-methylbutoxy)phenyl)-7-(4'-(trans,trans-4'-pentyl-
 bi(cyclohexan-4-)carbonyloxy)biphenyl-carbonyloxy)-10-(4-(4'-(trans-4-pentylcyclohexyl)biphenyl-4-ylcarbox-
 amido)phenyl)-3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran; and
 6-Methoxy-3-(4-methoxyphenyl)-13,13-dimethyl-3-(4-((S)-2-methylbutoxy)phenyl)-10-(4-(((3R,3aS,6S,6aS)-
 6-(4'-(trans-4-pentylcyclohexyl)biphenyl-carbonyloxy)hexahydrofuro[3,2-b]furan-3-yloxy)carbonyl)phenyl)-
 3,13-dihydroindeno[2',3':3,4]naphtho[1,2-b]pyran.

5. Eine photochrome Zusammensetzung umfassend eine photochrome Verbindung gemäß Anspruch 1 und wahlweise
 mindestens eine andere photochrome Verbindung, wobei diese Zusammensetzung umfasst:

- eine einzelne photochrome Verbindung;
- eine Mischung photochromer Verbindungen;
- ein Material, welches mindestens eine photochrome Verbindung umfasst;
- ein Material, an welches mindestens eine photochrome Verbindung chemisch gebunden ist;
- Material (c) oder (d), weiterhin umfassend eine Beschichtung, um im Wesentlichen einen Kontakt der min-
 destens einen photochromen Verbindung mit externen Materialien zu verhindern;
- ein photochromes Polymer oder
- Mischungen derselben.

6. Eine photochrome Zusammensetzung, umfassend mindestens eine photochrome Verbindung gemäß Anspruch 1,
 die in mindestens einen Teil eines organischen Materials eingebracht ist, wobei dieses organische Material ein
 polymeres Material, ein oligomeres Material, ein monomeres Material oder eine Mischung oder Kombination der-
 selben ist.

7. Die photochrome Zusammensetzung gemäß Anspruch 6, wobei dieses polymere Material flüssigkristalline Materi-
 alien, selbstassemblierende Materialien, Polycarbonat, Polyamid, Polyimid, Poly(meth)acrylat, polycyclisches Alken,
 Polyurethan, Poly(harnstoff)urethan, Polythiourethan, Polythio(harnstoff)urethan, Polyol(allylcarbonat), Cellulose-
 acetat,

Cellulosediacetat, Cellulosetriacetat, Celluloseacetatpropionat, Celluloseacetatbutyrat, Polyalken, Polyalkylen-Vi-
 nylacetat, Poly(vinylacetat), Poly(vinylalkohol), Poly(vinylchlorid), Poly(vinylformal), Poly(vinylacetal), Poly(vinyl-
 idenchlorid), Poly(ethylenterephthalat), Polyester, Polysulfon, Polyolefin, Copolymere derselben und/oder Mischun-
 gen derselben umfasst oder

wobei die photochrome Zusammensetzung weiterhin mindestens ein Additiv umfasst, welches aus Farbstoffen, Ausrichtungsförderern, Antioxidantien, die Kinetik verbessernde Additiven, Photoinitiatoren, thermischen Initiatoren, Polymerisationsinhibitoren, Lösungsmitteln, Lichtstabilisatoren, Wärmestabilisatoren, Formtrennmitteln, Rheologiesteuerungsmitteln, Verlaufsmitteln, Radikalfängern, Geliermitteln und Haftvermittlern ausgewählt ist.

- 5
8. Die photochrome Zusammensetzung gemäß Anspruch 6, umfassend eine Beschichtungszusammensetzung, die aus flüssigkristallinen Materialien, selbstassemblierenden Materialien und filmbildenden Materialien ausgewählt ist.
- 10
9. Ein photochromer Gegenstand umfassend ein Substrat und eine photochrome Verbindung gemäß Anspruch 1, die mit mindestens einem Teil des Substrats verbunden ist.
- 15
10. Der photochrome Gegenstand gemäß Anspruch 9, umfassend ein optisches Element, wobei dieses optische Element mindestens eines von einem ophthalmologischen Element, einem Anzeigeelement, einem Fenster, einem Spiegel, Verpackungsmaterial und einem aktiven oder passiven Flüssigkristallelement ist, wobei das ophthalmologische Element vorzugsweise korrigierende Gläser, nichtkorrigierende Gläser, Kontaktlinsen, intraokulare Linsen, Vergrößerungsgläser, Schutzgläser oder Visiere umfasst.
- 20
11. Der photochrome Gegenstand gemäß Anspruch 9, wobei das Substrat ein polymeres Material umfasst und das photochrome Material zumindest in einen Teil des polymeren Materials eingebracht ist, wobei das photochrome Material vorzugsweise mit mindestens einem Teil des polymeren Materials vermischt ist, an mindestens einen Teil des polymeren Materials gebunden ist und/oder von mindestens einem Teil des polymeren Materials aufgenommen ist.
- 25
12. Der photochrome Gegenstand gemäß Anspruch 9, wobei der photochrome Gegenstand eine Beschichtung oder einen Film umfasst, die bzw. der mit mindestens einem Teil des Substrats verbunden ist, wobei diese Beschichtung oder dieser Film das photochrome Material umfasst, wobei das Substrat vorzugsweise aus organischen Materialien, anorganischen Materialien oder Kombinationen derselben gebildet ist.
- 30
13. Der photochrome Gegenstand gemäß Anspruch 9, weiterhin umfassend mindestens eine zusätzliche zumindest teilweise Beschichtung, die aus photochromen Beschichtungen, antireflektierenden Beschichtungen, linear polarisierenden Beschichtungen, Übergangsbeschichtungen, Primerbeschichtungen, haftenden Beschichtungen, reflektierenden Beschichtungen, Antibeschlagbeschichtungen, Sauerstoffbarrierebeschichtungen, ultraviolettes Licht absorbierenden Beschichtungen und schützende Beschichtungen ausgewählt ist.
- 35
14. Ein photochromer Gegenstand, umfassend ein Substrat;
mindestens eine teilweise Beschichtung eines Ausrichtungsmaterials; mindestens eine zusätzliche zumindest teilweise Beschichtung eines flüssigkristallinen Materials und
mindestens eine photochrome Verbindung gemäß Anspruch 1.
- 40
15. Der photochrome Gegenstand gemäß Anspruch 14, weiterhin umfassend mindestens ein Additiv, welches aus dichroitischen Farbstoffen, nichtdichroitischen Farbstoffen, Ausrichtungsförderern, Antioxidantien, die Kinetik verbessernden Additiven, Photoinitiatoren, thermischen Initiatoren, Polymerisationsinhibitoren, Lösungsmitteln, Lichtstabilisatoren, Wärmestabilisatoren, Formtrennmitteln, Rheologiesteuerungsmitteln, Verlaufsmitteln, Radikalfängern, Geliermitteln und Haftvermittlern ausgewählt ist.
- 45
16. Der photochrome Gegenstand gemäß Anspruch 14, wobei
- das Substrat aus Glas, Quarz und polymeren organischen Materialien ausgewählt ist,
 - das mindestens eine Ausrichtungsmaterial ein Polymernetzwerk umfasst, welches ausgerichtet werden kann, indem es mindestens einem von einem magnetischen Feld, einem elektrischen Feld, linear polarisierter Infrarotstrahlung, linear polarisierter ultravioletter Strahlung, linear polarisierter sichtbarer Strahlung und einer Scher-
kraft ausgesetzt wird, oder
 - dieses flüssigkristalline Material ein flüssigkristallines Polymer ist.
- 50
- 55
17. Der photochrome Gegenstand gemäß Anspruch 14, weiterhin umfassend mindestens eine Primerbeschichtung, Übergangsbeschichtung, schützende Beschichtung oder eine Kombination derselben, wobei vorzugsweise

- die Übergangsbeschichtung ein Acrylatpolymer umfasst,
- die schützende Beschichtung mindestens ein Siloxanderivat umfasst oder
- die mindestens eine Primerbeschichtung ein Polyurethan umfasst.

5

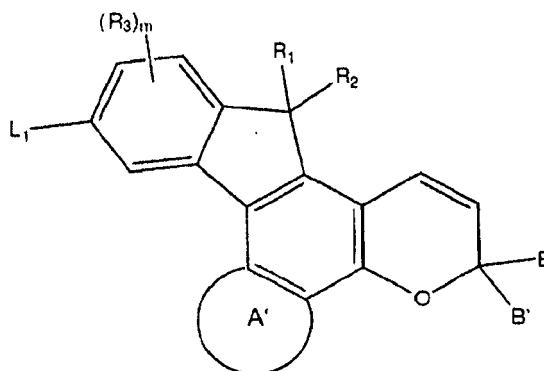
Revendications

1. Composé représenté par la formule graphique I suivante :

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Formule I

25

dans laquelle

A' est choisi parmi les groupes hétéroaryle facultativement substitué et aryle facultativement substitué, A' étant éventuellement substitué par L₂ ;

30

R₁ et R₂ sont chacun choisis indépendamment parmi un atome d'hydrogène, un groupe hydroxy et les groupes chiraux ou non chiraux choisis parmi les groupes hétéroalkyle éventuellement substitué, alkyle éventuellement substitué, alcényle éventuellement substitué, alcynyle éventuellement substitué, aryle éventuellement substitué, hétéroaryle éventuellement substitué, cycloalkyle éventuellement substitué, hétérocycloalkyle éventuellement substitué, un atome d'halogène, les groupes amino éventuellement substitué, carboxy, alkylcarbonyle, alcoxy-carbonyle, alcoxy éventuellement substitué et aminocarbonyle, ou R₁ et R₂ peuvent être pris ensemble avec des atomes intermédiaires quelconques pour former un groupe choisi parmi les groupes oxo, cycloalkyle éventuellement substitué et hétérocycloalkyle éventuellement substitué ; et

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R₃ dans chaque cas est choisi indépendamment parmi les groupes chiraux ou non chiraux choisis parmi les groupes formyle, alkylcarbonyle, alcoxycarbonyle, aminocarbonyle, arylcarbonyle, aryloxycarbonyle, aminocarbonyloxy, alcoxycarbonylamino, aryloxycarbonylamino, acide boronique, esters d'acide boronique, cycloalkoxy-carbonylamino, hétérocycloalkyloxycarbonylamino, hétéroaryloxycarbonylamino, alkyle éventuellement substitué, alcényle éventuellement substitué, alcynyle éventuellement substitué, un atome d'halogène, les groupes cycloalkyle éventuellement substitué, aryle éventuellement substitué, hétéroaryle éventuellement substitué, alcoxy éventuellement substitué, hétéroalkyle éventuellement substitué, hétérocycloalkyle substitué et amino éventuellement substitué ;

40

m est un nombre entier de 0 à 3 ;

45

B et B' sont chacun choisis indépendamment parmi L₃, un atome d'hydrogène, un atome d'halogène, et les groupes chiraux ou non chiraux choisis parmi les groupes métallocényle, alkyle éventuellement substitué, alcényle éventuellement substitué, alcynyle éventuellement substitué, hétéroalkyle éventuellement substitué, alcoxy éventuellement substitué, aryle éventuellement substitué, hétéroaryle éventuellement substitué, hétérocycloalkyle éventuellement substitué et cycloalkyle éventuellement substitué, ou B et B' sont pris ensemble avec des atomes intermédiaires quelconques pour former un groupe choisi parmi les groupes cycloalkyle éventuellement substitué et hétérocycloalkyle éventuellement substitué ; et

50

L₁, L₂ et L₃ dans chaque cas sont choisis indépendamment parmi un groupe d'allongement chiral ou non chiral représenté par :

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- [S₁]_c-[Q₁-[S₂]_d]_d-[Q₂-[S₃]_e]_e-[Q₃-[S₄]_f]_f-S₅-P dans laquelle :

(a) Q₁, Q₂ et Q₃, dans chaque cas sont choisis indépendamment parmi un groupe divalent choisi parmi les groupes aryle éventuellement substitué, hétéroaryle éventuellement substitué, cycloalkyle éventuellement substitué et hétérocycloalkyle éventuellement substitué ;

où les substituants sont indépendamment choisis parmi P, les mésogènes cristallins liquides, un atome d'halogène, les groupes polyalcoxy en C₁ à C₁₈, (alcoxy en C₁ à C₁₈) carbonyle, (alkyle en C₁ à C₁₈) carbonyle, (alcoxy en C₁ à C₁₈) carbonyloxy, aryloxy-carbonyloxy, perfluoroalcoxy en C₁ à C₁₈, perfluoro(alcoxy en C₁ à C₁₈) carbonyle, perfluoro(alkyle en C₁ à C₁₈) carbonyle, perfluoro(alkyle en C₁ à C₁₈) amino, di(perfluoro(alkyle en C₁ à C₁₈) alkyl)amino, perfluoro(alkyle en C₁ à C₁₈) thio, (alkyle en C₁ à C₁₈)thio, acétyle en C₁ à C₁₈, cycloalkyle en C₃ à C₁₀, cycloalcoxy en C₃ à C₁₀, alkyle en C₁ à C₁₈ à chaîne linéaire et alkyle en C₁ à C₁₈ à chaîne ramifiée ;

où ledit groupe alkyle en C₁ à C₁₈ à chaîne linéaire et ledit groupe alkyle en C₁ à C₁₈ à chaîne ramifiée sont mono-substitués par un groupe choisi parmi un groupe cyano, un atome d'halogène et un groupe alcoxy en C₁ à C₁₈ ; ou

où ledit groupe alkyle en C₁ à C₁₈ à chaîne linéaire et ledit groupe alkyle en C₁ à C₁₈ à chaîne ramifiée sont poly-substitués par au moins deux groupes choisis indépendamment parmi un atome d'halogène, -M(T)_(t-1) et -M(OT)_(t-1), où M est choisi parmi l'aluminium, l'antimoine, le tantale, le titane, le zirconium et le silicium, T est choisi parmi les radicaux organofonctionnels, les radicaux hydrocarbonés organofonctionnels, les radicaux hydrocarbonés aliphatiques et les radicaux hydrocarbonés aromatiques, et t est la valence de M ;

(b) c, d, e et f sont chacun choisis indépendamment parmi un nombre entier de 1 à 20 ; et chaque S₁, S₂, S₃, S₄ et S₅ est choisi indépendamment dans chaque cas parmi un motif d'espacement choisi parmi :

(i) les groupes alkylène éventuellement substitué, halogénoalkylène éventuellement substitué, -Si(CH₂)_g- et -(Si[(CH₂)₂O]_h)_n-, où g dans chaque cas est choisi indépendamment parmi un nombre entier de 1 à 20 ; h dans chaque cas est choisi indépendamment parmi un nombre entier de 1 à 16 ; et lesdits substituants pour les groupes alkylène et halogénoalkylène sont choisis indépendamment parmi les groupes alkyle en C₁ à C₁₈, cycloalkyle en C₃ à C₁₀ et aryle ;

(ii) -N(Z)-, -C(Z)=C(Z)-, -C(Z)=N-, -C(Z')₂-C(Z')₂- et une liaison simple, où Z dans chaque cas est choisi indépendamment parmi un atome d'hydrogène, les groupes alkyle en C₁ à C₁₈, cycloalkyle en C₃ à C₁₀ et aryle, et Z' dans chaque cas est choisi indépendamment parmi les groupes alkyle en C₁ à C₁₈, cycloalkyle en C₃ à C₁₀ et aryle ; et

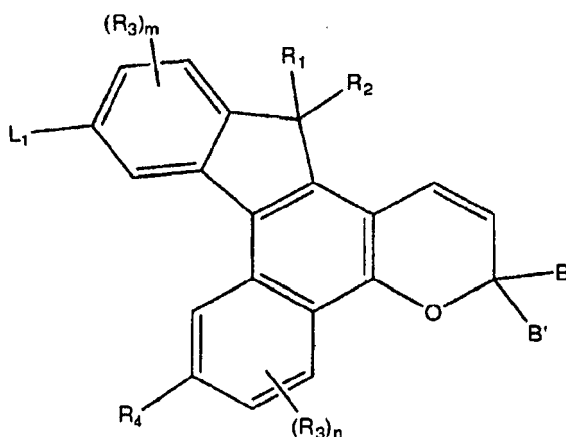
(iii) -O-, -C(=O)-, -C=C-, -N=N-, -S-, -S(=O)-, -(O=)S(=O)-, -(O=)S(=O)O-, -O(O=)S(=O)O- et un résidu alkylène en C₁ à C₂₄ à chaîne linéaire ou ramifiée, ledit résidu alkylène en C₁ à C₂₄ étant non substitué, monosubstitué par un groupe cyano ou un atome d'halogène ou poly-substitué par un atome d'halogène,

à condition que lorsque deux motifs d'espacement comprenant des hétéroatomes sont liés entre eux, les motifs d'espacement sont reliés de manière à ce que les hétéroatomes ne soient pas directement liés les uns aux autres, chaque liaison entre S₁ et le composé représenté par la formule graphique I ne comporte pas deux hétéroatomes liés entre eux, et la liaison entre S₅ et P ne comporte pas deux hétéroatomes liés l'un à l'autre ;

(c) P dans chaque cas est choisi indépendamment parmi les groupes hydroxy, amino, alcényle en C₂ à C₁₈, alcynyle en C₂ à C₁₈, azido, silyle, siloxy, hydrure de silyle, (tétrahydro-2H-pyran-2-yl)oxy, thio, isocyanato, thio-isocyanato, acryloyloxy, méthacryloyloxy, 2-(acryloyloxy)éthylcarbamide, 2-(méthacryloyloxy)éthylcarbamide, aziridinyle, allyloxy-carbonyloxy, époxy, acide carboxylique, ester carboxylique, acryloylamino, méthacryloylamino, aminocarbonyloxy, (alkyle en C₁ à C₁₈)aminocarbonyloxy, aminocarbonylalkyle en C₁ à C₁₈, (alkyloxy en C₁ à C₁₈)carbonyloxy, halogénocarbonyloxy, un atome d'hydrogène, les groupes aryle, hydroxyalkyle en C₁ à C₁₈, alkyle en C₁ à C₁₈, alcoxy en C₁ à C₁₈, aminoalkyle en C₁ à C₁₈, (alkyle en C₁ à C₁₈) amino, di(alkyle en C₁ à C₁₈) amino, (alkyle en C₁ à C₁₈) alcoxy en C₁ à C₁₈, (alcoxy en C₁ à C₁₈) alcoxy en C₁ à C₁₈, nitro, éther poly(alkyle en C₁ à C₁₈), (alkyle en C₁ à C₁₈) (alcoxy en C₁ à C₁₈)alkyle en C₁ à C₁₈, polyéthylèneoxy, polypropylèneoxy, éthylène, acryloyloxy, acryloyloxyalkyle en C₁ à C₁₈, méthacryloyloxy, méthacryloyloxyalkyle en C₁ à C₁₈, 2-chloroacryloyloxy, 2-phénylacryloyloxy, acryloyloxyphényle, 2-chloroacryloylamino, 2-phénylacryloylamino, aminocarbonyloxy, oxétanyle, glycidyle, cyano, isocyanatoalkyle en C₁ à C₁₈, ester de l'acide itaconique, éther vinylique, ester de vinyle, un dérivé du styrène, les polymères à cristaux liquides de chaîne principale et de chaîne latérale, les dérivés de siloxane, les dérivés d'éthylèneimine, les dérivés d'acide maléique, les dérivés de maléimide, les dérivés d'acide fumarique, les dérivés d'acide cinnamique non substitués, les dérivés d'acide cinnamique qui sont substitués avec au moins un des groupes méthyle,

méthoxy, cyano et d'un atome d'halogène, et les groupes monovalents ou divalents chiraux ou non chiraux substitués ou non substitués choisis parmi les radicaux stéroïdes, les radicaux terpénoïdes, les radicaux alcaloïdes et des mélanges de ceux-ci, où les substituants sont choisis indépendamment parmi les groupes alkyle en C₁ à C₁₈, alcoxy en C₁ à C₁₈, amino, cycloalkyle en C₃ à C₁₀, (alkyle en C₁ à C₁₈) alcoxy en C₁ à C₁₈, fluoroalkyle en C₁ à C₁₈, cyano, cyanoalkyle en C₁ à C₁₈, cyanoalcoxy en C₁ à C₁₈ ou des mélanges de ceux-ci, ou P est une structure ayant de 2 à 4 groupes réactifs ou P est un précurseur de polymérisation par métathèse ouvrant un cycle non substitué ou substitué ou P est un composé photochromique substitué ou non substitué ; et (d) d', e' et f' sont chacun choisis indépendamment parmi 0, 1, 2, 3 et 4, à condition qu'une somme de d'+e'+f' soit au moins égale à 2.

2. Composé selon la revendication 1, représenté par la formule graphique IA :



Formule IA

dans laquelle

R₄ est choisi parmi un atome d'hydrogène, R₃ et L₂ ; et

n est un nombre entier de 0 à 3,

de préférence dans laquelle

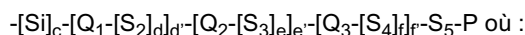
R₁ et R₂ sont chacun choisis indépendamment parmi un atome d'hydrogène, un groupe hydroxy et les groupes chiraux ou non chiraux choisis parmi les groupes hétéroalkyle éventuellement substitué, alkyle éventuellement substitué, aryle éventuellement substitué, hétéroaryle éventuellement substitué, cycloalkyle éventuellement substitué, un atome d'halogène, les groupes amino éventuellement substitué, carboxy, alkylcarbonyle, alcoxycarbonyle, alcoxy éventuellement substitué et aminocarbonyle, ou R₁ et R₂ peuvent être pris ensemble avec des atomes intermédiaires quelconques pour former un groupe choisi parmi les groupes oxo, cycloalkyle éventuellement substitué et hétérocycloalkyle éventuellement substitué ;

R₃ dans chaque cas est choisi indépendamment parmi les groupes formyle, alkylcarbonyle, alcoxycarbonyle, aminocarbonyle, arylcarbonyle, aryloxy carbonyle, alkyle éventuellement substitué, ester de l'acide boronique, un atome d'halogène, les groupes cycloalkyle éventuellement substitué, aryle éventuellement substitué, alcoxy éventuellement substitué, hétéroalkyle éventuellement substitué, hétérocycloalkyle substitué et amino éventuellement substitué ;

m et n sont chacun indépendamment un nombre entier de 0 à 2 ;

B et B' sont chacun choisis indépendamment parmi L₃, un atome d'hydrogène, un atome d'halogène, les groupes chiraux ou non chiraux choisis parmi les groupes alkyle éventuellement substitué, alcényle éventuellement substitué, hétéroalkyle éventuellement substitué, alcoxy éventuellement substitué, aryle éventuellement substitué, hétéroaryle éventuellement substitué et cycloalkyle éventuellement substitué, ou B et B' sont pris ensemble avec des atomes intermédiaires quelconques pour former un groupe choisi parmi un groupe cycloalkyle éventuellement substitué et un groupe hétérocycloalkyle éventuellement substitué ; et

L₁, L₂ et L₃ dans chaque cas sont choisis indépendamment parmi un groupe d'allongement chiral ou non chiral représenté par :



(a) Q_1 , Q_2 et Q_3 dans chaque cas sont choisis indépendamment parmi un groupe divalent choisi parmi les groupes aryle éventuellement substitué, hétéroaryle éventuellement substitué, cycloalkyle éventuellement substitué et hétérocycloalkyle éventuellement substitué ;

où les substituants sont choisis indépendamment parmi P, les mésogènes cristallins liquides, un atome d'halogène, les groupes poly (alcoxy en C_1 à C_{12}), (alcoxy en C_1 à C_{12}) carbonyle, (alkyle en C_1 à C_{12}) carbonyle, perfluoroalcoxy en C_1 à C_{12} , perfluoro (alcoxy en C_1 à C_{12}) carbonyle, perfluoro (alkyle en C_1 à C_{12}) carbonyle, acétyle en C_1 à C_{18} , cycloalkyle en C_3 à C_7 , cycloalcoxy en C_3 à C_7 , alkyle en C_1 à C_{12} à chaîne linéaire et alkyle en C_1 à C_{12} à chaîne ramifiée ;

où ledit groupe alkyle en C_1 à C_{12} à chaîne linéaire et ledit groupe alkyle en C_1 à C_{12} à chaîne ramifiée sont mono-substitués par un groupe choisi parmi un atome d'halogène et un groupe alcoxy en C_1 à C_{12} ou où ledit groupe alkyle en C_1 à C_{12} à chaîne linéaire et ledit groupe alkyle en C_1 à C_{12} à chaîne ramifiée sont poly-substitués par au moins deux groupes choisis indépendamment parmi un atome d'halogène ;

(b) c, d, e et f sont chacun choisis indépendamment parmi un nombre entier de 1 à 10 ; et chaque S_1 , S_2 , S_3 , S_4 et S_5 est choisi indépendamment dans chaque cas parmi un motif d'espacement choisi parmi :

(i) les groupes alkylène substitué ou non substitué, halogénoalkylène substitué ou non substitué, $-\text{Si}(\text{CH}_2)_g-$ et $-\text{Si}[(\text{CH}_3)_2\text{O}]_h-$, où g dans chaque cas est choisi indépendamment parmi un nombre entier de 1 à 10 ; h dans chaque cas est choisi indépendamment parmi un nombre entier de 1 à 8 ; et lesdits substituants pour les groupes alkylène et halogénoalkylène sont choisis indépendamment parmi les groupes alkyle en C_1 à C_{12} , cycloalkyle en C_3 à C_7 et phényle ;

(ii) $-\text{N}(\text{Z})-$, $-\text{C}(\text{Z})=\text{C}(\text{Z})-$ et une liaison simple, où dans chaque cas Z est choisi indépendamment parmi un atome d'hydrogène, les groupes alkyle en C_1 à C_{12} , cycloalkyle en C_3 à C_7 et phényle ; et

(iii) $-\text{O}-$, $-\text{C}(\text{=O})-$, $-\text{C}=\text{C}-$, $-\text{N}=\text{N}-$, $-\text{S}-$ et $-\text{S}(\text{=O})-$, à condition que lorsque deux motifs d'espacement comprenant des hétéroatomes sont liés entre eux, les motifs d'espacement sont reliés de manière à ce que les hétéroatomes ne soient pas directement liés les uns aux autres, chaque liaison entre S_1 et le composé représenté par la formule graphique IA ne comporte pas deux hétéroatomes liés entre eux, et la liaison entre S_5 et P ne comporte pas deux hétéroatomes liés l'un à l'autre ;

(c) P dans chaque cas est choisi indépendamment parmi les groupes hydroxy, amino, alcényle en C_2 à C_{12} , silyle, siloxy, (tétrahydro-2H-pyran-2-yl)oxy, isocyanato, acryloyloxy, méthacryloyloxy, époxy, acide carboxylique, ester carboxylique, (alkyloxy en C_1 à C_{12})carbonyloxy, halogénocarbonyle, un atome d'hydrogène, les groupes aryle, hydroxyalkyle en C_1 à C_{12} , alkyle en C_1 à C_{12} , alcoxy en C_1 à C_{12} , éthylène, acryloyle, acryloyloxyalkyle en C_1 à C_{12} , méthacryloyle, méthacryloyloxyalkyle en C_1 à C_{12} , oxétanyle, glycidyle, éther vinylique, les dérivés de siloxane, les dérivés d'acide cinnamique non substitués, les dérivés d'acide cinnamique qui sont substitués avec au moins un des groupes méthyle, méthoxy, cyano et d'un atome d'halogène, et les groupes monovalents ou divalents chiraux ou non chiraux substitués ou non substitués choisis parmi les radicaux stéroïdes, où chaque substituant est choisi indépendamment parmi les groupes alkyle en C_1 à C_{12} , alcoxy en C_1 à C_{12} , amino, cycloalkyle en C_3 à C_7 , (alkyle en C_1 à C_{12}) alcoxy en C_1 à C_{12} ou fluoroalkyle en C_1 à C_{12} , ou P est une structure ayant de 2 à 4 groupes réactifs ; et

(d) d', e' et f' sont chacun choisis indépendamment parmi 0, 1, 2, 3 et 4, à condition qu'une somme de $d'+e'+f'$ soit au moins égale à 2,

plus préférablement dans laquelle :

R_1 et R_2 sont chacun choisis indépendamment parmi un atome d'hydrogène, un groupe hydroxy et les groupes chiraux ou non chiraux choisis parmi les groupes hétéroalkyle éventuellement substitué, alkyle éventuellement substitué, aryle éventuellement substitué, cycloalkyle éventuellement substitué, un atome d'halogène, les groupes carboxy, alkylcarbonyle, alcoxycarbonyle, alcoxy éventuellement substitué et aminocarbonyle, ou R_1 et R_2 peuvent être pris ensemble avec des atomes intermédiaires quelconques pour former un groupe choisi parmi les groupes oxo et cycloalkyle éventuellement substitué ; et

R_3 dans chaque cas est choisi indépendamment parmi les groupes alkylcarbonyle, alcoxycarbonyle, aminocarbonyle, alkyle éventuellement substitué, ester de l'acide boronique, un atome d'halogène, les groupes cycloalkyle éventuellement substitué, aryle éventuellement substitué, alcoxy éventuellement substitué, hétérocycloalkyle éventuellement substitué et amino éventuellement substitué ;

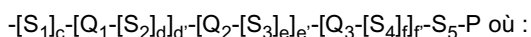
m et n sont chacun indépendamment un nombre entier de 0 à 2 ;

B et B' sont chacun choisis indépendamment parmi L_3 , un atome d'hydrogène, les groupes chiraux choisis parmi les groupes alkyle éventuellement substitué, alcényle éventuellement substitué, aryle éventuellement substitué, hétéroaryle éventuellement substitué et cycloalkyle éventuellement substitué, ou B et B' sont pris

ensemble avec des atomes intermédiaires quelconques pour former un groupe cycloalkyle éventuellement substitué ;

L₁, L₂ et L₃ dans chaque cas sont choisis indépendamment parmi un groupe d'allongement chiral ou non chiral représenté par :

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(a) Q₁, Q₂ et Q₃ dans chaque cas sont choisis indépendamment parmi un groupe divalent choisi parmi les groupes aryle éventuellement substitué, hétéroaryle éventuellement substitué, cycloalkyle éventuellement substitué et hétérocycloalkyle éventuellement substitué ;

où les substituants sont choisis indépendamment parmi P, les groupes (alcoxy en C₁ à C₆)carbonyle, perfluoroalcoxy en C₁ à C₆, cycloalkyle en C₃ à C₇, cycloalcoxy en C₃ à C₇, alkyle en C₁ à C₆ à chaîne linéaire et alkyle en C₁ à C₆ à chaîne ramifiée ;

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où ledit groupe alkyle en C₁ à C₆ à chaîne linéaire et ledit groupe alkyle en C₁ à C₆ à chaîne ramifiée sont mono-substitués par un groupe choisi parmi un atome d'halogène et un groupe alcoxy en C₁ à C₁₂ ou

où ledit groupe alkyle en C₁ à C₆ à chaîne linéaire et ledit groupe alkyle en C₁ à C₆ à chaîne ramifiée sont poly-substitués par au moins deux groupes choisis indépendamment parmi un atome d'halogène ;

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(b) c, d, e et f sont chacun choisis indépendamment parmi un nombre entier de 1 à 10 ; et chaque S₁, S₂, S₃, S₄ et S₅ est choisi indépendamment dans chaque cas parmi un motif d'espacement choisi parmi :

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(i) un groupe alkylène substitué ou non substitué ;

(ii) -N(Z)-, -C(Z)=C(Z)- et une liaison simple, où dans chaque cas Z est choisi indépendamment parmi un atome d'hydrogène et un groupe alkyle en C₁ à C₆ ; et

(iii) -O-, -C(=O)-, -C=C- et -N=N-, -S- ;

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à condition que lorsque deux motifs d'espacement comprenant des hétéroatomes sont liés entre eux, les motifs d'espacement sont reliés de manière à ce que les hétéroatomes du premier motif d'espacement ne soient pas directement liés aux hétéroatomes du second motif d'espacement, et,

à condition que lorsque S₁ et S₅ sont respectivement liés à la formule I et P, ils sont liés de sorte que les deux hétéroatomes ne soient pas directement liés l'un à l'autre ;

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(c) P dans chaque cas est choisi indépendamment parmi les groupes hydroxy, amino, alcényle en C₂ à C₆, siloxy, (tétrahydro-2H-pyran-2-yl)oxy, isocyanato, acryloyloxy, méthacryloyloxy, époxy, acide carboxylique, ester carboxylique, (alkyloxy en C₁ à C₆) carbonyloxy, un atome d'hydrogène, les groupes aryle, hydroxyalkyle en C₁ à C₆, alkyle en C₁ à C₆, éthylène, acryloyle, acryloyloxyalkyle en C₁ à C₁₂, oxétanyle, glycidyle, éther vinylique, les dérivés de siloxane et les groupes monovalents ou divalents chiraux ou non chiraux substitués ou non substitués choisis parmi les radicaux stéroïdes, où chaque substituant est choisi indépendamment parmi les groupes alkyle en C₁ à C₆, alcoxy en C₁ à C₆, amino et cycloalkyle en C₃ à C₇,

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et encore plus préférablement dans laquelle R₁ et R₂ sont chacun choisis indépendamment parmi les groupes méthyle, éthyle, propyle et butyle ; R₃ et R₄ dans chaque cas sont chacun choisis indépendamment parmi les groupes méthyle, éthyle, bromo, chloro, fluoro, méthoxy, éthoxy et CF₃ ; B et B' sont chacun choisis indépendamment parmi un groupe phényle substitué par un ou plusieurs groupes indépendamment choisis parmi les groupes aryle, hétéroaryle, hétérocycloalkyle, alkyle, alcényle, alcynyle, alcoxy, un atome d'halogène, les groupes amino, alkylcarbonyle, carboxy et alcoxycarbonyle ; et pour L₁ : Q₁ est un groupe aryle non substitué ; e' vaut 1 ou 2 ; e dans chaque cas vaut 1 ; S₃ dans chaque cas est une liaison simple ; Q₂ dans chaque cas est choisi indépendamment parmi un groupe aryle éventuellement substitué ; f vaut 1 ; f vaut 1 ; S₄ est une liaison simple ; et Q₃ est un groupe cycloalkyle éventuellement substitué ; S₅ est -(CH₂)_g- où g est un nombre entier de 1 à 20 ; et P est un atome d'hydrogène.

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3. Composé selon la revendication 1, dans lequel L₁ est choisi parmi les groupes :

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4-[4-(4-butyl-cyclohexyl)-phényl]-cyclohexyloxy ;
 4"-butyl-[1,1',4',1"]tercyclohexan-4-yloxy ;
 4-[4-(4-butyl-phényl)-cyclohexyloxy-carbonyl]-phénoxy ;
 4'-(4-butyl-benzoyloxy)-biphényl-4-carbonyloxy ;
 4-(4-pentyl-phénylazo)-phénylcarbamoyle ;

4-(4-diméthylamino-phénylazo)-phénylcarbamoyle ;
 4-[5-(4-propyl-benzoyloxy)-pyrimidin-2-yl]-phényle ;
 4-[2-(4'-méthyl-biphényl-4-carbonyloxy)-1,2-diphényl-éthoxycarbonyl]-phényle ;
 4-(1,2-diphényl-2-[3-[4-(4-propyl-benzoyloxy)-phényl]-acryloyloxy]-éthoxycarbonyl)-phényle ;
 4-[4-(4-[4-[3-(6-[4-[4-(4-nonyl-benzoyloxy)-phénoxy-carbonyl]-phénoxy)-hexyloxy-carbonyl]propionyloxy]-benzoyloxy)-benzoyloxy)-phényl]-pipérazin-1-yle ;
 4-[4-(4-[4-[4-(4-nonyl-benzoyloxy)-benzoyloxy]-benzoyloxy]-benzoyloxy)-phényl]-pipérazin-1-yle ;
 4-(4'-propyl-biphényl-4-yléthynyl)-phényle ;
 4-(4-fluoro-phénoxy-carbonyloxy)-pipéridin-1-yle ;
 2-[17-(1,5-diméthyl-hexyl)-10,13-diméthyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tétradécahydro-1H-cyclopenta[a]phénanthrène-3-yloxy]-indan-5-yle ;
 4-[17-(1,5-diméthyl-hexyl)-10,13-diméthyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tétradécahydro-1H-cyclopenta[a]phénanthrène-3-yloxy-carbonyloxy]-pipéridin-1-yle ;
 4-(biphényl-4-carbonyloxy)-pipéridin-1-yle ;
 4-(naphthalène-2-carbonyloxy)-pipéridin-1-yle ;
 4-(4-phénylcarbamoyle-phénylcarbamoyle)-pipéridin-1-yle ;
 4-(4-(4-phénylpipéridin-1-yl)-benzoyloxy)-pipéridin-1-yle ;
 4-butyl-[1,1';4',1'']terphényl-4-yle ;
 4-(4-pentadécafluoroheptyloxy-phénylcarbamoyle)-benzoyloxy ;
 4-(3-pipéridin-4-yl-propyl)-pipéridin-1-yle ;
 4-(4-(4-[17-(1,5-diméthyl-hexyl)-10,13-diméthyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tétradécahydro-1H-cyclopenta[a]phénanthrène-3-yloxy-carbonyloxy]-benzoyloxy)-phénoxy-carbonyl)phénoxy-méthyle ;
 4-[4-(4-cyclohexyl-phénylcarbamoyle)-benzoyloxy]-pipéridin-1-yle ;
 4-[4-(4-cyclohexyl-phénylcarbamoyle)-benzoyloxy]-pipéridin-1-yle ;
 N-{4-[(4-pentyl-benzylidène)amino]-phényl}-acétamidyloxy ;
 4-(3-pipéridin-4-yl-propyl)pipéridin-1-yle ;
 4-(4-hexyloxy-benzoyloxy)-pipéridin-1-yle ;
 4-(4'-hexyloxy-biphényl-4-carbonyloxy)-pipéridin-1-yle ;
 4-(4-butyl-phénylcarbamoyle)-pipéridin-1-yle ;
 4-[4-[4-[4-pipéridinyl-4-oxy]-phényl]phénoxy]pipéridin-4-yle ;
 4-(4-(9-(4-butylphényl)-2,4,8,10-tétraoxaspiro[5.5]undéc-3-yl)phényl)pipérazin-1-yle ;
 4-(6-(4-butylphényl)carbonyloxy-(4,8-dioxabicyclo[3.3.0]oct-2-yl)oxycarbonyl)phényle ;
 1-[4-[5-(4-butyl-phényl)-[1,3]dioxan-2-yl]-phényl]-4-méthyl-pipérazin-1-yle ;
 4-(7-(4-propylphénylcarbonyloxy)bicyclo[3.3.0]oct-2-yl)oxycarbonyl)phényle ;
 4-[17-(1,5-diméthyl-hexyl)-10,13-diméthyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tétradécahydro-1H-cyclopenta[a]phénanthrène-3-yloxy-carbonyloxy ;
 (4-trans-(4-pentylcyclohexyl)benzamido)phényle ;
 (4-(4-trans-(4-pentylcyclohexyl)phénoxy)carbonyl)-phényle ;
 4-(4-(4-trans-(4-pentylcyclohexyl)phényl)benzamido)-phényle ;
 4-((trans-(4'-pentyl-[1,1'-bi(cyclohexane)]-4-yl)oxy)carbonyl)phényle ;
 4-(4'-(4-pentylcyclohexyl)-[1,1'-biphényl]-4-ylcarboxamido)phényle ;
 4-((4'-(4-pentylcyclohexyl)-[1,1'-biphényl]-4-carbonyl)oxy)benzamido ;
 4-(4'-(4-pentylcyclohexyl)-[1,1'-biphényl]-4-carbonyl)pipérazin-1-yle ;
 4-(4-(4-(4-pentylcyclohexyl)phényl)benzamido)-2-(trifluorométhyl)phényle ;
 2-méthyl-4-trans-(4-((4'-trans-(4-pentylcyclohexyl)-biphényl-4-yloxy)carbonyl)cyclohexanecarboxamido)phényle ;
 4'-((1r,1's,4R,4'R)-4'-pentylbi(cyclohexane-4-)carbonyloxy)biphénylcarbonyloxy ;
 4-(((3S,8S,9S,10R,13R,14S,17R)-10,13-diméthyl-17-(R)-6-méthylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tétradécahydro-1H-cyclopenta[a]phénanthrène-3-yloxy)carbonyl)pipérazin-1-yle ; et
 4-((S)-2-méthylbutoxy)phényl)-10-(4-(((3R,3aS,6S,6aS)-6-(4'-trans-(4-pentylcyclohexyl)biphénylcarbonyloxy)-hexahydrofuro[3,2-b]furan-3-yloxy)carbonyl)phényle.

4. Composé selon la revendication 1, choisi parmi :

3,3-Bis(4-méthoxyphényl)-10-[4-(4-(trans-4-pentylcyclohexyl)benzamido)phényl]-13,13-diméthyl-12-bromo-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3,3-Bis(4-méthoxyphényl)-10-[4-((4-(trans-4-pentylcyclohexyl)phénoxy)carbonyl)phényl]-6,13,13-triméthyl-

3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Fluorophényl)-3-(4-pipéridinophényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-6-
 trifluorométhyl-11,13,13-triméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3,3-Bis(4-méthoxyphényl)-10-[4-(4-(trans-4-pentylcyclohexyl)benzamido)phényl]-5,7-difluoro-13,13-diméthyl-
 5 3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Méthoxyphényl)-3-(4-pipéridinophényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-
 5,7-difluoro-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Méthoxyphényl)-3-(4-morpholinophényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phé-
 10 nyl]-5,7-difluoro-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Fluorophényl)-3-(4-pipéridinophényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phénoxy)carbonyl)phényl]-12-
 bromo-5,7-difluoro-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-Phényl-3-(4-pipéridinophényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-12-bromo-
 5,7-difluoro-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-Phényl-3-(4-pipéridinophényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phénoxy)carbonyl)phényl]-12-bromo-
 15 5,7-difluoro-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Fluorophényl)-3-(4-pipéridinophényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-
 12-bromo-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3,3-Bis(4-méthoxyphényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-12-bromo-6,7-di-
 méthoxy-11,13,13-triméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 20 3,3-Bis(4-méthoxyphényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-6-trifluorométhyl-
 12-bromo-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3,3-Bis(4-méthoxyphényl)-10,12-bis[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-6-trifluoro-
 méthyl-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 25 3,3-Bis(4-méthoxyphényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-5,7-difluoro-
 13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3,3-Bis(4-méthoxyphényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-6-trifluorométhyl-
 13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3,3-Bis(4-méthoxyphényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-5,7-difluoro-12-
 bromo-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 30 3-(4-Fluorophényl)-3-(4-morpholinophényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-
 6-trifluorométhyl-13-méthyl-13-butyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Fluorophényl)-3-(4-morpholinophényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-
 5,7-difluoro-12-bromo-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-Phényl-3-(4-méthoxyphényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-6-trifluoro-
 35 méthyl-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-Phényl-3-(4-morpholinophényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-6-trifluoro-
 méthyl-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3,3-Bis(4-fluorophényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-6-trifluorométhyl-12-
 bromo-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 40 3,3-Bis(4-fluorophényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-6-trifluorométhyl-
 13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Méthoxyphényl)-3-(4-butoxyphényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-6-
 trifluorométhyl-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Fluorophényl)-13,13-diméthyl-3-(4-morpholinophényl)-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphé-
 45 nyl]-4-ylcarboxamido)phényl)-6-(trifluorométhyl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Butoxyphényl)-3-(4-fluorophényl)-13,13-diméthyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphényl]-4-yl-
 carboxamido)phényl)-6-(trifluorométhyl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-(4-(4-Méthoxyphényl)pipérazin-1-yl)phényl)-13,13-diméthyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-bi-
 50 phényl]-4-ylcarboxamido)phényl)-3-phényl-6-(trifluorométhyl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-
 b]pyrane ;
 3-(4-Butoxyphényl)-3-(4-fluorophényl)-13,13-diméthyl-10-(4-(((trans,trans-4'-pentyl-[1,1'-bi(cyclohexan)]-4-
 yl)oxy)carbonyl)phényl)-6-(trifluorométhyl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Fluorophényl)-13,13-diméthyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphényl]-4-ylcarboxamido)phé-
 nyl)-3-(4-butoxyphényl)-6-(trifluorométhyl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 55 3-(4-Méthoxyphényl)-13,13-diméthyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphényl]-4-ylcarboxami-
 do)phényl)-3-(4-(trifluorométhoxy)phényl)-6-(trifluorométhyl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-
 b]pyrane ;
 3,3-Bis(4-hydroxyphényl)-10-[4-(4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido)phényl]-6-trifluorométhyl-

13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 12-Bromo-3-(4-butoxyphényl)-3-(4-fluorophényl)-13,13-diméthyl-10-(4-((4'-(trans-4-pentylcyclohexyl)-[1,1'-biphényl]-4-carbonyl)oxy)benzamido)-6-(trifluorométhyl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Butoxyphényl)-5,7-dichloro-11-méthoxy-3-(4-méthoxyphényl)-13,13-diméthyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphényl]-4-ylcarboxamido)phényl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Butoxyphényl)-3-(4-fluorophényl)-13,13-diméthyl-10-(4-((4'-(trans-4-pentylcyclohexyl)-[1,1'-biphényl]-4-carbonyl)oxy)benzamido)-6-(trifluorométhyl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 5,7-Dichloro-3,3-bis(4-hydroxyphényl)-11-méthoxy-13,13-diméthyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphényl]-4-ylcarboxamido)phényl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 6,8-Dichloro-3,3-bis(4-hydroxyphényl)-11-méthoxy-13,13-diméthyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphényl]-4-ylcarboxamido)phényl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Butoxyphényl)-5,8-difluoro-3-(4-fluorophényl)-13,13-diméthyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphényl]-4-ylcarboxamido)phényl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Butoxyphényl)-3-(4-fluorophényl)-13,13-diméthyl-10-(4-(4'-(trans-4-pentylcyclohexyl)-[1,1'-biphényl]-4-carbonyl)pipérazin-1-yl)-6-(trifluorométhyl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Morpholinophényl)-3-(4-méthoxyphényl)-10,7-bis[4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido]phényl]-5-fluoro-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Morpholinophényl)-3-(4-méthoxyphényl)-10-[4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido]-2-(trifluorométhyl)phényl]-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3,3-Bis(4-méthoxyphényl)-10-[4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido]-2-(trifluorométhyl)phényl]-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Morpholinophényl)-3-(4-méthoxyphényl)-10-[4-(4-(trans-4-pentylcyclohexyl)phényl)benzamido]-2-(trifluorométhyl)phényl]-13,13-diméthyl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3,3-Bis(4-méthoxyphényl)-13,13-diméthyl-10-(2-méthyl-4-(trans-4-((4'-(trans-4-pentylcyclohexyl)biphényl-4-yloxy)carbonyl)cyclohexanecarboxamido)phényl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-(4-(4-Butylphényl)pipérazin-1-yl)phényl)-3-(4-méthoxyphényl)-13,13-diméthyl-10-(4-(4'-(trans-4-pentylcyclohexyl)biphényl-4-ylcarboxamido)-2-(trifluorométhyl)phényl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-(4-(4-Butylphényl)pipérazin-1-yl)phényl)-3-(4-méthoxyphényl)-13,13-diméthyl-10-(2-méthyl-4-(4'-(trans-4-pentylcyclohexyl)biphényl-4-ylcarboxamido)phényl)-7-(4-(4-(trans-4-pentylcyclohexyl)benzamido)phényl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-(4-Méthoxyphényl)-13,13-diméthyl-7,10-bis(4-(4'-(trans-4-pentylcyclohexyl)biphényl-4-ylcarboxamido)phényl)-3-phényl-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 3-p-Tolyl-3-(4-méthoxyphényl)-6-méthoxy-13,13-diméthyl-7-(4'-(trans,trans-4'-pentylbi(cyclohexane-4-)carbonyloxy)biphénylcarbonyloxy)-10-(4-(4'-(trans-4-pentylcyclohexyl)biphényl-4-ylcarboxamido)phényl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 10-(4-(((3S,8S,9S,10R,13R,14S,17R)-10,13-Diméthyl-17-(R)-6-méthylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tétradécahydro-1H-cyclopenta[a]phénanthrèn-3-yloxy)carbonyl)pipérazin-1-yl)-3-(4-méthoxyphényl)-13,13-diméthyl-3-(4-morpholinophényl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 6-Méthoxy-3-(4-méthoxyphényl)-13,13-diméthyl-3-(4-((S)-2-méthylbutoxy)phényl)-10-(4-(4'-(trans-4-pentylcyclohexyl)biphényl-4-ylcarboxamido)phényl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
 6-Méthoxy-3-(4-méthoxyphényl)-13,13-diméthyl-3-(4-((S)-2-méthylbutoxy)phényl)-7-(4'-(trans,trans-4'-pentylbi(cyclohexane-4-)carbonyloxy)biphénylcarbonyloxy)-10-(4-(4'-(trans-4-pentylcyclohexyl)biphényl-4-ylcarboxamido)phényl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane ; et
 6-Méthoxy-3-(4-méthoxyphényl)-13,13-diméthyl-3-(4-((S)-2-méthylbutoxy)phényl)-10-(4-(((3R,3aS,6S,6aS)-6-(4'-(trans-4-pentylcyclohexyl)biphénylcarbonyloxy)hexahydrofuro[3,2-b]furan-3-yloxy)carbonyl)phényl)-3,13-dihydro-indéno[2',3':3,4]naphto[1,2-b]pyrane.

5. Composition photochromique comprenant un composé photochromique selon la revendication 1 et éventuellement au moins un autre composé photochromique, dans laquelle ladite composition comprend :

- (a) un composé photochromique unique ;
- (b) un mélange de composés photochromiques ;
- (c) un matériau comprenant au moins un composé photochromique ;
- (d) un matériau auquel au moins un composé photochromique est chimiquement lié ;
- (e) le matériau (c) ou (d) comprenant en outre un revêtement pour sensiblement empêcher le contact de l'au moins un composé photochromique avec des matériaux externes ;

- (f) un polymère photochromique ; ou
 (g) des mélanges de ceux-ci.

- 5 6. Composition photochromique comprenant au moins un composé photochromique selon la revendication 1, incorporé dans au moins une partie d'une substance organique, ladite substance organique étant une substance polymère, une substance oligomère, une substance monomère ou un mélange ou une combinaison de celles-ci.
- 10 7. Composition photochromique selon la revendication 6, dans laquelle ladite substance polymère comprend les substances cristallines liquides, les substances d'auto-assemblage, un polycarbonate, un polyamide, un polyimide, un poly(méth)acrylate, un alcène polycyclique, un polyuréthane, un poly(urée)uréthane, un polythiouréthane, un polythio(urée)uréthane, un polyol(carbonate d'allyle), un acétate de cellulose, un diacétate de cellulose, un triacétate de cellulose, un propionate d'acétate de cellulose, un butyrate d'acétate de cellulose, un polyalcène, un mélange de polyalcylène-acétate de vinyle, un poly(acétate de vinyle), un alcool polyvinylique, un polychlorure de vinyle, un poly(vinylformaldéhyde), un poly(vinylacétal), un polychlorure de vinylidène, un polytéréphtalate d'éthylène, un polyester, une polysulfone, une polyoléfine, des copolymères de ceux-ci et/ou des mélanges de ceux-ci, ou la composition photochromique comprend en outre au moins un additif choisi parmi les colorants, les promoteurs d'alignement, les antioxydants, les additifs renforçant la cinétique, les photo-initiateurs, les initiateurs thermiques, les inhibiteurs de polymérisation, les solvants, les photostabilisants, les stabilisants thermiques, les agents de démoulage, les agents de contrôle de rhéologie, les agents d'aplanissement, les piègeurs de radicaux libres, les agents gélifiants et les promoteurs d'adhérence.
- 20 8. Composition photochromique selon la revendication 6, comprenant une composition de revêtement choisi parmi les substances cristallines liquides, les substances d'auto-assemblage et les substances de formation de film.
- 25 9. Article photochromique comprenant un substrat et un composé photochromique selon la revendication 1 lié à au moins une partie d'un substrat.
- 30 10. Article photochromique selon la revendication 9, comprenant un élément optique, ledit élément optique étant au moins un élément ophtalmique, un élément d'affichage, une fenêtre, un miroir, un matériau d'emballage et une élément cellulaire à cristaux liquides actif ou passif, dans lequel l'élément ophtalmique comprend de préférence les lentilles correctives, les lentilles non correctives, les lentilles de contact, les lentilles intra-oculaires, les lentilles à effet de loupe, les lentilles protectrices ou les visières.
- 35 11. Article photochromique selon la revendication 9, dans lequel le substrat comprend une substance polymère et la substance photochrome est incorporée dans au moins une partie de la substance polymère, dans lequel la substance photochrome est de préférence mélangée avec au moins une partie de la substance polymère, liée à au moins une partie de la substance polymère, et/ou imbibée dans au moins une partie de la substance polymère.
- 40 12. Article photochromique selon la revendication 9, dans lequel l'article photochrome comprend un revêtement ou un film lié à au moins une partie du substrat, ledit revêtement ou film comprenant la substance photochrome, dans lequel ledit substrat est de préférence formé à partir de substances organiques, de substances inorganiques ou de combinaisons de celles-ci.
- 45 13. Article photochromique selon la revendication 9, comprenant en outre au moins un revêtement partiel choisi parmi les revêtements photochromiques, les revêtements antireflets, les revêtements linéairement polarisant, les revêtements de transition, les revêtements primaires, les revêtements adhésifs, les revêtements réfléchissants, les revêtements antibuée, les revêtements barrières contre l'oxygène, les revêtements absorbant la lumière ultraviolette et les revêtements protecteurs.
- 50 14. Article photochromique comprenant un substrat ; au moins un revêtement partiel d'une substance d'alignement ; au moins un revêtement partiel supplémentaire d'une substance cristalline liquide ; et au moins un composé photochromique selon la revendication 1.
- 55 15. Article photochromique selon la revendication 14, comprenant en outre au moins un additif choisi parmi les colorants dichroïde, les colorants non dichroïdes, les promoteurs d'alignement, les antioxydants, les additifs renforçant la cinétique, les photo-initiateurs, les initiateurs thermiques, les inhibiteurs de polymérisation, les solvants, les pho-

tostabilisants, les stabilisants thermiques, les agents de démoulage, les agents de contrôle de rhéologie, les agents d'aplanissement, les piègeurs de radicaux libres, les agents gélifiants et les promoteurs d'adhérence.

16. Article photochromique selon la revendication 14, dans lequel

- 5
- le substrat est choisi parmi le verre, le quartz et les substances organiques polymères,
 - l'au moins une substance d'alignement comprend un réseau polymère orientable par exposition à au moins un de : un champ magnétique, un champ électrique, un rayonnement infrarouge linéairement polarisé, un rayonnement ultraviolet linéairement polarisé, un rayonnement visible linéairement polarisé et une force de cisaillement, ou
 - ladite substance cristalline liquide est un polymère à cristaux liquides.
- 10

17. Article photochromique selon la revendication 14, comprenant en outre au moins un revêtement primaire, un revêtement de transition, un revêtement protecteur ou une combinaison de ceux-ci, de préférence dans lequel

- 15
- le revêtement de transition comprend un polymère d'acrylate,
 - le revêtement protecteur comprend au moins un dérivé de siloxane, ou
 - l'au moins un revêtement primaire comprend un polyuréthane.
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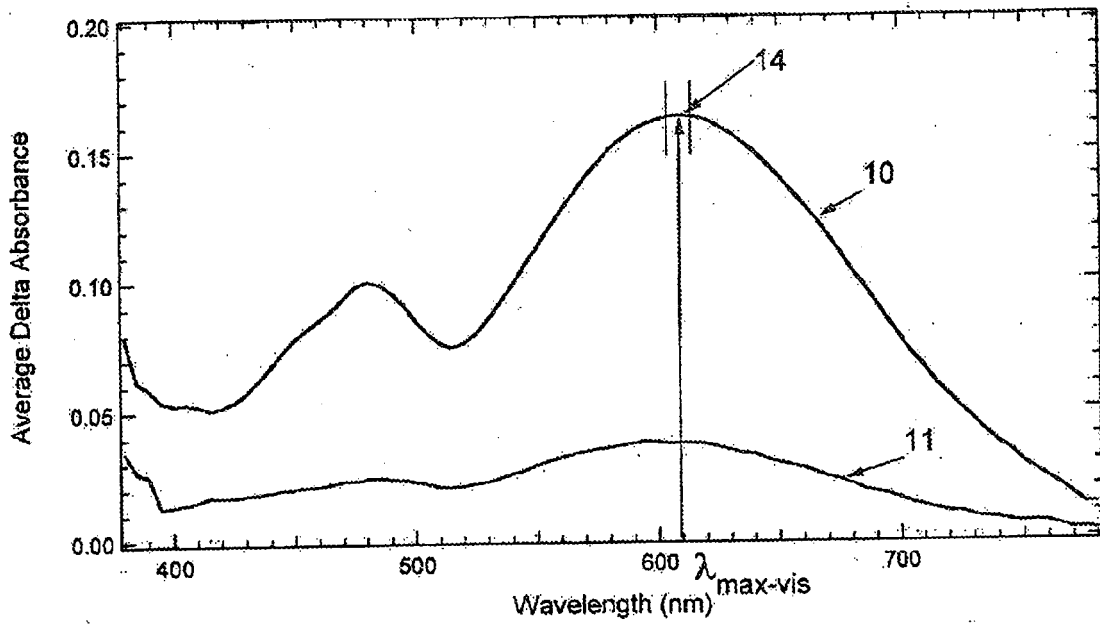
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FIG. 1



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