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(54) PHOTOCHROMIC COMPOUNDS

PHOTOCHROMISCHE VERBINDUNGEN

COMPOSES PHOTOCHROMIQUES

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Description

BACKGROUND

[0001] Various non-limiting embodiments disclosed herein relate generally to photochromic compounds. Other non-limiting embodiments relate to devices and elements made using the photochromic compounds disclosed herein.

[0002] 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.

[0003] 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.

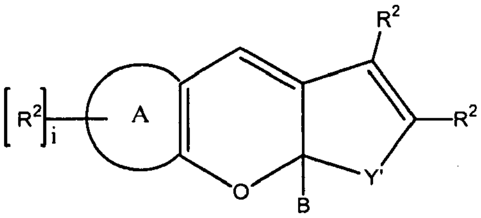
[0004] In contrast to the dichroic compounds, it is generally not necessary to position or arrange the molecules of conventional photochromic compounds to form a conventional photochromic element. Thus, for example, conventional photochromic elements, such as lenses for photochromic eyewear, can be formed, 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.

[0005] 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.

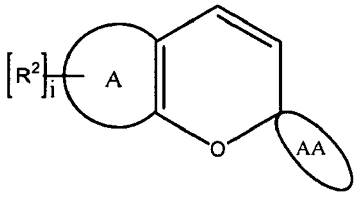
[0006] Document US 5 395 567 A discloses photochromic spironaphthopyran compounds and document WO 96/04576 A discloses photochromic phenanthropyran derivatives.

SUMMARY OF THE INVENTION

[0007] The present invention relates to a non-thermally reversible photochromic compound represented by one of Formula X and Formula XI:



X



XI

as defined below.

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

[0008] Various non-limiting embodiments of the present invention will be better understood when read in conjunction with the drawings, in which:

Fig. 1 shows two average difference absorption spectrum obtained for a photochromic compound according to various non-limiting embodiments disclosed herein using the CELL METHOD.

DETAILED DESCRIPTION

[0009] 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.

[0010] Further, while the numerical ranges and parameters setting forth the broad scope of the invention 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.

[0011] Various non-limiting embodiments of the invention will now be described. One non-limiting embodiment provides a thermally reversible, 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 2.3 in at least one state as determined according to the CELL METHOD, which is described in detail below. Further, according various non-limiting embodiments, the thermally reversible, photochromic compound has an average absorption ratio greater than 2.3 in an activated state as determined according to the CELL METHOD. As used herein, the term "photochromic compound" includes both thermally reversible and non-thermally reversible (or photo-reversible) photochromic compounds. 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. Further, as used herein the term "compound" means a substance formed by the union of two or more elements, components, ingredients, or parts and includes, without limitation, molecules and macromolecules (for example polymers or oligomers) formed by the union of two or more elements, components, ingredients, or parts.

[0012] 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 an unactived 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 (22.8 °C +/- 0.5 °C or better) (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).

[0013] 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.

[0014] 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 spectum obtained for the same photochromic compound in the orthogonal polarization plane.

[0015] 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 $\lambda_{max\text{-}vis}$ +/- 5 nanometers (generally indicated as 14 in Fig. 1), wherein $\lambda_{max\text{-}vis}$ is the wavelength at which the photochromic compound had the highest average absorbance in any plane, is calculated according to the following equation:

$$AR_{\lambda i} = Ab^{1}_{\lambda i} / Ab^{2}_{\lambda i} \qquad \text{Eq.1}$$

wherein, $AR_{\lambda i}$ is the absorption ratio at wavelength λ_i, $Ab^1_{\lambda i}$ is the average absorption at wavelength λ_i in the polarization direction (i.e., 0° or 90°) having the higher absorbance, and $Ab^2_{\lambda i}$ 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.

[0016] 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., $\lambda_{max\text{-}vis}$ +/- 5 nanometers) according to the following equation:

$$AR = (\Sigma AR_{\lambda i}) / n_i \qquad \text{Eq. 2}$$

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

[0017] 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.

[0018] As discussed above, non-limiting embodiments disclosed herein provide a thermally reversible photochromic compound having an average absorption ratio greater than 2.3 in at least one state as determined according to CELL METHOD. Thus, the thermally reversible photochromic compound according to this non-limiting embodiment can display both useful photochromic properties and useful dichroic properties. That is, the thermally reversible, photochromic compound can be a thermally reversible, 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.

[0019] 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 2.5 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.

[0020] Another non-limiting embodiment provides a thermally reversible, photochromic compound that is free of oxazines and adapted to have at least a first state and a second state, wherein the photochromic compound has an average absorption ratio of at least 1.5 in at least one state as determined according to CELL METHOD. Further, according to this non-limiting embodiment, the average average absorption ratio can range from 1.5 to 50 in at least one state as determined according to CELL METHOD.

[0021] Other non-limiting embodiments disclosed herein provide a photochromic compound, which may be a thermally reversible photochromic compound, comprising: (a) at least one photochromic group (PC) chosen from pyrans, oxazines, and fulgides; and (b) at least one lengthening agent attached to the at least one photochromic group, wherein the lengthening agent (L) is represented by the following Formula I (which is described in detail below):

$$- [S_1]_c\text{-}[Q_1\text{-}[S_2]_d]_{d'}\text{-}[Q_2\text{-}[S_3]_e]_{e'}\text{-}[Q_3\text{-}[S_4]_f]_{f'}\text{-}S_5\text{-}P \qquad \mathrm{I}$$

[0022] As used herein, the term "attached" means directly bonded to or indirectly bonded to through another group. Thus, for example, according to various non-limiting embodiments disclosed herein, L can be directly bonded to PC as a substituent on PC, or L can be a substituent on another group (such as a group represented by R^1, which is discussed below) that is directly bonded to PC (i.e., L is indirectly bonded to PC). Although not limiting herein, according to various non-limiting embodiments, L can be attached to PC so as to extend or lengthen PC in an activated state such that the absorption ratio of the extended PC (i.e., the photochromic compound) is enhanced as compared to PC alone. Although not limiting herein, according to various non-limiting embodiments, the location of attachment of L on PC can be chosen such that L lengthens PC in at least one of a direction parallel to or a direction perpendicular to a theoretical transitional dipole moment of the activated form of PC. As used herein the term "theoretical transitional dipole moment" refers to transient dipolar polarization created by interaction of electromagnetic radiation with the molecule. See, for example, IUPAC Compendium of Chemical Technology, 2nd Ed., International Union of Pure and Applied Chemistry (1997).

[0023] With reference to Formula I above, each Q_1, Q_2, and Q_3 can be independently chosen for each occurrence from: a divalent group chosen from an unsubstituted or a substituted aromatic group, an unsubstituted or a substituted alicyclic group, an unsubstituted or a substituted heterocyclic group, and mixtures thereof, wherein substituents are chosen from: a group represented by P (as set forth below), aryl, thiol, amide, liquid crystal mesogens, halogen, C_1-C_{18}alkoxy, poly(C_1-C_{18}alkoxy), amino, amino(C_1-C_{18})alkylene, C_1-C_{18}alkylamino, di-(C_1-C_{18})alkylamino, C_1-C_{18}alkyl, C_2-C_{18} alkene, C_2-C_{18} alkyne, C_1-C_{18} alkyl(C_1-C_{18})alkoxy, C_1-C_{18} alkoxycarbonyl, C_1-C_{18} alkylcarbonyl, C_1-C_{18} alkyl carbonate, aryl carbonate, C_1-C_{18} acetyl, C_3-C_{10}cycloalkyl, C_3-C_{10} cycloalkoxy, isocyanato, amido, cyano, nitro, a straight-chain or branched C_1-C_{18} alkyl group that is mono-substituted with cyano, halo, or C_1-C_{18}alkoxy, or poly-substituted with halo, and a group represented by one of the following formulae: $-M(T)_{(t-1)}$ 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. As used herein, the prefix "poly" means at least two.

[0024] As discussed above, Q_1, Q_2, and Q_3 can be independently chosen for each occurrence from a divalent group, such as an unsubstituted or a substituted aromatic group, unsubstituted or substituted heterocyclic group, and an unsubstituted or substituted alicylic group. Non-limiting examples of useful aromatic groups include: benzo, naphtho, phenanthro, biphenyl, tetrahydro naphtho, terphenyl, and anthraceno.

[0025] As used herein the term "heterocyclic group" means a compound having a ring of atoms, wherein at least one atom forming the ring is different than the other atoms forming the ring. Further, as used herein, the term heterocyclic group specifically excludes fused heterocyclic groups. Non-limiting examples of suitable heterocyclic groups from which Q_1, Q_2, and Q_3 can be chosen include: isosorbitol, dibenzofuro, dibenzothieno, benzofuro, benzothieno, thieno, furo, dioxino, carbazolo, anthranilyl, azepinyl, benzoxazolyl, diazepinyl, dioazlyl, imidazolidinyl, imidazolyl, imidazolinyl, indazolyl, indoleninyl, indolinyl, indolizinyl, indolyl, indoxazinyl, isobenzazolyl, isoindolyl, isooxazolyl, isooxazyl, isopyrroyl, isoquinolyl, isothiazolyl, morpholino, morpholinyl, oxadiazolyl, oxathiazolyl, oxathiazyl, oxathiolyl, oxatriazolyl, oxazolyl, piperazinyl, piperazyl, piperidyl, purinyl, pyranopyrrolyl, pyrazinyl, pyrazolidinyl, pyrazolinyl, pyrazolyl, pyrazyl, pyridazinyl, pyridazyl, pyridyl, pyrimidinyl, pyrimidyl, pyridenyl, pyrrolidinyl, pyrrolinyl, pyrroyl, quinolizinyl, quinuclidinyl, quinolyl, thiazolyl, triazolyl, triazyl, N-arylpiperazino, aziridino, arylpiperidino, thiomorpholino, tetrahydroquinolino, tetrahydroisoquinolino, pyrryl, unsubstituted, mono- or di- substituted C_4-C_{18} spirobicyclic amines, and unsubstituted, mono- or di-substituted C_4-C_{18} spirotricyclic amines.

[0026] As discussed above, according to various non-limiting embodiments Q_1, Q_2, and Q_3 can be chosen from mono- or di- substituted C_4-C_{18} spirobicyclic amine and C_4-C_{18} spirotricyclic amine. Non-limiting examples of suitable substituents include aryl, C_1-C_6 alkyl, C_1-C_6 alkoxy or phenyl (C_1-C_6)alkyl. Specific non-limiting examples of mono- or di-substituted spirobicyclic amines include: 2-azabicyclo[2.2.1]hept-2-yl; 3-azabicyclo[3.2.1]oct-3-yl; 2-azabicyclo[2.2.2]oct-2-yl; and 6-azabicyclo[3.2.2]nonan-6-yl. Specific non-limiting examples of mono- or di-substituted tricyclic amines include: 2-azatricyclo[3.3.1.1(3,7)]decan-2-yl; 4-benzyl-2-azatricyclo[3.3.1.1(3,7)]decan-2-yl; 4-methoxy-6-methyl-2-azatricyclo[3.3.1.1(3,7)]decan-2-yl; 4-azatricyclo[4.3.1.1(3,8)]undecan-4-yl; and 7-methyl-4-azatricyclo[4.3.1.1(3,8)]undecan-4-yl.

[0027] Examples of alicyclic groups from which Q_1, Q_2, and Q_3 can be chosen include, without limitation, cyclohexyl, cyclopropyl, norbornenyl, decalinyl, adamantanyl, bicyclooctane, per-hydrofluorene, and cubanyl.

[0028] With continued reference to Formula I, and each S_1, S_2, S_3, S_4, and S_5 is independently chosen for each occurrence from a spacer unit chosen from:

(1) $-(CH_2)_g-$, $-(CF_2)_h-$, $-Si(CH_2)_g-$, $-(Si[(CH_3)_2]O)_h-$, wherein g is independently chosen for each occurrence from 1 to 20; h is chosen from 1 to 16;
(2) -N(Z)-, -C(Z)=C(Z)-, -C(Z)=N-, -C(Z’)-C(Z’)-, wherein Z is independently chosen for each occurrence from hydrogen, C_1-C_6 alkyl, cycloalkyl and aryl, and Z’ is independently chosen for each occurrence from C_1-C_6 alkyl, cycloalkyl and aryl; and
(3) -O-, -C(O)-, -C≡C-, -N=N-, -S-, -S(O)-, -S(O)(O)-, straight-chain or branched C_1-C_{24} alkylene residue, said C_1-C_{24} alkylene residue being unsubstituted, mono-substituted by cyano or halo, or poly-substituted by halo;

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 and when S_1 and S_5 are linked to PC and P, respectively, they are linked so that two heteroatoms are not directly linked to each other. As used herein the term "heteroatom" means atoms other than carbon or hydrogen.

[0029] According to various non-limiting embodiments disclosed herein, in Formula I, c, d, e, and f each can be independently chosen from an integer ranging from 1 to 20, inclusive; and d’, e’ and f each can be independently chosen from 0, 1, 2, 3, and 4, provided that the sum of d’ + e’ + f’ is at least 1. According to other non-limiting embodiments disclosed herein, c, d, e, and f each can be independently chosen from an integer ranging from 0 to 20, inclusive; and d’, e’ and f’ each can be independently chosen from 0, 1, 2, 3, and 4, provided that the sum of d’ + e’ + f’ is at least 2. According to still other non-limiting embodiments disclosed herein, c, d, e, and f each can be independently chosen from an integer ranging from 0 to 20, inclusive; and d’, e’ and f’ each can be independently chosen from 0, 1, 2, 3, and 4, provided that the sum of d’ + e’ + f’ is at least 3. According to still other non-limiting embodiments disclosed herein, c, d, e, and f each can be independently chosen from an integer ranging from 0 to 20, inclusive; and d’, e’ and f each can be independently chosen from 0, 1, 2, 3, and 4, provided that the sum of d’ + e’ + f’ is at least 1.

[0030] Further, in Formula I, P can be chosen from: aziridinyl, hydrogen, hydroxy, aryl, alkyl, alkoxy, amino, alkylamino, alkylalkoxy, alkoxyalkoxy, nitro, polyalkyl ether, $(C_1$-$C_6)$alkyl$(C_1$-$C_6)$alkoxy$(C_1$-$C_6)$alkyl, polyethyleneoxy, polypropyleneoxy, ethylene, acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, acryloylphenylene, acrylamide, methacrylamide, 2-chloroacrylamide, 2-phenylacrylamide, epoxy, isocyanate, thiol, thioisocyanate, itaconic acid ester, vinyl ether, vinyl ester, a styrene derivative, siloxane, main-chain and side-chain liquid crystal polymers, ethyleneimine derivatives, maleic acid 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 and unsubstituted chiral and non-chiral monovalent or divalent groups chosen from steroid radicals, terpenoid radicals, alkaloid radicals and mixtures thereof, wherein the substituents are independently chosen from alkyl, alkoxy, amino, cycloalkyl, alkylalkoxy, fluoroalkyl, cyanoalkyl, cyanoalkoxy and mixtures thereof.

[0031] According to various non-limiting embodiments disclosed herein, when P is a polymerizable group, the polymerizable group can be any functional group adapted to participate in a polymerization reaction. Non-limiting examples of polymerization reactions include those described in the definition of "polymerization" in Hawley’s Condensed Chemical Dictionary Thirteenth Edition, 1997, John Wiley & Sons, pages 901-902. For example, although not limiting herein, polymerization reactions include: "addition polymerization," in which free radicals are the initiating agents that react with the double bond of a monomer by adding to it on one side at the same time producing a new free electron on the other side; "condensation polymerization," in which two reacting molecules combine to form a larger molecule with elimination of a small molecule, such as a water molecule; and "oxidative coupling polymerization." Further, non-limiting examples of polymerizable groups include hydroxy, acryloxy, methacryloxy, 2-(acryloxy)ethylcarbamyl, 2-(methacryloxy)ethylcarbamyl, isocyanate, aziridine, allylcarbonate, and epoxy, e.g., oxiranylmethyl.

[0032] According to one specific, non-limiting embodiment, P can be chosen from a main-chain or a side-chain liquid crystal polymer and a liquid crystal mesogen. As used herein, the term liquid crystal "mesogen" means rigid rod-like or disc-like liquid crystal molecules. Further, as used herein the term "main-chain liquid crystal polymer" refers to a polymer having liquid crystal mesogens within the backbone (i.e., the main chain) structure of the polymer. As used herein the term "side-chain liquid crystal polymer" refers to a polymer having liquid crystal mesogens attached to the polymer at the side chains. Although not limiting herein, generally, the mesogens are made up of two or more aromatic rings that restrict the movement of a liquid crystal polymer. Examples of suitable rod-like liquid crystal mesogens include without limitation: substituted or unsubstituted aromatic esters, substituted or unsubstituted linear aromatic compounds, and substituted or unsubstituted terphenyls.

[0033] According to another specific, non-limiting embodiment, P can be chosen from a steroid radical, for example and without limitation, a cholesterolic compound.

[0034] As is discussed above, various non-limiting embodiments disclosed herein provide a photochromic compound comprising (a) a photochromic group (PC) chosen from pyrans, oxazines, and fulgides, and (b) at least one lengthening agent (L) represented by Formula I (above) attached to PC. According to the present invention, which are discussed herein below in more detail, PC is a non-thermally reversible, photochromic group. As used herein, the term "non-thermally reversible" means 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 actinic radiation.

[0035] According to one specific, non-limiting embodiment, wherein the photochromic group comprises at least two PCs, the PCs can be linked to one another via linking group substituents on the individual PCs. For example, the PCs can be polymerizable photochromic groups or photochromic groups that are adapted to be compatible with a host material ("compatibilized photochromic group"). Non-limiting examples of polymerizable photochromic groups from which PC can be chosen and that are useful in conjunction with various non-limiting embodiments disclosed herein are disclosed in U.S. Patent 6,113,814. Non-limiting examples of compatiblized photochromic groups from which PC can be chosen and that are useful in conjunction with various non-limiting embodiments disclosed herein are disclosed in U.S. Patent 6,555,028.

[0036] Other suitable photochromic groups and complementary photochromic groups are described in U.S. Patents 6,080,338 at column 2, line 21 to column 14, line 43; 6,136,968 at column 2, line 43 to column 20, line 67; 6,296,785 at column 2, line 47 to column 31, line 5; 6,348,604 at column 3, line 26 to column 17, line 15; 6,353,102 at column 1, line 62 to column 11, line 64; and 6,630,597 at column 2, line 16 to column 16, line 23.

[0037] Additionally, as previously discussed, according to various non-limiting embodiments disclosed herein, the photochromic compound comprising the at least one photochromic group (PC) and the at least one lengthening agent (L) represented by Formula I (above) and attached to PC, can be a photochromic-dichroic compound. For example, according to various non-limiting embodiments the photochromic compound can be a photochromic-dichroic compound having an average absorption ratio greater than 2.3 in an activated state as determined according to the CELL METHOD (described above). According to other non-limiting embodiments, the photochromic compound can be a photochromic-dichroic compound having an average absorption ratio ranging from 4 to 20, 3 to 30, or 2.5 to 50 in an activated state as determined according to CELL METHOD.

[0038] Further, in addition to at least one lengthening agent (L), the photochromic compounds according to various non-limiting embodiments disclosed herein can further comprise at least one group represented by R^1 that is directly bonded to PC. Further, although not required, as previously discussed, according to various non-limiting embodiments, the at least one lengthening agent (L) can be indirectly bonded to PC through the at least one group represented by R^1. That is, according to various non-limiting embodiments, L can be a substituent on at least one group R^1 that is bonded to PC.

[0039] According to various non-limiting embodiments disclosed herein, R^1 can be independently chosen for each occurrence from:

(i) hydrogen, C_1-C_{12} alkyl, C_2-C_{12} alkylidene, C_2-C_{12} alkylidyne, vinyl, C_3-C_7 cycloalkyl, C_1-C_{12} haloalkyl, allyl, halogen, and benzyl that is unsubstituted or mono-substituted with at least one of C_1-C_{12} alkyl and C_1-C_{12} alkoxy;

(ii) phenyl that is mono-substituted at the *para* position with at least one substituent chosen from: C_1-C_7 alkoxy, linear or branched chain C_1-C_{20} alkylene, linear or branched chain C_1-C_4 polyoxyalkylene, cyclic C_3-C_{20} alkylene, phenylene, naphthylene, C_1-C_4 alkyl substituted phenylene, mono- or poly-urethane(C_1-C_{20})alkylene, mono- or poly-ester(C_1C_{20})alkylene, mono- or poly-carbonate(C_1-C_{20})alkylene, polysilanylene, polysiloxanylene and mixtures thereof, wherein the at least one substituent is connected to an aryl group of a photochromic material;

(iii) -CH(CN)$_2$ and -CH(COOX$_1$)$_2$, wherein X_1 is chosen from at least one of a lengthening agent L represented by Formula I above, hydrogen, C_1-C_{12} alkyl that is unsubstituted or mono-substituted with phenyl, phenyl(C_1-C_{12})alkyl that is mono-substituted with C_1-C_{12} alkyl or C_1-C_{12} alkoxy, and an aryl group that is unsubstituted, mono- or di-substituted, wherein each aryl substituent is independently chosen from C_1-C_{12} alkyl and C_1-C_{12} alkoxy;

(iv) -CH(X_2)(X_3), wherein:

(A) X_2 is chosen from at least one of a lengthening agent L represented by Formula I above, hydrogen, C_1-C_{12} alkyl and an aryl group that is unsubstituted, mono- or di-substituted, wherein each aryl substituent is independently chosen from C_1-C_{12}alkyl and C_1-C_{12} alkoxy; and

(B) X_3 is chosen from at least one of -COOX$_1$, -COX$_1$, -COX$_4$, and -CH$_2$OX$_5$, wherein:

(1) X_4 is chosen from at least one of morpholino, piperidino, amino that is unsubstituted, mono- or di-

substituted with C_1-C_{12} alkyl, and an unsubstituted, mono or di- substituted group chosen from phenylamino and diphenylamino, wherein each substituent is independently chosen from C_1-C_{12} alkyl or C_1-C_{12} alkoxy; and

(2) X_5 is chosen from a lengthening agent L represented by Formula I above, hydrogen, -C(O)X_2, C_1-C_{12} alkyl that is unsubstituted or mono-substituted with (C_1-C_{12})alkoxy or phenyl, phenyl(C_1-C_{12})alkyl that is mono-substituted with (C_1-C_{12})alkoxy, and an aryl group that is unsubstituted, mono- or di-substituted, wherein each aryl substituent is independently chosen from C_1-C_{12} alkyl and C_1-C_{12} alkoxy;

(v) an unsubstituted, mono-, di-, or tri- substituted aryl group, such as phenyl, naphthyl, phenanthryl, or pyrenyl; 9-julolidinyl; or an unsubstituted, mono- or di-substituted heteroaromatic group chosen from pyridyl, furanyl, benzofuran-2-yl, benzofuran-3-yl, thienyl, benzothien-2-yl, benzothien-3-yl, dibenzofuranyl, dibenzothienyl, carbazoyl, benzopyridyl, indolinyl, and fluorenyl; wherein the substituents are independently chosen for each occurrence from:

(A) a lengthening agent L represented by Formula I above;

(B) -C(O)X_6, wherein X_6 is chosen from at least one of: a lengthening agent L represented by Formula I above, hydrogen, C_1-C_{12} alkoxy, phenoxy that is unsubstituted, mono- or di- substituted with C_1-C_{12} alkyl or C_1-C_{12} alkoxy, an aryl group that is unsubstituted, mono- or di-substituted with C_1-C_{12} alkyl or C_1-C_{12} alkoxy, an amino group that is unsubstituted, mono- or di-substituted with C_1-C_{12} alkyl, and a phenylamino group that is unsubstituted, mono- or di-substituted with C_1-C_{12} alkyl or C_1-C_{12} alkoxy;

(C) aryl, haloaryl, C_3-C_7 cycloalkylaryl, and an aryl group that is mono- or di-substituted with C_1-C_{12} alkyl or C_1-C_{12} alkoxy;

(D) C_1-C_{12} alkyl, C_3-C_7 cycloalkyl, C_3-C_7 cycloalkyloxy(C_1-C_{12})alkyl, aryl(C_1-C_{12})alkyl, aryloxy(C_1-C_{12})alkyl, mono- or di- (C_1-C_{12})alkylaryl(C_1-C_{12})alkyl, mono- or di- (C_1-C_{12})alkoxyaryl(C_1-C_{12})alkyl, haloalkyl, and mono(C_1-C_{12})alkoxy(C_1-C_{12})alkyl;

(E) C_1-C_{12} alkoxy, C_3-C_7 cycloalkoxy, cycloalkyloxy(C_1-C_{12})alkoxy, aryl(C_1-C_{12})alkoxy, aryloxy(C_1-C_{12})alkoxy, mono- or di-(C_1-C_{12})alkylaryl(C_1-C_{12})alkoxy, and mono- or di- (C_1-C_{12})alkoxyary)(C_1-C_{12})alkoxy;

(F) amido, amino, mono- or di-alkylamino, diarylamino, piperazino, N-(C_1-C_{12})alkylpiperazino, N-arylpiperazino, aziridino, indolino, piperidino, morpholino, thiomorpholino, tetrahydroquinolino, tetrahydroisoquinolino, pyrrolidyl, hydroxy, acryloxy, methacryloxy, and halogen;

(G) -OX_7 and -N(X_7)$_2$, wherein X_7 is chosen from:

(1) a lengthening agent L represented by Formula I above, hydrogen, C_1-C_{12} alkyl, C_1-C_{12}acyl, phenyl(C_1-C_{12})alkyl, mono(C_1-C_{12})akyl substituted phenyl(C_1-C_{12})alkyl, mono(C_1-C_{12})alkoxy substituted phenyl(C_1-C_{12})alkyl; C_1-C_{12}alkoxy(C_1-C_{12})alkyl; C_3-C_7 cycloalkyl; mono(C_1-C_{12})alkyl substituted C_3-C_7 cycloalkyl, C_1-C_{12} haloalkyl, allyl, benzoyl, mono-subsituted benzoyl, naphthoyl or mono-substituted naphthoyl, wherein each of said benzoyl and naphthoyl substituents are independently chosen from C_1-C_{12} alkyl, and C_1-C_{12} alkoxy;

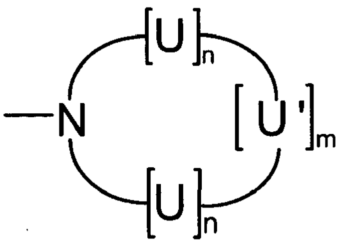
(2) -CH(X_8)X_9, wherein X_8 is chosen from a lengthening agent L represented by Formula I above, hydrogen or C_1-C_{12} alkyl; and X_9 is chosen from a lengthening agent L represented by Formula I above, -CN, -CF_3, or -COOX_{10}, wherein X_{10} is chosen from a lengthening agent L represented by Formula I above, hydrogen or C_1-C_{12} alkyl;

(3) -C(O)X_6; and

(4) tri(C_1-C_{12})alkylsilyl, tri(C_1-C_{12})alkoxysilyl, di(C_1-C_{12})alkyl(C_1-C_{12}alkoxy)silyl, or di(C_1-C_{12})alkoxy(C_1-C_{12} alkyl)silyl;

(H) -SX_{11}, wherein X_{11} is chosen from a lengthening agent L represented by Formula I above, C_1-C_{12} alkyl, an aryl group that is unsubstituted, or mono- or di- substituted with C_1-C_{12}alkyl, C_1-C_{12}alkoxy or halogen;

(I) a nitrogen containing ring represented by Formula i:

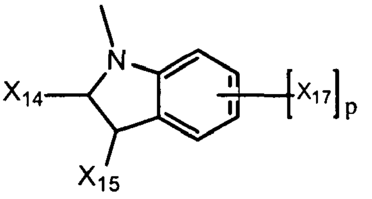


i

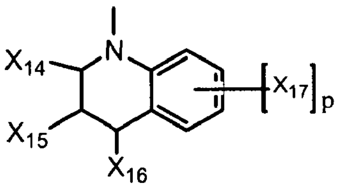
wherein:

(1) n is an integer chosen from 0, 1, 2, and 3, provided that if n is 0, U' is U, and each U is independently chosen for each occurrence from $-CH_2-$, $-CH(X_{12})-$, $-C(X_{12})_{2-}$, $-CH(X_{13})-$, $-C(X_{13})_2-$, and $-C(X_{12})(X_{13})-$, wherein X_{12} is chosen from a lengthening agent L represented by Formula I above and C_1-C_{12} alkyl, and X_{13} is chosen from a lengthening agent L represented by Formula I above, phenyl and naphthyl, and
(2) U' is chosen from U, -O-, -S-, -S(O)-, -NH-,$-N(X_{12})-$ or $-N(X_{13})-$, and m is an integer chosen from 1, 2, and 3; and

(J) a group represented by one of Formula ii or iii:



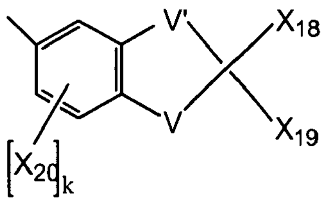
ii



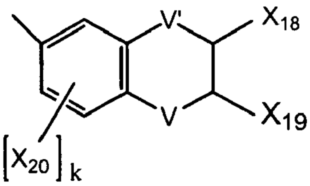
iii

wherein X_{14}, X_{15}, and X_{16} are independently chosen for each occurrence from a lengthening agent L represented by Formula I above, C_1-C_{12} alkyl, phenyl and naphthyl, or X_{14} and X_{15} together form a ring of 5 to 8 carbon atoms; p is an integer chosen from 0, 1, or 2, and X_{17} is independently chosen for each occurrence from a lengthening agent L represented by Formula I above, C_1-C_{12} alkyl, C_1-C_{12} alkoxy and halogen;

(vi) an unsubstituted or mono-substituted group chosen from pyrazolyl, imidazolyl, pyrazolinyl, imidazolinyl, pyrrolidinyl, phenothiazinyl, phenoxazinyl, phenazinyl and acridinyl, wherein each substituent is independently chosen from a lengthening agent L represented by Formula I above, C_1-C_{12} alkyl, C_1-C_{12} alkoxy, phenyl, hydroxy, amino and halogen;
(vii) a group represented by one of Formula iv or v:



iv

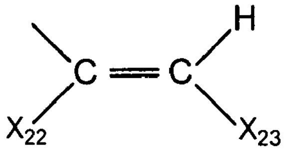


v

wherein

(A) V' is independently chosen in each formula from -O-, -CH-, C_1-C_6 alkylene, and C_3-C_7 cycloalkylene,
(B) V is independently chosen in each formula from -O- or $-N(X_{21})-$, wherein X_{21} is from a lengthening agent L represented by Formula I above, hydrogen, C_1-C_{12} alkyl, and C_2-C_{12} acyl, provided that if V is $-N(X_{21})-$, V' is $-CH_2-$,
(C) X_{18} and X_{19} are each independently chosen from a lengthening agent L represented by Formula I above, hydrogen and C_1-C_{12} alkyl, and
(D) k is chosen from 0, 1, and 2, and each X_{20} is independently chosen for each occurrence from a lengthening agent L represented by Formula I above, C_1-C_{12} alkyl, C_1-C_{12} alkoxy, hydroxy and halogen;

(viii) a group represented by Formula vi:

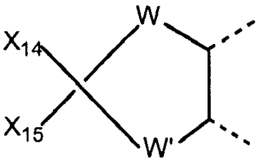


vi

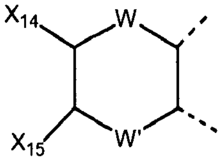
wherein

(A) X_{22} is chosen from a lengthening agent L represented by Formula I above, hydrogen and C_1-C_{12} alkyl, and
(B) X_{23} is chosen from a lengthening agent L represented by Formula I above or an unsubstituted, mono-, or di-substituted group chosen from naphthyl, phenyl, furanyl and thienyl, wherein each substituent is independently chosen for each occurrence from C_1-C_{12} alkyl, C_1-C_{12} alkoxy, and halogen;

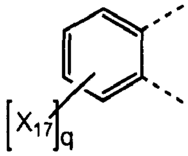
(ix) -C(O)X_{24}, wherein X_{24} is chosen from a lengthening agent L represented by Formula I above, hydroxy, C_1-C_{12} alkyl, C_1-C_{12} alkoxy, phenyl that is unsubstituted or mono-substituted with C_1-C_{12} alkyl or C_1-C_{12} alkoxy, amino that is unsubstituted, mono- or di-substituted with at least one of C_1-C_{12} alkyl, phenyl, benzyl, and naphthyl;
(x) -OX_7 and -N(X_7)$_2$, wherein X_7 is as set forth above;
(xi) -SX_{11}, wherein X_{11} is as set forth above;
(xii) the nitrogen containing ring represented by Formula iv, which is set forth above;
(xiii) the group represented by one of Formula v or vi, which are set forth above; and
(xiv) immediately adjacent R^1 groups together a group represented by one of Formula vii, viii, and ix:



vii



viii



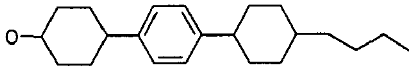
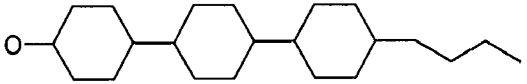
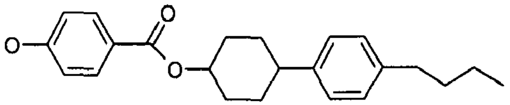
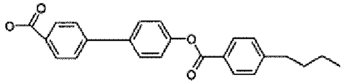
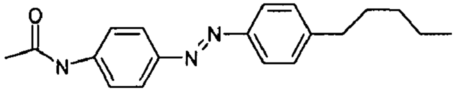
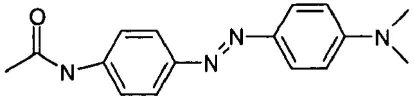
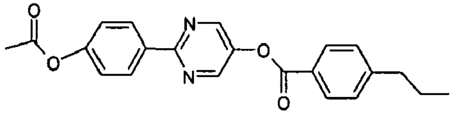
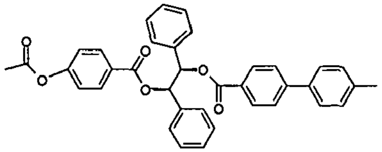
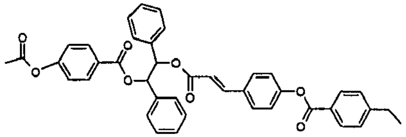
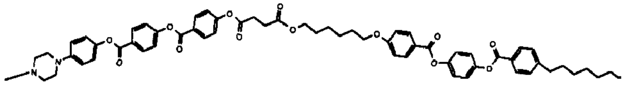
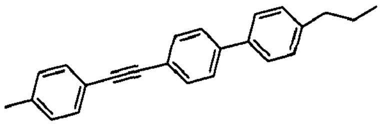
ix

wherein

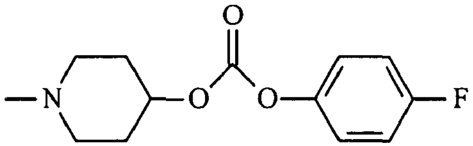
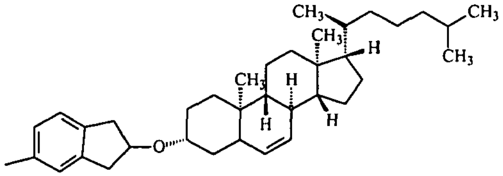
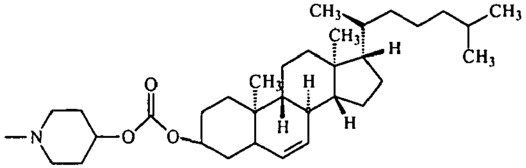
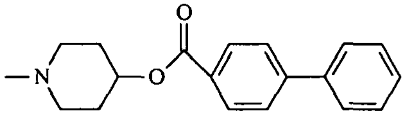
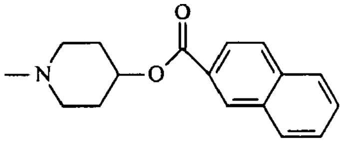
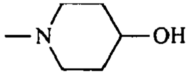
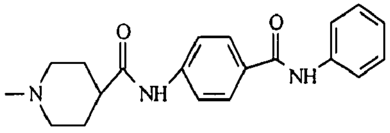
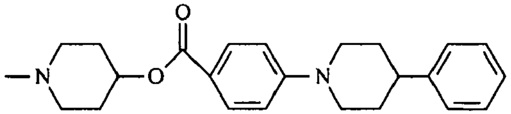
(A) W and W' are independently chosen for each occurrence from -O-, -N(X_7)-, -C(X_{14})-, -C(X_{17})-, (wherein X_7, X_{14}, and X_{17} are as set forth above),
(B) X_{14}, X_{15} and X_{17} are as set forth above, and
(C) q is an integer chosen from 0, 1, 2, 3, and 4.

[0040] According to non-limiting embodiments the at least one lengthening agent is chosen from one of the following compounds listed (and graphically represented) below in Table I.

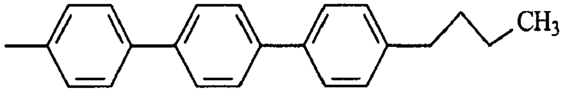
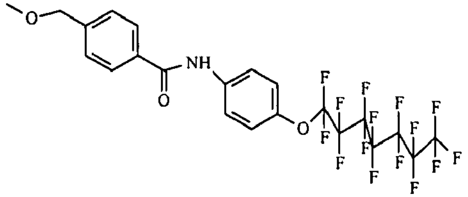
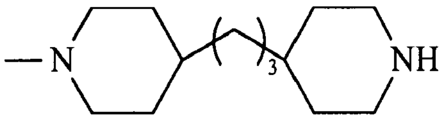
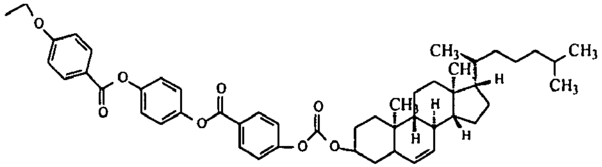
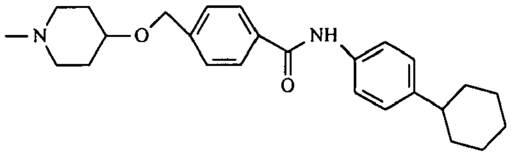
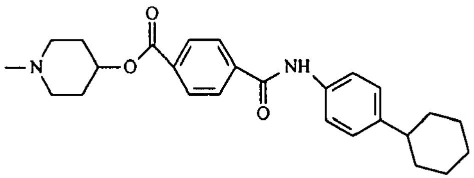
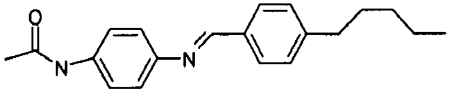
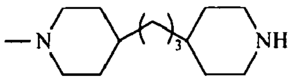
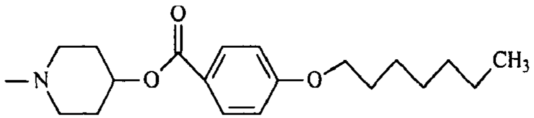
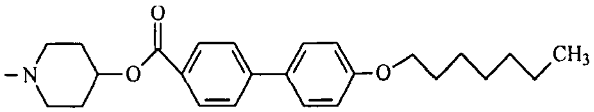
Table I:

(1) 4-[4-(4-butyl-cyclohexyl)-phenyl]-cyclohexyloxy 	(2) 4"-butyl-[1,1';4',1"]tercyclohexan-4-yloxy 
(3) 4-[4-(4-butyl-phenyl)-cylohexyloxycarbonyl]-phenoxy 	(4) 4'-(4-butyl-benzoyloxy)-biphenyl-4-carbonyloxy 
(5) 4-(4-pentyl-phenylazo)-phenylcarbamoyl 	(6) 4-(4-dimethylamino-phenylazo)-phenylcarbamoyl 
(7) {4-[5-(4-propyl-benzoyloxy)-pyrimidin-2-yl]-phenyl} ester 	(8) {4-[2-(4'-methyl-biphenyl-4-carbonyloxy)-1,2-diphenyl-ethoxycarbonyl]-phenyl} ester 
(9) [4-(1,2-diphenyl-2-{3-[4-(4-propyl-benzoyloxy)-phenyl]-acryloyloxy}-ethoxycarbonyl)-phenyl] ester 	(10) 4-[4-(4-{4-[3-(6-{4-[4-(4-nonyl-benzoyloxy)-phenoxycarbonyl]-phenoxy}-hexyloxycarbonyl)-propionyloxy]-benzoyloxy}-benzoyloxy)-phenyl]-piperazin-1-yl 
(11) {4-[4-(4-{4-[4-(4-nonyl-benzoyloxy)-benzoyloxy]-benzoyloxy}-benzoyloxy)-phenyl]-piperazin-1-yl}	(12) 4-(4'-propyl-biphenyl-4-ylethynyl)-phenyl 

(continued)

(13) 4-(4-fluoro-phenoxycarbonyloxy)-piperidin-1-yl 	(14) 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-yloxycarbonyloxy]-piperidin-1-yl 	(16) 4-(biphenyl-4-carbonyloxy)-piperidin-1-yl 
(17) 4-(naphthalene-2-carbonyloxy)-piperidin-1-yl 	(18) 4-hydroxy-piperidin-1-yl 
(19) 4-(4-phenylcarbamoyl-phenylcarbamoyl)-piperidin-1-yl 	(20) 4-(4-(4-phenylpiperidin-1-yl)-benzoyloxy)-piperidin-1-yl 
(21) 4-butyl-[1,1';4',1"]terphenyl-4-yl	(22) 4-(4-pentadecafluoroheptyloxy-phenylcarbamoyl)-benzyloxy

(continued)

	
(23) 4-(3-piperidin-4-yl-propyl)-piperidin-1-yl 	(24) 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-1 H-cyclopenta[a]phenanthren-3-yloxycarbonyloxy]-benzoyloxy}-phenoxycarbonyl)-phenoxymethyl 
(25) 4-[4-(4-cyclohexyl-phenylcarbamoyl)-benzyloxy]-piperidin-1-yl 	(26) 4-[4-(4-cyclohexyl-phenylcarbamoyl)-benzoyloxy]-piperidin-1-yl 
(27) N-{4-[(4-pentyl-benzylidene)-amino]-phenyl}-acetamidyl 	(28) 4-(3-piperidin-4-yl-propyl)-piperidin-1-yl 
(29) 4-(4-hexyloxy-benzoyloxy)-piperidin-1-yl] 	(30)4-(4'-hexyloxy-biphenyl-4-carbonyloxy)-piperidin-1-yl 
(31) 4-(4-butyl-phenylcarbamoyl)-piperidin-1-yl	(32) biphenyl-4,4'-dicarboxylic acid bis-[1-Name of PC Group]-piperidin-4-yl]ester

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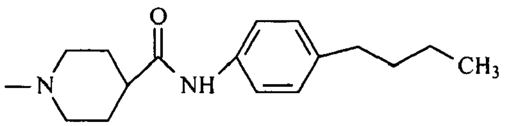
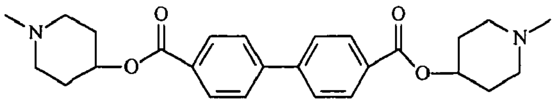
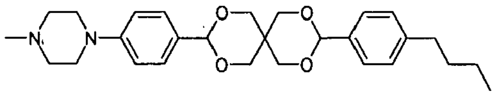
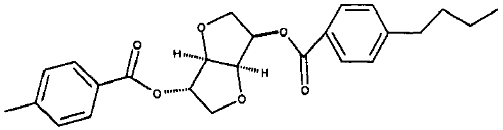
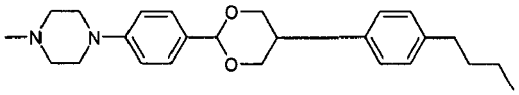
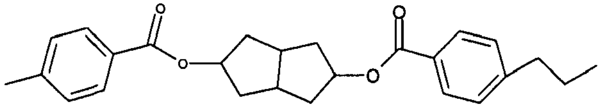
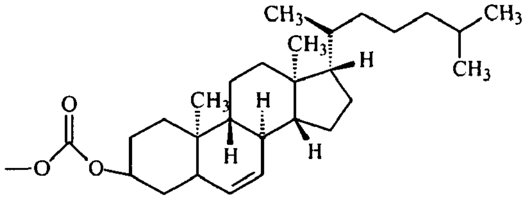
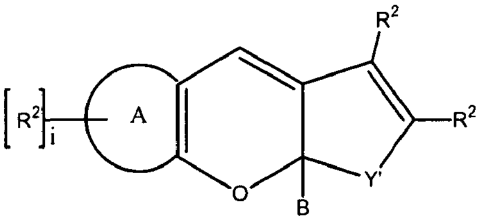
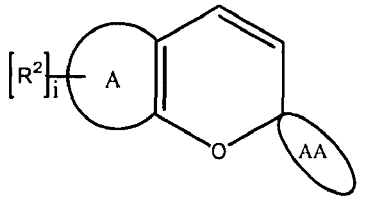
	
(33) 4-(4-(9-(4-butylphenyl)-2,4,8,10-tetraoxaspiro[5.5]undec-3-yl)phenyl)piperazin-1-yl 	(34) 4-(6-(4-butylphenyl)carbonyloxy-(4,8-dioxabicyclo[3.3.0]oct-2-yl))oxycarbonyl)pheny 
(35) 1-{4-[5-(4-butyl-phenyl)-[1,3]dioxan-2-yl]-phenyl}-4-methyl-piperazin-1-yl 	(36) 4-(7-(4-propylphenylcarbonyloxy)bicyclo[3.3.0]oct-2-yl)oxycarbonyl)phenyl 
(37) 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 	

[0041] The present invention provides a non-thermally reversible photochromic compound represented by one of Formula X and Formula XI:



X

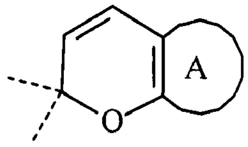


XI

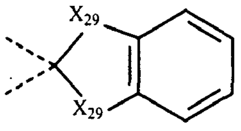
wherein:

(a) A is chosen from naphtho, benzo, phenanthro, fluorantheno, antheno, quinolino, thieno, furo, indolo, indolino, indeno, benzofuro, benzothieno, thiopheno, indeno-fused naphtho, heterocyclic-fused naphtho, and heterocyclic-fused benzo;

(b) AA is a group represented by one of Formula xv and xvi:



xv



xvi

wherein X_{29} is independently chosen from each occurrence form -C(R")(R")-, -O-, -S-, and -N(R"')-, wherein R" is independently chosen for each occurrence from hydrogen, a substituted or unsubstituted alkyl, cycloalkyl, arylalkyl, or together form cycloalkyl that is substituted or unsubstituted; R"' is independently chosen for each occurrence from an alkyl, aryl or arylalkyl group that is unsubstituted or substituted with at least one of:

(i) $-CH(CN)_2$ or $-CH(COOX_1)_2$ wherein X_1 is as set forth above;
(ii) $-CH(X_2)(X_3)$, wherein X_2 and X_3 are as set forth above;
(iii) $-C(O)X_{24}$, wherein X_{24} is as set forth above; and
(iv) halogen, hydroxy, ester, or amine;

(c) Y' is chosen from: $-(Y_1)C=C(Y_2)-$, -O-,-S-,-S(O)(O)-, and $-N(X_7)-$, wherein Y_1 and Y_2 together form benzo, naphtho, phenanthro, furo, thieno, benzofuro, benzothieno, and indolo; and X_7 is as set forth above;

(d) B is as set forth above;

(e) i is an integer chosen from 0 to 4, and each R^2 is independently chosen for each occurrence from the R^2 groups set forth above;

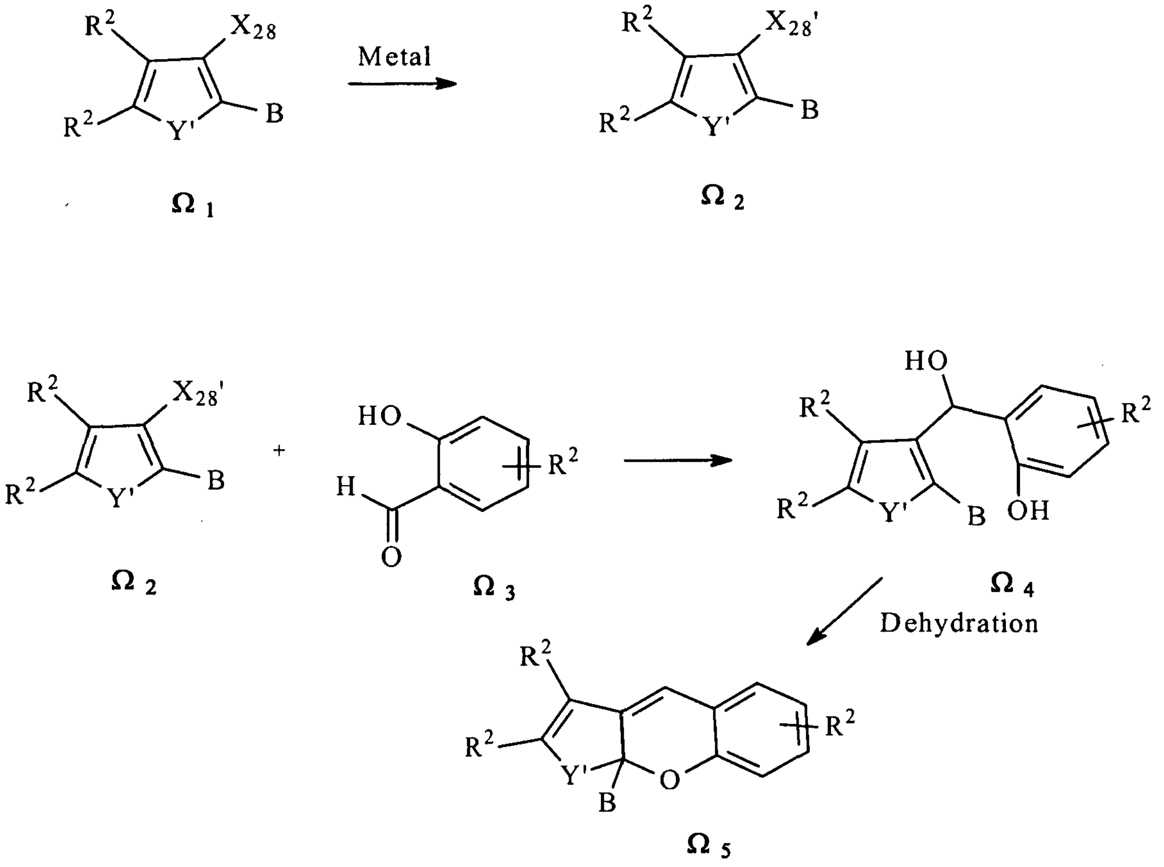
wherein lengthening agent L is independently chosen for each occurrence from a compound represented by Formula I.

[0042] Additionally, according to various non-limiting embodiments disclosed herein, the photochromic compound represented either of Formula X or XI comprises at least one lengthening agent (L) represented by Formula I above. As previously discussed, in Formula I, c, d, e, and f each can be independently chosen from an integer ranging from 1 to 20, inclusive; and d', e' and f' each can be independently chosen from 0, 1, 2, 3, and 4, provided that the sum of d' + e' + f' is at least 1. According to other non-limiting embodiments disclosed herein, c, d, e, and f each can be independently chosen from an integer ranging from 0 to 20, inclusive; and d', e' and f' each can be independently chosen from 0, 1, 2, 3, and 4, provided that the sum of d' + e' + f' is at least 2. According to still other non-limiting embodiments disclosed herein, c, d, e, and f each can be independently chosen from an integer ranging from 0 to 20, inclusive; and d', e' and f' each can be independently chosen from 0, 1, 2, 3, and 4, provided that the sum of d' + e' + f' is at least 3. According to still other non-limiting embodiments disclosed herein, c, d, e, and f each can be independently chosen from an integer ranging from 0 to 20, inclusive; and d', e' and f' each can be independently chosen from 0, 1, 2, 3, and 4, provided that the sum of d' + e' + f' is at least 1.

[0043] Thus, for example, in either of Formula X or XI, "i" can be at least 1 and at least one of the R^2 groups can be a lengthening agent L. Additionally or alternatively, the photochromic compound can comprise at least one R^2 group that is substituted with a lengthening agent L. Moreover, although not limiting herein, according to various non-limiting embodiments disclosed herein, the lengthening agent (L) can be attached to a photochromic group at any available position such that L extends or lengthens the photochromic group in an activated state such that the absorption ratio of the extended photochromic group (i.e., the photochromic compound) is enhanced as compared to the unextended photochromic group. Thus, for example and without limitation, according to various non-limiting embodiments wherein the photochromic compound is represented by Formula X, L can be directly bonded to the pyran group, for example, wherein i is at least 1 and R^2 is L, or it can be indirectly bonded to the pyran group, for example, as a substiutent on an R^2 or B group such that L extends the pyran group in an activated state such that the absorption ratio of the photochromic compound is enhanced as compared to the unextended pyran group. Further, for example and without limitation, according to various non-limiting embodiments wherein the photochromic compound is represented by Formula XI, L can be directly bonded to the pyran group, for example, wherein i is at least 1 and R^2 is L, or it can be indirectly bonded to the pyran group, for example, as a substiutent on an R^2 or the AA group such that L extends the pyran group in an activated state such that the absorption ratio of the photochromic compound is enhanced as compared to the unextended pyran group.

[0044] For example, although not limiting herein, a general reaction sequence for forming a non-thermally reversible photochromic compound represented by Formula X above (wherein A is benzo) is as follows:

Reaction Sequence W



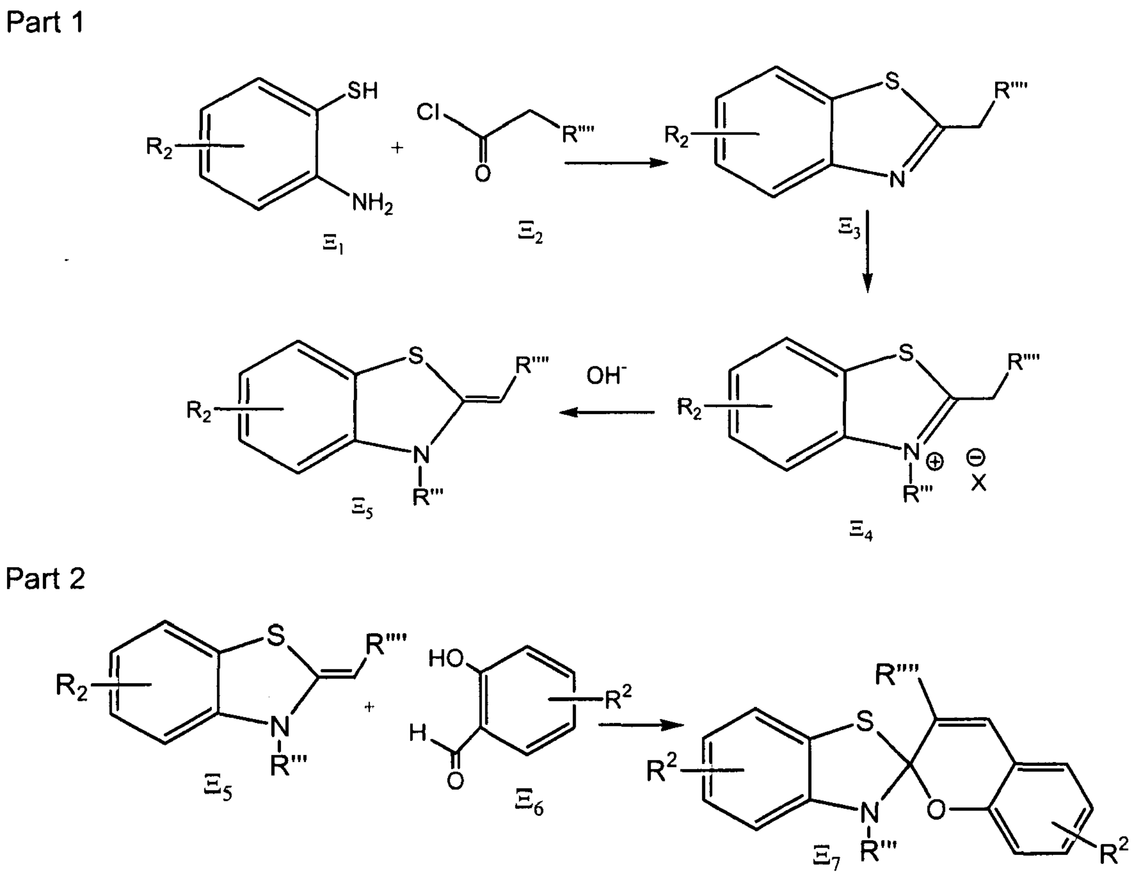
[0045] In Part 1 of Reaction Sequence W, X_{28} is a halogen such as Br, I, and Cl; and the metal is chosen from Li, Mg, Zn, and Sn; and X_{28}' is a metal salt, such as: LiX_{28}, MgX_{28}, ZnX_{28}, and SnX_{28}. Further, in Part A of Reaction Sequence

W, the B and halogen substituted compound represented by Formula Ω_1 is reacted with a metal in a halogen metal exchange reaction in an ether-like solvent such as, but not limited to, tetrahydrofuran to produce the metalated compound represented by Formula Ω_2.

[0046] In Part 2 of Reaction Sequence W, the metalated compound represented by Formula Ω_2 is reacted with an R^2 substituted salicylaldehyde derivative (represented by Formula Ω_3) in an ether-like sovent (such as but not limited to tetrahydrofuran) to produce the diol compound represented by Formula Ω_4. Thereafter, the diol compound represented by Formula Ω_4 is dehydrated with dehydration agents, such as but not limited to, magnesium sulfate, sodium sulfate, P_2O_5, molecular sieves, p-toluene sulfonic acids to produce the non-thermally reversible photochromic compound according to one non-limiting embodiment disclosed herein and represented by Formula Ω_5. Further, as discussed above with respect to Formula X, at least one R^2 group in the photochromic compound represented by Formula Ω_5, can be a lengthening agent L, or at least one R^2 group, B or Y' can comprise a group that is substituted with a lengthening agent L.

[0047] For example, although not limiting herein, a general reaction sequence for forming a non-thermally reversible photochromic compound represented by Formula XI above is as follows:

Reaction Sequence X



[0048] In Part 1 of Reaction Sequence X, an orthoaminothiophenol represented by Formula Ξ_1 is condensed with an acid chloride represented by Formula Ξ_2, wherein R'''' is chosen from hydrogen, a substituted or unsubstituted alkyl, cycloalkyl, and arylalkyl, in a solvet such as, but not limited to, chloroform to form the benzothiazole derivative represented by Formula Ξ_3. The benzothiazole derivative represented by Formula Ξ_3 is reacted with an alkyl halide, tosylate, or methylsulfonate, with or without solvents, to form the benzothiazolium quaternary salt represented by Formula Ξ_4. The benzothiazolium quaternary salt represented by Formula Ξ_4 is then reacted with a base, such as amine or hydroxide (which is shown) to give the benzothiozoline derivative represented by Formula Ξ_5.

[0049] In Part 2 of Reaction Sequence X, the benzothiozoline derivative represented by Formula Ξ_5 is condensed with an R^2 substituted salicylaldehyde derivative (represented by Formula Ξ_6) to produce the non-thermally reversible photochromic compound according to one non-limiting embodiment disclosed herein and represented by Formula Ξ_7. As previously discussed with respect to Formula XI above, in the photochoromic compound represented by Formula Ξ_7, at least one R^2 group can be a lengthening agent L (represented by Formula I above) or can be a group substituted with a lengthening agent L.

[0050] Another non-limiting embodiment provides a photochromic compound chosen from:

(a) 3-phenyl-3-(4-(4-piperidinopiperidino)phenyl)-13,13-dimethyl-indeno[2',3':3,4]naphtho[1,2-b]pyran;
(b) 3-phenyl-3-(4-(4-benzylpiperidino)phenyl)-13,13-dimethyl-indeno[2',3':3,4]naphtho[1,2-b]pyran;
(c) 3-phenyl-3-(4-(4-(3-piperidin-4-yl-propyl)piperidino)phenyl)-13,13-dimethyl-indeno[2',3':3,4]-naphtho[1,2-b]pyran;
(d) 3-phenyl-3-(4-(4-(3-(1-(2-hydroxyethyl)piperidin-4-yl)propyl)piperidino)phenyl)-13,13-dimethyl-indeno[2',3':3,4]naphtho[1,2-b]pyran;
(e) 3-phenyl-3-(4-(4-phenylpiperazine)phenyl)-13,13-dimethyl-indeno[2',3':3,4]naphtho[1,2-b]pyran;
(f) 3-phenyl-3-(4-(4-benzylpiperazine)phenyl)- 13,13-dimethyl-indeno[2',3':3,4]naphtho[1,2-b]pyran;
(g) 3-phenyl-3-(4-(4-hexyloxymethyl piperidino)phenyl)-13,13-dimethyl-indeno[2',3':3,4]naphtho[1,2-b]pyran;
(h) 3-phenyl-3-(4-(4-(4-butyl-phenylcarbamoyl)-piperidin-1-yl) phenyl)-13,13-dimethyl-6-methoxy-7-(4-phenyl-piperazin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran;
(i) 3-phenyl-3-(4-pyrrolidin-1-yl-phenyl)-13,13-dimethyl-6-methoxy-7-(4-phenyl-piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;
(j) 3-phenyl-3-(4-pyrrolidin-1-yl-phenyl)-13,13-dimethyl-6-methoxy-7-([1,4']bipiperidinyl-1"-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;
(k) 3-phenyl-3-(4-([1 ,4']bipiperidinyl-1'-yl)phenyl)-13,13-dimethyl-6-methoxy-7-([1,4']bipiperidinyl-1'-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;
(l) 3-phenyl-3-(4-([1,4']bipiperidinyl-1'-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-benzylpiperidin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran;
(m) 3-phenyl-3-(4-([1,4']bipiperidinyl-1'-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(piperadin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;
(n) 3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-phenyl-piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;
(o) 3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(biphenyl-4-carbonyloxy)-piperidin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;
(p) 3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-hexyloxy-benzoyloxy)-piperidin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran;
(q) 3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-hexylbenzoyloxy)-piperidin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran;
(r) 3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4'-octyloxy-biphenyl-4-carbonyloxy)-piperidin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;
(s) 3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-{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}-indeno[2',3':3,4]naphtho[1,2-b]pyran;
(t) 3-phenyl-3-(4-(4-pyrrolidinylphenyl)- 13,13-dimethyl-6-methoxy-7-(-{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}indeno[2',3':3,4]naphtho[1,2-b]pyran;
(u) 3-phenyl-3-(4-(1-hydroxypiperidin-1-yl)-phenyl)-13,13-dimethyl-6-methoxy-7-(4-phenyl-piperazin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran;
(v) 3-phenyl-3-{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}-phenyl)-13,13-dimethyl-6-methoxy-7-(4-phenyl-piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;
(w) 3-phenyl-3-(4-(4-hexylbenzoyloxy)-piperidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-hexylbenzoyloxy)-piperidin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;
(x) 3-phenyl-3-(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]-piperidin-1-yl}-phenyl)-13,13-dimethyl-6-methoxy-7-{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}-)indeno[2',3':3,4]naphtho[1,2-b]pyran;
(y) 3-phenyl-3-(4-{4-(biphenyl-4-carbonyloxy]-piperidin-1-yl}-phenyl)-13,13-dimethyl-6-methoxy-7-4-(4-(biphenyl-4-carbonyloxy)-piperidin-1-yl}-)indeno[2',3':3,4]naphtho[1,2-b]pyran;
(z) 3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(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-yloxycarbonyl]-piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;
(aa) 3-phenyl-3-(4-(4-hexylbenzoyloxy)-piperadin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-phenyl-piperazin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran;
(bb) 3-phenyl-3-(4-(4-fluorobenzoyloxy)-piperadin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-phenyl-piper-

azin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran;

(cc) 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-3-hydroxy-13-ethyl-6-methoxy-7-(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]-piperadin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran;

(dd) 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-hexylbenzoyloxy-piperadin-1-yl)-indeno[2',3':3,4] naphtho[1,2-b]pyran;

(ee) 3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-hexylbenzoyloxy)phenyl)piperazin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran;

(ff) 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(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-yloxycarbonyl]-piperazin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran;

(gg) 3-phenyl-3-(4-(4-phenylpiperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-phenyl-piperazin-1-yl)-4-oxo-butanoyl)-piperazine-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran;

(hh) 3-phenyl-3-(4-(4-phenylpiperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-fluorobenzoyloxy)phenyl)piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;

(ii) 3-phenyl-3-(4-(4-phenylpiperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-biphenylcarbonyloxy)phenyl)piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;

(jj) 3-phenyl-3-(4-(4-phenylpiperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4'-octyloxy-biphenyl-4-carbonyloxy)phenyl)piperazin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran;

(kk) 3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-hexyloxyphenylcarbonyloxy)phenyl) piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;

(ll) 3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-{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]-phenyl)-piperidin-1-yl}-indeno[2',3':3,4]naphtho[1,2-b]pyran;

(mm) 3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-(4-hexylbenzoyloxy)benzoyloxy)-phenyl)piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;

(nn) 3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-(4-(4-hexylbenzoyloxy)phenyl)piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;

(oo) 3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-(2-fluorobenzoyloxy)benzoyloxy)phenyl) piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;

(pp) 3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-(4-fluorobenzoyloxy)benzoyloxy)-phenyl)piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;

(qq) 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-(4-(4-hexylbenzoyloxy)phenyl)piperazin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran;

(rr) 3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-(4-(4-hexylbenzoyloxy)benzoyloxy)-benzoyloxy)phenyl)piperazin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran;

(ss) 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-hexylbenzoyloxy)-indeno[2',3':3,4] naphtho[1,2-b]pyran;

(tt) 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-hexylbenzoyloxy)benzoyloxy)-indeno[2',3':3,4]naphtho[1,2-b]pyran;

(uu) 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-hexylbenzoyloxy)benzoyloxy)benzoyloxy)indeno[2',3':3,4] naphtho[1,2-b]pyran;

(vv) 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-(4-hexylbenzoyloxy)benzoyloxy)-benzoyloxy)benzoyloxy)-indeno[2',3':3,4]naphtho[1,2-b]pyran;

(ww)3-phenyl-3-(4-(4-(4-methoxyphenyl)-piperazin-1-yl))phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(3-phenylprop-2-ynoyloxy)phenyl)piperazin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran;

(xx) 3-phenyl-3-(4-(4-(4-hexylbenzoyloxy)phenyl)piperazin-1-yl)phenyl-13,13-dimethyl-6-methoxy-7-(4-phenylpiperazin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran;

(yy) 3-phenyl-3-(4-(4'-octyloxybiphenyl-4-carbonyloxy)-piperazin-1-yl))phenyl)-13,13-dimethyl-6-methoxy-7-(4-(phenyl)-piperazin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran;

(zz) 3-phenyl-3-(4-(4-methoxyphenyl)piperazin-1-yl))phenyl)-13,13-dimethyl-6-methoxy-7-(3-(4-hexylbenzoyloxyphenyl)piperazin-1-yl)-indeno[2',3':3,4] naphtho[1,2-b]pyran;

(aaa) 3-(4-methoxyphenyl)-3-(4-(4-methoxyphenyl)piperazin-1-yl)phenyl)-13-ethyl-13-hydroxy-6-methoxy-7-(4-(4-(4-hexylbenzoyloxy)phenyl)piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran;

(bbb) 3-phenyl-3-{4-(pyrrolidin-1-yl)phenyl)-13-[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]-13-ethyl-6-methoxy-7-(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-yloxycarbonyloxy]-piperadin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran;

(ccc) 3-phenyl-3-(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]-piperidin-1-yl}-phenyl)-13-ethyl-13-hydroxy-6-methoxy-7-{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}-)indeno[2’,3’:3,4]naphtho[1,2-b]pyran;

(ddd) 3-phenyl-3-{4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-(3-phenyl-3-{4-(pyrrolidin-1-yl)phenyl}-13,13-dimethyl-6-methoxy-indeno[2’,3’:3,4]naphtho[1,2-b]pyran-7-yl)-piperadin-1-yl)oxycarbonyl)phenyl)phenyl)cabonyloxy)-indeno[2’,3’:3,4]naphtho[1,2-b]pyran;

(eee) 3-{4-[4-(4-methoxy-phenyl)-piperazin-1-yl]-phenyl}-3-phenyl-7-methoxycarbonyl-3H-naphtho[2,1-b]pyran;

(fff) 3-{4-[4-(4-methoxy-phenyl)-piperazin-1-yl]-phenyl}-3-phenyl-7-hydroxycarbonyl-3H-naphtho[2,1-b]pyran;

(ggg) 3-{4-[4-(4-methoxy-phenyl)-piperazin-1-yl]-phenyl}-3-phenyl-7-(4-phenyl-(phen-1-oxy)carbonyl)-3H-naphtho[2,1-b]pyran;

(hhh) 3-{4-[4-(4-methoxy-phenyl)-piperazin-1-yl]-phenyl}-3-phenyl-7-(N-(4-((4-dimethylamino)phenyl)diazenyl)phenyl)carbamoyl-3H-naphtho[2,1-b]pyran;

(iii) 2-phenyl-2-{4-[4-(4-methoxy-phenyl)-piperazin-1-yl]-phenyl}-benzofuro[3’,2’:7,8] benzo[b]pyran;

(jjj) 2-phenyl-2-{4-[4-(4-methoxy-phenyl)-piperazin-1-yl]-phenyl}-benzothieno[3’,2’:7,8] benzo[b]pyran;

(kkk) 7-{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}-2-phenyl-2-(4-pyrrolidin-1-yl-phenyl)-6-methoxycarbonyl-2H-benzo[b]pyran;

(lll) 2-phenyl-2-{4-[4-(4-methoxy-phenyl)-piperazin-1-yl]-phenyl}-9-hydroxy-8-methoxycarbonyl-2H-naphtho[1,2-b]pyran;

(mmm) 2-phenyl-2-{4-[4-(4-methoxy-phenyl)-piperazin-1-yl]-phenyl}-9-hydroxy-8-(N-(4-butyl-phenyl))carbamoyl-2H-naphtho[1,2-b]pyran;

(nnn) 2-phenyl-2-{4-[4-(4-methoxy-phenyl)-piperazin-1-yl]-phenyl}-9-hydroxy-8-(N-(4-phenyl)phenyl) carbamoyl-2H-naphtho[1,2-b]pyran;

(ooo) 1,3,3-trimethyl-6’-(4-ethoxycarbonyl)-piperidin-1-yl)-spiro[indoline-2,3’-3H-naphtho[2,1-b][1,4]oxazine];

(ppp) 1,3,3-trimethyl-6’-(4-[N-(4-butylphenyl)carbamoyl]-piperidin-1-yl)-spiro[indoline-2,3’-3H-naphtho[2,1-b][1,4]oxazine];

(qqq) 1,3,3-trimethyl-6’-(4-(4-methoxyphenyl)piperazin-1-yl)-spiro[indoline-2,3’-3H-naphtho[2,1-b][1,4]oxazine];

(rrr) 1,3,3-trimethyl-6’-(4-(4-hydroxyphenyl)piperazin-1-yl)-spiro[indoline-2,3’-3H-naphtho[2,1-b][1,4]oxazine];

(sss) 1,3,3,5,6-pentamethyl-7’-(4-(4-methoxyphenyl)piperazin-1-yl)-spiro[indoline-2,3’-3H-naphtho[2,1-b][1,4]oxazine];

(ttt) 1,3-diethyl-3-methyl-5-methoxy-6’-(4-(4’-Hexyloxy-biphenyl-4-carbonyloxy)-piperidin-1-yl)-spiro[indoline-2,3’-3H-naphtho[2,1-b][1,4]oxazine];

(uuu) 1,3-diethyl-3-methyl-5-[4-(4-pentadecafluoroheptyloxy-phenylcarbamoyl)-benzyloxy]-6’-(4-(4’-hexyloxy-biphenyl-4-carbonyloxy)-piperidin-1-yl)-spiro[indoline-2,3’-3H-naphtho[2,1-b][1,4]oxazine];

(vvv) 2-phenyl-2-{4-[4-(4-methoxy-phenyl)-piperazin-1-yl]-phenyl}-5-carbomethoxy-8-(N-(4-phenyl)phenyl) carbamoyl-2H-naphtho[1,2-b]pyran;

(www) 2-phenyl-2-{4-[4-(4-methoxy-phenyl)-piperazin-1-yl]-phenyl}-5-carbomethoxy-8-(N-(4-phenyl)phenyl) carbamoyl-2H-fluoantheno[1,2-b]pyran;

(xxx) 2-phenyl-2-{4-[4-(4-methoxy-phenyl)-piperazin-1-yl]-phenyl}-5-carbomethoxy-11-(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}phenyl)-2H-fluoantheno[1,2-b]pyran;

(yyy) 1-(4-carboxybutyl)-6-(4-(4-propylphenyl)carbonyloxy)phenyl)-3,3-dimethyl-6’-(4-ethoxycarbonyl)-piperidin-1-yl)-spiro[(1,2-dihydro-9H-dioxolano[4’,5’:6,7]indoline-2,3’-3H-naphtho[2,1-b][1,4]oxazine];

(zzz) 1-(4-carboxybutyl)-6-(4-(4-propylphenyl)carbonyloxy)phenyl)-3,3-dimethyl-7’-(4-ethoxycarbonyl)-piperidin-1-yl)-spiro[(1,2-dihydro-9H-dioxolano[4’,5’:6,7]indoline-2,3’-3H-naphtho[1,2-b][1,4]oxazine];

(aaaa) 1,3-diethyl-3-methyl-5-(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}phenyl)-6’-(4-(4’-hexyloxy-biphenyl-4-carbonyloxy)-piperidin-1-yl)-spiro[indoline-2,3’-3H-naphtho[2,1-b][1,4]oxazine];

(bbbb) 1-butyl-3-ethyl-3-methyl-5-methoxy-7’-(4-(4’-Hexyloxy-biphenyl-4-carbonyloxy)-piperidin-1-yl)-spiro[indoline-2,3’-3H-naphtho[1,2-b][1,4]oxazine];

(cccc) 2-phenyl-2-{4-[4-(4-methoxy-phenyl)-piperazin-1-yl]-phenyl}-5-methoxycarbonyl-6-methyl-2H-9-(4-(4-propylphenyl)carbonyloxy)phenyl)(1,2-dihydro-9H-dioxolano[4’,5’:6,7] naphtho[1,2-b]pyran;

(dddd) 3-(4-methoxyphenyl)-3-(4-(4-methoxyphenyl)piperazin-1-yl)phenyl)-13-ethyl-13-hydroxy-6-methoxy-7-(4-(4-propylphenyl)carbonyloxy)phenyl)-[1,2-dihydro-9H-dioxolano[4",5":6,7]][indeno[2’,3’:3,4]]naphtho[1,2-b]pyran;

(eeee) 3-phenyl-3-(4-(4-methoxyphenyl)piperazin-1-yl)phenyl)-13-ethyl-13-hydroxy-6-methoxy-7-(4-(4-hexylphenyl)carbonyloxy)phenyl)-[1,2-dihydro-9H-dioxolano[4",5":5,6]][indeno[2’,3’:3,4]] naphtho[1,2-b]pyran;

(ffff) 4-(4-((4-cyclohexylidene-1-ethyl-2,5-dioxopyrrolin-3-ylidene)ethyl)-2-thienyl)phenyl-(4-propyl)benzoate;

(gggg) 4-(4-((4-adamantan-2-ylidene-1-(4-(4-hexylphenyl)carbonyloxy)phenyl)-2,5-dioxopyrrolin-3-ylidene)ethyl)-2-thienyl)phenyl-(4-propyl)benzoate;

(hhhh) 4-(4-((4-adamantan-2-ylidene-2,5-dioxo-1-(4-(4-(4-propylphenyl)piperazinyl)phenyl)pyrrolin-3-ylidene)ethyl)-2-thienyl)phenyl (4-propyl)benzoate;

(iiii) 4-(4-((4-adamantan-2-ylidene-2,5-dioxo-1-(4-(4-(4-propylphenyl)piperazinyl)phenyl)pyrrolin-3-ylidene)ethyl)-1-methylpyrrol-2-yl)phenyl (4-propyl)benzoate;

(jjjj) 4-(4-((4-adamantan-2-ylidene-2,5-dioxo-1-(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}phenyl)pyrrolin-3-ylidene)ethyl)-1-methylpyrrol-2-yl)phenyl (4-propyl)benzoate;

(kkkk) 4-(4-methyl-5,7-dioxo-6-(4-(4-(4-propylphenyl)piperazinyl)phenyl)spiro[8,7a-dihydrothiapheno[4,5-f]isoindole-8,2'-adamentane]-2-yl)phenyl (4-propyl) phenyl benzoate;

(llll) N-(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}phenyl -6,7-dihydro-4-methyl-2-phenylspiro(5,6-benzo[b]thiophenedicarboxyimide-7,2-tricyclo[3.3.1.1]decane);

(mmmm) N-cyanomethyl-6,7-dihydro-2-(4-(4-(4-propylphenyl)piperazinyl)phenyl)-4-methylspiro(5,6- benzo[b]thiophenedicarboxyimide-7,2-tricyclo[3.3.1.1] decane);

(nnnn) N-phenylethyl-6,7-dihydro-2-(4-(4-(4-hexylbenzoyloxy)phenyl)piperazin-1-yl)phenyl-4-methylspiro(5,6- benzo[b]thiophenedicarboxyimide-7,2-tricyclo[3.3.1.1] decane);

(oooo) N-phenylethyl-6,7-dihydro-2-(4-(4-(4-hexylbenzoyloxy)phenyl)piperazin-1-yl)phenyl-4-cyclopropyl spiro(5,6-benzo[b]thiophenedicarboxyimide-7,2-tricyclo[3.3.1.1] decane);

(pppp) N-phenylethyl-6,7-dihydro-2-(4-(4-(4-hexylbenzoyloxy)phenyl)piperazin-1-yl)phenyl-4-cyclopropyl spiro(5,6-benzo[b]furodicarboxyimide-7,2-tricyclo[3.3.1.1] decane);

(qqqq) N-cyanomethyl-6,7-dihydro-4-(4-(4-(4-hexylbenzoyloxy)phenyl)piperazin-1-yl)phenyl-2-phenylspiro(5,6-benzo[b]thiophenedicarboxyimide-7,2-tricyclo[3.3.1.1] decane);

(rrrr) N-[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-yloxycarbonyl -6,7-dihydro-2-(4-methoxyphenyl)phenyl-4-methylspiro(5,6-benzo[b]thiophenedicarboxyimide-7,2-tricyclo[3.3.1.1] decane);

(ssss) N-cyanomethyl-2-(4-(6-(4-butylphenyl)carbonyloxy-(4,8-dioxabicyclo[3.3.0]oct-2-yl))oxycarbonyl)phenyl -6,7-dihydro-4-cyclopropylspiro(5,6-benzo[b] thiophenedicarboxyimide-7,2-tricyclo[3.3.1.1]decane);

(tttt) 6,7-dihydro-N-methoxycarbonylmethyl-4-(4-(6-(4-butylphenyl)carbonyloxy-(4,8-dioxabicyclo[3.3.0]oct-2-yl))oxycarbonyl)phenyl-2-phenylspiro(5,6-benzo[b]thiophenedicarboxyimide-7,2-tricyclo[3.3.1.1] decane);

(uuuu) 3-phenyl-3-(4-(4-phenyi-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-(4-(6-(4-(4-(4-(4-nonylphenylcabonyloxy)phenyl)oxycarbonyl)phenoxy)hexyloxy)benzoyloxy)phenyl) piperazin-1-yl)indeno[2',3':3,4] naphtho[1 ,2-b]pyran;

(vvvv) 3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-(4-(4-(4-(6-(4-(4-(4-(4-nonylphenylcabonyloxy)phenyl)oxycarbonyl)phenoxy)hexyloxy)benzoyloxy)phenyl) piperazin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran; and

(wwww) 3-phenyl-3-(4-pyrrolidinylphenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-(4-(6-(4-(4-(4-nonylphenylcabonyloxy)phenyl)oxycarbonyl)phenoxy)hexyloxy)phenyl)piperazin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran.

[0051] The thermally reversible photochromic compounds according to various non-limiting embodiments disclosed herein can be used in a variety of applications to provide photochromic and/or dichroic properties.

[0052] One non-limiting embodiment provides a photochromic article comprising an organic host material and a photochromic amount of the photochromic compound comprising at least one photochromic group chosen from pyrans, oxazines, and fulgides; and (b) at least one lengthening agent L represented by Formula I and attached to the at least one photochromic group, 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, according to this non-limiting embodiment, 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.

[0053] Non-limiting examples of organic host materials that may be used in conjunction with various non-limiting embodiments disclosed herein include polymeric materials, for example, 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. For example, such 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.

[0054] According to one specific non-limiting embodiment, the organic host material is chosen from polyacrylates, polymethacrylates, poly(C_1-C_{12}) 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(styreneacrylonitrile), 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.

[0055] 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.

[0056] 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, and active and passive liquid crystal cell elements and devices.

[0057] 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.

[0058] For example, in one non-limiting embodiment, the organic host material is an ophthalmic element, and more particularly, is an ophthalmic lens.

[0059] 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 those photochromic pyrans, oxazines, fulgides, and fulgimides set forth above. Other complementary photochromic compounds include, for example, photochromic metal-dithizonates, for example mercury dithizonate, which are described in U.S. Patent No. 3,361,706.

[0060] 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.

[0061] Another non-limiting embodiment 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 comprising (a) at least one photochromic group chosen from pyrans, oxazines, and fulgides; and (b) at least one lengthening agent L represented by Formula I and attached to the at least one photochromic group, 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.

[0062] 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.

[0063] 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.

[0064] Still other non-limiting embodiments provide optical elements comprising a substrate and an at least partial coating comprising at least one photochromic compound comprising (a) at least one photochromic group chosen from pyrans, oxazines, and fulgides; and (b) at least one lengthening agent L represented by Formula I and attached to the at least one photochromic group, 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, according to one non-limiting embodiment, the optical element is an ophthalmic element, and the substrate is an ophthalmic substrate chosen from corrective and non-corrective lenses, partially formed lenses, and lens blanks.

[0065] Although not limiting herein, the optical elements according to various non-limiting embodiments disclosed herein 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.

[0066] 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, and reflective substrates. 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.

[0067] 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, in one non-limiting embodiment, 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.

[0068] One specific non-limiting embodiment provides an optical element comprising a substrate and an at least partial coating comprising at least one photochromic compound comprising (a) at least one photochromic group chosen from pyrans, oxazines, and fulgides; and (b) at least one lengthening agent L represented by Formula I and attached to the at least one photochromic group connected to at least a portion of the substrate. Further, according to this non-limiting embodiment, the at least one thermally reversible photochromic compound can be a photochromic-dichroic compound having an average absorption ratio greater than 2.3 in an activated state as determined according to CELL METHOD.

[0069] As discussed above, the optical elements according to various non-limiting embodiments disclosed herein can be display elements, such as, but not limited to screens, monitors, and security elements. For example, one non-limiting embodiment provides 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 comprising (a) at least one photochromic group chosen from pyrans, oxazines, and fulgides; and (b) at least one lengthening agent L represented by Formula I and attached to the at least one photochromic group 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 2.3 in an activated state as determined according to CELL METHOD.

[0070] 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.

[0071] Another non-limiting embodiment provides a security element comprising a substrate and at least one photochromic compound comprising (a) at least one photochromic group chosen from pyrans, oxazines, and fulgides; and (b) at least one lengthening agent L represented by Formula I and attached to the at least one photochromic group 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.

[0072] Although not limiting herein, according to this non-limiting embodiment, the security element can be connected to at least a portion of a substrate chosen from a transparent substrate and a reflective substrate. Alternatively, according to certain non-limiting embodiments 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.

[0073] Additionally, according to the aforementioned non-limiting embodiment the at least one photochromic compound can be a thermally reversible photochromic-dichroic compound having an average absorption ratio greater than 2.3 in the activated state as determined according to CELL METHOD.

[0074] Furthermore, security element according to the aforementioned non-limiting embodiment can further comprise one or more other coatings or sheets to form a multilayer reflective security element with viewing angle dependent characteristics as described in U.S. Patent 6,641,874.

[0075] 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.

[0076] 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.

[0077] 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 preformed film having a generally uniform thickness and capable of self-support.

[0078] 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. According to one non-limiting embodiment, a coating comprising the photochromic compound is applied to a mold and the substrate is 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.

[0079] 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.

[0080] 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.

EXAMPLES

[0081] Various embodiments disclosed herein will now be illustrated in the following non-limiting examples.

Example 1

Step 1

[0082] 4-Fluorobenzophenone (64.5 g) and anhydrous dimethyl sulfoxide (DMSO) (200 ml) were added to a reaction flask under nitrogen. 1-phenylpiperazine (36.2 g) was added, and the suspension was heated to 180 °C. After 2 hours, heat was removed, and the mixture was poured into 4 liters of water. The precipitate was collected by vacuum filtration, washed with water, dried in vacuum and recrystallized from acetone/methanol. GC/MS data showed that the resulting product (55 g, 89 % yield), recovered as off-white crystals, has a structure consistent with 4-(4-phenylpiperazin-1-yl)benzophenone.

Step 2

[0083] 4-(4-phenylpiperazin-1-yl)benzophenone (55 g) from Step 1 and dimethylformamide (DMF) (300 mL, saturated with acetylene) were added to a reaction flask. A sodium acetylide suspension (64 g of a 18 weight percent slurry in toluene, obtained from Aldrich) was added to the mixture with stirring. After 20 minutes, the reaction was poured into a stirred mixture of deionized water (3 L) and hexanes (500 ml). The solid formed was collected by vacuum filtration and dried in vacuum. An NMR spectrum showed that the final product (59 g, 99.7 % yield), an off-white powder, had a structure consistent with 1-phenyl-1-(4-phenylpiperazin-1-yl)phenyl)-prop-2-yn-1-ol.

Step 3

[0084] N-Phenylpiperazine (31.3 g, 187 millimole (mmol)), 2,3-dimethoxy-7,7-dimethyl-7H-benzo[c]fluoren-5-ol (40 g, 125 mmol) and THF (200 mL) were added to a 2 liter round-bottomed flask equipped with a bubbler and magnetically stirred at room temperature. A solution of 1.6 M methyl lithium in ethyl ether (234 mL, 375 mmol) was added to the mixture slowly via a dropping funnel under a nitrogen atmosphere. Gas evolution and boiling of the solvent was observed and 200 mL of the solvent was removed from the flask by distillation. The remaining mixture was refluxed for 10 hours and then poured into 400 mL water. Hydrochloric acid (HCl) (3 N) was added to the mixture with stirring until a pH value of 4-6 was obtained. Ethyl acetate (300 mL) was then added to the mixture. The crystalline precipitate was collected by vacuum filtration. The organic layer was separated, dried and concentrated. The resulting oil was crystallized by the addition of ethyl acetate and collected by vacuum filtration. The recovered solids were combined and washed with acetone. White crystals (45.7 g) were obtained as the product. The product was characterized by NMR and MS to have a structure consistent with 7,7-dimethyl-2-(4-phenylpiperazin-1-yl)-3-methoxy-7H-benzo[c]fluoren-5-ol.

Step 4

[0085] 1-phenyl-1-(4-phenylpiperazin-1-yl)phenyl)-prop-2-yn-1-ol (1.84 g, 5 mmol) from step 2, 7,7-dimethyl-2-(4-phenylpiperazin-1-yl)-3-methoxy-7H-benzo[c]fluoren-5-ol from Step 3 (1.5 g, 3.33 mmol), 3 Å molecular sieves (2 g) and chloroform (80 mL) were added to a 250 mL flask equipped with a dropping funnel and stirred at room temperature. A chloroform solution of trifluoroacetic acid (0.3 M, 4 mL) was added dropwise to the reaction flask via the dropping funnel. A gray color was obtained. The resulting reaction mixture was refluxed for 8 hours. Molecular sieves were removed by filtration over a pad of Celite. The chloroform solution was washed with a saturated sodium bicarbonate water solution, dried over magnesium sulfate and concentrated. The recovered product was purified by flash chromatography on silica gel (eluent: 20/80 ethyl acetate/hexanes). The recovered solid was further purified by dissolution in $CHCl_3$ and precipitation from methanol to yield a gray solid (2.1 g). The final product was identified by NMR as having a structure consistent with 3-phenyl-3-(4-pyrrolidin-1-yl-phenyl)-13,13-dimethyl-6-methoxy-7-(4-phenyl-piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 2

[0086] The procedures of Step 1, Step 2 and Step 4 of Example 1 were followed except that in Step 1, 4-piperidinopiperidine was used in place of 1-phenylpiperazine and in Step 4, 7,7-dimethyl-7H-benzo[c]fluoren-5-ol was used in place of 7,7-dimethyl-2-(4-phenylpiperazin-1-yl)-3-methoxy-7H-benzo[c]fluoren-5-ol. The recovered final product was a blue solid. An NMR spectrum showed that the final product had a structure consistent with 3-phenyl-3-(4-(4-piperidinopiperidino)phenyl)-13,13-dimethyl-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 3

Step 1

[0087] 2,3-Dimethoxy-5-hydroxy-7H-benzo[C]fluoren-7-one, the product of Step 5 of Example 14 of U.S. Patent 6,296,785 (50.13 g, 0.164 mol) and THF (500 ml) were added to a flask equipped with a bubbler under a nitrogen atmosphere and stirred at room temperature. A solution of 25 weight percent ethylmagnesium chloride in THF (124 ml, 0.36 mol) was added slowly and carefully causing the evolution of gas. The addition was completed in 30 minutes. The reaction was exothermic and caused the THF to boil. After 10 minutes, a water solution of 3 N HCl was added slowly with vigorous stirring until a slightly acidic mixture was obtained. A saturated sodium bicarbonate water solution was added. The organic layer was separated and the water layer was extracted with ethyl acetate. The recovered organic solutions were combined, dried over magnesium sulfate and concentrated. Crystals precipitated during the evaporation of the solvent. Chloroform was added to help with crystallization. The product was collected by vacuum filtration as white crystals (47.7 g). An NMR spectrum showed the product to have a structure consistent with 7-ethyl-2,3-dimethoxy-7H-benzo[c]fluorene-5,7-diol.

Step 2

[0088] N-Phenylpiperazine (7.23 g, 44.6 mmol), 7-ethyl-2,3-dimethoxy-7H-benzo[c]fluorene-5,7-diol (10 g, 30 mmol) from Step 1 and THF (200 mL) were added to a flask and magnetically stirred at room temperature under a nitrogen atmosphere. A solution of 1.6 M methyl lithium in ethyl ether (93 mL, 149 mmol) was added to the mixture slowly via a dropping funnel. A 100 mL amount of the solvents was distilled out of the flask. The remaining mixture was refluxed for 2 days. The resulting reaction mixture was poured into a flask containing water (200 mL), acidified to pH 4 by the addition of 3 N HCl. Ethyl acetate (100 mL) was added to the mixture and the resulting crystalline precipitate was collected by vacuum filtration, washed with water and acetone and air-dried. White crystals (6.77 g) were recovered as the product. An NMR spectrum showed that the resulting product had a structure consistent with 7-ethyl-3-methoxy-2-(4-phenylpiperazin-1-yl)-7H-benzo[c]fluorene-5,7-diol.

Step 3

[0089] The procedure of Step 4 of Example 1 was followed except that 1-phenyl-1-(4-(4-hydroxypiperidin-1-yl)-phenyl)-prop-2-yn-1-ol from Example 6 was used in place of 1-phenyl-1-(4-phenylpiperazin-1-yl)phenyl)-prop-2-yn-1-ol and 7-ethyl-3-methoxy-2-(4-phenyl-piperazin-1-yl)-7H-benzo[c]fluorene-5,7-diol was used in place of 7,7-dimethyl-2-(4-phenylpiperazin-1-yl)-3-methoxy-7H-benzo[c]fluoren-5-ol. An NMR spectrum showed that the resulting product, a black solid, had a structure consistent with 3-phenyl-3-(4-(4-hydroxypiperadin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-phenyl-piperazin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Step 4

[0090] The product of Step 3 (0.5 g, 0.66 mmol), 4-hexylbenzoylchloride (0.42 g, 1.9 mmol) and pyridine (10 mL) were added to a reaction flask and stirred at room temperature for 4 hours. The resulting mixture was poured into a beaker containing 100 mL of water. The resulting precipitate was dissolved in chloroform, dried over magnesium sulfate, concentrated and flash-chromatographed from silica gel using as an eluent: 2/8 (volume/volume) ethyl acetate/hexanes. The recovered solid was further purified by dissolution in $CHCl_3$ and precipitation from methanol to yield a black solid (0.44 g). An NMR spectrum showed that the final product had a structure consistent with 3-phenyl-3-(4-(4-(4-hexylbenzoyloxy)-piperadin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-phenyl-piperazin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 4

Step 1

[0091] The procedure of Example 1 was followed except that in Step 1, pyrrolidine was used in place of 1-phenylpiperazine and in Step 3, 4-hydroxypiperidine was used in place of 1-phenylpiperazine. An NMR spectrum showed that the final product, recovered as purple crystals, had a structure consistent with 3-phenyl-3-(4-(pyrrolidin-1-yl)-phenyl)-13,13-dimethyl-6-methoxy-7-(4-hydroxypiperadin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran.

Step 2

[0092] 3-phenyl-3-(4-(pyrrolidin-1-yl)-phenyl)-13,13-dimethyl-6-methoxy-7-(4-hydroxypiperadin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran from Step 1 (1.5 g, 2.3 mmol), 4,4'-biphenyldicarboxylic acid (0.27 g, 1.1 mmol), dicyclohexyl carbodiimide (0.48 g, 2.3 mmol), 4-(dimethylamino)-pyridine (0.03 g, 0.23 mmol) and dichloromethane (40 mL) were added to a flask and heated under reflux for 36 hours. The solid produced was removed by filtration and the remaining solution was concentrated. The resulting solid crude product was purified by flash chromatography (3/7 ethyl acetate/hexanes, volume ratio). The recovered solid was further purified by dissolution in $CHCl_3$ and precipitation from methanol. An NMR spectrum showed that the final product, a purple solid (0.47 g), had a structure consistent with Biphenyl-4,4'-dicarboxylic acid bis-{1-[6-methoxy-13,13-dimethyl-3-phenyl-3-(4-pyrrolidin-1-yl-phenyl)-3H,13H-indeno[2',3':3,4]naphtha[1,2-b]pyran-7-yl]-piperidin-4-yl} ester.

Example 5

Step 1

[0093] The procedure of Step 1, Step 2 and Step 3 of Example 7 was followed except that 4-hydroxypiperidine was used in place of N-phenylpiperazine in Step 2 and 1-phenyl-1-(4-pyrrolidin-1-yl-phenyl)-prop-2-yn-1-ol (one intermediate from Step 1 of Example 4) was used in place of 1-phenyl-1-(4-(4-hydroxypiperidin-1-yl)-phenyl)-prop-2-yn-1-ol in Step 3. An NMR spectrum showed that the final product, a purple solid, had a structure consistent with 3-phenyl-3-(4-pyrrolidinophenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-hydroxypiperadin-1-yl)-indeno[2',3':3,4] naphtho[1,2-b]pyran.

Step 2

[0094] A mixture of 3-phenyl-3-(4-pyrrolidinophenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-hydroxypiperadin-1-yl)-indeno[2',3':3,4] naphtho[1,2-b]pyran from Step 1 (4.0 g, 6 mmol) and tetrahydrofuran (THF) (200 mL) was added to a reaction flask and stirred at room temperature under a nitrogen atmosphere. A 2 M solution of lithium diisopropyl amide in a mixture of THF and hexanes solvents available from ACROS Organics (12 mL, 24 mmol) was added via a syringe. Cholesteryl chloroformate (2.7 g, 6 mmol) was added at -78 °C and the resulting mixture was warmed up to room temperature and stirred for half an hour at room temperature. The reaction mixture was poured into water (1500 mL), acidified with 3 N HCl followed by neutralization of the excess acid by saturated sodium bicarbonate water solution, extracted with ethyl acetate, dried over magnesium sulfate, concentrated and flash chromatographed using 3:7 (volume:volume) ethyl acetate:hexanes as the eluent. Two products were obtained, which correspond to mono-adduct and di-adduct respectively. An NMR showed that the di-adduct product (0.666 g) had a structure consistent with 3-phenyl-3-{4-(pyrrolidin-1-yl)phenyl)-13-{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}-13-ethyl-6-methoxy-7-(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]-piperadin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 6

[0095] The procedure of Example 3 was followed except that 4-hydroxypiperidine was used in place of N-phenylpiperazine in Step 2 and cholesteryl chloroformate was used in place of hexylbenzoylchloride in Step 4. An NMR spectrum showed that the resulting product, an off-white solid, had a structure consistent with 3-phenyl-3-(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]-piperidin-1-yl}-phenyl)-13-ethyl-13-hydroxy-6-methoxy-7-{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}-)indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 7

Step 1

[0096] 4-Hydroxybenzoic acid (45 g, 0.326 mol), dodecylbenzenesulfonic acid (2 drops) and ethyl ether (500 mL) were added to a flask equipped with a dropping funnel and stirred at room temperature. Neat dihydropyran (DHP)(35 mL, 0.39 mol) was added dropwise via the dropping funnel within a 30 minute interval and a white crystalline precipitate formed. The resulting suspension was stirred overnight and the precipitate was collected by vacuum filtration. A white solid product (41 g) was recovered. An NMR spectrum showed that the resulting product had a structure consistent with 4-(2-tetrahydro-2H-pyranoxy)benzoic acid.

Step 2

[0097] 4-Hydroxypiperidine (19.5 g, 0.193 mol), 2,3-dimethoxy-7,7-dimethyl-7H-benzo[c]fluoren-5-ol (41.17 g, 0.128 mol) and THF (300 mL) were added to a 2 liter round-bottomed flask equipped with a bubbler and stirred magnetically at room temperature. A solution of 3 M methyl Grignard in THF (171 mL, 0.514 mmol) was added to the mixture slowly via a dropping funnel under a nitrogen atmosphere. The resulting mixture was concentrated to a viscous oil. The viscous oil was maintained under reflux and stirred for 5 days. Thin layer chromatography showed that 2 products were present in the reaction. The resulting reaction mixture was poured into a beaker containing water (1000 mL), neutralized with HCl (3 N) to a pH value of 4-6, extracted with ethyl acetate and flash-chromatographed using 2:8 (volume:volume) ethyl acetate:hexanes as the eluent. Both products were collected and obtained as white solids. An NMR spectrum showed that the major product had a structure consistent with 7,7-dimethyl-3-methoxy-7H-benzo[c]fluorene-2,5-diol and the minor product had a structure consistent with 7,7-dimethyl-3-methoxy-3-(4-hydroxypiperadin-1-yl)-7H-benzo[c]fluorene-5-ol.

Step 3

[0098] 7,7-Dimethyl-3-methoxy-7H-benzo[c]fluorene-2,5-diol from Step 1 (5.1 g), 1-phenyl-1-(4-pyrrolidin-1-yl-phenyl)-prop-2-yn-1-ol (5.1g), pyridinium p-toluenesulfonate (0.2 g), trimethyl orthoformate (4 g) and chloroform (100 mL) were added to a reaction flask and stirred at room temperature over the weekend. The reaction mixture was then concentrated and flash-chromatographed using 2:8 (volume:volume) ethyl acetate:hexanes as the eluent. A grey solid was recovered (9.1 g). An NMR spectrum showed that the resulting product had a structure consistent with 3-phenyl-3-(4-(4-pyrrolidinylphenyl)-13,13-dimethyl-6-methoxy-7-hydroxy-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Step 4

[0099] The procedure of Step 2 of Example 4 was used except that the reaction was conducted at room temperature, 4-(2-tetrahydro-2H-pyranoxy)benzoic acid from Step 1 was used in place of 4,4'-biphenyldicarboxylic acid, 3-phenyl-3-(4-(4-pyrrolidinylphenyl)-13,13-dimethyl-6-methoxy-7-hydroxy-indeno[2',3':3,4]naphtho[1,2-b]pyran from Step 3 was used in place of 3-phenyl-3-(4-(pyrrolidin-1-yl)-phenyl)-13,13-dimethyl-6-methoxy-7-(4-hydroxypiperadin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran and flash chromatography on silica gel was not used for the product purification. The product was purified by a technique of dissolution in chloroform followed by precipitation from methanol. An NMR spectrum showed that the resulting product, a blue solid, had a structure consistent with 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(2-tetrahydro-2H-pyranoxy)benzoyloxy)-indeno[2',3':3,4] naphtho[1,2-b]pyran.

Step 5

[0100] 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(2-tetrahydro-2H-pyranoxy)benzoyloxy)-indeno[2',3':3,4] naphtho[1,2-b]pyran, product of Step 4 (5 g, 6.5 mmol), pyridinium p-toluenesulfonate (0.16 g, 0.65 mmol), ethyl acetate (100 mL) and methanol (20 mL) were added to a reaction flask and refluxed for 24 hours. The resulting reaction mixture was extracted with water, dried over magnesium sulfate, concentrated and flash-chromatographed using 3/7 (volume/volume) ethyl acetate/hexane as the eluent. An NMR spectrum showed that the resulting product, a blue solid (4.4 g), had a structure consistent with 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-hydroxybenzoyloxy)-indeno[2',3':3,4] naphtho[1,2-b]pyran.

Step 6

[0101] The procedure of Step 4 and Step 5 of this example was used except that the product from Step 5 of this Example, 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-hydroxybenzoyloxy)-indeno[2',3':3,4] naphtho[1,2-b]pyran, was used in place of 3-phenyl-3-(4-(4-pyrrolidinylphenyl)-13,13-dimethyl-6-methoxy-7-hydroxy-indeno[2',3':3,4]naphtho[1,2-b]pyran. An NMR spectrum showed that the resulting product, a blue solid, had a structure consistent with 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-hydroxybenzoyloxy)benzoyloxy)-indeno[2',3':3,4] naphtho[1,2-b]pyran.

Step 7

[0102] The procedure of Step 4 and Step 5 of this Example was used except that the product from Step 6 of this Example, 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-hydroxybenzoyloxy)benzoyloxy)-indeno[2',3':3,4] naphtho[1,2-b]pyran, was used in place of 3-phenyl-3-(4-(4-pyrrolidinylphenyl)-13,13-dimethyl-6-methoxy-7-hydroxy-indeno[2',3':3,4]naphtho[1,2-b]pyran. An NMR spectrum showed that the resulting product, a blue solid, had a structure consistent with 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-hydroxybenzoyloxy)benzoyloxy)benzoyloxy)-indeno[2',3':3,4] naphtho[1,2-b]pyran.

Step 8

[0103] The procedure of Step 4 of Example 3 was used except that the product from Step 7, 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-hydroxybenzoyloxy)benzoyloxy)benzoyloxy)-indeno[2',3':3,4] naphtho[1,2-b]pyran, was used in place of 3-phenyl-3-(4-(4-hydroxypiperadin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-phenyl-piperazin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran. An NMR spectrum showed that the final product, a blue solid, had a structure consistent with 3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-(4-hexylbenzoyloxy)benzoyloxy)-benzoyloxy)benzoyloxy)-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 8

[0104] The procedure of Step 3 of Example 7 was used except that methyl 6-methoxy-1-naphthoate was used in place of 7,7-Dimethyl-3-methoxy-7H-benzo[c]fluorene-2,5-diol and 1-phenyl-1-(4-(4-(4-methoxyphenyl) piperazino)phenyl)-2-propyn-1-ol was used in place of 1-phenyl-1-(4-pyrrolidin-1-yl-phenyl)-prop-2-yn-1-ol. Light yellow crystals (2.4 g) were recovered. An NMR spectrum showed that the resulting product had a structure consistent with 3-(4-(4-(4-methoxy-phenyl)-piperazin-1-yl)-phenyl)-3-phenyl-7-methoxycarbonyl-3H-naphtho[2,1-b]pyran.

Example 9

Step 1

[0105] The procedure of Example 8 was followed except that 6-hydroxy-1-naphthoic acid was used in place of methyl 6-methoxy-1-naphthoate. A light orange color powder was recovered. An NMR spectrum showed that the resulting product had a structure consistent with 3-(4-(4-(4-methoxy-phenyl)-piperazin-1-yl)-phenyl)-3-phenyl-7-hydroxycarbonyl-3H-naphtho[2,1-b]pyran.

Step 2

[0106] The procedure of Step 2 of Example 4 was used except that the reaction was conducted at room temperature, 3-{4-[4-(4-Methoxy-phenyl)-piperazin-1-yl]-phenyl}-3-phenyl-7-hydroxycarbonyl-3H-naphtho[2,1-b]pyran was used in place of 4,4'-biphenyldicarboxylic acid and 4-phenylphenol was used in place of 3-phenyl-3-(4-(pyrrolidin-1-yl)-phenyl)-13,13-dimethyl-6-methoxy-7-(4-hydroxypiperadin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran. An NMR spectrum showed that the white solid product had a structure consistent with 3-{4-[4-(4-Methoxy-phenyl)-piperazin-1-yl]-phenyl}-3-phenyl-7-(4-phenyl-(phen-1-oxy)carbonyl)-3H-naphtho[2,1-b]pyran.

Example 10

[0107] The procedure of Step 3 of Example 7 was used except that 4-hydroxy-dibenzofuran was used in place of 7,7-Dimethyl-3-methoxy-7H-benzo[c]fluorene-2,5-diol and 1-phenyl-1-(4-(4-(4-methoxyphenyl) piperazino)phenyl)-2-propyn-1-ol was used in place of 1-phenyl-1-(4-pyrrolidin-1-yl-phenyl)-prop-2-yn-1-ol. An NMR spectrum showed that the final product, an off-white solid, had a structure consistent with 2-phenyl-2-{4-[4-(4-methoxy-phenyl)-piperazin-1-yl]-phenyl}-benzofuro[3',2':7,8] benzo[b]pyran.

Example 11

Step 1

[0108] The procedure of Step 3 of Example 7 was used except that methyl 2,4-dihydroxybenzoate was used in place of 7,7-Dimethyl-3-methoxy-7H-benzo[c]fluorene-2,5-diol. An NMR spectrum showed that the final product, a yellow solid, had a structure consistent with 7-hydroxy-2-phenyl-2-(4-pyrrolidin-1-yl-phenyl)- 6-methoxycarbonyl-2H-benzo[b]pyran.

Step 2

[0109] The procedure of Step 4 of Example 3 was followed except that the product from Step 1, 7-hydroxy-2-phenyl-2-(4-pyrrolidin-1-yl-phenyl)-6-methoxycarbonyl-2H-benzo[b]pyran was used in place of 3-phenyl-3-(4-(4-hydroxypiperadin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-phenyl-piperazin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran and cholesteryl chloroformate was used in place of 4-hexylbenzoylchloride. An NMR spectrum showed that the final product, an off-white solid, had a structure consistent with 7-{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}-2-phenyl-2-(4-pyrrolidin-1-yl-phenyl)-6-methoxycarbonyl-2H-benzo[b]pyran.

Example 12

[0110] The procedure of Step 3 of Example 7 was used except that methyl 3,5-dihydroxy-2-naphthoate was used in place of 7,7-Dimethyl-3-methoxy-7H-benzo[c]fluorene-2,5-diol and 1-phenyl-1-(4-(4-(4-methoxyphenyl) piperazino)phenyl)-2-propyn-1-ol was used in place of 1-phenyl-1-(4-pyrrolidin-1-yl-phenyl)-prop-2-yn-1-ol. An NMR spectrum showed that the final product, a grey solid, had a structure consistent with 2-phenyl-2-{4-[4-(4-methoxy-phenyl)-piperazin-1-yl]-phenyl}-9-hydroxy-8-methxycarbonyl-2H-naphtho[1,2-b]pyran.

Example 13

[0111] To a stirred mixture of 4-n-butylaniline (1.13 g, 7.6 mmol) and THF (20 ml) at room temperature, isopropylmagnesium bromide (2 M in ethyl ether, 3.8 ml) was added via a syringe. After 2 minutes, solid 2-phenyl-2-{4-[4-(4-Methoxy-phenyl)-piperazin-1-yl]-phenyl}-9-hydroxy-8-methxycarbonyl-2H-naphtho[1,2-b]pyran was added in one portion and the mixture obtained was kept stirring at room temperature for four more hours and then poured into water. The precipitate was collected, dissolved in chloroform, dried over magnesium sulfate and concentrated. The crude product was purified by flash chromatography. An NMR spectrum showed that the final product, a grey solid (0.71 g), had a structure consistent with 2-phenyl-2-{4-[4-(4-Methoxy-phenyl)-piperazin-1-yl]-phenyl}-9-hydroxy-8-(4-butyl-phenyl)carbamoyl-2H-naphtho[1,2-b]pyran.

Example 14

[0112] A mixture of 1-nitroso-2-naphthol (12.32 g, 71 mmol), ethyl isonipecotate (11.2 g, 71 mmol) and methanol (200 ml) was refluxed for 2 hours. Neat 1,3,3-trimethyl-2-methyleneindoline was added in one portion. The mixture was kept refluxing for 10 more minutes and then the solvent was removed by vacuum. Flash chromatography was used to separate the product. An NMR spectrum showed that the final product, a yellow solid (9 g, yield 25%). had a structure consistent with 1,3,3-trimethyl-6'-(4-ethoxycarbonyl)-piperidin-1-yl)-spiro[indoline-2,3'-3H-naphtho[2,1-b][1,4]oxazine].

Example 15

[0113] The procedure of Example 13 was used except that 1,3,3-trimethyl-6'-(4-ethoxycarbonyl)-piperidin-1-yl)-spiro[indoline-2,3'-3H-naphtho[2,1-b][1,4]oxazine] was used in place of 2-phenyl-2-{4-[4-(4-Methoxy-phenyl)-piperazin-1-yl]-phenyl}-9-hydroxy-8-methoxycarbonyl-2H-naphtho[1,2-b]pyran. An NMR spectrum showed that the final product, off-white crystals, had a structure consistent with 1,3,3-trimethyl-6'-(4-[N-(4-butylphenyl)carbamoyl]-piperidin-1-yl)-spiro[indoline-2,3'-3H-naphtho[2,1-b][1,4]oxazine].

Example 16

[0114] The procedure of Example 14 was used except that N-(4-methoxyphenyl)piperazine was used in place of ethyl isonipecotate. An NMR spectrum showed that the final product had a structure consistent with 1,3,3-trimethyl-6'-(4-(4-methoxyphenyl)piperazin-1-yl)-spiro[indoline-2,3'-3H-naphtho[2,1-b][1,4]oxazine].

Example 17

[0115] The procedure of Example 14 was used except that N-(4-hydroxyphenyl)piperazine was used in place of ethyl isonipecotate. An NMR spectrum showed that the final product had a structure consistent with 1,3,3-trimethyl-6'-(4-(4-hydroxyphenyl)piperazin-1-yl)-spiro[indoline-2,3'-3H-naphtho[2,1-b][1,4]oxazine].

Example 18

Part A

[0116] Testing was done with the photochromic compounds described in Examples 1-17 in the following manner. A quantity of photochromic compound calculated to yield a 1.5 x 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 photochromic compound was dissolved into the monomer blend by stirring and gentle heating, if necessary. After a clear solution was obtained, it 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, hold the temperature at 95°C for 3 hours, ramp down to 60°C over a 2 hour interval and then hold 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 B

[0117] Prior to response testing on an optical bench, the photochromic samples from Part A 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 molecules. The UVA irradiance at the sample 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 (500W, 120V) for about 10 minutes at a distance of about 36 cm from the lamp in order to bleach, or inactivate, the photochromic compound 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.

[0118] The optical bench was fitted with an Oriel Model #66011 300-watt Xenon arc lamp, an Oriel Model 71445 computer controlled shutter, a Schott 3mm 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 22.2 °C +/- 2 °C (72 °F +/-2 °F) for photochromic response testing. An Oriel Photofeedback unit, Model 68850 was used to control the intensity of the xenon arc lamp during activation of the sample.

[0119] An Ocean Optics LS-1 tungsten halogen light source was used as the monitoring light source for photochromic response measurement. Light, focused into a fiber optic cable was collimated and passed perpendicularly through the center of the sample, in the water cell. After passing through the sample, the light was refocused into a 5.1-cm (2-inch) integrating sphere and fed to an Ocean Optics S2000 spectrophotometer by fiber optic cables. Ocean Optics OOIBase 32 software and PPG proprietary software were used to measure response and control the operation of the optical bench.

[0120] Irradiance for response testing of the photochromic samples on the optical bench was established at the sample 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 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 30°-35° normal to its surface while being perpendicular to the monitoring light.

[0121] Samples were activated in the 22.2 °C (72 °F) 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.

[0122] 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.

[0123] 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 3 UV-Visible spectrophotometer or comparable equipment.

[0124] Some of the compounds of the Examples exhibited dual absorption peaks in the visible spectrum in distinct color regions. For each $\lambda_{max\text{-}vis}$ the corresponding sensitivity (Δ OD/Min), saturation optical density (Δ OD at saturation) and fade half life (T 1/2) for the compounds of the Examples are tabulated in Table II for Band A representing the major (more intense) absorption peak and B and B representing the minor absorption peak.

[0125] The ΔOD/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 fifteen 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.

Table II:

Example	Band	λmax-vis (nm)	Sensitivity (ΔOD/min)	ΔOD @ Saturation	T¼ (seconds)
Example 1	A	502	0.51	1.62	701
	B	589	0.35	1.15	716
Example 2	A	-	-	-	-
	B	592	0.68	1.32	219
Example 3	A	507	0.46	0.71	154
	B	597	0.34	0.54	154
Example 4	A	522	0.16	0.66	426
	B	620	0.16	0.66	430
Example 5	A	528	0.1	0.22	219
	B	624	0.1	0.23	208
Example 6	A	503	0.49	0.80	155
	B	601	0.36	0.58	159
Example 7	A	498	0.19	0.39	221
	B	631	0.37	0.74	210
Example 8*		-	-	-	-
		-	-	-	-
Example 9*		-	-	-	-
		-	-	-	-

(continued)

Example	Band	λmax-vis (nm)	Sensitivity (ΔOD/min)	ΔOD @ Saturation	T¼ (seconds)
Example 10	A	511	0.03	0.03	>2000
	B	573	0.03	0.03	>2000
Example 11*		-	-	-	-
		-	-	-	-
Example 12	A	565	0.12	0.54	1022
	B				
Example 13	A	560	0.05	0.29	1329
	B				
Example 14	A	437	0.06	0.02	17
	B	585	0.41	0.17	19
Example 15	A	437	0.05	0.02	17
	B	584	0.36	0.16	20
Example 16	A	585	0.36	0.16	21
	B	432	0.02	0.02	26
Example 17	A	579	0.35	0.16	22
	B				
*Fade rate too fast to permit measurement.					

Example 19

[0126] The average absorption ratio of each of the photochromic compounds of Examples 1-17, as well as the average absorption ratio of Photosol™ 0265 ("Comparative Example"), which is commercially available from PPG Industries, Inc. and reported to be 1,3,3,4,5 (or 1,3,3,5,6)-pentamethyl-spiro[indoline-2,3-[3H]naphth[2,1-b][1,4]oxazine, was deteremined according to the CELL METHOD.

[0127] 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.

[0128] The gap between the two glass substrates of the cell assembly was filled with a liquid crystal solution containing the one of the photochromic compounds of Examples 1-17 or the Comparative Example ("Test Material"). The liquid crystal solution was formed by mixing the following components in the weight percents listed in Table III with heating, if necessary, to dissolve the test material.

Table III:

Component	Weight Percent
Licristal™ E7	97-99.5
Test Material	0.5-3

[0129] 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 Melles Griot 04 IES 211 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.

[0130] 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 4" light pipe was attached to the single end of the cable to insure proper mixing.

[0131] 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 (22.8 °C +/- 5 °C or better) (73°F ± 5°F or better) maintained by the lab air conditioning system or a temperature controlled air cell.

[0132] To conduct the measurements, the cell assembly was exposed to 6.7 W/m^2 of UVA from the activating light source for 5 to 15 minutes to activate the Test Material. 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 2" integrating sphere, which was connected to an Ocean Optics 2000 spectrophotometer using a single function fiber optic cable. The spectral information, after passing through the sample, was collected using Ocean Optics OOIBase32 and OOIColor software, and PPG propriety software. While the photochromic-dichroic material was activated, the position of the polarizing sheet 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 3-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.

[0133] 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 photochromic response of the Test Material 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 $\lambda_{max-vis}$ +/- 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.

[0134] For each Test Material, 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. The results of these tests are present in Table IV below.

Table IV:

Example Number	Wavelength Range $\lambda_{max-vis}$ (nm) +/- 5 nm	Average Absorption Ratio (AR)
Comparative Example	623 +/- 5 nm	2.3
1	500 +/- 5 nm	3.9
2	601 +/- 5 nm	2.2
3	505 +/- 5 nm	3.7
4	628 +/- 5 nm	4.8
5	529 +/- 5 nm	3.3
6	507 +/- 5 nm	6.0
7	640 +/- 5 nm	6.6
8*	-	-

(continued)

Example Number	Wavelength Range $\lambda_{max\text{-}vis}$ (nm) +/- 5 nm	Average Absorption Ratio (AR)
9*	-	-
10	584 +/- 5 nm	3.9
11*	-	-
12	571 +/- 5 nm	2.7
13	590 +/- 5 nm	4.0
14	590 +/- 5 nm	6.0
15	590 +/- 5 nm	7.8
16	586 +/- 5 nm	8.3
17	587 +/- 5 nm	7.0
* Too fast fading to measure		

Example 20

[0135] The average absorption ratio for each of the named compounds in Table V was determined as set forth above in Example 19. It will be appreciated by those skilled in the art that the compounds listed in Table V may be made in accordance with the teachings and examples disclosed herein with appropriate modifications, which will be readily apparent to those skilled in the art. Further, those skilled in the art will recognize that various modifications to the disclosed methods, as well as other methods, can be used in making the named compounds set forth below in Table V.

Table V:

Compound Name	Wavelength Range λ_{max} (nm) (+/- 5 nm)	Average Absorption Ratio (AR)
3-phenyl-3-(4-(4-benzylpiperidino)phenyl)-13,13-dimethyl-indeno[2',3':3,4]naphtho[1,2-b]pyran	610	2.2
3-phenyl-3-(4-(4-(3-piperidin-4-yl-propyl)piperidino)phenyl)-13,13-dimethyl-indeno[2',3':3,4]-naphtho[1,2-b]pyran	590	2.0
3-phenyl-3-(4-(4-hexyloxymethyl piperidino)phenyl)-13,13-dimethyl-indeno[2',3':3,4]naphtho[1,2-b]pyran	606	2.2
3-phenyl-3-(4-([1,4']bipiperidinyl-1'-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(piperadin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran	515	2.3
3-phenyl-3-(4-([1,4']bipiperidinyl-1'-yl)phenyl)-13,13-dimethyl-6-methoxy-7-([1,4']bipiperidinyl-1'-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran	513	3.4
3-phenyl-3-(4-pyrrolidin-1-yl-phenyl)-13,13-dimethyl-6-methoxy-7-([1,4']bipiperidinyl-1"-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran	630	2.8
3-phenyl-3-(4-([1,4']bipiperidinyl-1'-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-benzylpiperidin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran	515	2.7
3-phenyl-3-(4-(4-phenylpiperazine)phenyl)-13,13-dimethyl-indeno[2',3':3,4]naphtho[1,2-b]pyran	592	2.2
3-phenyl-3-(4-(4-benzylpiperazine)phenyl)-13,13-dimethyl-indeno[2',3':3,4]naphtho[1,2-b]pyran	598	2.1
3-phenyl-3-(4-pyrrolidin-1-yl-phenyl)-13,13-dimethyl-6-methoxy-7-(4-phenyl-piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran	632	4.5

(continued)

Compound Name	Wavelength Range λ_{max} (nm) (+/- 5 nm)	Average Absorption Ratio (AR)
3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-hexyloxy-benzoyloxy)-piperidin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran	501	3.9
3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-hexylbenzoyloxy)-piperidin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran	503	3.9
3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(biphenyl-4-carbonyloxy)-piperidin-1-yl])indeno[2',3':3,4]naphtho[1,2-b]pyran	501	4.2
3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4'-octyloxybiphenyl-4-carbonyloxy)-piperidin-1-yl)indeno[2',3':3,4]naphtho[1,2-b] pyran	499	4.1
3-phenyl-3-(4-(4-hexylbenzoyloxy)-piperidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-hexylbenzoyloxy)-piperidin-1-yl)indeno[2',3':3,4]naphtho[1,2-b] pyran	505	4.3
3-phenyl-3-(4-(4-(4-butyl-phenylcarbamoyl)-piperidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-phenyl-piperazin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran	506	5.0
3-phenyl-3-(4-(1-hydroxypiperidin-1-yl)-phenyl)-13,13-dimethyl-6-methoxy-7-(4-phenyl-piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran	512	4.0
3-phenyl-3-{4-(4-fluorobenzoyloxy)-piperadin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-phenyl-piperazin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran	507	3.5
3-phenyl-3-(4-(4-pyrrolidinylphenyl)-13,13-dimethyl-6-methoxy-7-(-{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} indeno[2',3':3,4]naphtho[1,2-b]pyran	525	6.3
3-phenyl-3-(4-{4-(biphenyl-4-carbonyloxy]-piperidin-1-yl}-phenyl)-13,13-dimethyl-6-methoxy-7-{44-(biphenyl-4-carbonyloxy)-piperidin-1-yl}-)indeno[2',3':3,4]naphtho [1,2-b]pyran	503	4.6
3-phenyl-3-{4-(pyrrolidin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-hexylbenzoyloxy-piperadin-1-yl)-indeno[2',3':3,4] naphtho[1,2-b]pyran	635	3.4
3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-{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-yloxycarbonyloxy]-piperidin-1-yl}-indeno[2',3':3,4]naphtho[1,2-b]pyran	502	6.0
3-phenyl-3-{4-(pyrrolidin-1-yl)phenyl)-3-hydroxy-13-ethyl-6-methoxy-7-(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]-piperadin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran	635	5.2
3-phenyl-3-{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}-phenyl)-13,13-dimethyl-6-methoxy-7-(4-phenyl-piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran	505	4.4
3-phenyl-3-{4-(pyrrolidin-1-yl)phenyl)-13-[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]-13-ethyl-6-methoxy-7-(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]-piperadin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b] pyran	529	3.3

(continued)

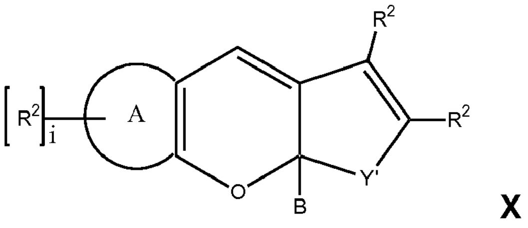
Compound Name	Wavelength Range λ_{max} (nm) (+/- 5 nm)	Average Absorption Ratio (AR)
3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-[17-(1,5-dimethylhexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yloxycarbonyl]-piperazin-1-yl) indeno[2',3':3,4]naphtho[1,2-b]pyran	503	7.1
3-phenyl-3-{4-(pyrrolidin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(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-yloxycarbonyl]-piperazin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran	637	5.3
3-phenyl-3-(4-(4-phenylpiperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-phenyl-piperazin-1-yl)-4-oxo-butanoyl)-piperazine-1-yl)-indeno[2',3':3,4] naphtho[1,2-b]pyran	499	4.6
3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-hexylbenzoyloxy)phenyl)piperazin-1-yl)indeno[2',3':3,4] naphtho[1,2-b] pyran	496	5.9
3-phenyl-3-(4-(4-phenylpiperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-fluorobenzoyloxy)phenyl)piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b] pyran	497	5.3
3-phenyl-3-(4-(4-phenylpiperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-biphenylcarbonyloxy)phenyl)piperazin-1-yl)indeno[2',3':3,4]naphtho[1,2-b]pyran	497	5.8
3-phenyl-3-(4-(4-phenylpiperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4'-octyloxybiphenyl-4-carbonyloxy)phenyl)piperazin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran	497	6.3
3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-hexyloxyphenylcarbonyloxy)phenyl)piperazin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran	496	5.8
3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-{4-(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-yloxycarbonyloxy]-phenyl)-piperidin-1-yl}-indeno[2',3':3,4]naphtho[1,2-b]pyran	499	5.6
3-phenyl-3-(4-(4-(4-(4-hexylbenzoyloxy)phenyl)piperazin-1-yl)phenyl-13,13-dimethyl-6-methoxy-7-(4-phenylpiperazin-1-yl)-indeno[2',3':3,4]naphtho[1,2-b]pyran	499	4.8
3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-(4-hexylbenzoyloxy)benzoyloxy)-phenyl)piperazin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran	493	6.1
3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-(4-(4-hexylbenzoyloxy)phenyl)piperazin-1-yl)indeno[2',3':3,4] naphtho[1,2-b] pyran	499	5.7
3-phenyl-3-(4-(4-methoxyphenyl)-piperazin-1-yl))phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(3-phenylprop-2-ynoyloxy)phenyl)piperazin-1-yl)-indeno[2',3':3,4] naphtho[1,2-b]pyran	499	6.3
3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-(2-fluorobenzoyloxy)benzoyloxy)phenyl)piperazin-1-yl)indeno[2',3':3,4] naphtho[1,2-b]pyran	497	5.8

(continued)

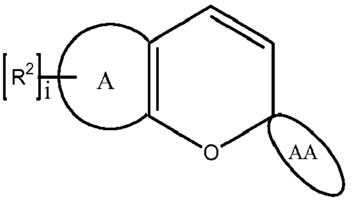
Compound Name	Wavelength Range λ_{max} (nm) (+/- 5 nm)	Average Absorption Ratio (AR)
3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-(4-fluorobenzoyloxy)benzoyloxy)-phenyl)piperazin-1-yl)indeno[2’,3’:3,4] naphtho[1,2-b]pyran	498	6.1
3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-(4-(4-hexylbenzoyloxy)phenyl)piperazin-1-yl)indeno[2’,3’:3,4] naphtho[1,2-b]pyran	629	6.3
3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-hexylbenzoyloxy)-indeno[2’,3’:3,4] naphtho[1,2-b]pyran	645	4.7
3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-hexylbenzoyloxy)benzoyloxy)-indeno[2’,3’:3,4]naphtho[1,2-b]pyran	639	5.9
3-phenyl-3-(4-(4-methoxyphenyl)piperazin-1-yl))phenyl)-13,13-dimethyl-6-methoxy-7-(3-(4-hexylbenzoyloxyphenyl)piperazin-1-yl)-indeno[2’,3’:3,4]naphtho [1,2-b]pyran	500	2.8
3-phenyl-3-(4-(pyrrolidin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-hexylbenzoyloxy)benzoyloxy)benzoyloxy)indeno[2’, 3’:3,4] naphtho[1,2-b]pyran	646	6.4
3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-(4-(4-hexylbenzoyloxy)benzoyloxy)-benzoyloxy)phenyl)piperazin-1-yl) indeno[2’,3’:3,4] naphtho[1,2-b]pyran	497	7.1
3-(4-methoxyphenyl)-3-(4-(4-methoxyphenyl)piperazin-1-yl)phenyl)-13-ethyl-13-hydroxy-6-methoxy-7-(4-(4-(4-hexylbenzoyloxy)phenyl)piperazin-1-yl)indeno[2’,3’:3,4]naphtho[1,2-b]pyran	499	5.4
2-phenyl-2-{4-[4-(4-Methoxy-phenyl)-piperazin-1-yl]-phenyl}-benzofuro[3’,2’:7,8] benzo[b]pyran	583	4.2
2-phenyl-2-{4-[4-(4-Methoxy-phenyl)-piperazin-1-yl]-phenyl}-benzothieno[3’,2’:7,8] benzo[b]pyran	510	4.1
3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-(4-(6-(4-(4-(4-(4-nonylphenylcabonyloxy)phenyl)oxycarbonyl) phenoxy) hexyloxy)benzoyloxy)phenyl)piperazin-1-yl)indeno[2’,3’:3,4]naphtho[1,2-b]pyran	495	6.1
3-phenyl-3-(4-(4-phenyl-piperazin-1-yl)phenyl)-13-hydroxy-13-ethyl-6-methoxy-7-(4-(4-(4-(4-(6-(4-(4-(4-(4-nonylphenylcabonyloxy)phenyl) oxycarbonyl)phenoxy) hexyloxy)benzoyloxy)phenyl)piperazin-1-yl)indeno[2’,3’:3,4]naphtho[1,2-b]pyran	500	6.0
3-phenyl-3-(4-pyrrolidinylphenyl)-13,13-dimethyl-6-methoxy-7-(4-(4-(4-(4-(6-(4-(4-(4-nonylphenylcabonyloxy)phenyl)oxycarbonyl)phenoxy) hexyloxy)phenyl)piperazin-1-yl)indeno[2’,3’:3,4] naphtho[1,2-b]pyran	627	6.5

Claims

1. A non-thermally reversible photochromic compound represented by one of Formula X and Formula XI:



X

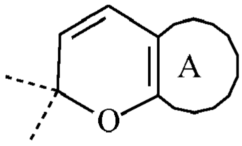


XI

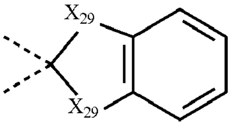
wherein:

(a) A is chosen from naphtho, benzo, phenanthro, fluorantheno, antheno, quinolino, thieno, furo, indolo, indolino, indeno, benzofuro, benzothieno, thiopheno, indeno-fused naphtho, heterocyclic-fused naphtho, and heterocyclic-fused benzo;

(b) AA is a group represented by one of Formula xv and xvi:



xv



xvi

wherein X_{29} is independently chosen from each occurrence from -C(R")(R")-,-O-, -S-, and -N(R"')-, wherein R" is independently chosen for each occurrence from hydrogen, a substituted or unsubstituted alkyl, cycloalkyl, arylalkyl, or together form cycloalkyl that is substituted or unsubstituted; R"' is independently chosen for each occurrence from an alkyl, aryl or arylalkyl group that is unsubstituted or substituted with at least one of:

(i) $-CH(CN)_2$ or $-CH(COOX_1)_2$ wherein X_1 is chosen from at least one of a lengthening agent L, hydrogen, C_1-C_{12} alkyl that is unsubstituted or mono-substituted with phenyl, phenyl(C_1-C_{12})alkyl that is mono-substituted with C_1-C_{12} alkyl or C_1-C_{12} alkoxy, and an aryl group that is unsubstituted, mono- or di-substituted, wherein each aryl substituent is independently chosen from C_1-C_{12} alkyl and C_1-C_{12} alkoxy;

(ii) $-CH(X_2)(X_3)$ wherein

(A) X_2 is chosen from at least one of a lengthening agent L, hydrogen, C_1-C_{12} alkyl, and an aryl group that is unsubstituted, mono- or di-substituted, wherein each aryl substituent is independently chosen from C_1-C_{12} alkyl and C_1-C_{12} alkoxy; and

(B) X_3 is chosen from at least one of $-COOX_1$, $-COX_1$, $-COX_4$, and $-CH_2OX_5$, wherein:

(1) X_4 is chosen from at least one of morpholino, piperidino, amino that is unsubstituted, mono- or di- substituted with C_1-C_{12} alkyl, and an unsubstituted, mono or di- substituted group chosen from phenylamino and diphenylamino, wherein each substituent is independently chosen from C_1-C_{12} alkyl or C_1-C_{12} alkoxy; and

(2) X_5 is chosen from a lengthening agent L, hydrogen, $-C(O)X_2$, C_1-C_{12} alkyl that is unsubstituted or mono-substituted with (C_1-C_{12})alkoxy or phenyl, phenyl(C_1-C_{12})alkyl that is mono-substituted with (C_1-C_{12})alkoxy, and an aryl group that is unsubstituted, mono- or di-substituted, wherein each aryl substituent is independently chosen from C_1-C_{12} alkyl and C_1-C_{12} alkoxy;

(iii) $-C(O)X_{24}$; wherein X_{24} is chosen from a lengthening agent L, hydroxy, C_1-C_{12} alkyl, C_1-C_{12} alkoxy,

phenyl that is unsubstituted or mono-substituted with C_1-C_{12} alkyl or C_1-C_{12} alkoxy, amino that is unsubstituted, mono- or di-substituted with at least one of C_1-C_{12} alkyl, phenyl, benzyl, and naphthyl; or
(iv) halogen, hydroxy, ester, or amine;

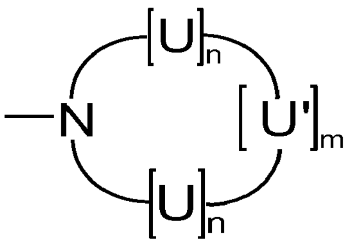
(c) Y' is chosen from: -(Y_1)C=C(Y_2)-, -O-,-S-,-S(O)(O)-, and -N(X_7)-, wherein Y_1 and Y_2 together form benzo, naphtho, phenanthro, furo, thieno, benzofuro, benzothieno and indolo, and X_7 is chosen from:

(i) a lengthening agent L, hydrogen, C_1-C_{12} alkyl, C_1-C_{12} acyl, phenyl(C_1-C_{12})alkyl, mono(C_1-C_{12})alkyl substituted phenyl(C_1-C_{12})alkyl, mono(C_1-C_{12})alkoxy substituted phenyl(C_1-C_{12})alkyl; C_1-C_{12}alkoxy(C_1-C_{12})alkyl; C_3-C_7 cycloalkyl; mono(C_1-C_{12})alkyl substituted C_3-C_7 cycloalkyl, C_1-C_{12} haloalkyl, allyl, benzoyl, mono-subsituted benzoyl, naphthoyl or mono-substituted naphthoyl, wherein each of said benzoyl and naphthoyl substituents are independently chosen from C_1-C_{12} alkyl, and C_1-C_{12} alkoxy;
(ii) -CH(X_8)X_9, wherein X_8 is chosen from a lengthening agent L, hydrogen or C_1-C_{12} alkyl; and X_9 is chosen from a lengthening agent L, -CN, -CF_3, or -COOX_{10}, wherein X_{10} is chosen from a lengthening agent L, hydrogen or C_1-C_{12} alkyl;
(iii) -C(O)X_6, wherein X_6 is chosen from at least one of: a lengthening agent L, hydrogen, C_1-C_{12} alkoxy, phenoxy that is unsubstituted, mono- or di-substituted with C_1-C_{12} alkyl or C_1-C_{12} alkoxy, an aryl group that is unsubstituted, mono- or di-substituted with C_1-C_{12} alkyl or C_1-C_{12} alkoxy, an amino group that is unsubstituted, mono- or di-substituted with C_1-C_{12} alkyl, and a phenylamino group that is unsubstituted, mono- or di-substituted with C_1-C_{12} alkyl or C_1-C_{12} alkoxy;
(iv) tri(C_1-C_{12})alkylsilyl, tri(C_1-C_{12})alkoxysilyl, di(C_1-C_{12})alkyl(C_1-C_{12}alkoxy)silyl, or di(C_1-C_{12})alkoxy(C_1-C_{12} alkyl)silyl;

(d) B is chosen from:

(i) hydrogen, C_1-C_{12} alkyl, C_2-C_{12} alkylidene, C_2-C_{12} alkylidyne, vinyl, C_3-C_7 cycloalkyl, C_1-C_{12} haloalkyl, allyl, halogen, and benzyl that is unsubstituted or mono-substituted with at least one of C_1-C_{12} alkyl and C_1-C_{12} alkoxy;
(ii) phenyl that is mono-substituted at the *para* position with at least one substituent chosen from: C_1-C_7 alkoxy, linear or branched chain C_1-C_{20} alkylene, linear or branched chain C_1-C_4 polyoxyalkylene, cyclic C_3-C_{20} alkylene, phenylene, naphthylene, C_1-C_4 alkyl substituted phenylene, mono- or poly-urethane(C_1-C_{20})alkylene, mono- or poly-ester(C_1-C_{20})alkylene, mono- or poly-carbonate(C_1-C_{20})alkylene, polysilanylene, polysiloxanylene and mixtures thereof, wherein the at least one substituent is connected to an aryl group of a photochromic material;
(iii) -CH$(CN)_2$ and -CH$(COOX_1)_2$;
(iv) -CH(X_2)(X_3);
(v) an unsubstituted, mono-, di-, or tri- substituted aryl group; 9-julolidinyl; or an unsubstituted, mono- or di-substituted heteroaromatic group chosen from pyridyl, furanyl, benzofuran-2-yl, benzofuran-3-yl, thienyl, benzothien-2-yl, benzothien-3-yl, dibenzofuranyl, dibenzothienyl, carbazoyl, benzopyridyl, indolinyl, or fluorenyl; wherein each substituent is independently chosen for each occurrence from:

(A) a lengthening agent L;
(B) -C(O)X_6;
(C) aryl, haloaryl, C_3-C_7 cycloalkylaryl, and an aryl group that is mono- or di-substituted with C_1-C_{12} alkyl or C_1-C_{12} alkoxy;
(D) C_1-C_{12} alkyl, C_3-C_7 cycloalkyl, C_3-C_7 cycloalkyloxy(C_1-C_{12})alkyl, aryl(C_1-C_{12})alkyl, aryloxy(C_1-C_{12})alkyl, mono- or di- (C_1-C_{12})alkylaryl(C_1-C_{12})alkyl, mono- or di- (C_1-C_{12})alkoxyaryl(C_1-C_{12})alkyl, haloalkyl, and mono(C_1-C_{12})alkoxy(C_1-C_{12})alkyl;
(E) C_1-C_{12} alkoxy, C_3-C_7 cycloalkoxy, cycloalkyloxy(C_1-C_{12})alkoxy, aryl(C_1-C_{12})alkoxy, aryloxy(C_1-C_{12})alkoxy, mono- or di- (C_1-C_{12})alkylaryl(C_1-C_{12})alkoxy, and mono- or di- (C_1-C_{12})alkoxyaryl(C_1-C_{12})alkoxy;
(F) amido, amino, mono- or di-alkylamino, diarylamino, piperazino, N-(C_1-C_{12})alkylpiperazino, N-arylpiperazino, aziridino, indolino, piperidino, morpholino, thiomorpholino, tetrahydroquinolino, tetrahydroisoquinolino, pyrrolidyl, hydroxy, acryloxy, methacryloxy, and halogen;
(G) -OX_7 or -N$(X_7)_2$;
(H) -SX_{11}, wherein X_{11} is chosen from a lengthening agent L, C_1-C_{12} alkyl, an aryl group that is unsubstituted, or mono- or di- substituted with C_1-C_{12} alkyl, C_1-C_{12} alkoxy, or halogen;
(I) a nitrogen containing ring represented by Formula i:



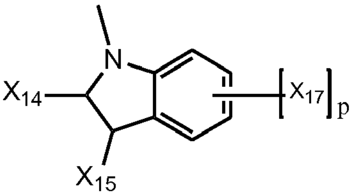
i

wherein

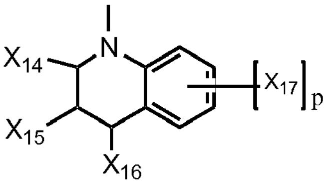
(1) n is an integer chosen from 0, 1, 2, and 3, provided that if n is 0, U' is U, and each U is independently chosen for each occurrence from $-CH_2-$, $-CH(X_{12})-$, $-C(X_{12})_2-$, $-CH(X_{13})-$, $-C(X_{13})_2-$, and $-C(X_{12})(X_{13})-$, wherein X_{12} is chosen from a lengthening agent L represented by Formula I below and C_1-C_{12} alkyl, and X_{13} is chosen from a lengthening agent L represented by Formula I below, phenyl and naphthyl, and

(2) U' is chosen from U, -O-, -S-, -S(O)-, -NH-,$-N(X_{12})-$ or $-N(X_{13})-$, and m is an integer chosen from 1, 2, and 3, and

(J) a group represented by Formula ii or iii:



ii

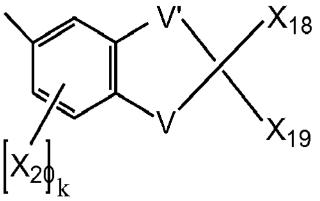


iii

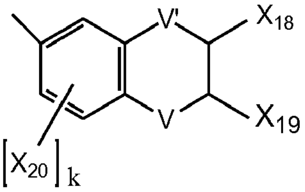
wherein X_{14}, X_{15}, and X_{16} are independently chosen for each occurrence from a lengthening agent L, C_1-C_{12} alkyl, phenyl or naphthyl, or X_{14} and X_{15} together form a ring of 5 to 8 carbon atoms; p is an integer chosen from 0, 1, or 2, and X_{17} is independently chosen for each occurrence from a lengthening agent L, C_1-C_{12} alkyl, C_1-C_{12} alkoxy, or halogen;

(vi) an unsubstituted or mono-substituted group chosen from pyrazolyl, imidazolyl, pyrazolinyl, imidazolinyl, pyrrolidinyl, phenothiazinyl, phenoxazinyl, phenazinyl, or acridinyl, wherein each substituent is independently chosen from a lengthening agent L, C_1-C_{12} alkyl, C_1-C_{12} alkoxy, phenyl, hydroxy, amino or halogen;

(vii) a group represented by Formula iv or v:



iv



v

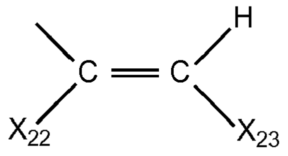
(A) V' is independently chosen in each formula from -O-, -CH-, C_1-C_6 alkylene, and C_3-C_7 cycloalkylene,

(B) V is independently chosen in each formula from -O- or $-N(X_{21})-$, wherein X_{21} is chosen from a lengthening agent L represented by Formula I below, hydrogen, C_1-C_{12} alkyl, and C_2-C_{12} acyl, provided that if V is $-N(X_{21})-$, V' is $-CH_2-$,

(C) X_{18} and X_{19} are each independently chosen from a lengthening agent L, hydrogen and C_1-C_{12} alkyl, and

(D) k is chosen from 0, 1, and 2, and each X_{20} is independently chosen for each occurrence from a lengthening agent L, C_1-C_{12} alkyl, C_1-C_{12} alkoxy, hydroxy and halogen; and

(viii) a group represented by Formula vi:

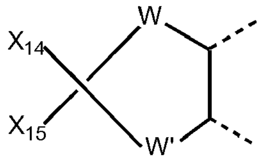

vi

wherein

(A) X_{22} is chosen from a lengthening agent L, hydrogen and C_1-C_{12} alkyl, and
(B) X_{23} is chosen from a lengthening agent L and an unsubstituted, mono-, or di-substituted group chosen from naphthyl, phenyl, furanyl and thienyl, wherein each substituent is independently chosen for each occurrence from C_1-C_{12} alkyl, C_1-C_{12} alkoxy, and halogen; and

(e) i is an integer chosen from 0 to 4, and each R^2 is independently chosen for each occurrence from:

(i) a group represented by B;
(ii) -C(O)X_{24};
(iii) -OX_7 and -N$(X_7)_2$;
(iv) -SX_{11};
(v) the nitrogen containing ring represented by Formula i;
(vi) the group represented by Formula ii or iii;
(vii) immediately adjacent R^2 groups together form at a group represented by Formula vii, viii, or ix: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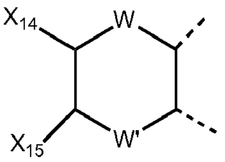
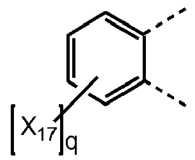

viii

ix



wherein

(A) W and W' are independently chosen for each occurrence from -O-, -N(X_7)-, -C(X_{14})-, -C(X_{17})-,
(B) X_{14}, X_{15} and X_{17} are as set forth above, and
(C) q is an integer chosen from 0, 1, 2, 3, and 4; and

(viii) a lengthening agent L;

provided that the non-thermally reversible photochromic compound comprises at least one lengthening agent L and each lengthening agent L is independently chosen for each occurrence from a compound represented by Formula I:

$$-[S_1]_c-[Q_1-[S_2]_d]_{d'}-[Q_2-[S_3]_e]_{e'}-[Q_3-[S_4]_f]_{f'}-S_5-P \qquad \text{I}$$

wherein:

(a) each Q_1, Q_2, and Q_3 is independently chosen for each occurrence from: a divalent group chosen from: an unsubstituted or a substituted aromatic group, an unsubstituted or a substituted alicyclic group, an unsubstituted or a substituted heterocyclic group, and mixtures thereof, wherein substituents are chosen from: a group represented by P, thiol, amide, liquid crystal mesogens, halogen, C_1-C_{18} alkoxy, poly(C_1-C_{18} alkoxy), amino, amino(C_1-C_{18})alkylene, C_1-C_{18}alkylamino, di-(C_1-C_{18})alkylamino, C_1-C_{18} alkyl, C_2-C_{18} alkene, C_2-C_{18} alkyne, C_1-C_{18} alkyl(C_1-C_{18})alkoxy, C_1-C_{18} alkoxycarbonyl, C_1-C_{18} alkylcarbonyl, C_1-C_{18} alkyl carbonate, aryl carbonate, C_1-C_{18} acetyl, C_3-C_{10} cycloalkyl, C_3-C_{10} cycloalkoxy, isocyanato, amido, cyano, nitro, a straight-chain or branched C_1-C_{18} alkyl group that is mono-substituted with cyano, halo, or C_1-C_{18} alkoxy, or poly-substituted with halo, and a group represented by one of the following formulae: $-M(T)_{(t-1)}$ 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 ranging from 0 to 20, inclusive; and each S_1,

S_2, S_3, S_4, and S_5 is independently chosen for each occurrence from a spacer unit chosen from:

(i) -$(CH_2)_g$-, -$(CF_2)_h$-, -$Si(CH_2)_g$-, -$(Si[(CH_3)_2]O)_h$-, wherein g is independently chosen for each occurrence from 1 to 20; h is a whole number from 1 to 16 inclusive;
(ii) -N(Z)-, -C(Z)=C(Z)-, -C(Z)=N-, -C(Z')-C(Z')-, wherein Z is independently chosen for each occurrence from hydrogen, C_1-C_6 alkyl, cycloalkyl and aryl, and Z' is independently chosen for each occurrence from C_1-C_6 alkyl, cycloalkyl and aryl; and
(iii) -O-, -C(O)-, -C≡C-, -N=N-, -S-, -S(O)-, -S(O)(O)-, straight-chain or branched C_1-C_{24} alkylene residue, said C_1-C_{24} alkylene residue being unsubstituted, mono-substituted by cyano or halo, or poly-substituted by halo;

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 and when S_1 and S_5 are linked to PC and P, respectively, they are linked so that two heteroatoms are not directly linked to each other;
(c) P is chosen from: aziridinyl, hydrogen, hydroxy, aryl, alkyl, alkoxy, amino, alkylamino, alkylalkoxy, alkoxyalkoxy, nitro, polyalkyl ether, $(C_1$-$C_6)$alkyl$(C_1$-$C_6)$alkoxy$(C_1$-$C_6)$alkyl, polyethyleneoxy, polypropyleneoxy, ethylene, acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, acryloylphenylene, acrylamide, methacrylamide, 2-chloroacrylamide, 2-phenylacrylamide, epoxy, isocyanate, thiol, thioisocyanate, itaconic acid ester, vinyl ether, vinyl ester, a styrene derivative, siloxane, main-chain and side-chain liquid crystal polymers, ethyleneimine derivatives, maleic acid 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 and unsubstituted chiral and non-chiral monovalent or divalent groups chosen from steroid radicals, terpenoid radicals, alkaloid radicals and mixtures thereof, wherein the substituents are independently chosen from alkyl, alkoxy, amino, cycloalkyl, alkylalkoxy, fluoroalkyl, cyanoalkyl, cyanoalkoxy and mixtures thereof; 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 1.

2. The non-thermally reversible photochromic compound according to claim 1, wherein in either of Formula X or XI the integer i is at least 1 and at least one of the R^2 groups is a lengthening agent L.

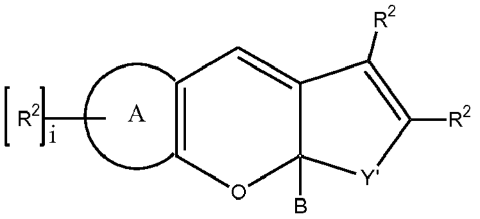
3. The non-thermally reversible photochromic compound of any of the preceding claims, wherein the photochromic compound comprises at least one R^2 group that is substituted with a lengthening agent L.

4. The non-thermally reversible photochromic compound according to claim 1 represented by Formula X, wherein said lengthening agent L is substituted on a R^2 or B group.

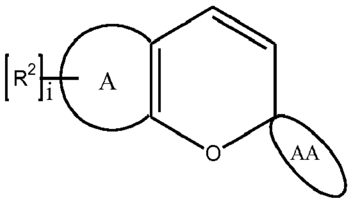
5. The non-thermally reversible photochromic compound according to claim 1 represented by Formula XI, wherein said lengthening agent L is substituted on a R^2 or AA group.

Patentansprüche

1. Eine nicht thermisch reversible photochrome Verbindung dargestellt durch eine der Formel X und Formel XI:



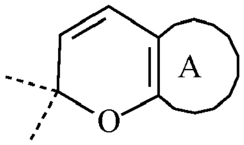
X



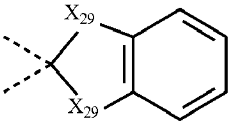
XI

wobei:

(a) A aus Naphtho, Benzo, Phenanthro, Fluorantheno, Antheno, Chinolino, Thieno, Furo, Indolo, Indolino, Indeno, Benzofuro, Benzothieno, Thiopheno, indenokondensiertem Naphtho, heterocyclisch kondensiertem Naphtho und heterocyclisch kondensiertem Benzo ausgewählt ist;
(b AA eine Gruppe ist, die durch eine der Formeln xv und xvi dargestellt ist:



xv



xvi

wobei X_{29} unabhängig voneinander bei jedem Auftreten aus -C(R")(R")-,-O-, -S- und -N(R''')- ausgewählt ist, wobei R" unabhängig voneinander bei jedem Auftreten aus Wasserstoff, einem substituierten oder unsubstituierten Alkyl, Cycloalkyl, Arylalkyl ausgewählt ist, oder zusammengenommen Cycloalkyl bildet, das substituiert oder unsubstituiert ist; R''' unabhängig voneinander bei jedem Auftreten aus einer Alkyl-, Aryl- oder Arylalkylgruppe ausgewählt ist, die unsubstituiert oder substituiert ist mit mindestens einem von:

(i) $-CH(CN)_2$ oder $-CH(COOX_1)_2$, wobei X_1 aus mindestens einem von einem Verlängerungsmittel L, Wasserstoff, C_1-C_{12}-Alkyl, das unsubstituiert oder mit Phenyl monosubstituiert ist, Phenyl(C_1-C_{12})alkyl, das mit C_1-C_{12}-Alkyl oder C_1-C_{12}-Alkoxy monosubstituiert ist und einer Arylgruppe, die unsubstituiert, mono- oder disubstituiert ist, wobei jeder Arylsubstituent unabhängig aus C_1-C_{12}-Alkyl und C_1-C_{12}-Alkoxy ausgewählt ist, ausgewählt ist;
(ii) $-CH(X_2)(X_3)$, wobei

(A) X_2 aus mindestens einem von einem Verlängerungsmittel L, Wasserstoff, C_1-C_{12}-Alkyl und einer Arylgruppe, die unsubstituiert, mono- oder disubstituiert ist, wobei jeder Arylsubstituent unabhängig aus C_1-C_{12}-Alkyl und C_1-C_{12}-Alkoxy ausgewählt ist, ausgewählt ist; und
(B) X_3 aus mindestens einem von $-COOX_1$, $-COX_1$, $-COX_4$ und $-CH_2OX_5$ ausgewählt ist, wobei:

(1) X_4 aus mindestens einem von Morpholino, Piperidino, Amino, welches unsubstituiert, mono- oder disubstituiert mit C_1-C_{12}-Alkyl ist und einer unsubstituierten, mono- oder disubstituierten Gruppe, die aus Phenylamino und Diphenylamino ausgewählt ist, wobei jeder Substituent unabhängig aus C_1-C_{12}-Alkyl oder C_1-C_{12}-Alkoxy ausgewählt ist, ausgewählt ist; und
(2) X_5 aus einem Verlängerungsmittel L, Wasserstoff, $-C(O)X_2$, C_1-C_{12}-Alkyl, das unsubstituiert oder mit (C_1-C_{12})Alkoxy oder Phenyl monosubstituiert ist, Phenyl(C_1-C_{12})alkyl, das mit (C_1-C_{12})Alkoxy monosubstituiert ist und einer Arylgruppe, die unsubstituiert, mono- oder disubstituiert ist, wobei jeder Arylsubstituent unabhängig aus C_1-C_{12}-Alkyl und C_1-C_{12}-Alkoxy ausgewählt ist, ausgewählt ist;

(iii) $-C(O)X_{24}$; wobei X_{24} aus einem Verlängerungsmittel L, Hydroxy, C_1-C_{12}-Alkyl, C_1-C_{12}-Alkoxy, Phenyl, das unsubstituiert oder mit C_1-C_{12}-Alkyl oder C_1-C_{12}-Alkoxy monosubstituiert ist, Amino, das unsubstituiert, mono- oder disubstituiert mit mindestens einem von C_1-C_{12}-Alkyl, Phenyl, Benzyl und Naphthyl ist, ausgewählt ist; oder
(iv) Halogen, Hydroxy, Ester oder Amin;

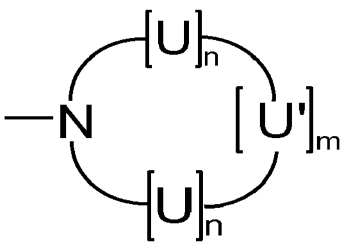
(c) Y' ausgewählt ist aus: $-(Y_1)C=C(Y_2)-$, -O-,-S-,-S(O)(O)- und $-N(X_7)-$, wobei Y_1 und Y_2 zusammen Benzo, Naphtho, Phenanthro, Furo, Thieno, Benzofuro, Benzothieno und Indolo bilden, und X_7 ausgewählt ist aus:

(i) einem Verlängerungsmittel L, Wasserstoff, C_1-C_{12}-Alkyl, C_1-C_{12}-Acyl, Phenyl(C_1-C_{12})alkyl, mono(C_1-C_{12})alkylsubstituiertem Phenyl(C_1-C_{12})alkyl, mono(C_1-C_{12})alkoxysubstituiertem Phenyl(C_1-C_{12})alkyl; C_1-C_{12}-Alkoxy(C_1-C_{12})alkyl; C_3-C_7-Cycloalkyl; mono(C_1-C_{12})alkylsubstituiertem C_3-C_7-Cycloalkyl, C_1-C_{12}-Halogenalkyl, Allyl, Benzoyl, monosubstituiertem Benzoyl, Naphthoyl oder monosubstituiertem Naphthoyl, wobei diese Benzoyl- und Naphthoylsubstituenten jeweils unabhängig aus C_1-C_{12}-Alkyl und C_1-C_{12}-Alkoxy ausgewählt sind;
(ii) -CH(X_8)X_9, wobei X_8 aus einem Verlängerungsmittel L, Wasserstoff oder C_1-C_{12}-Alkyl ausgewählt ist; und X_9 aus einem Verlängerungsmittel L, -CN, -CF_3 oder -COOX_{10}, wobei X_{10} aus einem Verlängerungsmittel L, Wasserstoff oder C_1-C_{12}-Alkyl ausgewählt ist, ausgewählt ist;
(iii) -C(O)X_6, wobei X_6 ausgewählt ist aus mindestens einem von: einem Verlängerungsmittel L, Wasserstoff, C_1-C_{12}-Alkoxy, Phenoxy, das unsubstituiert, mono- oder disubstituiert mit C_1-C_{12}-Alkyl oder C_1-C_{12}-Alkoxy ist, einer Arylgruppe, die unsubstituiert, mono- oder disubstituiert mit C_1-C_{12}-Alkyl oder C_1-C_{12}-Alkoxy ist, einer Aminogruppe, die unsubstituiert, mono- oder disubstituiert mit C_1-C_{12}-Alkyl ist und einer Phenylaminogruppe, die unsubstituiert, mono- oder disubstituiert mit C_1-C_{12}-Alkyl oder C_1-C_{12}-Alkoxy ist;
(iv) Tri(C_1-C_{12})alkylsilyl, Tri(C_1-C_{12})alkoxysilyl, Di(C_1-C_{12})alkyl-(C_1-C_{12}alkoxy)silyl oder Di(C_1-C_{12})alkoxy(C_1-C_{12} alkyl)silyl;

(d) B ausgewählt ist aus:

(i) Wasserstoff, C_1-C_{12}-Alkyl, C_2-C_{12}-Alkyliden, C_2-C_{12}-Alkylidin, Vinyl, C_3-C_7-Cycloalkyl, C_1-C_{12}-Halogenalkyl, Allyl, Halogen und Benzyl, das unsubstituiert oder mit mindestens einem von C_1-C_{12}-Alkyl und C_1-C_{12}-Alkoxy monosubstituiert ist;
(ii) Phenyl, welches in der *para* -Position monosubstituiert mit mindestens einem Substituenten ist, der ausgewählt ist aus: C_1-C_7-Alkoxy, linearem oder verzweigtkettigem C_1-C_{20}-Alkylen, linearem oder verzweigtkettigem C_1-C_4-Polyoxyalkylen, cyclischem C_3-C_{20}-Alkylen, Phenylen, Naphthylen, C_1-C_4-alkylsubstituiertem Phenylen, Mono- oder Polyurethan-(C_1-C_{20})alkylen, Mono- oder Polyester(C_1-C_{20})alkylen, Mono- oder Polycarbonat(C_1-C_{20})alkylen, Polysilanylen, Polysiloxanylen und Mischungen davon, wobei der mindestens eine Substituent mit einer Arylgruppe eines photochromen Materials verbunden ist;
(iii) -CH$(CN)_2$ und -CH$(COOX_1)_2$;
(iv) -CH(X_2)(X_3);
(v) einer unsubstituierten, mono-, di- oder trisubstituierten Arylgruppe; 9-Julolidinyl; oder einer unsubstituierten, mono- oder disubstituierten heteroaromatischen Gruppe ausgewählt aus Pyridyl, Furanyl, Benzofuran-2-yl, Benzofuran-3-yl, Thienyl, Benzothien-2-yl, Benzothien-3-yl, Dibenzofuranyl, Dibenzothienyl, Carbazoyl, Benzopyridyl, Indolinyl oder Fluorenyl; wobei jeder Substituent unabhängig voneinander bei jedem Auftreten ausgewählt ist aus:

(A) einem Verlängerungsmittel L;
(B) -C(O)X_6,
(C) Aryl, Halogenaryl, C_3-C_7-Cycloalkylaryl und einer Arylgruppe, die mit C_1-C_{12}-Alkyl oder C_1-C_{12}-Alkoxy mono- oder disubstituiert ist;
(D) C_1-C_{12}-Alkyl, C_3-C_7-Cycloalkyl, C_3-C_7-Cycloalkyloxy-(C_1-C_{12})alkyl, Aryl(C_1-C_{12})alkyl, Aryloxy(C_1-C_{12})alkyl, Mono- oder Di(C_1-C_{12})alkylaryl(C_1-C_{12})alkyl, Mono- oder Di(C_1-C_{12})alkoxyaryl(C_1-C_{12})alkyl, Halogenalkyl und Mono(C_1-C_{12})alkoxy(C_1-C_{12})alkyl;
(E) C_1-C_{12}-Alkoxy, C_3-C_7-Cycloalkoxy, Cycloalkyloxy-(C_1-C_{12})alkoxy, Aryl(C_1-C_{12})alkoxy, Aryloxy(C_1-C_{12})alkoxy, Mono- oder Di(C_1-C_{12})alkylaryl(C_1-C_{12})alkoxy und Mono- oder Di(C_1-C_{12})alkoxyaryl(C_1-C_{12})alkoxy,
(F) Amido, Amino, Mono- oder Dialkylamino, Diarylamino, Piperazino, N-(C_1-C_{12})Alkylpiperazino, N-Arylpiperazino, Aziridino, Indolino, Piperidino, Morpholino, Thiomorpholino, Tetrahydrochinolino, Tetrahydroisochinolino, Pyrrolidyl, Hydroxy, Acryloxy, Methacryloxy und Halogen;
(G) -OX_7 oder -N$(X_7)_2$;
(H) -SX_{11}, wobei X_{11} aus einem Verlängerungsmittel L, C_1-C_{12}-Alkyl, einer Arylgruppe, die unsubstituiert oder mit C_1-C_{12}-Alkyl, C_1-C_{12}-Alkoxy oder Halogen mono- oder disubstituiert ist;
(I) einem stickstoffhaltigen Ring dargestellt durch Formel i:



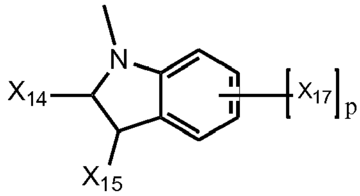
i

wobei

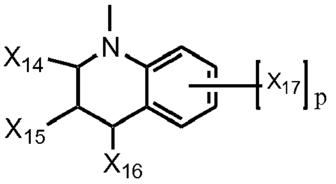
(1) n eine ganze Zahl ausgewählt aus 0, 1, 2 und 3 ist, vorausgesetzt, dass, wenn n 0 ist, U' U ist und jedes U unabhängig voneinander bei jedem Auftreten ausgewählt ist aus: $-CH_2-$, $-CH(X_{12})-$, $-C(X_{12})_2-$, $-CH(X_{13})-$, $-C(X_{13})_2-$ und $-C(X_{12})(X_{13})-$, wobei X_{12} aus einem Verlängerungsmittel L dargestellt durch nachfolgende Formel I und C_1-C_{12}-Alkyl ausgewählt ist und X_{13} aus einem Verlängerungsmittel L dargestellt durch nachfolgende Formel I. Phenyl und Naphthyl ausgewählt ist und

(2) U' aus U, -O-, -S-, -S(O)-, -NH-,$-N(X_{12})-$ oder $-N(X_{13})-$ ausgewählt ist und m eine ganze Zahl ist, die aus 1, 2 und 3 ausgewählt ist und

(J) einer Gruppe dargestellt durch die Formel ii oder iii:



ii

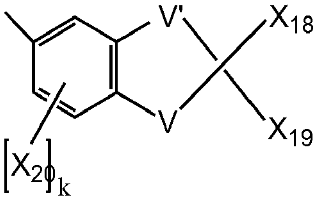


iii

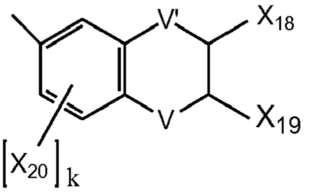
wobei X_{14}, X_{15} und X_{16} unabhängig voneinander bei jedem Auftreten aus einem Verlängerungsmittel L, C_1-C_{12}-Alkyl, Phenyl oder Naphthyl ausgewählt sind oder X_{14} und X_{15} zusammen einen Ring mit 5 bis 8 Kohlenstoffatomen bilden; p eine ganze Zahl ausgewählt aus 0, 1 oder 2 ist und X_{17} unabhängig voneinander bei jedem Auftreten aus einem Verlängerungsmittel L, C_1-C_{12}-Alkyl, C_1-C_{12}-Alkoxy oder Halogen ausgewählt ist;

(vi) einer unsubstituierten oder monosubstituierten Gruppe ausgewählt aus Pyrazolyl, Imidazolyl, Pyrazolinyl, Imidazolinyl, Pyrrolidinyl, Phenothiazinyl, Phenoxazinyl, Phenazinyl oder Acridinyl, wobei jeder Substituent unabhängig aus einem Verlängerungsmittel L, C_1-C_{12}-Alkyl, C_1-C_{12}-Alkoxy, Phenyl, Hydroxy, Amino oder Halogen ausgewählt ist;

(vii) einer Gruppe dargestellt durch Formel iv oder v:



iv



v

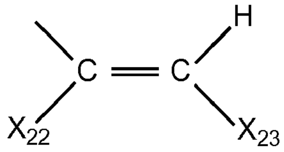
(A) V' unabhängig in jeder Formel aus -O-, -CH-, C_1-C_6-Alkylen und C_3-C_7-Cycloalkylen ausgewählt ist,

(B) V unabhängig in jeder Formel aus -O- oder $-N(X_{21})-$ ausgewählt ist, wobei X_{21} aus einem Verlängerungsmittel L dargestellt durch nachfolgende Formel I, Wasserstoff, C_1-C_{12}-Alkyl und C_2-C_{12}-Acyl ausgewählt ist, vorausgesetzt, dass, wenn V $-N(X_{21})-$ ist, V' $-CH_2-$ ist,

(C) X_{18} und X_{19} jeweils unabhängig voneinander aus einem Verlängerungsmittel L, Wasserstoff und C_1-C_{12}-Alkyl ausgewählt sind und

(D) k aus 0, 1 und 2 ausgewählt ist und jedes X_{20} unabhängig voneinander bei jedem Auftreten aus einem Verlängerungsmittel L, C_1-C_{12}-Alkyl, C_1-C_{12}-Alkoxy, Hydroxy und Halogen ausgewählt ist; und

(viii) einer Gruppe dargestellt durch Formel vi:



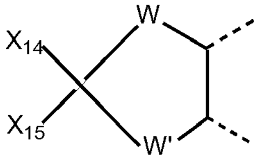
vi

wobei

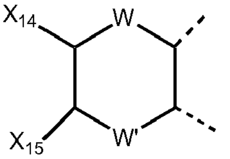
(A) X_{22} aus einem Verlängerungsmittel L, Wasserstoff und C_1-C_{12}-Alkyl ausgewählt ist und
(B) X_{23} aus einem Verlängerungsmittel L und einer unsubstituierten, mono- oder disubstituierten Gruppe ausgewählt aus Naphthyl, Phenyl, Furanyl und Thienyl ausgewählt ist, wobei jeder Substituent unabhängig voneinander bei jedem Auftreten aus C_1-C_{12}-Alkyl, C_1-C_{12}-Alkoxy und Halogen ausgewählt ist; und

(e) i eine ganze Zahl ausgewählt aus von 0 bis 4 ist und jedes R^2 jeweils unabhängig voneinander bei jedem Auftreten ausgewählt ist aus:

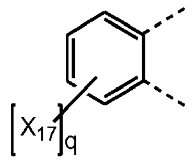
(i) einer Gruppe dargestellt durch B;
(ii) -C(O)X_{24};
(iii) -OX_7 und -N$(X_7)_2$;
(iv) -SX_{11};
(v) dem stickstoffhaltigen Ring dargestellt durch Formel i;
(vi) der Gruppe dargestellt durch Formel ii oder iii;
(vii) unmittelbar benachbarte R^2-Gruppen eine Gruppe bilden, die durch Formel vii, viii oder ix dargestellt ist:



vii



viii



ix

wobei

(A) W und W' unabhängig voneinander bei jedem Auftreten aus -O-, -N(X_7)-, -C(X_{14})-, -C(X_{17})- ausgewählt sind,
(B) X_{14}, X_{15} und X_{17} wie oben definiert sind, und
(C) q eine ganze Zahl ausgewählt aus 0, 1, 2, 3 und 4 ist; und

(viii) einem Verlängerungsmittel L,
vorausgesetzt, dass die nicht thermisch reversible photochrome Verbindung mindestens ein Verlängerungsmittel L umfasst und jedes Verlängerungsmittel L unabhängig voneinander bei jedem Auftreten aus einer Verbindung ausgewählt ist, die durch Formel I dargestellt ist:

$$- [S_1]_c -[Q_1 -[S_2]_d]_{d'}-[Q_2 -[S_3]_e]_{e'}-[Q_3 -[S_4]_f]_{f'} -S_5 -P \qquad \text{I}$$

wobei:

(a) jedes Q_1, Q_2 und Q_3 unabhängig voneinander bei jedem Auftreten ausgewählt ist aus: einer divalenten Gruppe ausgewählt aus: einer unsubstituierten oder einer substituierten aromatischen Gruppe, einer unsubstituierten oder einer substituierten alicyclischen Gruppe, einer unsubstituierten oder substituierten heterocyclischen Gruppe und Mischungen davon, wobei die Substituenten ausgewählt sind aus: einer Gruppe dargestellt durch P, Thiol, Amide, Flüssigkristallmesogenen, Halogen, C_1-C_{18}-Alkoxy, Poly(C_1-C_{18} alkoxy), Amino, Amino(C_1-C_{18})alkylen, C_1-C_{18}-Alkylamino, Di(C_1-C_{18})alkylamino, C_1-C_{18}-Alkyl, C_2-C_{18}-Alken, C_2-C_{18}-Alkin, C_1-C_{18}-Alkyl(C_1-C_{18})alkoxy, C_1-C_{18}-Alkoxycarbonyl, C_1-C_{18}-Alkylcarbonyl, C_1-C_{18}-Alkylcarbonat, Arylcarbonat, C_1-C_{18}-Acetyl, C_3-C_{10}-Cycloalkyl, C_3-C_{10}-Cycloalkoxy, Isocyanato, Amido, Cyano, Nitro, einer geradkettigen oder verzweigten C_1-C_{18}-Alkylgruppe, die mit Cyano, Halogen oder C_1-C_{18}-Alkoxy monosubstituiert ist oder mit Halogen polysubstituiert ist und eine Gruppe dargestellt durch eine der folgenden Formeln: $-M(T)_{(t-1)}$ und $-M(OT)_{(t-1)}$, wobei M aus Aluminum, Antimon, Tantal, Titan, Zirconium und Silicium ausgewählt ist, T aus organofunktionellen Resten, organofunktionellen Kohlenwasserstoffresten, aliphatischen Kohlenwasserstoffresten und aromatischen Kohlenwasserstoffresten ausgewählt ist und t die Wertigkeit von M ist;

(b) c, d, e und f jeweils unabhängig voneinander aus einer ganzen Zahl, die von 0 bis inklusive 20 reicht, ausgewählt sind; und jedes S_1, S_2, S_3, S_4 und S_5 unabhängig voneinander bei jedem Auftreten aus einer Abstandshaltereinheit ausgewählt ist, die ausgewählt ist aus:

> (i) $-(CH_2)_g-$, $-(CF_2)_h-$, $-Si(CH_2)_g-$, $-(Si[(CH_3)_2]O)_h-$, wobei g unabhängig voneinander bei jedem Auftreten aus von 1 bis 20 ausgewählt ist; h eine ganze Zahl von 1 bis inklusive 16 ist;
>
> (ii) -N(Z)-, -C(Z)=C(Z)-, -C(Z)=N-, -C(Z')-C(Z')-, wobei Z unabhängig voneinander bei jedem Auftreten aus Wasserstoff, C_1-C_6-Alkyl, Cycloalkyl und Aryl ausgewählt ist und Z' unabhängig voneinander bei jedem Auftreten aus C_1-C_6-Alkyl, Cycloalkyl und Aryl ausgewählt ist; und
>
> (ii) -O-, -C(O)-, -C≡C-, -N=N-, -S-, -S(O)-, -S(O)(O)-, geradkettigem oder verzweigtem C_1-C_{24}-Alkylenrest, wobei der C_1-C_{24}-Alkylenrest unsubstituiert, mit Cyano oder Halogen monosubstituiert oder mit Halogen mehrfachsubstituiert ist; vorausgesetzt, dass, wenn zwei Abstandshaltereinheiten umfassend Heteroatome miteinander verknüpft sind, die Abstandshaltereinheiten in einer solchen Weise miteinander verknüpft sind, dass die Heteroatome nicht direkt miteinander verknüpft sind und wenn S_1 und S_5 mit PC beziehungsweise P verknüpft sind, sie in einer solchen Weise verknüpft sind, dass zwei Heteroatome nicht direkt miteinander verbunden sind;

(c) P ausgewählt ist aus: Aziridinyl, Wasserstoff, Hydroxy, Aryl, Alkyl, Alkoxy, Amino, Alkylamino, Alkylalkoxy, Alkoxyalkoxy, Nitro, Polyalkylether, $(C_1$-$C_6)$Alkyl$(C_1$-$C_6)$alkoxy$(C_1$-$C_6)$alkyl, Polyethylenoxy, Polypropylenoxy, Ethylen, Acrylat, Methacrylat, 2-Chloracrylat, 2-Phenylacrylat, Acryloylphenylen, Acrylamid, Methacrylamid, 2-Chloracrylamid, 2-Phenylacrylamid, Epoxy, Isocyanat, Thiol, Thioisocyanat, Itaconsäureester, Vinylether, Vinylester, einem Styrolderivat, Siloxan, Hauptketten- und Seitenkettenflüssigkristallpolymeren, Ethyleniminderivaten, Maleinsäurederivaten, Fumarsäurederivaten, unsubstituierten Zimtsäurederivaten, Zimtsäurederivaten, die mit mindestens einem von Methyl, Methoxy, Cyano und Halogen substituiert sind, und substituierten und unsubstituierten, chiralen und nichtchiralen monovalenten oder divalenten Gruppen, die aus Steroidresten, Terpenoidresten, Alkaloidresten und Mischungen davon ausgewählt sind, wobei die Substituenten unabhängig voneinander aus Alkyl, Alkoxy, Amino, Cycloalkyl, Alkylalkoxy, Fluoralkyl, Cyanoalkyl, Cyanoalkoxy und Mischungen derselben ausgewählt sind; und

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

2. Die nicht thermisch reversible photochrome Verbindung gemäß Anspruch 1, wobei entweder in Formel X oder XI die ganze Zahl i mindestens eins ist und mindestens eine der R^2-Gruppen ein Verlängerungsmittel L ist.

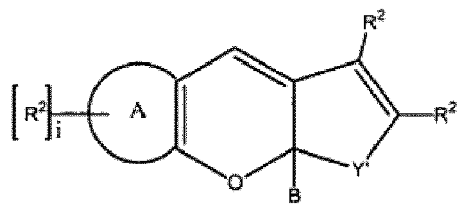
3. Die nicht thermisch reversible photochrome Verbindung gemäß einem der vorhergehenden Ansprüche, wobei die photochrome Verbindung mindestens eine R^2-Gruppe umfasst, die mit einem Verlängerungsmittel L substituiert ist.

4. Die nicht thermisch reversible photochrome Verbindung gemäß Anspruch 1 dargestellt durch Formel X, wobei das Verlängerungsmittel L an einer R^2- oder B-Gruppe substituiert ist.

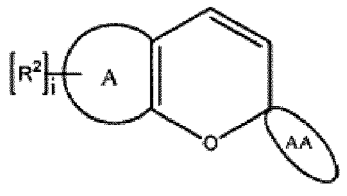
5. Die nicht thermisch reversible photochrome Verbindung gemäß Anspruch 1 dargestellt durch Formel XI, wobei das Verlängerungsmittel L an einer R^2- oder AA-Gruppe substituiert ist.

Revendications

1. Composé photochromique non thermiquement réversible, représenté par l'une des formules X et XI :



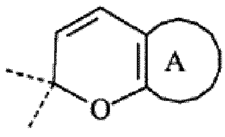
X



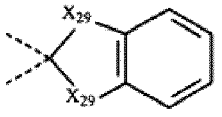
XI

dans lesquelles :

(a) A est choisi parmi les groupes naphto, benzo, phénanthro, fluoranthéno, anthéno, quinolino, thiéno, furo, indolo, indolino, indéno, benzofuro, benzothiéno, thiophéno, naphto soudé à indéno, naphto soudé à un groupe hétérocyclique, et benzo soudé à un groupe hétérocyclique ;
(b) AA est un groupe représenté par l'une des formules xv et xvi :



xv



xvi

où les radicaux X_{29} sont choisis indépendamment pour chaque occurrence parmi les groupes -C(R")(R")-, -O-, -S- et -N(R"')-, où les radicaux R" sont choisis indépendamment pour chaque occurrence chacun parmi un atome d'hydrogène, un groupe alkyle, cycloalkyle, arylalkyle, substitué ou non substitué, ou forment ensemble un groupe cycloalkyle qui est substitué ou non substitué ; R'" est choisi indépendamment pour chaque occurrence parmi un groupe alkyle, aryle ou arylalkyle qui est non substitué ou porte au moins un substituant parmi :

(i) un groupe $-CH(CN)_2$ ou $-CH(COOX_1)_2$ dans lequel X_1 est choisi parmi au moins un de l'ensemble constitué par un agent d'extension L, un atome d'hydrogène, un groupe alkyle en C_1-C_{12} qui est non substitué ou monosubstitué par phényle, un groupe phényl-alkyle(C_1-C_{12}) qui est monosubstitué par alkyle en C_1-C_{12} ou alcoxy en C_1-C_{12}, et un groupe aryle qui est non substitué, mono- ou disubstitué, chaque substituant du groupe aryle étant choisi indépendamment parmi alkyle en C_1-C_{12} et alcoxy en C_1-C_{12} ;
(ii) un groupe $-CH(X_2)(X_3)$ dans lequel

(A) X_2 est choisi parmi au moins un de l'ensemble constitué par un agent d'extension L, un atome d'hydrogène, un groupe alkyle en C_1-C_{12}, et un groupe aryle qui est non substitué, mono- ou disubstitué, chaque substituant du groupe aryle étant choisi indépendamment parmi alkyle en C_1-C_{12} et alcoxy en C_1-C_{12} ; et
(B) X_3 est choisi parmi au moins un de l'ensemble constitué par les groupes $-COOX_1$, $-COX_1$, $-COX_4$ et $-CH_2OX_5$, dans lesquels :

(1) X_4 est choisi parmi au moins un de l'ensemble constitué par les groupes morpholino, pipéridino, amino qui est non substitué, mono- ou disubstitué par alkyle en C_1-C_{12}, et un groupe non substitué, mono- ou disubstitué, choisi parmi les groupes phénylamino et diphénylamino, chaque substituant étant choisi indépendamment parmi alkyle en C_1-C_{12} et alcoxy en C_1-C_{12} ; et
(2) X_5 est choisi parmi un agent d'extension L, un atome d'hydrogène, un groupe $-C(O)X_2$, un groupe alkyle en C_1-C_{12} qui est non substitué ou monosubstitué par alcoxy en C_1-C_{12} ou phényle, un groupe phényl-alkyle(C_1-C_{12}) qui est monosubstitué par alcoxy en C_1-C_{12}, et un groupe aryle qui est non substitué, mono- ou disubstitué, chaque substituant du groupe aryle étant choisi indé-

pendamment parmi alkyle en C_1-C_{12} et alcoxy en C_1-C_{12};

(iii) un groupe -C(O)X_{24}; dans lequel X_{24} est choisi parmi un agent d'extension L, un groupe hydroxy, alkyle en C_1-C_{12}, alcoxy en C_1-C_{12}, un groupe phényle qui est non substitué ou monosubstitué par alkyle en C_1-C_{12} ou alcoxy en C_1-C_{12}, un groupe amino qui est non substitué, mono- ou disubstitué par au moins un de l'ensemble constitué par les groupes alkyle en C_1-C_{12}, phényle, benzyle et naphtyle ; ou
(iv) un atome d'halogène, un groupe hydroxy, ester ou amino ;

(c) Y' est choisi parmi : les groupes -(Y_1)C=C(Y_2)-, -O-, -S-, -S(O)(O)- et -N(X_7)-, Y_1 et Y_2 formant ensemble un groupe benzo, naphto, phénanthro, furo, thiéno, benzofuro, benzothiéno ou indolo, et X_7 étant choisi parmi :

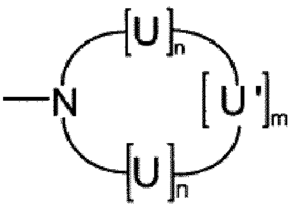
(i) un agent d'extension L, un atome d'hydrogène, un groupe alkyle en C_1-C_{12}, acyle en C_1-C_{12}, phényl-alkyle(C_1-C_{12}), un groupe phényl-alkyle(C_1-C_{12}) monosubstitué par alkyle en C_1-C_{12}, un groupe phényl-alkyle(C_1-C_{12}) monosubstitué par alcoxy en C_1-C_{12}; un groupe alcoxy(C_1-C_{12})-alkyle(C_1-C_{12}); un groupe cycloalkyle en C_3-C_7 ; un groupe cycloalkyle en C_3-C_7 monosubstitué par alkyle en C_1-C_{12}, un groupe halogénoalkyle(C_1-C_{12}), allyle, benzoyle, benzoyle monosubstitué, naphtoyle ou naphtoyle monosubstitué, chacun desdits substituants des groupes benzoyle et naphtoyle étant choisi indépendamment parmi des groupes alkyle en C_1-C_{12} et alcoxy en C_1-C_{12} ;
(ii) un groupe -CH(X_8)X_9, dans lequel X_8 est choisi parmi un agent d'extension L, un atome d'hydrogène ou un groupe alkyle en C_1-C_{12} ; et X_9 est choisi parmi un agent d'extension L, un groupe -CN, -CF_3 ou -COOX_{10}, dans lequel X_{10} est choisi parmi un agent d'extension L, un atome d'hydrogène ou un groupe alkyle en C_1-C_{12} ;
(iii) un groupe -C(O)X_6, dans lequel X_6 est choisi parmi au moins un de l'ensemble constitué par : un agent d'extension L, un atome d'hydrogène, un groupe alcoxy en C_1-C_{12}, un groupe phénoxy qui est non substitué, mono- ou disubstitué par alkyle en C_1-C_{12} ou alcoxy en C_1-C_{12}, un groupe aryle qui est non substitué, mono- ou disubstitué par alkyle en C_1-C_{12} ou alcoxy en C_1-C_{12}, un groupe amino qui est non substitué, mono- ou disubstitué par alkyle en C_1-C_{12}, et un groupe phénylamino qui est non substitué, mono- ou disubstitué par alkyle en C_1-C_{12} ou alcoxy en C_1-C_{12} ;
(iv) un groupe trialkyl(C_1-C_{12})silyle, trialcoxy(C_1-C_{12})silyle, dialkyl(C_1-C_{12})(alcoxy(C_1-C_{12}))silyle, ou dialcoxy(C_1-C_{12})-(alkyl(C_1-C_{12}))silyle ;

(d) B est choisi parmi :

(i) un atome d'hydrogène, un groupe alkyle en C_1-C_{12}, alkylidène en C_2-C_{12}, alkylidyne en C_2-C_{12}, vinyle, cycloalkyle en C_3-C_7, halogénoalkyle(C_1-C_{12}), allyle, un atome d'halogène, et un groupe benzyle qui est non substitué ou monosubstitué par au moins un de l'ensemble constitué par un groupe alkyle en C_1-C_{12} et un groupe alcoxy en C_1-C_{12} ;
(ii) un groupe phényle qui est monosubstitué en position *para* par au moins un substituant choisi parmi : un groupe alcoxy en C_1-C_7, un groupe alkylène en C_1-C_{20} à chaîne linéaire ou ramifiée, un groupe polyoxy-alkylène en C_1-C_4 à chaîne linéaire ou ramifiée, un groupe alkylène en C_3-C_{20} cyclique, un groupe phénylène, un groupe naphtylène, un groupe phénylène substitué par alkyle en C_1-C_4, un groupe mono- ou poly-uréthane-alkylène(C_1-C_{20}), un groupe mono- ou poly-ester-alkylène(C_1-C_{20}), un groupe mono- ou poly-carbonate-alkylène(C_1-C_{20}), un groupe polysilanylène, un groupe polysiloxanylène et des mélanges de ceux-ci, ledit au moins un substituant étant relié à un groupe aryle de la substance photochromique ;
(iii) un groupe -CH$(CN)_2$ et un groupe -CH$(COOX_1)_2$;
(iv) un groupe -CH(X_2)(X_3) ;
(v) un groupe aryle non substitué, mono-, di- ou trisubstitué ; un groupe 9-julolidinyle ; ou un groupe hétéroaromatique non substitué, mono- ou disubstitué, choisi parmi les groupes pyridyle, furanyle, benzofuran-2-yle, benzofuran-3-yle, thiényle, benzothién-2-yle, benzothién-3-yle, dibenzofuranyle, dibenzothiényle, carbazoyle, benzopyridyle, indolinyle ou fluorényle ; chaque substituant étant choisi indépendamment pour chaque occurrence parmi :

(A) un agent d'extension L ;
(B) un groupe -C(O)X_6 ;
(C) un groupe aryle, halogénoaryle, cycloalkyl(C_3-C_7)aryle, et un groupe aryle qui est mono- ou disubstitué par alkyle en C_1-C_{12} ou alcoxy en C_1-C_{12} ;
(D) des groupes alkyle en C_1-C_2, cycloalkyle en C_3-C_7, cycloalkyloxy(C_3-C_7)alkyle(C_1-C_{12}), aryl-alkyle(C_1-C_{12}), aryloxy-alkyle(C_1-C_{12}), mono- ou di-alkyl(C_1-C_{12})aryl-alkyle(C_1-C_{12}), mono- ou di-al-

coxy(C_1-C_{12})aryl-alkyle(C_1-C_{12}), halogénoalkyle et monoalcoxy(C_1-C_{12})alkyle(C_1-C_{12}) ;
(E) des groupes alcoxy en C_1-C_{12}, cycloalcoxy en C_3-C_7, cycloalkyloxy-alcoxy(C_1-C_{12}), arylalcoxy(C_1-C_{12}), aryloxy-alcoxy(C_1-C_{12}), mono- ou di-alkyl(C_1-C_{12})aryl-alcoxy(C_1-C_{12}), et mono- ou di-alcoxy(C_1-C_{12})arylalcoxy(C_1-C_{12}) ;
(F) un groupe amido, amino, mono- ou di-alkylamino, diarylamino, pipérazino, N-alkyl(C_1-C_{12})pipérazino, N-arylpipérazino, aziridino, indolino, pipéridino, morpholino, thiomorpholino, tétrahydroquinolino, tétrahydroisoquinolino, pyrrolidyle, hydroxy, acryloxy, méthacryloxy et un atome d'halogène ;
(G) un groupe $-OX_7$ ou $-N(X_7)_2$;
(H) un groupe $-SX_{11}$, dans lequel X_{11} est choisi parmi un agent d'extension L, un groupe alkyle en C_1-C_{12}, un groupe aryle qui est non substitué ou mono- ou disubstitué par alkyle en C_1-C_{12}, alcoxy en C_1-C_{12} ou halogéno ;
(I) un cycle contenant de l'azote, représenté par la formule i :

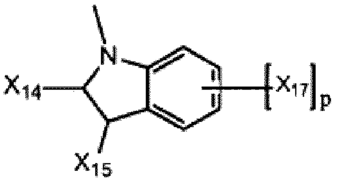


i

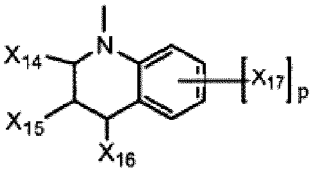
dans laquelle

(1) n est un nombre entier choisi parmi 0, 1, 2 et 3, étant entendu que si n est 0, U' est U, et chaque U est choisi indépendamment pour chaque occurrence parmi les groupes $-CH_2-$, $-CH(X_{12})-$, $-C(X_{12})_2-$, $-CH(X_{13})-$, $-C(X_{13})_2-$ et $-C(X_{12})(X_{13})-$, X_{12} étant choisi parmi un agent d'extension L représenté par la formule I ci-dessous et un groupe alkyle en C_1-C_{12}, et X_{13} étant choisi parmi un agent d'extension L représenté par la formule I ci-dessous, les groupes phényle et naphtyle, et
(2) U' est choisi parmi U, -O-, -S-, -S(O)-, -NH-, $-N(X_{12})-$ ou $-N(X_{13})-$, et m est un nombre entier choisi parmi 1, 2 et 3, et

(J) un groupe représenté par la formule ii ou iii :



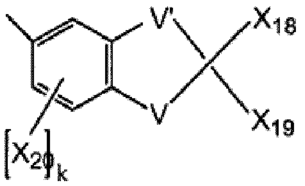
ii



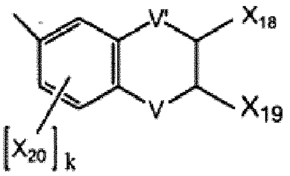
iii

formules dans lesquelles X_{14}, X_{15} et X_{16} sont choisis indépendamment pour chaque occurrence parmi un agent d'extension L, un groupe alkyle en C_1-C_{12}, phényle ou naphtyle, ou X_{14} et X_{15} ensemble forment un cycle à 5 à 8 atomes de carbone ; p est un nombre entier choisi parmi 0, 1 et 2, et X_{17} est choisi indépendamment pour chaque occurrence parmi un agent d'extension L, un groupe alkyle en C_1-C_{12}, un groupe alcoxy en C_1-C_{12} ou un atome d'halogène ;

(vi) un groupe non substitué ou monosubstitué choisi parmi un groupe pyrazolyle, imidazolyle, pyrazolinyle, imidazolinyle, pyrrolidinyle, phénothiazinyle, phénoxazinyle, phénazinyle ou acridinyle, chaque substituant étant choisi indépendamment parmi un agent d'extension L, un groupe alkyle en C_1-C_{12}, alcoxy en C_1-C_{12}, phényle, hydroxy, amino ou un atome d'halogène ;
(vii) un groupe représenté par la formule iv ou v :



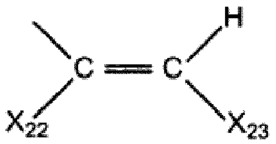
iv



v

(A) V' est choisi indépendamment dans chaque formule parmi -O-, -CH-, un groupe alkylène en C_1-C_6 et un groupe cycloalkylène en C_3-C_7,
(B) V est choisi indépendamment dans chaque formule parmi -O- ou -N(X_{21})-, X_{21} étant choisi parmi un agent d'extension L représenté par la formule I ci-dessous, un atome d'hydrogène, un groupe alkyle en C_1-C_{12}, et un groupe acyle en C_2-C_{12}, étant entendu que si V est un groupe -N(X_{21})-, V' est un groupe -CH_2-,
(C) X_{18} et X_{19} sont choisis chacun indépendamment parmi un agent d'extension L, un atome d'hydrogène et un groupe alkyle en C_1-C_{12}, et
(D) k est choisi parmi 0, 1 et 2, et chaque groupe X_{20} est choisi indépendamment pour chaque occurrence parmi un agent d'extension L, des groupes alkyle en C_1-C_{12}, alcoxy en C_1-C_{12}, hydroxy et des atomes d'halogène ; et

(viii) un groupe représenté par la formule vi :



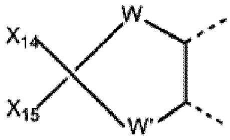
vi

dans laquelle

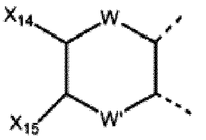
(A) X_{22} est choisi parmi un agent d'extension L, un atome d'hydrogène et un groupe alkyle en C_1-C_{12}, et
(B) X_{23} est choisi parmi un agent d'extension L et un groupe non substitué, mono- ou disubstitué, choisi parmi les groupes naphtyle, phényle, furanyle et thiényle, chaque substituant étant choisi indépendamment pour chaque occurrence parmi des groupes alkyle en C_1-C_{12}, alcoxy en C_1-C_{12} et des atomes d'halogène ; et

(e) i est un nombre entier valant de 0 à 4, et chaque radical R^2 est choisi indépendamment pour chaque occurrence parmi :

(i) un groupe représenté par B ;
(ii) un groupe -C(O)X_{24} ;
(iii) les groupes -OX_7 et -N(X_7)$_2$;
(iv) un groupe -SX_{11} ;
(v) le cycle contenant de l'azote représenté par la formule i ;
(vi) le groupe représenté par la formule ii ou iii ;
(vii) des groupes R^2 contigus forment ensemble un groupe représenté par la formule vii, viii ou ix ;

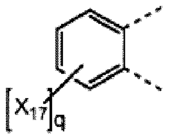


vii



viii

ix



formules dans lesquelles

(A) W et W' sont choisis indépendamment pour chaque occurrence parmi -O-, -N(X_7)-, -C(X_{14})-,

-C(X_{17})-,
(B) X_{14}, X_{15} et X_{17} sont tels que définis ci-dessus, et
(C) q est un nombre entier choisi parmi 0, 1, 2, 3 et 4 ; et

(viii) un agent d'extension L ;

étant entendu que le composé photochromique non thermiquement réversible comprend au moins un agent d'extension L et chaque agent d'extension L est choisi indépendamment pour chaque occurrence parmi les composés représentés par la formule I :

$$\mathbf{-\,[S_1]_c\text{-}[Q_1\text{-}[S_2]_d]_{d'}\text{-}[Q_2\text{-}[S_3]_e]_{e'}\text{-}[Q_3\text{-}[S_4]_f]_{f'}\text{-}S_5\text{-}P} \qquad \mathbf{I}$$

dans laquelle :

(a) chaque radical Q_1, Q_2 et Q_3 est choisi indépendamment pour chaque occurrence parmi : un groupe divalent choisi parmi : un groupe aromatique non substitué ou un groupe aromatique substitué, un groupe alicyclique non substitué ou un groupe alicyclique substitué, un groupe hétérocyclique non substitué ou un groupe hétérocyclique substitué, et des mélanges de ceux-ci, les substituants étant choisis parmi : un groupe représenté par P, un groupe thiol, un groupe amide, les mésogènes de cristaux liquides, un atome d'halogène, un groupe alcoxy en C_1-C_{18}, poly(alcoxy(C_1-C_{18})), amino, amino-alkylène(C_1-C_{18}), alkyl(C_1-C_{18})amino, dialkyl(C_1-C_{18})amino, alkyle en C_1-C_{18}, alcényle en C_2-C_{18}, alcynyle en C_2-C_{18}, alkyl(C_1-C_{18})alcoxy(C_1-C_{18}), alcoxy(C_1-C_{18})-carbonyle, alkyl(C_1-C_{18})carbonyle, alkyl(C_1-C_{18})carbonate, arylcarbonate, acétyle en C_1-C_{18}, cycloalkyle en C_3-C_{10}, cycloalcoxy en C_3-C_{10}, isocyanato, amido, cyano, nitro, un groupe alkyle en C_1-C_{18} à chaîne droite ou ramifié, qui est monosubstitué par cyano, halogéno ou alcoxy en C_1-C_{18}, ou polysubstitué par halogéno, et un groupe représenté par l'une des formules suivantes : -M(T)$_{(t-1)}$ et -M(OT)$_{(t-1)}$, dans lesquelles M est choisi parmi l'aluminium, l'antimoine, le tantale, le zirconium et le silicium, T est choisi parmi des radicaux organofonctionnels, des radicaux hydrocarbonés organofonctionnels, des radicaux hydrocarbonés aliphatiques et des radicaux hydrocarbonés aromatiques, et t est la valence de M ;
(b) c, d, e et f sont choisis chacun indépendamment parmi des nombres entiers valant de 0 à 20 inclus ; et chacun des radicaux S_1, S_2, S_3, S_4 et S_5 est choisi indépendamment pour chaque occurrence dans l'ensemble de groupes espaceurs constitué par :

(i) les groupes -(CH_2)$_g$-, -CF_2)$_h$-, -Si(CH_2)$_g$-, -(Si[(CH_3)$_2$]O)$_h$-, dans lesquels g est choisi indépendamment pour chaque occurrence entre 1 et 20 ; h est un nombre entier valant de 1 à 16 inclus ;
(ii) les groupes -N(Z)-, -C(Z)=C(Z)-, -C(Z)=N-, -C(Z')-C(Z')-, dans lesquels Z est choisi indépendamment pour chaque occurrence parmi un atome d'hydrogène, un groupe alkyle en C_1-C_6, un groupe cycloalkyle et un groupe aryle, et Z' est choisi indépendamment pour chaque occurrence parmi un groupe alkyle en C_1-C_6, un groupe cycloalkyle et un groupe aryle ; et
(iii) les groupes -O-, -C(O)-, -C=C-, -N=N-, -S-, -S(O)-, -S(O)(O)- un radical alkylène en C_1-C_{24} à chaîne droite ou ramifié, ledit radical alkylène en C_1-C_{24} étant non substitué, monosubstitué par cyano ou halogéno, ou polysubstitué par halogéno ;

étant entendu que lorsque deux groupes espaceurs comprenant des hétéroatomes sont liés ensemble, les groupes espaceurs sont liés de telle façon que les hétéroatomes ne sont pas liés directement entre eux et lorsque S_1 et S_5 sont liés à PC et P, respectivement, ils sont liés de telle façon que deux hétéroatomes ne sont pas liés directement entre eux ;
(c) P est choisi parmi : un groupe aziridinyle, un atome d'hydrogène, un groupe hydroxy, aryle, alkyle, alcoxy, amino, alkylamino, alkylalcoxy, alcoxyalcoxy, nitro, polyalkyléther, alkyl(C_1-C_6)alcoxy(C_1-C_6)alkyle(C_1-C_6), polyéthylène-oxy, polypropylène-oxy, éthylène, acrylate, méthacrylate, 2-chloroacrylate, 2-phénylacétate, acryloylphénylène, acrylamido, méthacrylamido, 2-chloro-acrylamido, 2-phénylacrylamido, époxy, isocyanate, thiol, thioisocyanate, ester d'acide itaconique, éther vinylique, ester vinylique, un dérivé de styrène, un siloxane, des polymères cristaux liquides à chaîne principale et chaîne latérale, des dérivés d'éthylène-imine, des dérivés d'acide maléique, des dérivés d'acide fumarique, des dérivés d'acide cinnamique non substitués, des dérivés d'acide cinnamique qui sont porteurs d'au moins un substituant choisi parmi les groupes méthyle, méthoxy, cyano et des atomes d'halogène, et des groupes monovalents ou divalents chiraux ou non chiraux, substitués ou non substitués, choisis parmi des radicaux stéroïdes, des radicaux terpénoïdes, des radicaux alcaloïdes et des mélanges de ceux-ci, les substituants étant choisis indépendamment parmi des groupes alkyle, alcoxy, amino, cycloalkyle, alkylalcoxy, fluoroalkyle, cyanoalkyle, cyanoalcoxy et des mélanges de ceux-ci ; et
(d) d', e' et f' sont choisis chacun indépendamment parmi 0, 1, 2, 3 et 4, étant entendu que la somme de d' + e' + f' est égale au moins à 1.

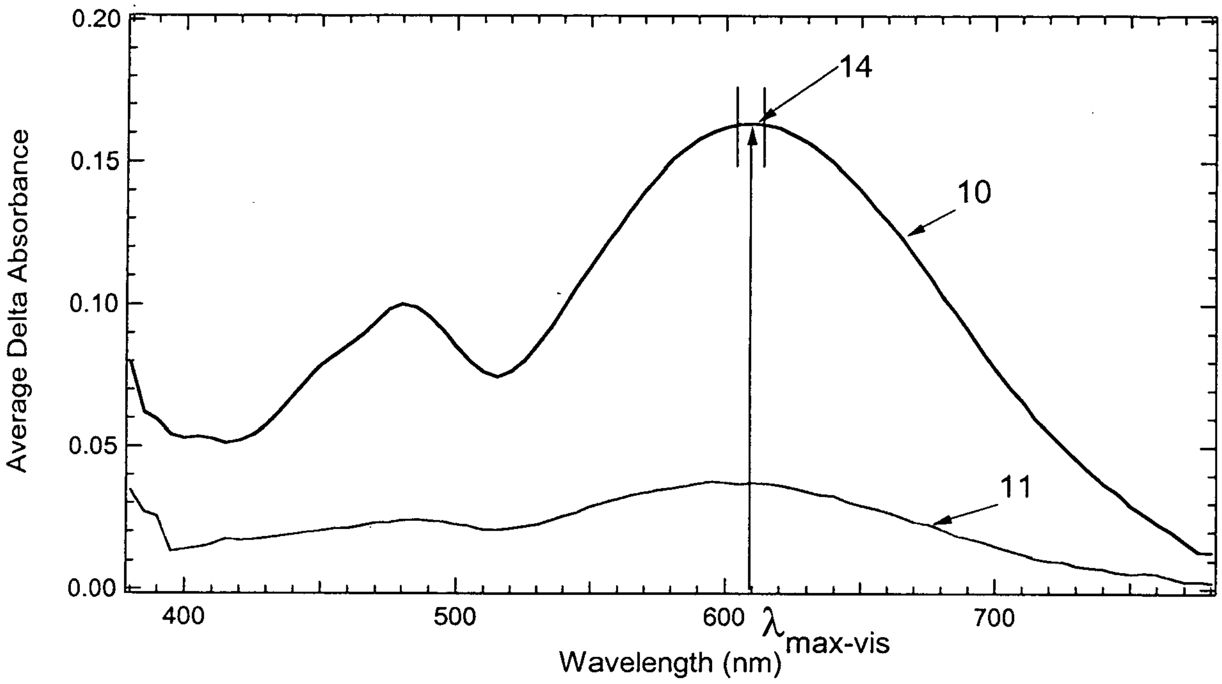
2. Composé photochromique non thermiquement réversible selon la revendication 1, dans lequel dans soit la formule X, soit la formule XI le nombre entier i est au moins égal à 1 et au moins l'un des groupes R^2 est un agent d'extension L.

3. Composé photochromique non thermiquement réversible selon l'une quelconque des revendications précédentes, où le composé photochromique comprend au moins un groupe R^2 qui est substitué par un agent d'extension L.

4. Composé photochromique non thermiquement réversible selon la revendication 1, représenté par la formule X, dans lequel l'agent d'extension L est un substituant sur un groupe R^2 ou B.

5. Composé photochromique non thermiquement réversible selon la revendication 1, représenté par la formule XI, dans lequel l'agent d'extension L est un substituant sur un groupe R^2 ou AA.

FIG. 1


0.20
0.15
0.10
0.05
0.00
Average Delta Absorbance
400
500
600
700
Wavelength (nm)
$\lambda_{max\text{-}vis}$
14
10
11

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