



(11) **EP 1 606 274 B9**

(12) **CORRECTED EUROPEAN PATENT SPECIFICATION**

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see
Description Paragraph(s) 23, 24, 133
Claims DE 4, 5, 6, 34
Claims EN 4, 5, 6, 34

(51) Int Cl.:
C07D 311/94 ^(2006.01) **G02B 5/23** ^(2006.01)
C08K 5/15 ^(2006.01) **C09K 9/02** ^(2006.01)

(86) International application number:
PCT/US2004/008156

(48) Corrigendum issued on:
16.01.2019 Bulletin 2019/03

(87) International publication number:
WO 2005/090327 (29.09.2005 Gazette 2005/39)

(45) Date of publication and mention
of the grant of the patent:
08.08.2018 Bulletin 2018/32

(21) Application number: **04749405.9**

(22) Date of filing: **16.03.2004**

(54) **INDENO-FUSED PHOTOCHROMIC NAPHTHOPYRANS, NAPHTHOLS AND PHOTOCHROMIC ARTICLES**

INDENOKONDENSIERTE PHOTOCHROME NAPHTHOPYRANE, NAPHTHOLE UND PHOTOCHROMISCHE ARTIKEL

NAPHTOPYRANES PHOTOCHROMES INDENO-FUSIONNEES, NAPHTOLS ET ARTICLES PHOTOCHROMES

(84) Designated Contracting States:
DE ES FR GB IT

(30) Priority: **20.03.2003 US 393177**

(43) Date of publication of application:
21.12.2005 Bulletin 2005/51

(60) Divisional application:
11001284.6 / 2 345 647
11001285.3 / 2 345 648

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(56) References cited:
EP-A- 1 054 010 WO-A-01/19813
WO-A-01/94336 DE-A- 19 741 705

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

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Description**BACKGROUND OF THE INVENTION**

[0001] The present invention relates to novel naphthopyran materials. More particularly, this invention relates to indeno-fused photochromic naphthopyran materials and to compositions and articles comprising such naphthopyran materials. This invention also relates to naphthols used in making the novel naphthopyrans. When exposed to light radiation containing ultraviolet rays, such as the ultraviolet radiation in sunlight or the light of a mercury lamp, many photochromic materials exhibit a reversible change in color. When the ultraviolet radiation is discontinued, such a photochromic material will return to its original color or colorless state.

[0002] Various classes of photochromic materials have been synthesized and suggested for use in applications in which a sunlight-induced reversible color change is desired. Although indeno-fused photochromic naphthopyrans are known, it has unexpectedly been discovered that materials demonstrating a bathochromic shift in the visible λ_{max} and/or an increase in sensitivity, which is measured as a change in optical density over time, can be prepared.

DETAILED DESCRIPTION OF THE INVENTION

[0003] It is noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless expressly and unequivocally limited to one referent.

[0004] For the purposes of this specification, unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and other parameters used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0005] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

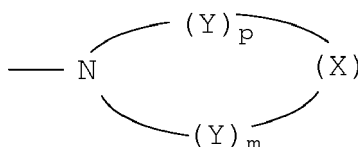
[0006] The phrase "an at least partial coating" means an amount of coating covering from a portion to the complete surface of the substrate. The phrase "an at least partially cured coating" refers to a coating in which the curable or crosslinkable components are at least partially cured, crosslinked and/or reacted. In alternate non-limiting embodiments of the present invention, the degree of reacted components, can vary widely, e.g., from 5% to 100% of all the possible curable, crosslinkable and/or reactable components. The phrase "being substantially free of spiro-substituents at the 13-position" means that a spiro-substituent such as fluoren-9-ylidene, adamantylidene, bornylidene or cyclooctylidene, is not present at the 13-position.

[0007] The phrase "an at least partially abrasion resistant coating or film" refers to a coating or film that demonstrates a Bayer Abrasion Resistance Index of from at least 1.3 to 10.0 in ASTM F-735 Standard Test Method for Abrasion Resistance of Transparent Plastics and Coatings Using the Oscillating Sand Method. The phrase "an at least partially antireflective coating" is a coating that at least partially improves the antireflective nature of the surface to which it is applied by increasing the percent transmittance as compared to an uncoated surface. The improvement in percent transmittance can range from 1 to 9 percent above the untreated surface. Put another way, the percent transmittance of the treated surface can range from a percentage greater than the untreated surface up to 99.9.

[0008] The present invention relates to a photochromic material of indeno [2',3':3,4]naphtho[1,2-b]pyran structure, characterized in that it comprises:

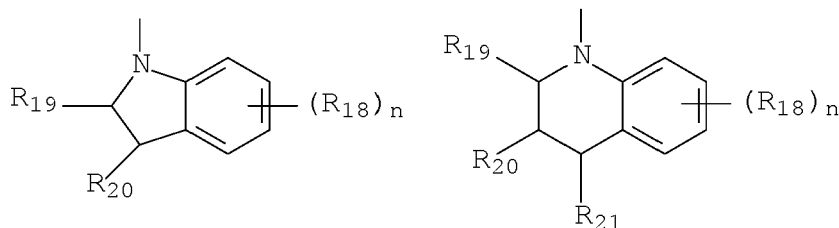
a nitrogen containing substituent selected from

- (i) $-N(R_{15})R_{16}$, R_{15} and R_{16} each being independently chosen from hydrogen, C_1-C_8 alkyl, aryl, furanyl, benzofuran-2-yl, benzofuran-3-yl, thienyl, benzothien-2-yl, benzothien-3-yl, dibenzofuranyl, dibenzothienyl, benzopyridyl, fluorenyl, C_1-C_8 alkylaryl, C_3-C_{20} cycloalkyl, C_4-C_{20} bicycloalkyl, C_5-C_{20} tricycloalkyl or C_1-C_{20} alkoxyalkyl and said aryl group being phenyl or naphthyl;
- (ii) a nitrogen containing ring represented by the following graphic formula:



wherein each Y being independently chosen for each occurrence from $-\text{CH}_2-$, $-\text{CH}(\text{R}_{17})-$, $-\text{C}(\text{R}_{17})(\text{R}_{17})-$, $-\text{CH}(\text{aryl})-$, $-\text{C}(\text{aryl})_2-$ or $-\text{C}(\text{R}_{17})(\text{aryl})-$; X being $-\text{Y}-$, $-\text{O}-$, $-\text{S}-$, $-\text{S}(\text{O})-$, $-\text{S}(\text{O}_2)-$, $-\text{NH}-$, $-\text{N}(\text{R}_{17})-$ or $-\text{N}(\text{aryl})-$; R_{17} being C_1 - C_6 alkyl; said aryl group being phenyl or naphthyl, m being chosen from the integer 1, 2 or 3 and p being chosen from the integer 0, 1, 2 or 3; provided that when p is 0, X is Y;

(iii) a group represented by one of the following graphic formulae:



wherein each R_{19} , R_{20} and R_{21} being chosen independently for each occurrence in each formula from hydrogen, C_1 - C_5 alkyl, phenyl or naphthyl; or the groups R_{19} and R_{20} together form a ring of 5 to 8 carbon atoms; R_{18} being chosen independently for each occurrence from C_1 - C_6 alkyl, C_{1-6} alkoxy, fluoro or chloro and n being chosen from the integer 0, 1 or 2;

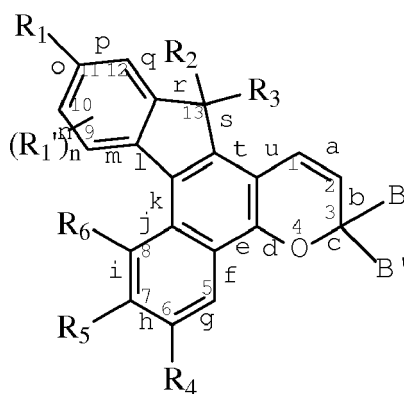
(iv) unsubstituted, mono- or di- substituted C_4 - C_{18} spirobicyclic amine; or

(v) unsubstituted, mono- or di- substituted C_4 - C_{18} spirotricyclic amine; said substituents for (iv) and (v) being independently chosen for each occurrence from aryl, C_1 - C_6 alkyl, C_{1-6} alkoxy or phenyl(C_1 - C_6)alkyl;

at the 11-position ring atom, said ring atoms being numbered according to the International Union of Pure and Applied Chemistry rules of nomenclature starting with the 1-position ring atom being the carbon atom para to the oxygen atom of the pyran ring and numbering clockwise therefrom, said photochromic material being free of spiro-substituents at the 13-position.

[0009] The ring atoms are numbered according to the International Union of Pure and Applied Chemistry rules of nomenclature starting with the 1-position ring atom being the carbon atom para to the oxygen atom of the pyran ring and numbering clockwise therefrom. In one non-limiting embodiment, the indeno [2',3':3,4]naphtho[1,2-b]pyran structure of the present invention has a nitrogen containing substituent as defined above at the 11 position and is substantially free of substituents at the other available positions. In another non-limiting embodiment, various substituents can be located at the 3-position of the pyran ring. In a further non-limiting embodiment, other substituents can be present at the number 6, 7, 8, 9, 10, 12 and/or 13 carbon atoms of the materials.

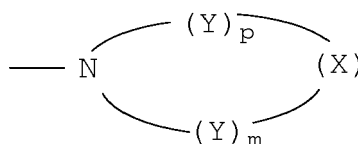
[0010] In one non-limiting embodiment, the naphthopyran materials of the present invention can be represented by the following graphic formula I in which the letters a through n represent the sides of the naphthopyran rings, and the numbers represent the numbers of the ring atoms of the naphthopyran and in the definitions of the substituents, like symbols have the same meaning unless stated otherwise.



I

[0011] In alternate non-limiting embodiments, R_1 in graphic formula I is represented by:

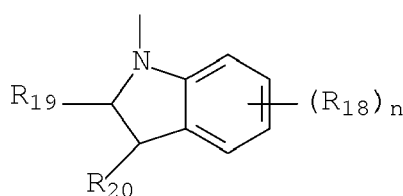
- (i) $-N(R_{15})R_{16}$, R_{15} and R_{16} each being independently chosen from C_1 - C_8 alkyl, C_1 - C_8 alkylaryl, C_3 - C_{20} cycloalkyl, C_4 - C_{20} bicycloalkyl, C_5 - C_{20} tricycloalkyl or C_1 - C_{20} alkoxyalkyl and said aryl group being phenyl or naphthyl;
 (ii) a nitrogen containing ring represented by the following graphic formula IIA:



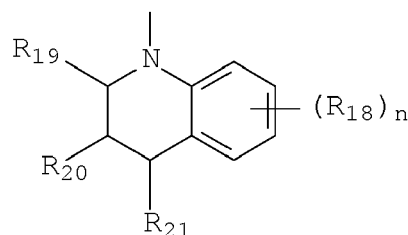
IIA

wherein each Y being independently chosen for each occurrence from $-CH_2-$, $-CH(R_{17})-$, $-C(R_{17})(R_{17})-$, $-CH(aryl)-$, $-C(aryl)_2-$ or $-C(R_{17})(aryl)-$; X being $-Y-$, $-O-$, $-S-$, $-S(O)-$, $-S(O)_2-$, $-NH-$, $-N(R_{17})-$ or $-N(aryl)-$; R_{17} being C_1 - C_6 alkyl; said aryl group being phenyl or naphthyl, m being chosen from the integer 1, 2 or 3 and p being chosen from the integer 0, 1, 2 or 3; provided that when p is 0, X is Y;

- (iii) a group represented by one of the following graphic formulae IIB or IIC:



IIB



IIC

wherein each R_{19} , R_{20} and R_{21} being chosen independently for each occurrence in each formula from hydrogen, C_1 - C_5 alkyl, phenyl or naphthyl; or the groups R_{19} and R_{20} together form a ring of 5 to 8 carbon atoms, for example, when R_{19} and R_{20} come together to form a ring of 6 carbon atoms on the group represented by graphic formula IIB, the resulting unsaturated group is carbazol-9-yl and the saturated group is tetrahydrocarbazol-9-yl, R_{18} being chosen independently for each occurrence from C_1 - C_6 alkyl, C_{1-6} alkoxy, fluoro or chloro and n being chosen from the integer 0, 1 or 2;

- (iv) unsubstituted, mono- or di- substituted C_4 - C_{18} spirobicyclic amine; or
 (v) unsubstituted, mono- or di- substituted C_4 - C_{18} spirotricyclic amine.

[0012] The substituents for (iv) and (v) are independently chosen for each occurrence from aryl, C_1 - C_6 alkyl, C_1 - C_6 alkoxy or phenyl (C_1 - C_6)alkyl. Non-limiting examples of mono- or di-substituted bicyclicamines include: 2-azabicyc-

lo[2.2.1]hept-2-yl; 3-azabicyclo[3.2.1]oct-3-yl; 2-azabicyclo[2.2.2]oct-2-yl; 6-azabicyclo[3.2.2]nonan-6-yl and tricyclicamines 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.

[0013] In one non-limiting embodiment, each R_1' in graphic formula I is independently chosen from each occurrence from C_1 - C_6 alkyl or C_1 - C_6 alkoxy and n being chosen from the integer 0, 1 or 2.

[0014] R_2 and R_3 are each independently chosen from the following alternate non-limiting embodiments:

(i) hydrogen, hydroxy, amino, mono- or di-substituted amino, C_1 - C_{12} alkyl, C_3 - C_{12} alkylidene, C_2 - C_{12} alkylidyne, vinyl, C_3 - C_7 cycloalkyl, C_1 - C_6 haloalkyl, allyl, benzyl, mono-substituted benzyl, chloro, fluoro or the group, $-C(O)W$, wherein W being hydroxy, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, mono-substituted phenyl, amino, mono(C_1 - C_6)alkylamino, di(C_1 - C_6)alkylamino, morpholino, piperidino or pyrrolidyl; said amino substituents being C_1 - C_6 alkyl, phenyl, benzyl or naphthyl; each of said benzyl and phenyl substituents being C_1 - C_6 alkyl or C_1 - C_6 alkoxy;

(ii) an unsubstituted, mono- di- or tri-substituted group chosen from phenyl, naphthyl, phenanthryl, pyrenyl, quinolyl, isoquinolyl, benzofuranyl, thienyl, benzothienyl, dibenzofuranyl, dibenzothienyl, carbazolyl or indolyl; each of said group substituents in (ii) being chosen independently for each occurrence from chloro, fluoro, C_1 - C_6 alkyl or C_1 - C_6 alkoxy;

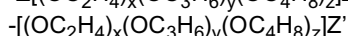
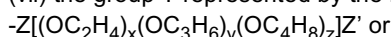
(iii) a mono-substituted phenyl, said phenyl having a substituent located at the para position being a linking group, $-(CH_2)_t-$ or $-O-(CH_2)_t-$, connected to an aryl group which is a member of another photochromic material, such as a naphthopyran or benzopyran, and t being chosen from the integer 1, 2, 3, 4, 5 or 6;

(iv) $-OR_8$, R_8 being chosen from C_1 - C_6 alkyl, C_1 - C_6 acyl, phenyl(C_1 - C_3)alkyl, mono(C_1 - C_6)alkyl substituted phenyl(C_1 - C_3)alkyl, mono(C_1 - C_6)alkoxy substituted phenyl(C_1 - C_3)alkyl, C_1 - C_6 alkoxy(C_2 - C_4)alkyl, C_3 - C_7 cycloalkyl, mono(C_1 - C_4)alkyl substituted C_3 - C_7 cycloalkyl, C_1 - C_6 chloroalkyl, C_1 - C_6 fluoroalkyl, allyl, tri(C_1 - C_6)alkylsilyl, tri(C_1 - C_6)alkoxysilyl, di(C_1 - C_6)alkyl (C_1 - C_6 alkoxy)silyl, di(C_1 - C_6)alkoxy(C_1 - C_6 alkyl)silyl, benzoyl, mono-substituted benzoyl, naphthoyl or mono-substituted naphthoyl; each of said benzoyl and naphthoyl substituents being independently chosen from C_1 - C_6 alkyl or C_1 - C_6 alkoxy; or R_8 being $-CH(R_9)Q$, wherein R_9 being chosen from hydrogen or C_1 - C_3 alkyl and Q being chosen from $-CN$, $-CF_3$, or $-COOR_{10}$ and R_{10} being chosen from hydrogen or C_1 - C_3 alkyl; or R_8 being $-C(O)V$, wherein V being chosen from hydrogen, C_1 - C_6 alkoxy, phenoxy, mono- or di-(C_1 - C_6)alkyl substituted phenoxy, mono- or di-(C_1 - C_6)alkoxy substituted phenoxy, an unsubstituted, mono- or di-substituted aryl group, phenyl or naphthyl, amino, mono(C_1 - C_6)alkylamino, di(C_1 - C_6)alkylamino, phenylamino, mono- or di-(C_1 - C_6)alkyl substituted phenylamino, or mono- or di-(C_1 - C_6)alkoxy substituted phenylamino; each of said aryl group substituents being independently chosen from C_1 - C_6 alkyl or C_1 - C_6 alkoxy;

(v) $-CH(Q')_2$, Q' being chosen from $-CN$ or $-COOR_{11}$ and R_{11} being chosen from hydrogen, C_1 - C_6 alkyl, phenyl(C_1 - C_3)alkyl, mono(C_1 - C_6)alkyl substituted phenyl(C_1 - C_3)alkyl, mono(C_1 - C_6)alkoxy substituted phenyl(C_1 - C_3)alkyl or an unsubstituted, mono- or di-substituted aryl group, phenyl or naphthyl; each of said aryl group substituents being independently chosen from C_1 - C_6 alkyl or C_1 - C_6 alkoxy;

(vi) $-CH(R_{12})G$, R_{12} being chosen from hydrogen, C_1 - C_6 alkyl or an unsubstituted, mono- or di-substituted aryl group, phenyl or naphthyl, and G being chosen from $-COOR_{11}$, $-COR_{13}$ or $-CH_2OR_{14}$, wherein R_{13} being chosen from hydrogen, C_1 - C_6 alkyl, an unsubstituted, mono- or di-substituted aryl group, phenyl or naphthyl, amino, mono(C_1 - C_6)alkylamino, di(C_1 - C_6)alkylamino, e.g., dimethyl amino, methyl propyl amino, etc., phenylamino, mono- or di-(C_1 - C_6)alkyl substituted phenylamino, e.g., each phenyl has one or two C_1 - C_6 alkyl substituents, mono- or di-(C_1 - C_6)alkoxy substituted phenylamino, diphenylamino, mono- or di-(C_1 - C_6)alkyl substituted diphenylamino, mono- or di-(C_1 - C_6)alkoxy substituted diphenylamino, morpholino or piperidino R_{14} being chosen from hydrogen, $-C(O)R_{11}$, C_1 - C_6 alkyl, C_1 - C_3 alkoxy(C_1 - C_6)alkyl, phenyl(C_1 - C_3)alkyl, mono(C_1 - C_6)alkoxy substituted phenyl(C_1 - C_3)alkyl or an unsubstituted, mono- or di-substituted aryl group, phenyl or naphthyl, each of said aryl group substituents being independently chosen from C_1 - C_6 alkyl or C_1 - C_6 alkoxy; or

(vii) the group T represented by the formula:



wherein -Z being chosen from $-C(O)-$ or $-CH_2-$, Z' being chosen from C_1 - C_3 alkoxy or a polymerizable group, defined herein as any functional group capable of participating in a polymerization reaction.

[0015] In one non-limiting embodiment, polymerization of the photochromic polymerizable materials can occur by mechanisms described in the definition of "polymerization" in Hawley's Condensed Chemical Dictionary Thirteenth Edition, 1997, John Wiley & Sons, pages 901-902, which disclosure is incorporated herein by reference. Those mechanisms include by "addition", in which free radicals are the initiating agents that react with the double bond of the monomer by adding to it on one side at the same time producing a new free electron on the other side, by "condensation", involving the splitting out of water molecules by two reacting monomers and by so-called "oxidative coupling".

[0016] Non-limiting examples of the polymerizable groups are hydroxy, (meth)acryloxy, 2-(methacryloxy)ethylcarbamyl, or epoxy, e.g., oxiranylmethyl. When there are 2 or more polymerizable groups on the naphthopyran, they may be the same or different.

[0017] In alternate non-limiting embodiments, the group, $-(OC_2H_4)_x-$, in the group T formulae, can represent poly(ethylene oxide); $-(OC_3H_6)_y-$, can represent poly(propylene oxide); and, $-(OC_4H_8)_z-$, can represent poly(butylene oxide). When used in combination, the poly(ethylene oxide), poly(propylene oxide) and poly(butylene oxide) groups of T can be in a random or block order within the T moiety. The letters x, y and z are each a number between 0 and 50 and the sum of x, y and z is between 2 and 50. The sum of x, y and z can be any number that falls within the range of 2 to 50, e.g., 2, 3, 4...50. This sum can also range from any lower number to any higher number within the range of 2 to 50, e.g., 6 to 50, 31 to 50. The numbers for x, y, and z are average values and can be partial numbers, e.g., 9.5.

[0018] In a further non-limiting embodiment, R_2 and R_3 can come together to form an oxo group.

[0019] R_4 in graphic formula I, in one non-limiting embodiment, is chosen from hydrogen, C_1 - C_6 alkyl or the group R_a chosen from:

(i) $-OR_8'$, R_8' being chosen from phenyl(C_1 - C_3)alkyl, C_1 - C_6 alkyl, mono(C_1 - C_6)alkyl substituted phenyl(C_1 - C_3)alkyl, mono(C_1 - C_6)alkoxy substituted phenyl(C_1 - C_3)alkyl, C_1 - C_6 alkoxy(C_2 - C_4)alkyl, C_3 - C_7 cycloalkyl, mono(C_1 - C_4)alkyl substituted C_3 - C_7 cycloalkyl, C_1 - C_6 chloroalkyl, C_1 - C_6 fluoroalkyl, allyl or $-CH(R_9)Q$, R_9 being chosen from hydrogen or C_1 - C_3 alkyl; or

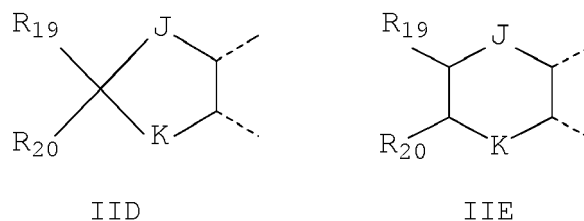
(ii) a group chosen from:

(1) $-N(R_{15})R_{16}$ wherein R_{15} and R_{16} being the same as described hereinbefore for R_1 ;

(2) a nitrogen containing ring represented by graphic formula IIA wherein Y, X, m and p being the same as described hereinbefore for R_1 ; or

(3) a group represented by graphic formulae IIB or IIC wherein R_{18} , R_{19} , R_{20} , R_{21} and n being the same as described hereinbefore for R_1 .

[0020] R_5 and R_6 are each chosen independently in one non-limiting embodiment from hydrogen, C_1 - C_6 alkyl or R_a , said R_a being the same as described hereinbefore for R_4 . In an alternate non-limiting embodiment, R_5 and R_6 can come together to form one of the following graphic formulae IID or IIE:



wherein J and K being independently chosen for each occurrence in each formula from oxygen or $-N(R_{15})-$, R_{15} , R_{19} and R_{20} each being the same as described hereinbefore for R_1 .

[0021] B and B' in graphic formula I, in one non-limiting embodiment, are each independently chosen from:

(i) mono-T-substituted phenyl, the group T being the same as described hereinbefore for R_2 and R_3 ;

(ii) an unsubstituted, mono-, di-, or tri-substituted aryl group, phenyl or naphthyl;

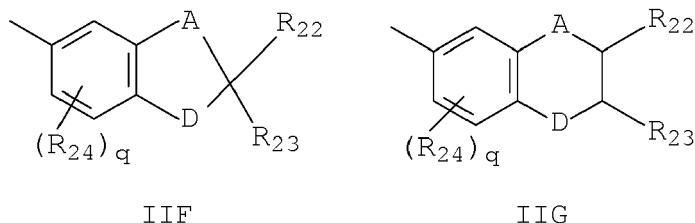
(iii) 9-julolidinyl or the unsubstituted, mono- or di-substituted heteroaromatic group chosen from pyridyl furanyl, benzofuran-2-yl, benzofuran-3-yl, thienyl, benzothien-2-yl, benzothien-3-yl, dibenzofuranyl, dibenzothienyl, carbazoyl, benzopyridyl, indolyl or fluorenyl, each of said aryl and heteroaromatic substituents in (ii) and (iii) being independently chosen from hydroxy, the group, $-C(O)W$, defined hereinbefore for R_2 and R_3 , aryl, mono (C_1 - C_6) alkoxyaryl, di(C_1 - C_6)alkoxyaryl, mono(C_1 - C_6)alkylaryl, di(C_1 - C_6)alkylaryl, chloroaryl, fluoroaryl, C_3 - C_7 cycloalkylaryl, C_3 - C_7 cycloalkyl, C_3 - C_7 cycloalkyloxy, C_3 - C_7 cycloalkyloxy(C_1 - C_6)alkyl, C_3 - C_7 cycloalkyloxy(C_1 - C_6)alkoxy, aryl(C_1 - C_6)alkyl, aryl(C_1 - C_6)alkoxy, aryloxy, aryloxy(C_1 - C_6)alkyl, aryloxy(C_1 - C_6)alkoxy, mono- or di-(C_1 - C_6)alkylaryl(C_1 - C_6)alkyl, mono- or di-(C_1 - C_6)alkoxyaryl(C_1 - C_6)alkyl, mono- or di-(C_1 - C_6)alkylaryl(C_1 - C_6)alkoxy, mono- or di-(C_1 - C_6)alkoxyaryl(C_1 - C_6)alkoxy, amino, mono(C_1 - C_6)alkylamino, di(C_1 - C_6)alkylamino, diarylamino, piperazino, N-(C_1 - C_6)alkylpiperazino, N-aryl piperazino, aziridino, indolino, piperidino, morpholino, thiomorpholino, tetrahydroquinolino, tetrahydroisoquinolino, pyrrolidyl, C_1 - C_6 alkyl, C_1 - C_6 chloroalkyl, C_1 - C_6 fluoroalkyl, C_1 - C_6 alkoxy, mono(C_1 - C_6)alkoxy(C_1 - C_4)alkyl, acryloxy, methacryloxy, bromo, chloro or fluoro, said aryl being chosen from phenyl or naphthyl;

(iv) an unsubstituted or mono-substituted group chosen from pyrazolyl, imidazolyl, pyrazolinyl, imidazolinyl, pyrrolinyl,

phenothiazinyl, phenoxazinyl, phenazinyl or acridinyl, each of said substituents being independently chosen from C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, fluoro, chloro or bromo;

(v) a monosubstituted phenyl, said phenyl having a substituent located at the para position being a linking group, -(CH₂)_t- or -O-(CH₂)_t-, connected to an aryl group which is a member of another photochromic material, such as a naphthopyran or benzopyran, and t being chosen from the integer 1, 2, 3, 4, 5 or 6;

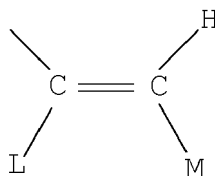
(vi) a group represented by one of the following graphic formulae IIF or IIG:



wherein A being independently chosen in each formula from methylene or oxygen and D being independently chosen in each formula from oxygen or substituted nitrogen, provided that when D is substituted nitrogen, A is methylene; said nitrogen substituents being chosen from hydrogen, C₁-C₆ alkyl, or C₂-C₆ acyl; each R₂₄ being independently chosen for each occurrence in each formula from C₁-C₆ alkyl, C₁-C₆ alkoxy, hydroxy, chloro or fluoro; R₂₂ and R₂₃ each being independently chosen in each formula from hydrogen or C₁-C₆ alkyl; and q being chosen from the integer 0, 1 or 2;

(vii) C₁-C₆ alkyl, C₁-C₆ chloroalkyl, C₁-C₆ fluoroalkyl, C₁-C₆ alkoxy(C₁-C₄)alkyl, C₃-C₆ cycloalkyl, mono(C₁-C₆)alkoxy(C₃-C₆)cycloalkyl, mono(C₁-C₆)alkyl(C₃-C₆)cycloalkyl, chloro(C₃-C₆)cycloalkyl, fluoro(C₃-C₆)cycloalkyl or C₄-C₁₂ bicycloalkyl; or

(viii) a group represented by the following graphic formula IIH:



wherein L being chosen from hydrogen or C₁-C₄ alkyl and M being chosen from an unsubstituted, mono-, or di-substituted group chosen from naphthyl, phenyl, furanyl, or thienyl; each of said group substituents being independently chosen from C₁-C₄ alkyl, C₁-C₄ alkoxy, fluoro, or chloro.

[0022] Alternatively, B and B' can together, in one nonlimiting embodiment, form fluoren-9-ylidene, mono-, or di-substituted fluoren-9-ylidene or a group being independently chosen from saturated C₃-C₁₂ spiro-monocyclic hydrocarbon rings, e.g., cyclopropylidene, cyclobutylidene, cyclopentylidene, cyclohexylidene, cycloheptylidene, cyclooctylidene, cyclononylidene, cyclodecylidene, cycloundecylidene or cyclododecylidene, saturated C₇-C₁₂ spiro-bicyclic hydrocarbon rings, e.g., bicyclo[2.2.1]heptylidene, i.e., norbornylidene, 1,7,7-trimethyl bicyclo[2.2.1]heptylidene, i.e., bornylidene, bicyclo[3.2.1]octylidene, bicyclo[3.3.1]nonan-9-ylidene or bicyclo[4.3.2]undecane, or saturated C₇-C₁₂ spiro-tricyclic hydrocarbon rings, e.g., tricyclo[2.2.1.0^{2,6}]heptylidene, tricyclo[3.3.1.1^{3,7}]decylidene, i.e., adamantylidene, and tricyclo[5.3.1.1^{2,6}]dodecylidene; each of said fluoren-9-ylidene substituents being independently chosen from C₁-C₄ alkyl, C₁-C₄ alkoxy, fluoro or chloro.

[0023] In alternate non-limiting embodiments, the substituents of the naphthopyran of the present invention can be chosen from the following:

(a) R₁ being represented by:

- (i) -N(R₁₅)R₁₆, R₁₅ and R₁₆ each being independently chosen from C₁-C₆ alkyl, or C₃-C₂₀ cycloalkyl;
- (ii) a nitrogen containing ring represented by the graphic formula IIA wherein each Y being -CH₂- and X being independently chosen from -Y-, -O-, -S-, -N(R₁₇)- and -N(phenyl)-, R₁₇ being C₁-C₆ alkyl, m being chosen from the integer 1, 2 or 3, and p being chosen from the integer 0, 1, 2 or 3;

(iii) a group represented by one of graphic formulae IIB or IIC wherein R_{19} , R_{20} and R_{21} each being independently chosen from hydrogen or C_1 - C_5 alkyl, R_{18} being independently chosen from hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, fluoro or chloro and n being chosen from the integer 0 or 1;

(iv) unsubstituted or mono-substituted C_5 - C_{18} spirobicyclic amine; or

(v) unsubstituted or mono-substituted C_5 - C_{18} spirotricyclic amine;

(b) R_1 being independently chosen from C_1 - C_4 alkyl or C_1 - C_4 alkoxy and n being chosen from the integer 0 or 1;
(c) R_2 and R_3 each being independently chosen from:

(i) hydrogen, hydroxy, C_3 - C_7 cycloalkyl, allyl, benzyl or the group, $-C(O)W$, wherein W being C_1 - C_6 alkyl or C_1 - C_6 alkoxy;

(ii) an unsubstituted or mono-substituted phenyl, said substituent being chosen from chloro, fluoro, C_1 - C_4 alkyl or C_1 - C_4 alkoxy;

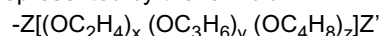
(iii) a monosubstituted phenyl, having a substituent at the para position that is a linking group chosen from $-(CH_2)_t-$ or $-O-(CH_2)_t-$, wherein t being chosen from the integer 2 or 3, connected to an aryl group which is a member of another photochromic naphthopyran;

(iv) $-OR_8$, R_8 being chosen from C_1 - C_6 alkyl, C_1 - C_6 acyl or phenyl(C_1 - C_3)alkyl; or R_8 being the group $-CH(R_9)Q$, wherein R_9 being hydrogen and Q being $-COOR_{10}$, R_{10} being C_1 - C_3 alkyl, or R_8 being the group, $-C(O)V$, wherein V being C_1 - C_6 alkoxy;

(v) $-CH(Q')_2$, Q' being $-COOR_{11}$, wherein R_{11} being C_1 - C_6 alkyl;

(vi) $-CH(R_{12})G$, R_{12} being hydrogen or C_1 - C_6 alkyl; G being $-COOR_{11}$ or $-CH_2OR_{14}$, wherein R_{14} being hydrogen, C_1 - C_6 alkyl, or C_1 - C_3 alkoxy(C_1 - C_6)alkyl;

(vii) the group T represented by the formula:



wherein $-Z$ being $-CH_2-$, Z' being C_1 - C_3 alkoxy or a polymerizable group, x , y and z each being independently chosen from a number between 0 and 30, and the sum of x , y and z being between 2 and 30; or

(viii) R_2 and R_3 together form an oxo group;

(d) R_4 being hydrogen, C_1 - C_6 alkyl or R_a , said R_a being chosen from:

(i) $-OR_8'$, R_8' being phenyl(C_1 - C_3)alkyl or C_1 - C_6 alkyl; or

(ii) $-N(R_{15})R_{16}$, R_{15} and R_{16} each being independently chosen from hydrogen, C_1 - C_6 alkyl, phenyl or C_3 - C_{20} cycloalkyl;

(iii) a nitrogen containing ring represented by graphic formula IIA wherein each Y being $-CH_2-$, and X being independently chosen from $-Y-$, $-O-$, $-S-$, $-NH-$, $-N(R_{17})-$ or $-N(aryl)-$, wherein R_{17} is C_1 - C_6 alkyl, said aryl being chosen from phenyl or naphthyl, m being chosen from the integer 1, 2 or 3, and p being chosen from the integer 0, 1, 2 or 3 provided that when p is 0, X is Y ; or

(iv) a group represented by one of graphic formulae IIB or IIC wherein R_{19} , R_{20} and R_{21} each being independently chosen from hydrogen, C_1 - C_5 alkyl or phenyl;

(e) R_5 being chosen from hydrogen, C_1 - C_4 alkyl or R_a , said R_a being described hereinbefore in (d);

(f) R_6 being chosen from hydrogen, C_1 - C_4 alkyl or R_a , said R_a being described hereinbefore in (d); or

(g) R_5 and R_6 together form one of graphic formula IID or IIE wherein J and K each being oxygen; and R_{19} and R_{20} being the same as described hereinbefore in (d)(iv);

(h) B and B' each being independently chosen from:

(i) mono- T -substituted phenyl;

(ii) an unsubstituted, mono-, di-, or tri-substituted aryl group, said aryl being phenyl or naphthyl;

(iii) 9-julolidinyl or the unsubstituted, mono- or di-substituted heteroaromatic group chosen from pyridyl, benzofuran-2-yl, benzofuran-3-yl, thienyl, benzothien-2-yl, benzothien-3-yl, dibenzofuranyl, dibenzothienyl, or carbazoyl, each of said aryl and heteroaromatic substituents in (h) (ii) and (iii) being independently chosen from hydroxy, C_3 - C_7 cycloalkyl, C_3 - C_7 cycloalkyloxy, aryl(C_1 - C_6)alkyl, aryloxy, aryloxy(C_1 - C_6)alkoxy, amino, mono(C_1 - C_6)alkylamino, di(C_1 - C_6)alkylamino, diarylamino, piperazino, N -aryl piperazino, indolino, piperidino, morpholino, thiomorpholino, pyrrolidyl, C_1 - C_6 alkyl, C_1 - C_6 alkoxy or fluoro;

(iv) an unsubstituted or mono-substituted group chosen from phenothiazinyl or phenoxazinyl, each of said substituents being independently chosen from C_1 - C_6 alkyl or C_1 - C_6 alkoxy;

(v) a monosubstituted phenyl, said phenyl having a substituent at the para position as described hereinbefore

in (c)(iii);

(vi) a group represented by one of graphic formulae IIF or IIG wherein A being independently chosen in each formula from methylene or oxygen and D being independently chosen in each formula from oxygen or substituted nitrogen, provided that when D is substituted nitrogen, A is methylene, said nitrogen substituents being chosen from hydrogen or C₁-C₄ alkyl; each R₂₄ being C₁-C₄ alkyl; R₂₂ and R₂₃ each being hydrogen; and q being the integer 0, 1 or 2;

(vii) C₁-C₆ alkyl, C₃-C₆ cycloalkyl or C₄-C₁₂ bicycloalkyl;

(viii) a group represented by graphic formula IIH wherein L being chosen from hydrogen or C₁-C₄ alkyl and M being chosen from an unsubstituted, mono-, or di-substituted phenyl; each of said phenyl substituents being independently chosen from C₁-C₄ alkyl or C₁-C₄ alkoxy; or

(i) B and B' taken together form fluoren-9-ylidene or mono-substituted fluoren-9-ylidene or a group being independently chosen from saturated C₃-C₁₂ spiro-monocyclic hydrocarbon rings, saturated C₇-C₁₂ spiro-bicyclic hydrocarbon rings or saturated C₇-C₁₂ spiro-tricyclic hydrocarbon rings; said fluoren-9-ylidene substituent being chosen from C₁-C₄ alkyl or C₁-C₄ alkoxy.

[0024] In further alternate non-limiting embodiments, the substituents of the naphthopyran can be chosen from:

(a) R₁ being represented by:

(i) -N(R₁₅)R₁₆, R₁₅ and R₁₆ each being independently chosen from C₁-C₄ alkyl;

(ii) a nitrogen containing ring represented by graphic formula IIA wherein each Y for each occurrence being -CH₂- and X being independently chosen from -Y-, -O-, and -N(R₁₇)-, R₁₇ being C₁-C₄ alkyl, m being chosen from the integer 1 or 2, and p being chosen from the integer 0, 1 or 2; or

(iii) a group represented by graphic formulae IIC or IIB wherein R₁₉, R₂₀, and R₂₁ each being hydrogen and n is 0;

(b) R₁, being C₁-C₂ alkyl or C₁-C₃ alkoxy;

(c) R₂ and R₃ each being independently chosen from:

(i) hydrogen, hydroxy or C₃-C₇ cycloalkyl;

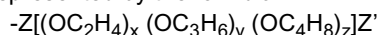
(ii) phenyl or mono-(C₁-C₄ alkoxy) substituted phenyl;

(iii) a monosubstituted phenyl, having a substituent at the para position being a linking group, -O-(CH₂)_t, t being chosen from the integer 2 or 3, connected to an aryl group being a member of another photochromic naphthopyran;

(iv) -OR₈, R₈ being C₁-C₆ alkyl or -CH(R₉)Q, R₉ being hydrogen, Q being -COOR₁₀, and R₁₀ being C₁-C₃ alkyl;

(v) -CH(R₁₂)G, R₁₂ being hydrogen; G being -COOR₁₁, wherein R₁₀ being C₁-C₆ alkyl or C₁-C₃ alkoxy(C₁-C₆)alkyl; or

(vi) the group T represented by the formula:



wherein -Z being -CH₂-, Z' being C₁-C₃ alkoxy, x, y and z each being independently chosen from a number between 0 and 20, and the sum of x, y and z being between 2 and 20;

(d) R₄ being hydrogen, C₁-C₆ alkyl or R_a, said R_a being chosen from:

(i) -OR₈', R₈' being C₁-C₄ alkyl;

(ii) -N(R₁₅)R₁₆, R₁₅ and R₁₆ each being independently chosen from C₁-C₄ alkyl or phenyl; or

(iii) a nitrogen containing ring represented by graphic formula IIA wherein each Y being -CH₂-, and X being independently chosen from -Y-, -O-, -S-, and -N(R₁₇)-, R₁₇ being C₁-C₄ alkyl, m being chosen from the integer 1, 2 or 3, and p being chosen from the integer 0, 1, 2 or 3;

(e) R₅ being hydrogen or C₁-C₄ alkyl;

(f) R₆ being hydrogen;

(g) B and B' each being independently chosen from:

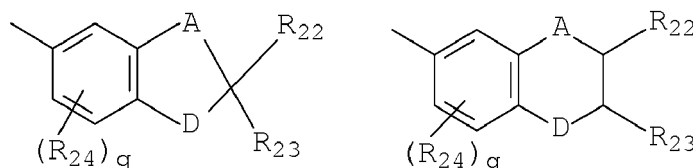
(i) mono-, di-, and tri-substituted phenyl;

(ii) an unsubstituted, mono- or di-substituted heteroaromatic group chosen from benzofuran-2-yl or dibenzofuranyl, each of said aryl and heteroaromatic substituents in (g) (i) and (ii) being independently chosen from C₃-C₇ cycloalkyl, aryloxy, aryloxy(C₁-C₆)alkoxy, di(C₁-C₆)alkylamino, piperazino, indolino, piperidino, mor-

pholino, pyrrolidyl, C₁-C₆ alkyl, C₁-C₆ alkoxy or fluoro;

(iii) a monosubstituted phenyl, said phenyl having a substituent at the para position as described hereinbefore in (c)(iii);

(iv) a group represented by one of the following graphic formulae:



wherein A being methylene and D being independently chosen in each formula from oxygen or substituted nitrogen, said nitrogen substituents being C₁-C₃ alkyl; each R₂₄ being C₁-C₃ alkyl; R₂₂ and R₂₃ each being hydrogen; and q being chosen from the integer 0, 1 or 2;

(v) C₁-C₄ alkyl or C₃-C₅ cycloalkyl;

(vi) the group represented by graphic formula IIH wherein L being hydrogen and M being chosen from an unsubstituted, mono-, or di-substituted phenyl, each of said phenyl substituents being C₁-C₄ alkoxy; or

(i) B and B' taken together form fluoren-9-ylidene, mono-substituted fluoren-9-ylidene or a saturated C₇-C₁₂ spiro-bicyclic hydrocarbon rings, each of said fluoren-9-ylidene substituents being C₁-C₄ alkoxy.

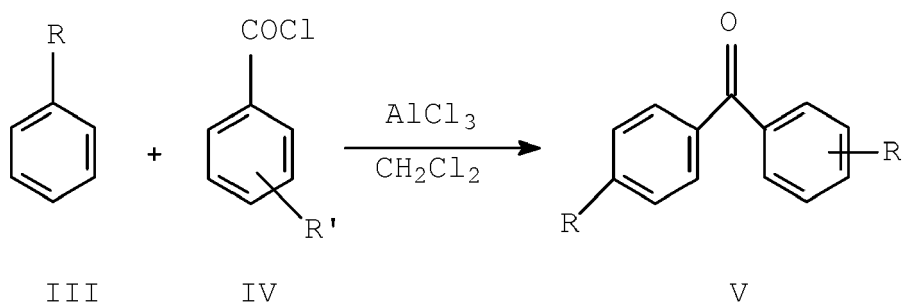
[0025] Materials represented by graphic formula I having substituents R₁-R₆, R₁', B and B' described hereinbefore, can be prepared by the methods of the following Reactions A through H. Additional methods for preparing materials of graphic formula I having substituents R₂-R₆, R₁', B and B' are disclosed in U.S. Patent 6,296,785B1 column 10, line 52 to column 29, line 18, which disclosure is incorporated herein by reference.

[0026] With reference to the following reactions, compounds represented by graphic formula V, VA, or VB are prepared by methods known to those skilled in the art, for example, by Friedel-Crafts methods shown in Reaction A using an appropriately substituted or unsubstituted benzoyl chloride of graphic formula IV with a commercially available substituted or unsubstituted benzene compound of graphic formula III. See the publication Friedel-Crafts and Related Reactions, George A. Olah, Interscience Publishers, 1964, Vol. 3, Chapter XXXI (Aromatic Ketone Synthesis), and "Regioselective Friedel-Crafts Acylation of 1,2,3,4-Tetrahydroquinoline and Related Nitrogen Heterocycles: Effect on NH Protective Groups and Ring Size" by Ishihara, Yugi et al, J. Chem. Soc., Perkin Trans. 1, pages 3401 to 3406, 1992.

[0027] By way of non-limiting illustration in Reaction A, the compounds represented by graphic formulae III and IV are dissolved in a solvent, such as carbon disulfide or methylene chloride, and reacted in the presence of a Lewis acid, such as aluminum chloride or tin tetrachloride, to form the corresponding substituted benzophenone represented by graphic formula V (VA in Reaction B or VB in Reaction C). R and R' represent possible substituents, as described hereinbefore with respect to B and B' of graphic formula I.

REACTION A

[0028]

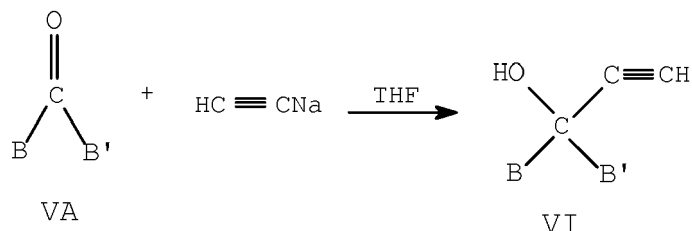


[0029] Further by way of non-limiting illustration in Reaction B, the substituted or unsubstituted ketone represented by graphic formula VA, in which B and B' can represent groups other than substituted or unsubstituted phenyl, as shown in graphic formula V, is reacted with sodium acetylide in a suitable solvent, such as anhydrous tetrahydrofuran (THF), to form the corresponding propargyl alcohol represented by graphic formula VI. Propargyl alcohols having B or B' groups

other than substituted and unsubstituted phenyl can, for example, be prepared from commercially available ketones or ketones prepared via reaction of an acyl halide with a substituted or unsubstituted benzene, naphthalene or heteroaromatic compound, e.g., 9-julolidinyl. Propargyl alcohols having a B or B' group represented by graphic formula IIH can be produced by methods known to those skilled in the art, for example, as described in U.S. Patent 5,274,132, column 2, lines 40 to 68.

REACTION B

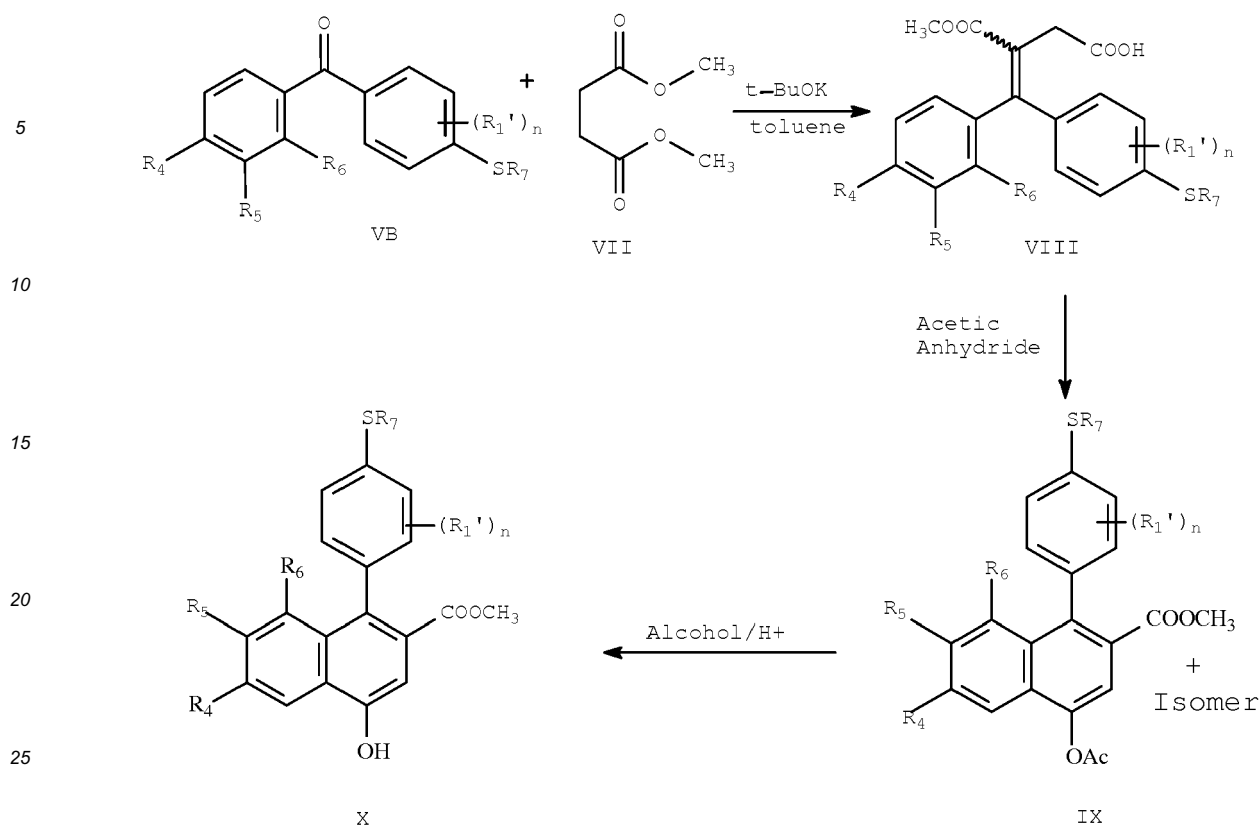
[0030]



[0031] Further by way of non-limiting illustration in Reaction C, a substituted benzophenone represented by graphic formula VB having SR_7 as the R_1 substituent (for illustrative purposes only, not belonging to the present invention) is reacted with an ester of succinic acid such as dimethyl succinate represented by graphic formula VII. Addition of the reactants to a solvent, e.g., toluene, containing potassium t-butoxide or sodium hydride as the base yields the Stobbe condensation half ester represented by graphic formula VIII. A mixture of cis and trans half esters forms, which then undergoes cyclodehydration in the presence of acetic anhydride to form a mixture of acetoxynaphthalenes. Further purification to isolate the distinct isomer represented by graphic formula IX may be desirable. This product is hydrolyzed in an aqueous alcoholic solution of base, such as sodium hydroxide, followed by treatment with aqueous hydrochloric acid (H^+) to form the carboxynaphthol represented by graphic formula X.

REACTION C

[0032]

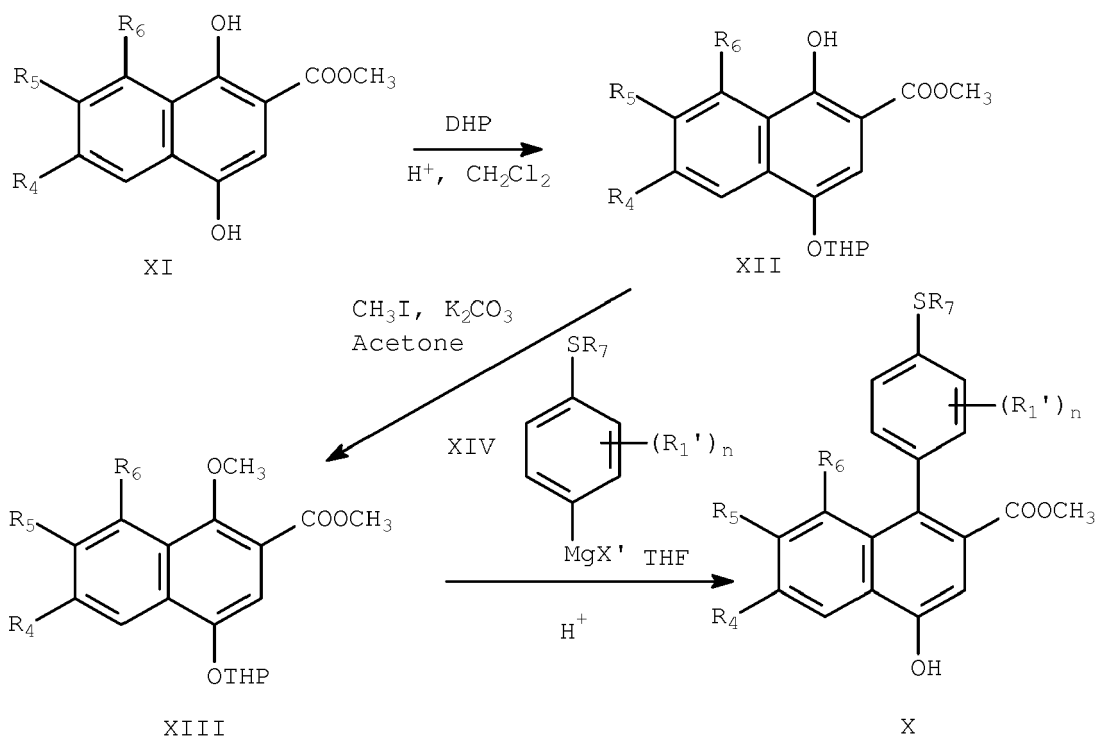


[0033] In Reaction D, a further non-limiting alternate method of preparing the compound represented by graphic formula X is disclosed. The substituted naphthol represented by graphic formula XI is reacted with dihydropyran (DHP) in methylene chloride in the presence of an acid (H⁺), such as para-toluene sulfonic acid (pTSA) or pyridium para toluene sulfonate (pPTS), to form the tetrahydropyran (THP) substituted naphthol represented by graphic formula XII. The compound represented by graphic formula XII is reacted with methyl iodide in the presence of anhydrous potassium carbonate in a suitable solvent such as anhydrous acetone to form compounds represented by graphic formula XIII. Alkylating reactions are further described in "Organic Synthesis". Vol.31 pages 90-93, John Wiley & Sons, Inc., New York, N.Y.

[0034] When an ester and methoxy group are arranged as such on the compound of graphic formula XIII, the methoxy substituent can be converted to a variety of different groups by reaction with Grignard reagents, represented by R^mMgX' wherein R^m is an organic group and X' is a halogen or by reaction with organolithium reagents. For example, the compound of graphic formula XIII is reacted with a benzene having SR₇ as the R₁ substituent (for illustrative purposes only, not belonging to the present invention) and (R₁')_n in a suitable solvent such as anhydrous tetrahydrofuran to form compounds represented by graphic formula X. This ester-mediated nucleophilic aromatic substitution reaction is done by methods known to those skilled in the art, for example, as further described in Synthesis, January 1995, pages 41-43; The Journal of Chemical Society Perkin Transaction I, 1995, pages 235-241.

REACTION D

[0035]

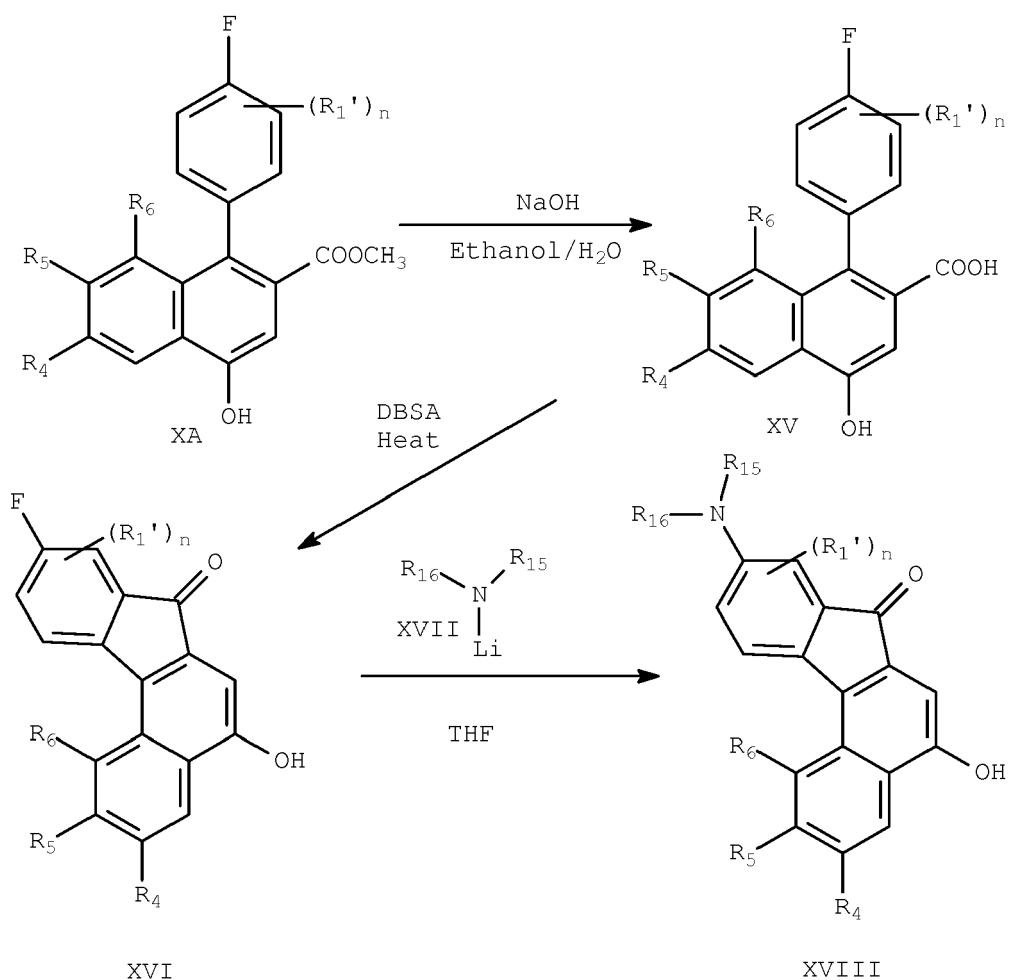


[0036] Further by way of non-limiting illustration in Reaction E, the compound represented by graphic formula XA having a fluoro substituent (or any other halo or similar replacement type substituent) in the R₁ position is treated with sodium hydroxide in boiling ethanol/water to form the carboxynaphthol of graphic formula XV. The compound represented by graphic formula XV is cyclized by heating, e.g., from about 110 to about 200°C, in the presence of an acid, such as dodecylbenzene sulfonic acid (DBSA), to a hydroxy-substituted benzo-fused fluorenone represented by graphic formula XVI. See the article by F.G. Baddar et al, in the J. Chem. Soc., page 986, 1958.

[0037] The compound represented by graphic formula XVI can be reacted with a lithium salt of N(R₁₅)R₁₆ (or any amine type substituent) represented by graphic formula XVII in a solvent such as tetrahydrofuran to produce an amino substituent as R₁ on the compound represented by graphic formula XVIII.

REACTION E

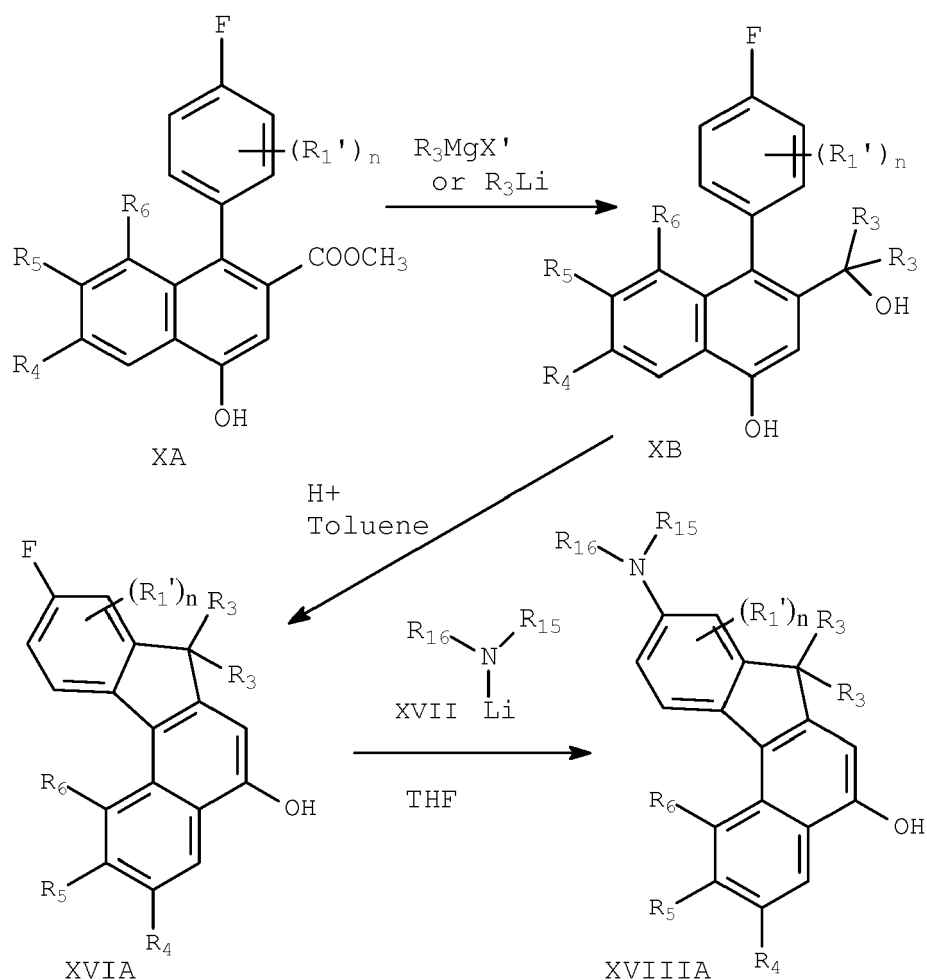
[0038]



[0039] In Reaction F, non-limiting methods for the preparation of materials having R₂ or R₃ substituents as well as an amino group as R₁ are disclosed. The compound represented by graphic formula XB, having the R₂ (or R₃) substituent present, is reacted with a Grignard reagent such as R₃MgX' (or R₂MgX') or a lithium reagent having an R₃ (or R₂) substituent to produce the compound represented by graphic formula XB. Compound XB is treated with acid in toluene until cyclized to produce the compound of graphic formula XVIA. The compound represented by graphic formula XVIA has fluorine, but in one non-limiting embodiment, could have any Leaving Group such as a different halogen, alkoxy or a sulfonate such as p-toluenesulfonate or tosyl, brosyl, mesyl or triflyl. The compound represented by graphic formula XVIA is reacted with a lithium salt of an amine represented by graphic formula XVII in a solvent such as tetrahydrofuran to produce an amino substituent as R₁ on the compound represented by graphic formula XVIII.

REACTION F

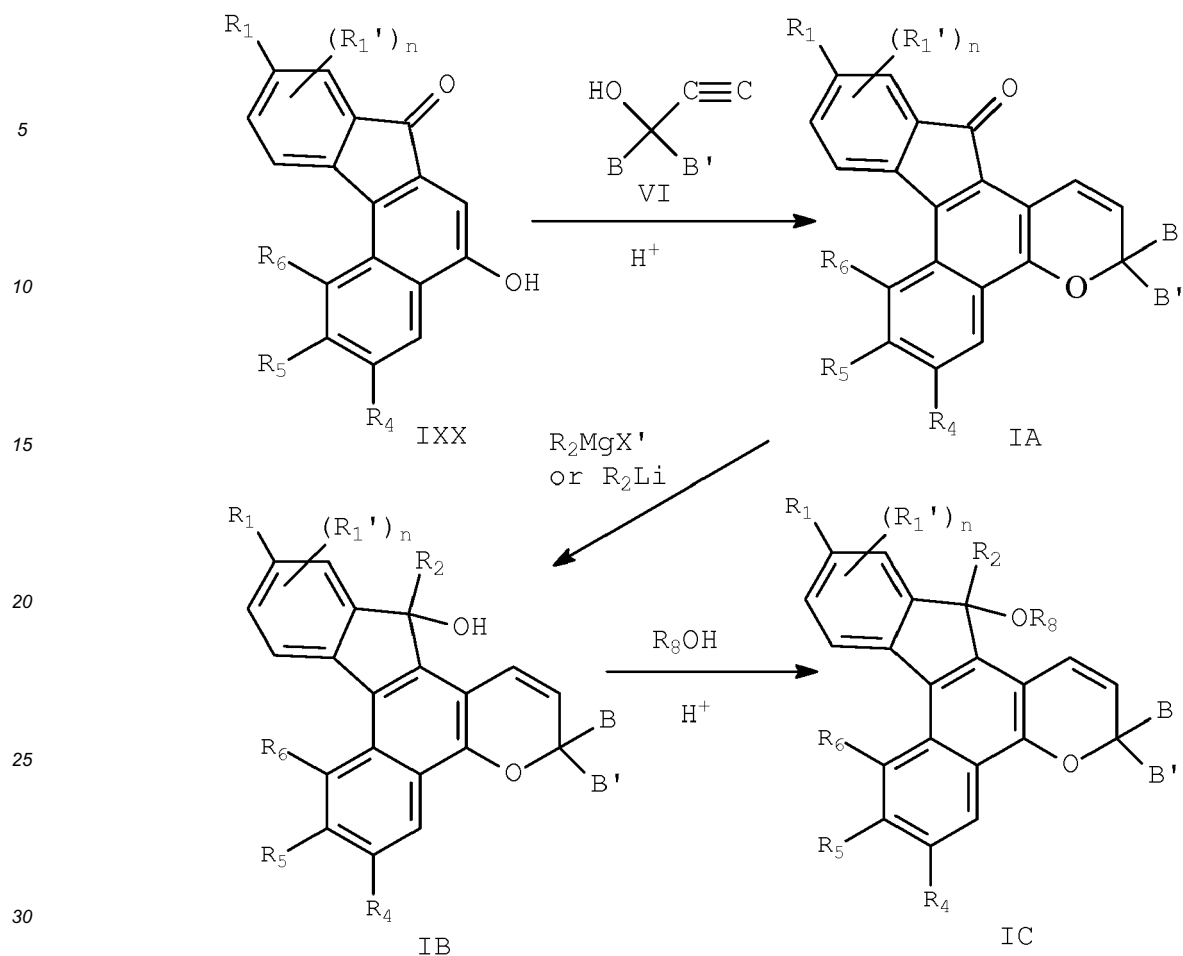
[0040]



[0041] Further by way of non-limiting illustration in Reaction G, the compound represented by graphic formula IXX is coupled with a propargyl alcohol represented by graphic formula VI in the presence of a catalytic amount of an acid, e.g., DBSA or pTSA, in a suitable solvent such as trichloromethane. This coupling reaction results in the indeno-fused naphthopyran represented by graphic formula IA. The compound represented by graphic formula IA is reacted with a Grignard reagent such as R_2MgX' (or R_3MgX') or a lithium reagent having an R_2 (or R_3) substituent to produce the compound represented by graphic formula IB. Subsequent reaction of the compound represented by graphic formula IB with an alcohol having a substituent R_8 in the presence of an acid such as hydrochloric acid results in the compound represented by graphic formula IC.

REACTION G

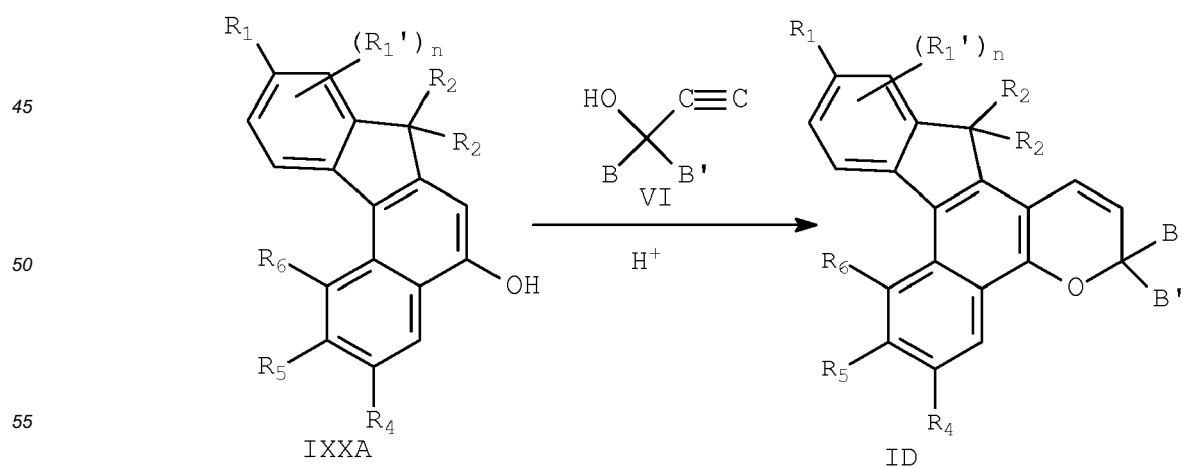
[0042]



[0043] Further by way of non-limiting illustration in Reaction H, the compound represented by graphic formula IXXA is coupled with a propargyl alcohol represented by graphic formula VI in the presence of a catalytic amount of an acid, e.g., DBSA, in a suitable solvent such as trichloromethane. This coupling reaction results in the indeno-fused naphthopyran represented by graphic formula ID.

REACTION H

[0044]

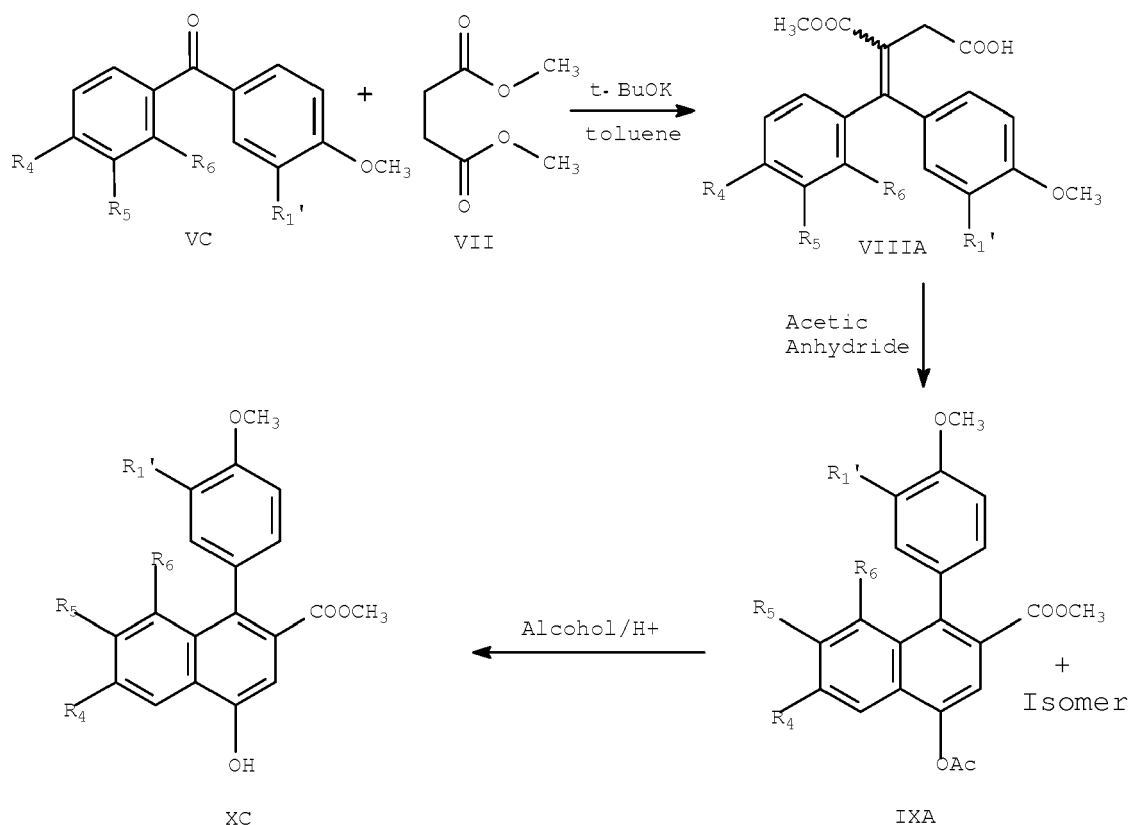


[0045] Further by way of non-limiting illustration in Reaction I, a substituted benzophenone represented by graphic

formula VC having methoxy as the R_1 substituent and R_1' located at what will become the 11 position of the indeno-fused naphthopyran is reacted with an ester of succinic acid such as dimethyl succinate represented by graphic formula VII. Addition of the reactants to a solvent, e.g., toluene, containing potassium t-butoxide or sodium hydride as the base yields the Stobbe condensation half ester represented by graphic formula VIIIA. A mixture of cis and trans half esters forms, which then undergoes cyclodehydration in the presence of acetic anhydride to form a mixture of acetoxynaphthalenes. Further purification to isolate the distinct isomer represented by graphic formula IXA may be desirable. This product is hydrolyzed in an alcoholic solution, followed by treatment with aqueous hydrochloric acid (H^+) to form the carboxynaphthol represented by graphic formula XC.

REACTION I

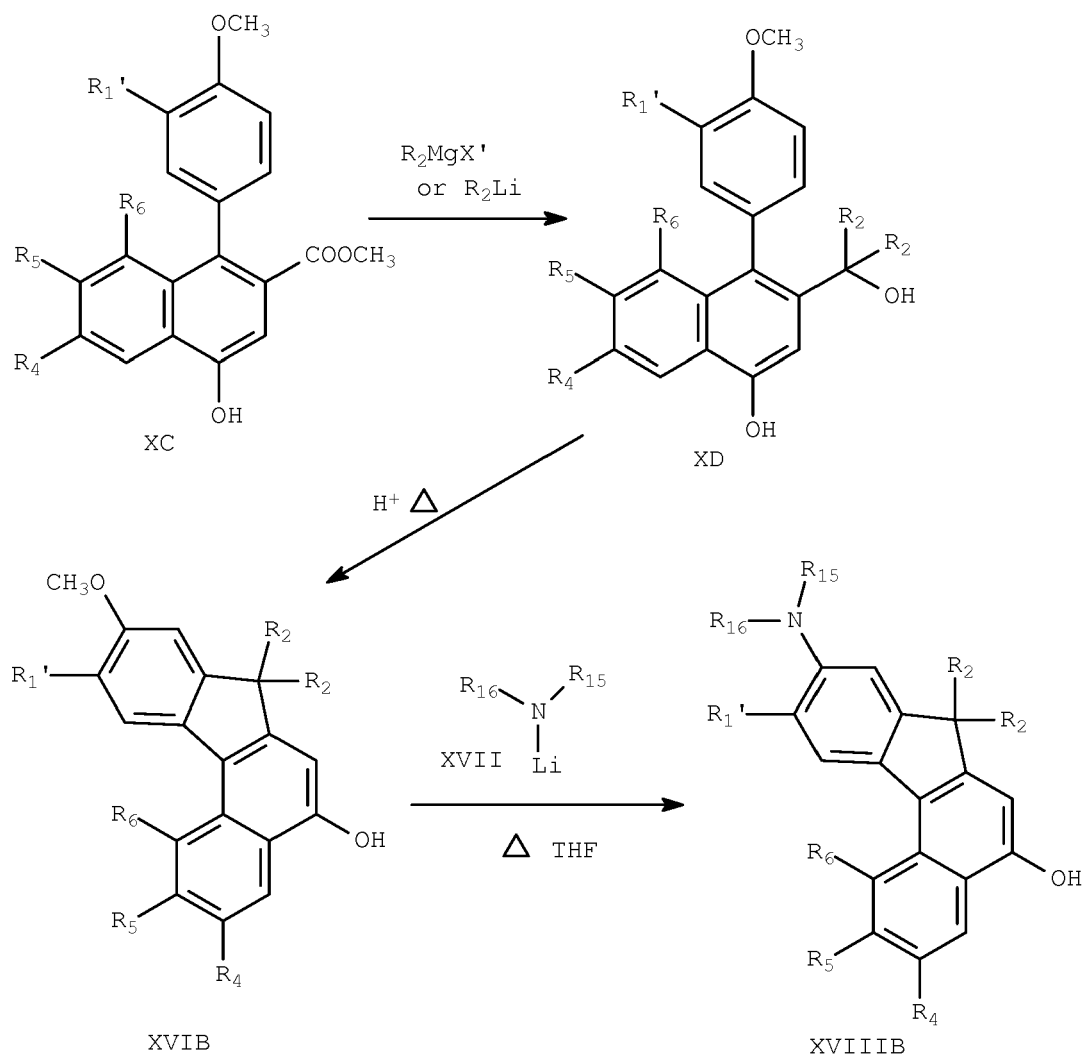
[0046]



[0047] In Reaction J, non-limiting methods for the preparation of materials having R_2 (or R_3) substituents as well as an amino group as R_1 are disclosed. The compound represented by graphic formula XC, is reacted with a Grignard reagent such as R_3MgX' (or R_2MgX') or a lithium reagent having an R_3 (or R_2) substituent to produce the compound represented by graphic formula XD. Such reactions are further described in the article "Direct Substitution of Aromatic Ethers by Lithium Amides. A New Aromatic Amination Reaction" by Wolter ten Hoeve et al, J. Org. Chem. 1993, 58, 5101-5106, which article is incorporated herein by reference. Compound XD is treated with acid in toluene until cyclized to produce the compound of graphic formula XVIB. The compound represented by graphic formula XVIB is reacted with a lithium salt of an amine represented by graphic formula XVII in a solvent such as tetrahydrofuran to produce an amino substituent as R_1 on the compound represented by graphic formula XVIIIIB.

REACTION J

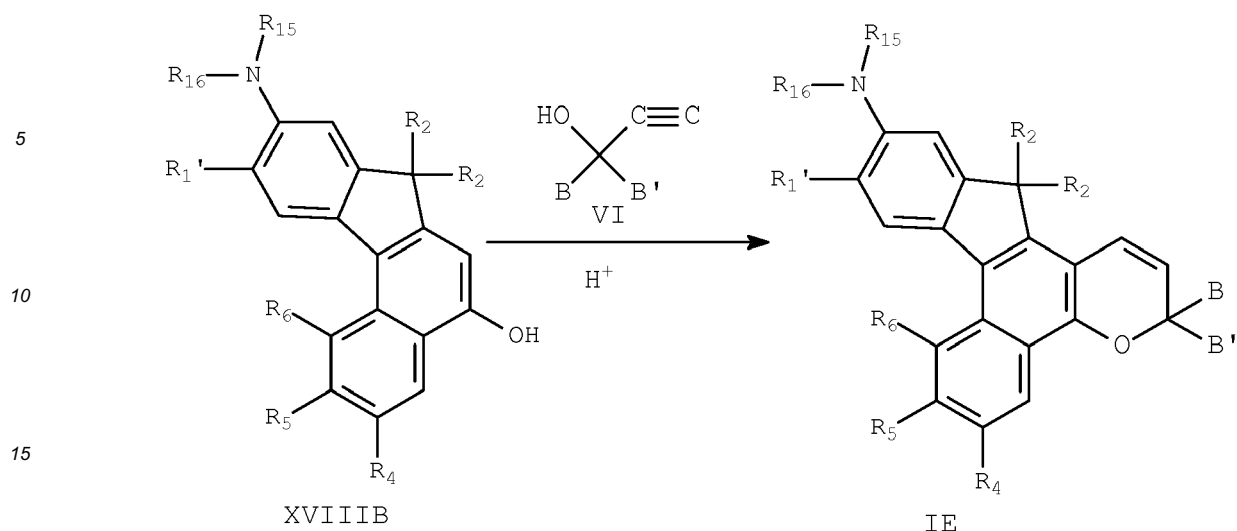
[0048]



[0049] Further by way of non-limiting illustration in Reaction K, the compound represented by graphic formula XVIIIIB is coupled with a propargyl alcohol represented by graphic formula VI in the presence of a catalytic amount of an acid, e.g., DBSA, in a suitable solvent such as trichloromethane. This coupling reaction results in the indeno-fused naphthopyran represented by graphic formula IE.

REACTION K

[0050]



[0051] The naphthols represented by graphic formula IXA and graphic formula XVI (modified by having the fluoro substituent replaced with a Leaving Group that includes halo, alkoxy or sulfonate groups as discussed hereinbefore) are useful, in one non-limiting embodiment, as intermediates in the preparation of the photochromic materials of the present invention. Specific naphthols that are included within the range of materials described by the aforementioned graphic formulae, in one non-limiting embodiment, are the naphthols of graphic formulae XVI, XVIII and XVIII B.

[0052] Non-limiting examples of the naphthols within the scope of the invention are chosen from the following:

- (a) 7,7-dimethyl-5-hydroxy-9-morpholino-7H-benzo[C]fluorene;
 (b) 7,7-dimethyl-5-hydroxy-10-methoxy-9-morpholino-7H-benzo[C]fluorene;
 (c) 7-dimethyl-7-methoxy-5-hydroxy-9-dimethylamino-7H-benzo[C]fluorene;
 (d) 7-ethyl-7-methoxy-5-hydroxy-9-piperidino-7H-benzo[C]fluorene;
 (e) 7,7-dimethyl-5-hydroxy-9-piperidino-7H-benzo[C]fluorene;
 (f) 7,7-dimethyl-3-methoxy-5-hydroxy-9-morpholino-7H-benzo[C]fluorene;
 (g) 7,7-dimethyl-3,4-dimethoxy-5-hydroxy-9-morpholino-7H-benzo[C]fluorene;
 (h) 7,7-dimethyl-3-methoxy-4-methyl-5-hydroxy-9-morpholino-7H-benzo[C]fluorene;
 (i) 7-phenyl-7-hydroxy-3-methoxy-4-methyl-5-hydroxy-9-morpholino-7H-benzo[C]fluorene;
 or
 (n) mixtures thereof.

[0053] Non-limiting examples of naphthopyrans within the scope of the invention are chosen from the following:

- (a) 3,3-di(4-methoxyphenyl)-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 (b) 3-phenyl-3-(4-morpholino-phenyl)-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho-[1,2-b]pyran;
 (c) 3,3-di(4-(2-methoxyethoxyphenyl))-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 (d) 3,3-di(4-methoxyphenyl)-11-morpholino-13-hydroxy-13-ethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 (e) 3,3-di(4-methoxyphenyl)-10-methoxy-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 (f) 3-(4-methoxyphenyl)-3-(4-morpholinophenyl)-10-methoxy-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
 (g) 3-(3,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; or
 (h) 3-(4-methoxyphenyl)-3-(4-morpholinophenyl)-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

[0054] Each of the naphthopyran materials with or without the other photochromic materials described herein can be used in amounts (or in a ratio) that can vary widely. Generally, an amount is used so that a host material or substrate to which the photochromic materials is associated, exhibits a desired resultant color, e.g., a substantially neutral color when activated with unfiltered sunlight, e.g., as near a neutral color as possible given the colors of the activated photo-

chromic materials. The photochromic materials, could be used to produce articles having a wide range of colors, e.g., pink. Further discussion of neutral colors and ways to describe colors can be found in U.S. Patent 5,645,767 column 12, line 66 to column 13, line 19.

[0055] In one non-limiting embodiment, it is contemplated that photochromic material of the present invention can be used alone or in combination with other such materials of the present invention, or in combination with one or more other organic photochromic materials, e.g., photochromic materials having at least one activated absorption maxima within the range of between about 400 and 700 nanometers.

[0056] In another non-limiting embodiment, the other photochromic materials can include the following classes of materials: chromenes, e.g., naphthopyrans, benzopyrans, indenonaphthopyrans, phenanthropyrans or mixtures thereof; spiropyrans, e.g., spiro(benzindoline)naphthopyrans, spiro(indoline)benzopyrans, spiro(indoline)naphthopyrans, spiro(indoline)quinopyrans and spiro(indoline)pyrans; oxazines, e.g., spiro(indoline)naphthoxazines, spiro(indoline)pyridobenzoxazines, spiro(benzindoline)pyridobenzoxazines, spiro(benzindoline)naphthoxazines and spiro(indoline)benzoxazines; mercury dithizonates, fulgides, fulgimides and mixtures of such photochromic compounds.

[0057] Such photochromic materials and complementary photochromic materials are described in U.S. Patents 4,931,220 at column 8, line 52 to column 22, line 40; 5,645,767 at column 1, line 10 to column 12, line 57; 5,658,501 at column 1, line 64 to column 13, line 17; 6,153,126 at column 2, line 18 to column 8, line 60; 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; and 6,353,102 at column 1, line 62 to column 11, line 64, the disclosures of the aforementioned patents are incorporated herein by reference. Spiro(indoline)pyrans are also described in the text, Techniques in Chemistry, Volume III, "Photochromism", Chapter 3, Glenn H. Brown, Editor, John Wiley and Sons, Inc., New York, 1971.

[0058] In a further non-limiting embodiment, the other photochromic materials can be polymerizable photochromic materials, such as polymerizable naphthoxazines disclosed in U.S. Patent 5,166,345 at column 3, line 36 to column 14, line 3; polymerizable spirobenzopyrans disclosed in U.S. Patent 5,236,958 at column 1, line 45 to column 6, line 65; polymerizable spirobenzopyrans and spirobenzothiopyrans disclosed in U.S. Patent 5,252,742 at column 1, line 45 to column 6, line 65; polymerizable fulgides disclosed in U.S. Patent 5,359,085 at column 5, line 25 to column 19, line 55; polymerizable naphthacenediones disclosed in U.S. Patent 5,488,119 at column 1, line 29 to column 7, line 65; polymerizable spirooxazines disclosed in U.S. Patent 5,821,287 at column 3, line 5 to column 11, line 39; polymerizable polyalkoxylated naphthopyrans disclosed in U.S. Patent 6,113,814 at column 2, line 23 to column 23, line 29; and the polymerizable photochromic compounds disclosed in WO97/05213 and allowed U.S. Application Serial No. 09/828,260 filed April 6, 2001. The disclosures of the aforementioned patents on polymerizable photochromic materials are incorporated herein by reference.

[0059] Other non-limiting embodiments of photochromic materials that can be used include organo-metal dithiozonates, e.g., (aryloxo)-thioformic arylhydrazidates, e.g., mercury dithizonates which are described in, for example, U.S. Patent 3,361,706 at column 2, line 27 to column 8, line 43; and fulgides and fulgimides, e.g., the 3-furyl and 3-thienyl fulgides and fulgimides, which are described in U.S. Patent 4,931,220 at column 1, line 39 through column 22, line 41, the disclosures of which are incorporated herein by reference.

[0060] An additional non-limiting embodiment of the other photochromic materials is a form of organic photochromic material resistant to the effects of a polymerization initiator that can also be used in the photochromic articles of the present invention. Such organic photochromic materials include photochromic compounds in admixture with a resinous material that has been formed into particles and encapsulated in metal oxides, which are described in United States Patents 4,166,043 and 4,367,170 at column 1 line 36 to column 7, line 12, which disclosure is incorporated herein by reference.

[0061] The photochromic materials described herein, e.g., the photochromic naphthopyrans of the present invention and other photochromic materials, can be chosen from a variety of materials. Non-limiting examples include: of course, a single photochromic compound; a mixture of photochromic compounds; a material comprising at least one photochromic compound, such as a plastic polymeric resin or an organic monomeric or oligomeric solution; a material such as a monomer or polymer to which at least one photochromic compound is chemically bonded; a material comprising and/or having chemically bonded to it at least one photochromic compound, the outer surface of the material being encapsulated (encapsulation is a form of coating), for example with a polymeric resin or a protective coating such as a metal oxide that prevents contact of the photochromic material with external materials such as oxygen, moisture and/or chemicals that have a negative effect on the photochromic material, such materials can be formed into a particulate prior to applying the protective coating as described in U.S. Patents 4,166,043 and 4,367,170; a photochromic polymer, e.g., a photochromic polymer comprising photochromic compounds bonded together; or mixtures thereof.

[0062] In one non-limiting embodiment, the amount of the photochromic materials to be incorporated into a polymeric coating composition and/or polymeric host material can vary widely. Generally a sufficient amount is used to produce a photochromic effect discernible to the naked eye upon activation. Generally such amount can be described as a photochromic amount. The particular amount used depends often upon the intensity of color desired upon irradiation thereof and upon the method used to incorporate the photochromic materials. Typically, in one non-limiting embodiment, the

more photochromic incorporated, the greater is the color intensity up to a certain limit. There is a point after which the addition of any more material will not have a noticeable effect, although more material may be added, if desired.

[0063] The relative amounts of the aforesaid naphthopyran materials or combinations of naphthopyran materials and other photochromic materials used will vary and depend in part upon the relative intensities of the color of the activated species of such materials, the ultimate color desired, and the method of application to the host material and/or substrate. In one non-limiting embodiment, the amount of total photochromic material which includes naphthopyran materials, other photochromic materials or both, incorporated by imbibition into a photochromic optical host material can vary widely. For example, it can range from about 0.01 to about 2.0, e.g., from 0.05 to about 1.0, milligrams per square centimeter of surface to which the photochromic material is incorporated or applied. The amount of total photochromic material incorporated or applied to the host material can range between any combination of these values, inclusive of the recited range, e.g., 0.015 to 1.999 milligrams per square centimeter.

[0064] In another non-limiting embodiment, the total amount of photochromic material incorporated into a polymerizable composition for forming a coating or polymerizate can vary widely. For example, it can range from 0.01 to 40 weight percent based on the weight of the solids in the polymerizable composition. In alternate non-limiting embodiments, the concentration of photochromic materials can range from 0.1 to 30 weight percent, from 1 to 20 weight percent, from 5 to 15 weight percent, or from 7 to 14 weight percent. The amount of photochromic material in the coating can range between any combination of these values, inclusive of the recited range, e.g., 0.011 to 39.99 weight percent.

[0065] In one non-limiting embodiment, compatible (chemically and color-wise) fixed tint dyes, can be added or applied to the host material, e.g., polymeric substrate, polymeric coating and/or polymeric film, used to produce the photochromic article to achieve a more aesthetic result, for medical reasons, or for reasons of fashion. The particular dye selected will vary and depend on the aforesaid need and result to be achieved. In one non-limiting embodiment, the dye can be selected to complement the color resulting from the activated photochromic materials, e.g., to achieve a more neutral color or absorb a particular wavelength of incident light. In another non-limiting embodiment, the dye can be selected to provide a desired hue to the host material when the photochromic materials are in an unactivated state.

[0066] In various non-limiting embodiments, adjuvant materials can also be incorporated into the host material used to produce the photochromic article. Such adjuvants can be used, prior to, simultaneously with or subsequent to application or incorporation of the photochromic material. For example, ultraviolet light absorbers can be admixed with photochromic materials before their addition to the composition or such absorbers can be superposed, e.g., superimposed, as a coating between the photochromic article and the incident light.

[0067] Further, stabilizers can be admixed with the photochromic materials prior to their addition to the composition to improve the light fatigue resistance of the photochromic materials provided that such stabilizers do not prevent the photochromic materials from activating. Non-limiting examples of stabilizers include hindered amine light stabilizers (HALS), asymmetric diaryloxalamide (oxanilide) compounds and singlet oxygen quenchers, e.g., a nickel ion complex with an organic ligand, polyphenolic antioxidants or mixtures of such stabilizers are contemplated. In one non-limiting embodiment, they can be used alone or in combination. Such stabilizers are described in U.S. Patents 4,720,356, 5,391,327 and 5,770,115.

[0068] The naphthopyran materials of the present invention, other photochromic materials or combinations thereof can be associated with the host material by various methods described in the art. In various non-limiting embodiments, the total amount of photochromic material can be incorporated into the host material used to form the photochromic article by various methods such as by adding the photochromic materials to one or more of the materials used to form the host material. In one non-limiting embodiment when the host material is a polymeric coating or film, the photochromic materials can be dissolved and/or dispersed in an aqueous or organic solvent prior to being incorporated into one or more of the components of the composition used to form the coating or film. Alternatively, the photochromic materials can be incorporated into the at least partially cured coating by imbibition, permeation or other transfer methods as known by those skilled in the art.

[0069] When at least partially cured polymers or polymerizates are used as the host material for the photochromic materials, various non-limiting embodiments include preparation of a photochromic article by injecting a polymerizable composition with photochromic materials with or without polymerizable substituents into a mold and polymerizing it by what, for example, is commonly referred to in the art as a cast-in-place process. In another non-limiting embodiment, photochromic materials can be added with the materials used to produce a polymeric film by extrusion or other methods known to those skilled in the art. Polymerizates, e.g., lenses, prepared by cast polymerization in the absence of a photochromic amount of a photochromic material can be used to prepare photochromic articles by applying or incorporating photochromic materials into the polymerizate by art-recognized methods.

[0070] Such non-limiting art-recognized methods include: (a) dissolving, dispersing and/or reacting the photochromic materials with or without polymerizable substituents with the materials used to form the polymerizate, e.g., addition of photochromic materials to a polymerizable composition or imbibition of the photochromic materials into the polymerizate by immersion of the polymerizate in a hot solution of the photochromic materials or by thermal transfer; (b) providing the photochromic material as a separate layer between adjacent layers of the polymerizate, e.g., as a part of a polymer

film; and (c) applying the photochromic material as part of a coating or film placed or laminated on the surface of the polymerizate. The term "imbibition" or "imbibe" is intended to mean and include permeation of the photochromic materials individually or with other non-photochromic materials into the polymerizate, solvent assisted transfer absorption of the photochromic materials into a polymerizate, vapor phase transfer, and other such transfer mechanisms.

[0071] In the context of the present invention, the nature of the polymeric substrate, polymeric film or polymeric coating, collectively referred to as the polymeric composition, can vary widely. Generally the polymeric composition is such that it allows the naphthopyran materials of the present invention and other photochromic materials to reversibly transform between their "open" and "closed" forms. In one non-limiting embodiment, the polymeric composition used to produce the photochromic articles of the present invention comprises compositions adapted to provide thermoplastic or thermosetting organic polymeric materials that are described in the Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Volume 6, pages 669 to 760, which disclosure is incorporated herein by reference. Such polymeric host materials can be transparent, translucent or opaque; but desirably are transparent or optically clear. In another non-limiting contemplated embodiment is a polymeric material that upon curing forms an at least partially cured polymeric coating chosen from polyurethanes, aminoplast resins, poly(meth)acrylates, e.g., polyacrylates and polymethacrylates, polyanhydrides, polyacrylamides, epoxy resins and polysilanes.

[0072] The various coating compositions described below are well known and are made with components and according to methods well understood and appreciated to those skilled in the art. Suitable substrates for the application of coatings containing the naphthopyran materials or a mixture of the naphthopyran materials and other photochromic materials include any type of substrate. Non-limiting examples include, paper, glass, ceramics, wood, masonry, textiles, metals and polymeric organic host materials.

[0073] The photochromic polyurethane coatings that can be used to prepare the photochromic coated articles of the present invention, in one non-limiting embodiment, can be produced by the catalyzed or uncatalyzed reaction of an organic polyol component and an isocyanate component in the presence of photochromic compound(s). Materials and methods for the preparation of polyurethanes are described in Ullmann's Encyclopedia of Industrial Chemistry, Fifth Edition, 1992, Vol. A21, pages 665 to 716. Non-limiting examples of methods and materials, e.g., organic polyols, isocyanates and other components, which can be used to prepare the polyurethane coating are disclosed in U.S. Patents 4,889,413 and 6,187,444B1.

[0074] The photochromic aminoplast resin coating composition that can be used to produce the photochromic coated articles of the present invention, in one non-limiting embodiment, can be prepared by combining a photochromic material with the reaction product of a functional component(s) having at least two functional groups chosen from hydroxyl, carbamate, urea or a mixture thereof and an aminoplast resin, e.g., crosslinking agent as described in U.S. Patents 4,756,973, 6,432,544B1 and 6,506,488.

[0075] Photochromic polysilane coating compositions contemplated for use in preparing the photochromic coated articles of the present invention, in one non-limiting embodiment, are prepared by hydrolyzing at least one silane monomer such as glycidoxypolytrimethoxysilane, vinyltrimethoxysilane, methacryloxypolytrimethoxysilane, tetramethoxysilane, tetraethoxysilane and/or methyltrimethoxysilane and combining the hydrolyzate with at least one photochromic material as described in U.S. Patent 4,556,605.

[0076] Photochromic poly(meth)acrylate coating compositions contemplated for use in preparing the photochromic coated articles of the present invention can be prepared, in one non-limiting embodiment, by combining photochromic compound(s) with mono-, di- or multi-functional (meth)acrylates as described in U.S. Patents 6,025,026 and 6,150,430 and WO publication 01/02449 A2.

[0077] The polyanhydride photochromic coating composition that can be used to prepare the photochromic coated articles of the present invention can be prepared in one non-limiting embodiment, by the reaction of a hydroxyl-functional component and a polymeric anhydride-functional component in a composition including at least one organic photochromic material as described in U.S. Patent 6,432,544B1. Non-limiting examples of hydroxyl-functional components, anhydride-functional component(s) and other components that can be used to prepare the polyanhydride photochromic coatings are disclosed in U.S. Patents 4,798,745, 4,798,746 and 5,239,012.

[0078] Photochromic polyacrylamide coating compositions contemplated for use in preparing the photochromic coated articles of the present invention, in one non-limiting embodiment, can be prepared by combining a photochromic component with the free radical initiated reaction product of a polymerizable ethylenically unsaturated composition comprising N-alkoxymethyl(meth)acrylamide and at least one other copolymerizable ethylenically unsaturated monomer as described in U.S. Patent 6,060,001. Methods for preparing N-alkoxymethyl(meth)acrylamide functional polymer are described in U.S. Patent 5,618,586.

[0079] The photochromic epoxy resin coating compositions that can be used to prepare the photochromic coated articles of the present invention, in one non-limiting embodiment, can be prepared by combining photochromic compound(s), epoxy resins or polyepoxides and curing agents as described in U.S. Patents 4,756,973 and 6,268,055B1.

[0080] In another non-limiting embodiment, the types of photochromic polymeric coatings comprising the film-forming polymers and the naphthopyran materials of the present invention with or without other photochromic compounds include

paints, e.g., a pigmented liquid or paste used for the decoration, protection and/or the identification of a substrate; and inks, e.g., a pigmented liquid or paste used for writing and printing on substrates such as in producing verification marks on security documents, e.g., documents such as banknotes, passport and drivers' licenses, for which authentication or verification of authenticity may be desired.

[0081] Application of the polymeric coating can be by any of the methods used in coating technology, non-limiting examples include, spray coating, spin coating, spin and spray coating, spread coating, curtain coating, dip coating, casting or roll-coating and methods used in preparing overlays, such as the method of the type described in U.S. Patent 4,873,029. The application method selected also depends on the thickness of the desired coating.

[0082] The thickness of the coatings on the photochromic articles of the present invention can vary widely. Coating having a thickness ranging from 1 to 50 microns can be applied by the methods used in coating technology. Coating of a thickness greater than 50 microns can require the application of multiple coatings or molding methods typically used for overlays. In alternate non-limiting embodiments, the coating may range in thickness from 1 to 10,000 microns, from 5 to 1000, from 8 to 400, or from 10 to 250 microns. The thickness of the polymeric coating can range between any combination of these values, inclusive of the recited range, e.g., a thickness of from 20 to 200 microns.

[0083] Following application of the polymeric coating to the surface of the substrate, in one non-limiting embodiment, the coating is at least partially cured. In another non-limiting embodiment, the methods used for curing the photochromic polymeric coating include the methods used for forming an at least partially cured polymer. Such methods include radical polymerization, thermal polymerization, photopolymerization or a combination thereof. Additional non-limiting methods include irradiating the coated substrate or at least partially cured polymer with infrared, ultraviolet, gamma or electron radiation so as to initiate the polymerization reaction of the polymerizable components with or without a catalyst or initiator. This can be followed by a heating step.

[0084] In one non-limiting embodiment, if required and if appropriate, the surface of the substrate to be coated is cleaned prior to applying the photochromic polymeric coating to produce the photochromic article of the present invention. This can be done for the purposes of cleaning and/or promoting adhesion of the coating. Effective treatment techniques for plastics and glass are known to those skilled in the art.

[0085] In some non-limiting embodiments, it may be necessary to apply a primer to the surface of the substrate before application of the photochromic polymeric coating. The primer can serve as a barrier coating to prevent interaction of the coating ingredients with the substrate and vice versa, and/or as an adhesive layer to adhere the photochromic polymeric coating to the substrate. Application of the primer can be by any of the methods used in coating technology such as, for example, spray coating, spin coating, spin and spray coating, spread coating, dip coating, casting or roll-coating.

[0086] The use of protective coatings, some of which can contain polymer-forming organosilanes, as primers to improve adhesion of subsequently applied coatings has been described in U.S. Patent 6,150,430, which disclosure is incorporated herein by reference. In one non-limiting embodiment, non-tintable coatings are used. Non-limiting examples of commercial coating products include SILVUE® 124 and HI-GARD® coatings, available from SDC Coatings, Inc. and PPG Industries, Inc., respectively. In addition, depending on the intended use of the coated article, in one non-limiting embodiment, it can be necessary to apply an appropriate protective coating(s), such as an abrasion resistant coating and/or coatings that can serve as oxygen barriers, onto the exposed surface of the coating composition to prevent scratches from the effects of friction and abrasion and interactions of oxygen with the photochromic materials, respectively.

[0087] In some cases, the primer and protective coatings are interchangeable, e.g., the same coating can be used as the primer and the protective coating(s). Non-limiting examples of hardcoats include those based on inorganic materials such as silica, titania and/or zirconia as well as organic hardcoats of the type that are ultraviolet light curable.

In one non-limiting embodiment, such protective coatings can be applied to the surface of photochromic articles comprising at least partially cured polymers containing photochromic materials.

[0088] In another non-limiting embodiment, the article of the present invention comprises a substrate to which a primer is applied followed by the photochromic polymeric coating and a protective hardcoat. In a further non-limiting embodiment, the protective hardcoat is a polysilane, e.g., an organosilane hardcoat.

[0089] In additional non-limiting embodiments, other coatings or surface treatments, e.g., a tintable coating, at least a partially antireflective coating, etc., can also be, applied to the photochromic articles of the present invention. An antireflective coating, e.g., a monolayer or multilayer of metal oxides, metal fluorides, or other such materials, can be deposited onto the photochromic articles, e.g., lenses, of the present invention through vacuum evaporation, sputtering, or some other method.

[0090] In a further non-limiting embodiment, the photochromic article comprising an at least partially cured polymer and a photochromic amount of at least one indeno[2',3':3,4]naphtho[1,2-b]pyran with or without other photochromic material further comprises a superstrate, e.g., a film or sheet comprising at least one organic polymeric material. The photochromic material can be located in the superstrate, the at least partially cured polymer or both.

The organic polymeric material of the superstrate is the same as the organic polymeric material described hereinafter as the substrate or host material. Non-limiting examples of the organic polymeric materials include thermosetting or

thermoplastic materials, for example a thermoplastic polyurethane superstrate.

[0091] In a still further non-limiting embodiment, the superstrate can be connected to the polymer surface directly, but does not become thermally fused to the substrate. In another non-limiting embodiment, the superstrate can be adheringly bonded to the substrate by becoming thermally fused with the subsurface of the substrate. General conditions under which superstrates are adheringly bonded to a substrate are known to those skilled in the art. Non-limiting conditions for adheringly laminating a superstrate to a substrate include heating to a temperature of from 250-350°F (121 - 177°C) and applying pressure of from 150 to 400 pounds per square inch (psi)(1034 to 2758 kPa). Sub-atmospheric pressures, e.g., a vacuum, can also be applied to draw down and conform the superstrate to the shape of the substrate as known to those skilled in the art. Non-limiting examples include applying at a sub-atmospheric pressure within the range of from 0.001 mm Hg to 20 mm Hg (0.13 Pa to 2.7 kPa) .

[0092] After a laminate comprising a superstrate applied to at least one surface of a substrate is formed, it can further comprise a protective coating or film superposed onto the superstrate. Such a protective coating or film, in one non-limiting embodiment, serves as an at least partially abrasion resistant coating or film. Non-limiting types of protective coatings include the aforescribed hardcoats that are curable by ultraviolet radiation and/or that contain organosilanes. The thickness of the protective coating can vary widely and include the the aforementioned range for the photochromic polymeric coatings. Non-limiting types of protective films include those made of organic polymeric materials such as thermosetting and thermoplastic materials. In another non-limiting embodiment, the protective film is a thermoplastic film made of polycarbonate. The thickness of the protective film or sheet can vary widely. Typically, such films have a thickness of from 1 to 20 mils (0.025 to 0.5 mm).

[0093] The host material for the naphthopyran materials of the present invention with or without other photochromic materials will usually be transparent, but may be translucent or even opaque. The host material need only be pervious to that portion of the electromagnetic spectrum, which activates the photochromic material, e.g., that wavelength of ultraviolet (UV) light that produces the open or colored form of the photochromic and that portion of the visible spectrum that includes the absorption maximum wavelength of the photochromic in its UV activated form, e.g., the open form. In one contemplated non-limiting embodiment, the host color should not be such that it masks the color of the activated form of the photochromic materials, e.g., so the change in color is readily apparent to the observer. Compatible tints may be applied to the host material as described in U.S. Patent 5,645,767 in column 13, line 59 to column 14, line 3.

[0094] In one contemplated non-limiting embodiment, the polymeric organic host material can be a solid transparent or optically clear material, e.g., materials having a luminous transmittance of at least 70 percent and are suitable for optical applications, such as optical elements chosen from plano and ophthalmic lenses, ocular devices such as ophthalmic devices that physically reside in or on the eye, e.g., contact lenses and intraocular lenses, windows, automotive transparencies, e.g., windshields, aircraft transparencies, plastic sheeting, polymeric films, etc.

[0095] Non-limiting examples of polymeric organic materials which can be used as a host material for the naphthopyran materials of the present invention with or without other photochromic materials or as a substrate for the photochromic polymeric coating include: poly(meth)acrylates, polyurethanes, polythiourethanes, poly(urea-urethanes), thermoplastic polycarbonates, polyesters, poly(ethylene terephthalate), polystyrene, poly(alpha methylstyrene), copoly(styrene-methyl methacrylate), copoly(styrene-acrylonitrile), polyvinylbutyral, poly(vinyl acetate), cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, polystyrene or polymers, such as homopolymers and copolymers prepared by polymerizing monomers chosen from bis(allyl carbonate) monomers, styrene monomers, diisopropenyl benzene monomers, vinylbenzene monomers, e.g., those described in U.S. Patent 5,475,074, diallylidene pentaerythritol monomers, polyol (allyl carbonate) monomers, e.g., diethylene glycol bis(allyl carbonate), vinyl acetate monomers, acrylonitrile monomers, mono- or polyfunctional, e.g., di- or multi-functional, (meth)acrylate monomers such as (C₁-C₁₂)alkyl (meth)acrylates, e.g., methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate etc., poly(oxyalkylene)(meth)acrylate, poly(alkoxylated phenol (meth)acrylates), diethylene glycol (meth)acrylates, ethoxylated bisphenol A (meth)acrylates, ethylene glycol (meth)acrylates, poly(ethylene glycol) (meth)acrylates, ethoxylated phenol (meth)acrylates, alkoxylated polyhydric alcohol (meth)acrylates, e.g., ethoxylated trimethylol propane triacrylate monomers, urethane (meth)acrylate monomers, such as those described in U.S. Patent 5,373,033, or a mixture thereof. Further examples of polymeric organic host materials are disclosed in the U.S. Patent 5,753,146, column 8, line 62 to column 10, line 34.

[0096] In another non-limiting embodiment, transparent copolymers and blends of transparent polymers are also suitable as polymeric materials. The host material can be an optically clear polymerized organic material prepared from a thermoplastic polycarbonate resin, such as the carbonate-linked resin derived from bisphenol A and phosgene, which is sold under the trademark, LEXAN; a polyester, such as the material sold under the trademark, MYLAR; a poly(methyl methacrylate), such as the material sold under the trademark, PLEXIGLAS; polymerizates of a polyol(allyl carbonate) monomer, especially diethylene glycol bis(allyl carbonate), which monomer is sold under the trademark CR-39, and polymerizates of copolymers of a polyol (allyl carbonate), e.g., diethylene glycol bis(allyl carbonate), with other copolymerizable monomeric materials, and copolymers with a polyurethane having terminal diacrylate functionality, as described in U.S. Patents 4,360,653 and 4,994,208; and copolymers with aliphatic urethanes, the terminal portion of which contain allyl or acrylyl functional groups, as described in U.S. Patent 5,200,483.

[0097] A further non-limiting embodiment is use of the naphthopyran materials of the present invention and other photochromic materials with optical organic resin monomers used to produce optically clear coatings and polymerizates, e.g., materials suitable for optical applications, such as for example plano and ophthalmic lenses, windows, and automotive transparencies. Examples of non-limiting embodiments include polymerizates of optical resins sold by PPG Industries, Inc. as TRIVEX monomers and under the CR- designation, e.g., CR-307, CR-407 and CR-607 and the resins used to prepare hard or soft contact lenses. Methods for producing both types of contact lenses are disclosed in U.S. Patent No. 5,166,345, column 11, line 52, to column 12, line 52.

[0098] Further non-limiting embodiments of optical resins include the resins used to form soft contact lenses with high moisture content described in U.S. Patent No. 5,965,630 and extended wear contact lenses described in U.S. Patent No. 5,965,631.

[0099] The present invention is more particularly described in the following examples which are intended as illustration only, since numerous modifications and variations therein will be apparent to those skilled in the art.

[0100] Examples 1-8 are of the photochromic materials of the present invention. Comparative Examples (CE) 1-5 represent photochromic materials prepared by methods disclosed in U.S. Patent 5,645,767 and 6,296,785B1. Example 9 describes the Indenonaphthopyran Photochromic Performance Test.

Example 1

Step 1

[0101] Methylene chloride (2 liters (L)), 1,4-dihydroxy-2-phenoxy-carbonyl-naphthalene (384 grams) and 152 grams of dihydropyran were added to a 3 L multi-necked flask at room temperature. The mixture was placed on a magnetic stirrer, and a solution of dodecylbenzenesulfonic acid (1.4 grams, in 15 milliliters (mL) of methylene chloride) was added with stirring. After 1 hour of mixing, the completed reaction was quenched by adding triethylamine (2.7 grams) and potassium carbonate (2.7 grams). The suspension was vacuum filtered and the solvent was removed by rotary evaporation. The recovered product was a thick oil. All of it was used as is, without purification, in the next step.

Step 2

[0102] The oily product from step 1 was added to a flask and dissolved in acetone (750 mL). Potassium carbonate (200 grams) and iodomethane (220 mL) were added and the reaction was stirred and heated to 40°C. The reaction was gradually heated to reflux and iodomethane was added 4 times, each time with 1 equivalent, until the reaction was complete. The mixture was vacuum filtered and the solvent was removed by rotary evaporation to yield a concentrated liquid. The liquid was poured into 2 L of water and formed a brown precipitate. The brown precipitate was vacuum filtered, dissolved in 2.5 L of ethyl acetate and the solvent was removed by rotary evaporation to yield 200 mL of solution. The solution was poured into 3:1 hexane:ethyl acetate to induce crystallization. Brown crystals (420 grams) of product were collected. A nuclear magnetic resonance (NMR) spectrum showed the product to have a structure consistent with 4-tetrahydropyranyloxy-1-methoxy-2-phenoxy-carbonyl naphthalene.

Step 3

[0103] The product of Step 2, 4-tetrahydropyranyloxy-1-methoxy-2-phenoxy-carbonyl naphthalene (200 grams) and tetrahydrofuran (800 mL) were added to a 3 L multi-necked flask and stirred at 0°C under a nitrogen blanket. To the reaction mixture was added a 1 molar (M) fluorophenylmagnesium bromide solution (690 mL) drop-wise over a 1 hour period. After an additional 4.5 hours of stirring, the reaction mixture was poured into 1.5 L of water and acidified to pH 2. After individual phase layers formed, the layers were separated and the aqueous layer was extracted 2 times, each with 200 mL of ethyl acetate. The organic layers were combined, washed with water and the solvent was removed by rotary evaporation to yield a wet red solid. The red solid was added to a flask containing methanol (500 mL) and 12.1 M hydrochloric acid (5 mL), and the resulting solution was heated to reflux for 1 hour. After cooling and setting overnight, the crystals that formed were collected by vacuum filtration and washed with hexane to yield 102 grams of reddish-orange crystals. An NMR spectrum showed the product to have a structure consistent with 4-hydroxy-1-(4-fluorophenyl)-2-phenoxy-carbonyl naphthalene.

Step 4

[0104] The product of Step 3, 4-hydroxy-1-(4-fluorophenyl)-2-phenoxy-carbonyl naphthalene (148 grams) and anhydrous THF (500 mL) were added to a 3 L multi-necked flask and placed on magnetic stirrer under nitrogen and stirred. The solution was cooled to 0°C and a 1.6 M methyl lithium solution (1.05 L) was added over 1 hour with stirring. After

an additional 1.5 hours of stirring, the completed reaction was poured into 2 L of ice water and allowed to set overnight. The resulting mixture was acidified to pH 4 and the phases that formed into layers were separated. The aqueous layer was extracted 3 times, each with 200 mL of ethyl acetate. The organic layers were combined, washed with water and the solvent was removed by rotary evaporation to yield a 132 g of dark oil. The material was used directly in the next step.

Step 5

[0105] The product from Step 4 (132 grams), xylenes (1.5 L) and dodecylbenzenesulfonic acid (9.2 grams) were added to a flask and heated to reflux. After 5 hours, the reaction mixture was cooled to room temperature and washed with a 5 weight percent solution of sodium bicarbonate (300 mL). The resulting emulsion was allowed to set overnight and the phase layers that formed were separated. The organic layer was dried over magnesium sulfate and the solvent was removed by rotary evaporation to yield a concentrated liquid. The concentrated liquid was eluted through a small silica plug column with 30:1 hexane: ethyl acetate. The solvent was removed from the resulting eluant by rotary evaporation to yield an oil. Crystallization was induced with toluene and hexane to yield 28 grams of a light tan product. An NMR spectrum showed the product to have a structure consistent with 7,7-dimethyl-5-hydroxy-9-fluoro-7H-benzo[C]fluorene.

Step 6

[0106] Anhydrous tetrahydrofuran (600 mL) and morpholine (70 mL) were added to a 3 L multi-necked flask which was placed on a magnetic stir under nitrogen and cooled to 0°C. A 1.6 M methyllithium solution (450 mL) was added drop-wise over a 1 hour period with stirring. After an additional 2 hours of stirring, ice was removed and the suspension was warmed to room temperature. A solution of 7,7-dimethyl-5-hydroxy-9-fluoro-7H-benzo[C]fluorene (20 grams) from Step 5 in 250 mL of anhydrous tetrahydrofuran was slowly added into the flask and stirred at 65°C. After 13 hours, reaction was cooled to room temperature and poured into 2 L of deionized water. Ethyl acetate (500 mL) was added to induce phase separation. The layers that formed were separated. The aqueous layer was made basic to pH 8 with 5 weight percent aqueous sodium hydroxide solution and extracted 2 times, each with 200 mL of ethyl acetate. The organic layers were combined, washed with water, the solvent was removed by rotary evaporation to yield an oil which was induced to crystallize in ethyl acetate. A brown precipitate (13 grams) was collected by vacuum filtration. An NMR spectrum showed the product to have a structure consistent with 7,7-dimethyl-5-hydroxy-9-morpholino-7H-benzo[c]fluorene.

Step 7

[0107] 7,7-Dimethyl-5-hydroxy-9-morpholino-7H-benzo[C]fluorene (2 grams) from Step 6, 1,1-di(4-methoxyphenyl)-2-propyn-1-ol (2 grams), two drops of dodecylbenzene sulfonic acid and chloroform (50 mL) were combined in a reaction vessel and stirred at ambient temperature overnight. Water (100 mL) was added to the reaction mixture and stirred for 30 minutes. The organic layer was separated and washed with a 10 weight percent sodium hydroxide solution followed by a wash with water. The organic layer was dried over magnesium sulfate and the solvent was removed by rotary evaporation to yield a residue. The residue was chromatographed on a silica gel using chloroform as the elutant. Photochromic fractions were collected, concentrated by rotary evaporation and the resulting solid was recrystallized from diethyl ether yielding 1.3 grams of crystals having a melting point of 258-261°C. An NMR spectrum showed the product to have a structure consistent with 3,3-di(4-methoxyphenyl)-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 2

[0108] The process of Example 1 was followed except that in Step 7, 1-phenyl-1-(4-morpholinophenyl)-2-propyn-1-ol was used instead of 1,1-di(4-methoxyphenyl)-2-propyn-1-ol. The recovered product had a melting point of 163-164°C. NMR analysis showed the product to have a structure consistent with 3-phenyl-3-(4-morpholino-phenyl)-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho-[1,2-b]pyran.

Example 3

[0109] The process of Example 1 was followed except that in Step 7, 1,1-di(4-(2-methoxyethoxyphenyl))-2-propyn-1-ol was used instead of 1,1-di(4-methoxyphenyl)-2-propyn-1-ol. The recovered product had a melting point of 153-155°C. NMR analysis showed the product to have a structure consistent with 3,3-di(4-(2-methoxyethoxyphenyl))-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 4Step 1

5 **[0110]** The product of Step 3 of Example 1, 4-hydroxy-1-(4-fluorophenyl)-2-phenoxy-carbonyl naphthalene (10 gm), a 10 weight percent aqueous sodium hydroxide solution (50 mL) and methanol (50 mL) were added to a reaction flask and heated to reflux for 3 hours and then cooled to room temperature. The reaction mixture was poured onto an aqueous solution of 4N hydrochloric acid/ice mixture (approximately 400 mL). A white precipitate formed and was collected by vacuum filtration, washed with water and was air-dried. Recrystallization from ethanol (95 weight percent) gave 1-(4-fluorophenyl)-4-hydroxy-2-naphthoic acid (7 grams).

Step 2

15 **[0111]** 1-(4-Fluorophenyl)-4-hydroxy-2-naphthoic acid, (7 grams) from Step 1, and dodecylbenzenesulfonic acid (1 gram) were added to a reaction flask containing xylene (1L) and heated to reflux and maintained at that temperature for 36 hours. The reaction was cooled and the resulting red precipitate was collected by vacuum filtration and washed with toluene. The red solid was air-dried yielding 4 grams of product. An NMR spectrum showed the product to have a structure consistent with 9-fluoro-5-hydroxy-7H-benzo[C]fluoren-7-one.

Step 3

20 **[0112]** The process of Example 1, Step 6 was followed except 9-fluoro-5-hydroxy-7H-benzo[C]fluoren-7-one from Step 2 above was used instead of 7,7-dimethyl-5-hydroxy-9-fluoro-7H-benzo[C]fluorene. NMR analysis showed the product to have a structure consistent with 9-morpholino-5-hydroxy-7H-benzo[C]fluoren-7-one.

Step 4

25 **[0113]** The process of Example 1, Step 7 was followed except 9-morpholino-5-hydroxy-7H-benzo[C]fluoren-7-one from Step 3 above was used instead of 7,7-dimethyl-5-hydroxy-9-morpholino-7H-benzo[C]fluorene. NMR analysis showed the product to have a structure consistent with 3,3 di(4-methoxyphenyl)-11-morpholino-13-oxo-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Step 5

35 **[0114]** The product of Step 4, 3,3 di(4-methoxyphenyl)-11-morpholino-13-oxo-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran (2 grams) was added to a reaction flask containing tetrahydrofuran (50 mL). Under a nitrogen atmosphere at 0°C, an excess of ethyl magnesium chloride (10 mL of a 2 M solution in tetrahydrofuran) was added to the reaction flask. The resulting reaction was stirred at 0°C for 30 minutes and then warmed to room temperature. The reaction mixture was poured onto 200 mL of ice water then acidified to pH 3 with an aqueous 2N hydrochloric acid solution. Diethylether (100 mL) was added and the organic phase separated. The solvents were removed by rotary evaporation and the resulting oil was chromatographed on a silica column using hexane:ethyl acetate (2:1) as eluant. The photochromic fractions were concentrated and the residue crystallized from methanol to give 1 gram of a white solid having a melting point of 222-225°C. An NMR spectrum showed the product to have a structure consistent with 3,3-di(4-methoxyphenyl)-13-hydroxy-13-ethyl-11-morpholino-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 5Step 1

50 **[0115]** 1,2-Dimethoxybenzene (292 grams) and a solution of benzoyl chloride (297 grams in 500 mL of methylene chloride) were added to a reaction flask under a nitrogen atmosphere. Solid anhydrous aluminum chloride (281 grams) was added portion wise to the reaction mixture occasionally cooling the reaction mixture in an ice/water bath. After the addition was completed, the reaction was stirred at room temperature for 3 hours. The reaction mixture was poured onto a 1:1 ice/1N HCl mixture (300 mL) and stirred vigorously for 15 minutes. After the different layers formed, the aqueous layer was separated and extracted into methylene chloride (100 mL) three times. The organic layers were combined and washed twice with 10 weight percent sodium hydroxide (100 mL each time), and then twice with water (100 mL each time). The solvent was removed by rotary evaporation to give a yellow solid. Recrystallization from 95% ethanol yielded 490 grams of beige needles having a melting point of 103-105 °C. NMR analysis showed the product to have a

structure consistent with 3,4-dimethoxybenzophenone.

Step 2

[0116] The product from Step 1, 3,4-dimethoxy benzophenone (490 grams) and diethyl succinate (354 grams) were combined in a reaction flask containing in 600 mL of toluene under a nitrogen atmosphere. The mixture was heated to 45 °C and then potassium t-butoxide (248 grams) was added portion wise over a 1-hour period. After completing the addition, the reaction mixture was heated to 45 °C and maintained at that temperature for 5 hours and then cooled to room temperature. Water (500 mL) was added to the reaction mixture and the phases separated into layers. The aqueous layer was collected and acidified to pH 2 with 4 N HCl. The resulting acidic solution was extracted five times into methylene chloride (50 mL each time). The organic extracts were combined and concentrated by rotary evaporation to provide a thick brown oil. NMR spectrum showed the desired product to have a structure consistent with 4-(3,4-dimethoxyphenyl)-4-phenyl-methoxycarbonyl-3-butenic acid. This material was not purified further but was used directly in the next step.

Step 3

[0117] The product from Step 2 (620 grams), was added to a reaction flask containing acetic anhydride (2.1 L) under a nitrogen atmosphere and heated to reflux. The reaction mixture was maintained at the reflux temperature for 6 hours, cooled to room temperature and the solvent (acetic anhydride) was removed by rotary evaporation to give a thick gum which solidified upon standing. The solid was added to a reaction flask and dissolved in boiling methanol (3 L). After cooling overnight, the crystals (249 grams) that formed were collected by vacuum filtration, washed with methanol and air-dried. NMR spectrum showed the crystals to have a structure consistent with 1-phenyl-2-methoxycarbonyl-4-acetoxy-6,7-dimethoxynaphthalene. The isomer 1-(3,4-dimethoxyphenyl)-2-methoxycarbonyl-4-acetoxy-naphthlene remained in the filtrate as an enriched mixture with 1-phenyl-2-methoxycarbonyl-4-acetoxy-6,7-dimethoxynaphthalene in methanol.

Step 4

[0118] The filtrate from Step 3 containing 1-(3,4-dimethoxyphenyl)-2-methoxycarbonyl-4-acetoxy-naphthlene and 5 mL of concentrated HCl were combined in a reaction flask and heated to reflux for 1 hour. The reaction was cooled and the precipitate that formed was collected by vacuum filtration washing with cold methanol yielding 27 grams of beige needles. NMR analysis showed the product to have structure consistent with 1-(3,4-dimethoxyphenyl)-2-methoxycarbonyl-4-hydroxynaphthalene.

Step 5

[0119] Anhydrous tetrahydrofuran (100 mL) was added to a reaction flask under a nitrogen atmosphere containing 1-(3,4-dimethoxyphenyl)-2-methoxycarbonyl-4-hydroxynaphthalene (25 grams) from Step 4. The reaction mixture was cooled in an ice bath and then 264 mL of a methyl lithium solution (1.4 M in tetrahydrofuran) was added dropwise over 40 minutes. The resulting yellow reaction mixture was stirred at 0°C for 2 hours and then slowly warmed to room temperature and stirred overnight. The reaction mixture was carefully poured onto 200 mL of an ice/water mixture. Ethyl acetate (100 mL) was added and the layers separated. The aqueous layer was collected and extracted with four 75 mL portions of ethyl acetate. The organic extracts were combined and washed with two 50 mL portions of water. The organic layer was collected, dried over anhydrous magnesium sulfate and then concentrated by rotary evaporation. The resulting oil was transferred into a reaction vessel (fitted with a Dean-Stark trap) with 500 mL of xylene and 200 mg of dodecylbenzene sulfonic acid. The reaction mixture was heated to reflux for 2 hours, cooled, and the xylene was removed by rotary evaporation. The resulting dark oil was crystallized from ethanol (95%) at reflux temperature and the resulting crystals were collected by vacuum filtration and washed with ethanol. A beige solid, 14 grams, was obtained. NMR analysis showed the product to have a structure consistent with 7,7-dimethyl-5-hydroxy-9,10-dimethoxy-7H-benzo[C]-fluorene.

Step 6

[0120] Morpholine (3.4 grams) was weighed into a dry reaction flask. Anhydrous tetrahydrofuran (50 mL) was added to the reaction flask and the resulting mixture was stirred under a nitrogen atmosphere at room temperature. Methyl lithium (25.1 mL of a 1.4 M solution in diethyl ether) was added dropwise to the reaction mixture over a 10-minute period. The temperature of the reaction mixture increased and a white solid precipitated out. 7,7-Dimethyl-5-hydroxy-9,10-dimethoxy-7H-benzo[C]-fluorene (2.5 grams) from step 5 was added over a 5-minute period to the reaction mixture. The resulting yellowish brown solution was heated overnight at reflux temperatures. After cooling to room temperature, the

reaction mixture was poured into 200 mL of water. The aqueous layer was collected and 10 weight percent hydrochloric acid was added until the pH was 6. A saturated sodium chloride solution (200 mL) was added to the aqueous layer. The resulting mixture was extracted with three 200 mL portions of ethyl acetate. The organic layers were collected, combined, washed once with a saturated sodium chloride solution (300 mL) and dried over anhydrous sodium sulfate. The solvent (ethyl acetate) was removed by rotary evaporation to yield a yellowish-brown oil that foamed upon drying. This material (identified as 7,7-dimethyl-5-hydroxy-9-morpholino-10-methoxy-7H-benzo[C]-fluorene) by mass spectroscopy was not purified further but was used directly in the next step.

Step 7

[0121] 7,7-Dimethyl-5-hydroxy-9-morpholino-10-methoxy-7H-benzo[C]-fluorene (1.30 grams) from Step 6, 1,1-bis(4-methoxyphenyl)-2-propyn-1-ol (1.16 grams), dodecylbenzene sulfonic acid (about 10 milligrams) and methylene chloride (200 mL) were combined in a reaction vessel and stirred at ambient temperature under a nitrogen atmosphere for 2 hours. The reaction mixture was washed twice with a saturated sodium bicarbonate solution (300 mL each time) and dried over anhydrous sodium sulfate. The solvent (methylene chloride) was removed by rotary evaporation. The resulting brown-black solid was purified by column chromatography and induced to crystallize from diethyl ether to yield 1.0 gram of a light yellow solid. NMR analysis showed the product to have a structure consistent with 3,3-di-(4-methoxyphenyl)-10-methoxy-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]-naphtho[1,2-b]pyran.

Example 6

[0122] The process of Example 6 was followed except that in Step 6, 1-(4-methoxyphenyl)-1-(4-morpholinophenyl)-2-propyn-1-ol (1.6 grams) was used in place of 1,1-bis(4-methoxyphenyl)-2-propyn-1-ol (1.16 grams). The resulting brown-black solid was purified by column chromatography and induced to crystallize from diethyl ether to yield 0.8 gram of a light yellow solid. NMR analysis showed the to have a structure consistent with 3-(4-methoxyphenyl)-3-(4-morpholinophenyl)-10-methoxy-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]-naphtho[1,2-b]pyran.

Example 7

[0123] The process of Example 1 was followed except that in Step 7, 1-(3,4-dimethoxyphenyl)-1-(4-methoxyphenyl)-2-propyn-1-ol was used instead of 1,1-di(4-methoxyphenyl)-2-propyn-1-ol to produce a solid having a melting point of 197-199°C. NMR analysis showed the product to have a structure consistent with 3-(3,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 8

[0124] The process of Example 1 was followed except that in Step 7, 1-(4-methoxyphenyl)-1-(4-morpholinophenyl)-2-propyn-1-ol was used instead of 1,1-di(4-methoxyphenyl)-2-propyn-1-ol. NMR analysis showed the product to have a structure consistent with 3-(4-methoxyphenyl)-3-(4-morpholinophenyl)-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran. When a portion of the recovered product was dissolved into diethylene glycol dimethyl ether and exposed to ultraviolet radiation, the solution became blue-green in color. When exposure to the ultraviolet radiation was discontinued, the solution became colorless.

Comparative Examples 1-5

[0125] Comparative Examples (CE) 1 through 5 were prepared following the procedures of U.S. Patent 5,645,767 and 6,296,785B1. NMR analysis showed the products to have structures consistent with the following names.

- CE-1 - 3,3-di(4-methoxyphenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.
- CE-2 - 3-phenyl-3-(4-morpholino-phenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.
- CE-3 - 3,3-di(4-(2-methoxyethoxyphenyl))-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.
- CE-4 - 3,3-di(4-methoxyphenyl)-13-hydroxy-13-ethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.
- CE-5 - 3-(4-methoxyphenyl)-3-(4-morpholinophenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 9

[0126] The Indenonaphthopyran Photochromic Performance Test comprises the preparation of photochromic polymeric test samples using the Examples of the present invention and Comparative Examples in Part A and testing the

photochromic performance as described in Part B.

Part A

[0127] Testing was done with the photochromic materials described in Examples 1 through 7 and Comparative Examples 1-6 in the following manner. A quantity of photochromic compound calculated to yield a 1.5×10^{-3} molal solution was added to a flask containing 50 grams of a monomer blend of 4 parts ethoxylated bisphenol A dimethacrylate (BPA 2EO DMA), 1 part poly(ethylene glycol) 600 dimethacrylate, and 0.033 weight percent 2,2'-azobis(2-methyl propionitrile) (AIBN). The 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 the interior dimensions of 2.2 mm x 6 inches (15.24 cm) x 6 inches (15.24 cm). The mold was sealed and placed in a horizontal air flow, programmable oven programmed to increase the temperature from 40°C to 95°C over a 5 hour interval, hold the temperature at 95°C for 3 hours, lower it to 60°C over a 2 hour interval and then hold it at 60°C for 16 hours. After the mold was opened, the polymer sheet was cut using a diamond blade saw into 2 inch (5.1 centimeters) test squares.

Part B

[0128] The photochromic test squares of Part A were tested for photochromic response on an optical bench. Prior to testing on the optical bench, the photochromic test squares were exposed to 365 nm ultraviolet light for about 10 minutes at a distance of about 14 cm from the lamps to activate the photochromic compound and then placed into a 75°C oven for 15 minutes to thermally bleach the photochromic compounds. The UVA (315 to 380 nm) irradiance at the sample was measured with a Licor Model Li-1800 spectroradiometer and found to be 22.2 Watts per square meter. The test squares were then cooled to room temperature, while exposed to fluorescent room lighting, approximately 1000 Lux for at least 2 hours and then kept covered for another 2 hours prior to testing on the optical bench.

[0129] The optical bench was fitted with an Oriel Model #66011 300 watt Xenon arc lamp, a remote controlled shutter, collimating lens, copper sulfate bath acting as a heat sink for the arc lamp, Schott WG-320 nm cut-off filter for removing short wavelength radiation; neutral density filter(s) and a sample holder. The air chamber in which testing was conducted was maintained at 72°F or 22°C. The irradiance at the sample was measured using a Licor Model Li-1800 spectroradiometer and found to be 2.5 watts per square meter UVA (315-380 nm) and 2.78 Klux. The irradiance consistency between experiments was verified by using a GRASEBY Optronics Model S-371 portable photometer and by running a preliminary response test with a photochromic test square reference standard before samples were run.

[0130] A Sorensen, Model SRL 20-50, DC power supply controlled the Nicolas Illuminator containing a 6 volt tungsten lamp that was used as the monitoring light source for photochromic response measurements. The collimated monitoring beam of light from the tungsten lamp was passed through the sample square at a small angle (approximately 30°) normal to the square and into a Model GM-200 monochromator from Spectral Energy Corporation. The monochromator was set at the previously determined visible lambda max of the photochromic compound being tested. The light at the set wavelength was measured upon exiting the monochromator by an attached International Light research radiometer system, Model IL1700 fitted with a high gain detector, Model SHD033. LabTech Notebook data acquisition and control software version 11.0 was used to process the data and control the operation of the optical bench.

[0131] Response measurements, in terms of a change in optical density (ΔOD) from the unactivated or bleached state to the activated or darkened state were determined by establishing the initial unactivated transmittance, opening the shutter from the Xenon lamp(s) and measuring the transmittance through activation at selected intervals of time, e.g., 30 seconds and 15 minutes, measuring the transmittance in the activated state, and calculating the change in optical density according to the formula: $\Delta OD = \log(\%T_b/\%T_a)$, where $\%T_b$ is the percent transmittance in the bleached state, $\%T_a$ is the percent transmittance in the activated state and the logarithm is to the base 10.

[0132] The $\Delta OD/\text{min.}$, which represents the sensitivity of the photochromic compound's response to ultraviolet light, was measured after the first five (5) seconds of UV exposure, then expressed on a per minute basis. The lambda max in the ultraviolet range ($\lambda \text{ max (UV)}$) is the wavelength of the major absorption peak in the ultraviolet range closest to the visible spectrum. The lambda max in the visible light range ($\lambda \text{ max (Vis)}$) is the wavelength in the visible spectrum at which the maximum absorption of the activated form of the photochromic compound occurs. The lambda max (Visible and UV) was determined by testing the photochromic test square polymerizates of Part A in a Varian Cary 3 UV-Visible spectrophotometer.

[0133] The Fade Half Life ($T_{1/2}$) is the time interval in seconds for the ΔOD of the activated form of the photochromic material in the test squares to reach one half the ΔOD measured after fifteen minutes of activation at 72°F, 22°C, after removal of the source of activating light, e.g., by closing the shutter. The results of the Indenonaphthopyran Photochromic Performance Test are included in Table 1.

TABLE 1

Example No.	λ max (UV)	λ max (Vis)	Sensitivity Δ OD/min.	Δ OD @		T $\frac{1}{2}$ (seconds)
				30sec.	15 min.	
1	395	604	0.54	0.26	1.10	363
CE 1	355	561	0.33	0.19	0.78	129
2	395	615	0.54	0.29	1.65	736
CE 2	355	583	0.42	0.21	1.23	248
3	395	602	0.54	0.29	1.27	369
CE 3	354	557	0.39	0.20	0.78	133
4	380	609	0.43	0.20	0.55	48
CE 4	360	562	0.29	0.12	0.27	47
5	391	603	0.58	0.29	1.07	236
CE 1	355	561	0.33	0.19	0.78	129
6	393	622	0.58	0.27	0.98	167
CE 5	356	589	0.36	0.17	0.61	99
7	363	604	0.63	0.31	1.43	490
CE 1	355	561	0.33	0.19	0.78	129

[0134] Table 1 shows that each of the Example compounds demonstrates a bathochromic shift in the visible lambda max and an increase in Sensitivity when compared to the respective Comparative Example compounds in the Indenonaphthopyran Photochromic Performance Test.

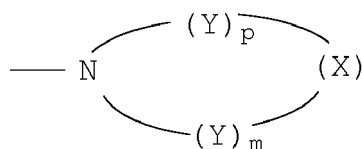
[0135] The present invention has been described with reference to specific details of particular embodiments thereof. It is not intended that such details be regarded as limitations upon the scope of the invention except insofar as to the extent that they are included in the accompanying claims.

Claims

1. A photochromic material of indeno [2',3':3,4]naphtho[1,2-b]pyran structure, **characterized in that** it comprises:

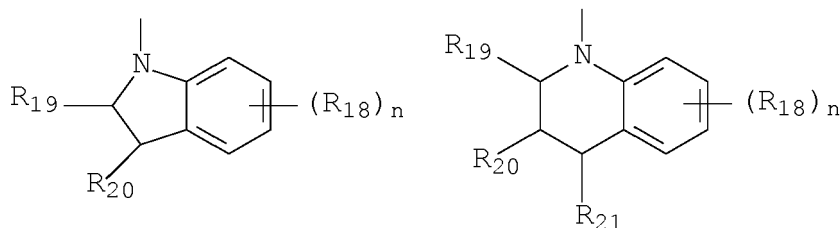
- a nitrogen containing substituent selected from

- (i) $-N(R_{15})R_{16}$, R_{15} and R_{16} each being independently chosen from C_1 - C_8 alkyl, C_1 - C_8 alkylaryl, C_3 - C_{20} cycloalkyl, C_4 - C_{20} bicycloalkyl, C_5 - C_{20} tricycloalkyl or C_1 - C_{20} alkoxyalkyl and said aryl group being phenyl or naphthyl;
- (ii) a nitrogen containing ring represented by the following graphic formula:



wherein each Y being independently chosen for each occurrence from $-\text{CH}_2-$, $-\text{CH}(\text{R}_{17})-$, $-\text{C}(\text{R}_{17})(\text{R}_{17})-$, $-\text{CH}(\text{aryl})-$, $-\text{C}(\text{aryl})_2-$ or $-\text{C}(\text{R}_{17})(\text{aryl})-$; X being $-\text{Y}-$, $-\text{O}-$, $-\text{S}-$, $-\text{NH}-$, $-\text{N}(\text{R}_{17})-$ or $-\text{N}(\text{aryl})-$; R_{17} being C_1 - C_6 alkyl; said aryl group being phenyl or naphthyl, m being chosen from the integer 1, 2 or 3 and p being chosen from the integer 0, 1, 2 or 3; provided that when p is 0, X is Y;

(iii) a group represented by one of the following graphic formulae:



wherein each R_{19} , R_{20} and R_{21} being chosen independently for each occurrence in each formula from hydrogen, C_1 - C_5 alkyl, phenyl or naphthyl; or the groups R_{19} and R_{20} together form a ring of 5 to 8 carbon atoms; R_{18} being chosen independently for each occurrence from C_1 - C_6 alkyl, C_{1-6} alkoxy, fluoro or chloro and n being chosen from the integer 0, 1 or 2;

(iv) unsubstituted, mono- or di- substituted C_4 - C_{18} spirobicyclic amine; or

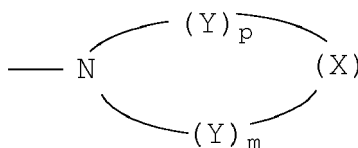
(v) unsubstituted, mono- or di- substituted C_4 - C_{18} spirotricyclic amine; said substituents for (iv) and (v) being independently chosen for each occurrence from aryl, C_1 - C_6 alkyl, C_{1-6} alkoxy or phenyl(C_1 - C_6)alkyl;

at the 11-position ring atom, said ring atoms being numbered according to the International Union of Pure and Applied Chemistry rules of nomenclature starting with the 1-position ring atom being the carbon atom para to the oxygen atom of the pyran ring and numbering clockwise therefrom, said photochromic material being free of spiro-substituents at the 13-position.

2. The photochromic material of claim 1 wherein the nitrogen containing substituent at the 11-position ring atom is represented by:

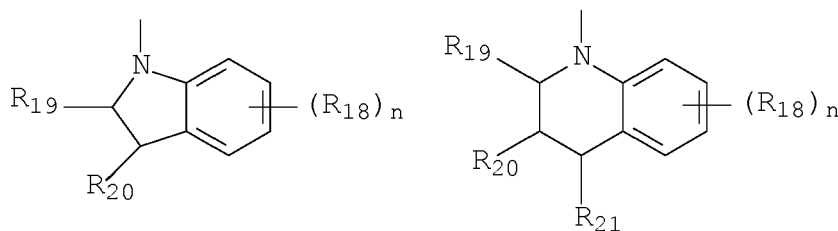
(i) $-\text{N}(\text{R}_{15})\text{R}_{16}$, R_{15} and R_{16} each being independently chosen from C_1 - C_6 alkyl;

(ii) a nitrogen containing ring represented by the following graphic formula:



wherein each Y being $-\text{CH}_2-$ and X being independently chosen from $-\text{Y}-$, $-\text{O}-$, $-\text{S}-$, $-\text{N}(\text{R}_{17})-$ and $-\text{N}(\text{phenyl})-$, R_{17} being C_1 - C_6 alkyl, m being chosen from the integer 1, 2 or 3, and p being chosen from the integer 0, 1, 2 or 3;

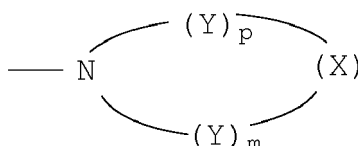
(iii) a group represented by one of the following graphic formulae:



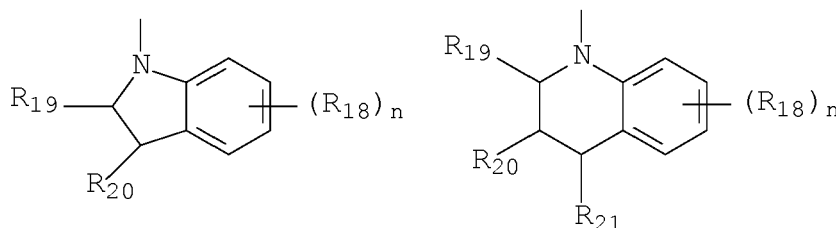
wherein R_{19} , R_{20} and R_{21} each being independently chosen from hydrogen or C_1 - C_5 alkyl, R_{18} being independently chosen from hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, fluoro or chloro and n being chosen from the integer 0 or 1;
 (iv) unsubstituted or mono-substituted C_5 - C_{18} spirobicyclic amine; or
 (v) unsubstituted or mono-substituted C_5 - C_{18} spirotricyclic amine; said substituents for (iv) and (v) being independently chosen for each occurrence from phenyl, C_1 - C_3 alkyl, C_1 - C_3 alkoxy or phenyl(C_1 - C_3)alkyl.

3. The photochromic material of claim 2 wherein the nitrogen containing substituent at the 11-position ring atom is represented by:

- (i) $-N(R_{15})R_{16}$, R_{15} and R_{16} each being C_1 - C_3 alkyl,
 (ii) a nitrogen containing ring represented by the following graphic formula:

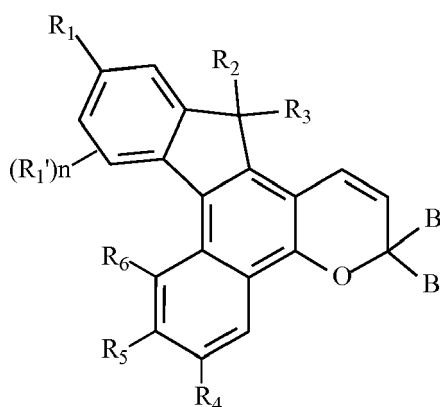


wherein each Y being $-CH_2-$ and X being independently chosen from $-Y-$, $-O-$, and $-N(R_{17})-$, R_{17} being C_1 - C_4 alkyl, m being chosen from the integer 1 or 2, and p being chosen from the integer 0, 1 or 2; or
 (iii) a group represented by the following graphic formulae:



wherein R_{19} , R_{20} , and R_{21} each being hydrogen and n is 0.

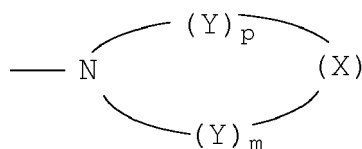
4. The naphthopyran of claim 1 represented by the following graphic formula:



wherein,

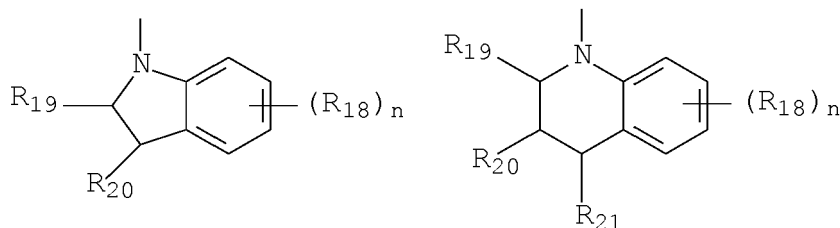
- (a) R_1 is represented by:

- (i) $-N(R_{15})R_{16}$, R_{15} and R_{16} each being independently chosen from C_1 - C_8 alkyl, C_1 - C_8 alkylaryl, C_3 - C_{20} cycloalkyl, C_4 - C_{20} bicycloalkyl, C_5 - C_{20} tricycloalkyl or C_1 - C_{20} alkoxyalkyl and said aryl group being phenyl or naphthyl;
 (ii) a nitrogen containing ring represented by the following graphic formula:



wherein each Y being independently chosen for each occurrence from $-\text{CH}_2-$, $-\text{CH}(\text{R}_{17})-$, $-\text{C}(\text{R}_{17})(\text{R}_{17})-$, $-\text{CH}(\text{aryl})-$, $-\text{C}(\text{aryl})_2-$ or $-\text{C}(\text{R}_{17})(\text{aryl})-$; X being $-\text{Y}-$, $-\text{O}-$, $-\text{S}-$, $-\text{NH}-$, $-\text{N}(\text{R}_{17})-$ or $-\text{N}(\text{aryl})-$; R_{17} being C_1 - C_6 alkyl; said aryl group being phenyl or naphthyl, m being chosen from the integer 1, 2 or 3 and p being chosen from the integer 0, 1, 2 or 3; provided that when p is 0, X is Y;

(iii) a group represented by one of the following graphic formulae:



wherein each R_{19} , R_{20} and R_{21} being chosen independently for each occurrence in each formula from hydrogen, C_1 - C_5 alkyl, phenyl or naphthyl; or the groups R_{19} and R_{20} together form a ring of 5 to 8 carbon atoms; R_{18} being chosen independently for each occurrence from C_1 - C_6 alkyl, C_1 - C_6 alkoxy, fluoro or chloro and n being chosen from the integer 0, 1 or 2;

(iv) unsubstituted, mono- or di- substituted C_4 - C_{18} spirobicyclic amine; or

(v) unsubstituted, mono- or di- substituted C_4 - C_{18} spirotricyclic amine; said substituents for (v) and (iv) being independently chosen for each occurrence from aryl, C_1 - C_6 alkyl, C_1 - C_6 alkoxy or phenyl(C_1 - C_6)alkyl;

(b) R_1' is independently chosen for each occurrence from C_1 - C_6 alkyl or C_1 - C_6 alkoxy and n being chosen from the integer 0, 1 or 2;

(c) R_2 and R_3 are each independently chosen from:

(i) hydrogen, hydroxy, amino, mono- or di-substituted amino, C_1 - C_{12} alkyl, C_3 - C_{12} alkylidene, C_2 - C_{12} alkylidyne, vinyl, C_3 - C_7 cycloalkyl, C_1 - C_6 haloalkyl, allyl, benzyl, mono-substituted benzyl, chloro, fluoro or $-\text{C}(\text{O})\text{W}$, wherein W being hydroxy, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, mono-substituted phenyl, amino, mono(C_1 - C_6)alkylamino, di(C_1 - C_6)alkylamino, morpholino, piperidino or pyrrolidyl; said amino substituents being C_1 - C_6 alkyl, phenyl, benzyl or naphthyl; each of said benzyl and phenyl substituents being C_1 - C_6 alkyl or C_1 - C_6 alkoxy;

(ii) an unsubstituted, mono- di- or tri-substituted group chosen from phenyl, naphthyl, phenanthryl, pyrenyl, quinolyl, isoquinolyl, benzofuranyl, thienyl, benzothienyl, dibenzofuranyl, dibenzothienyl, carbazolyl or indolyl; each of said group substituents in (c)(ii) being chosen independently for each occurrence from chloro, fluoro, C_1 - C_6 alkyl or C_1 - C_6 alkoxy;

(iii) a monosubstituted phenyl, said phenyl having a substituent located at the para position being $-(\text{CH}_2)_t-$ or $-\text{O}-(\text{CH}_2)_t-$, connected to an aryl group which is a member of another photochromic material, and t being chosen from the integer 1, 2, 3, 4, 5 or 6;

(iv) $-\text{OR}_8$, R_8 being chosen from C_1 - C_6 alkyl, C_1 - C_6 acyl, phenyl(C_1 - C_3)alkyl, mono(C_1 - C_6)alkyl substituted phenyl(C_1 - C_3)alkyl, mono(C_1 - C_6)alkoxy substituted phenyl(C_1 - C_3)alkyl, C_1 - C_6 alkoxy(C_2 - C_4)alkyl, C_3 - C_7 cycloalkyl, mono(C_1 - C_4)alkyl substituted C_3 - C_7 cycloalkyl, C_1 - C_6 chloroalkyl, C_1 - C_6 fluoroalkyl, allyl, tri(C_1 - C_6)alkylsilyl, tri(C_1 - C_6)alkoxysilyl, di(C_1 - C_6)alkyl (C_1 - C_6)alkoxysilyl, di(C_1 - C_6)alkoxy(C_1 - C_6)alkylsilyl, benzoyl, mono-substituted benzoyl, naphthoyl or mono-substituted naphthoyl; each of said benzoyl and naphthoyl substituents being independently chosen from C_1 - C_6 alkyl or C_1 - C_6 alkoxy; or R_8 being $-\text{CH}(\text{R}_9)\text{Q}$, wherein R_9 being chosen from hydrogen or C_1 - C_3 alkyl and Q being chosen from $-\text{CN}$, $-\text{CF}_3$,

or $-\text{COOR}_{10}$ and R_{10} being chosen from hydrogen or C_1 - C_3 alkyl; or R_8 being $-\text{C}(\text{O})\text{V}$, wherein V being chosen from hydrogen, C_1 - C_6 alkoxy, phenoxy, mono- or di-(C_1 - C_6)alkyl substituted phenoxy, mono- or di-(C_1 - C_6)alkoxy substituted phenoxy, an unsubstituted, mono- or di-substituted aryl group, phenyl or naphthyl, amino, mono(C_1 - C_6)alkylamino, di(C_1 - C_6)alkylamino, phenylamino, mono- or di-(C_1 - C_6)alkyl substituted phenylamino, or mono- or di-(C_1 - C_6)alkoxy substituted phenylamino; each of said aryl group substit-

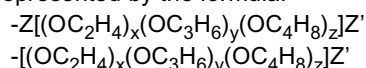
uents being independently chosen from C₁-C₆ alkyl or C₁-C₆ alkoxy;

(v) -CH(Q')₂, Q' being chosen from -CN or -COOR₁₁ and R₁₁ being chosen from hydrogen, C₁-C₆ alkyl, phenyl(C₁-C₃)alkyl, mono(C₁-C₆)alkyl substituted phenyl(C₁-C₃)alkyl, mono(C₁-C₆)alkoxy substituted phenyl(C₁-C₃)alkyl or an unsubstituted, mono- or di-substituted aryl group, phenyl or naphthyl; each of said

aryl group substituents being independently chosen from C₁-C₆ alkyl or C₁-C₆ alkoxy;

(vi) -CH(R₁₂)G, R₁₂ being chosen from hydrogen, C₁-C₆ alkyl or an unsubstituted, mono- or di-substituted aryl group, phenyl or naphthyl, and G being chosen from -COOR₁₁, -COR₁₃ or -CH₂OR₁₄, wherein R₁₃ being chosen from hydrogen, C₁-C₆ alkyl, an unsubstituted, mono- or di-substituted aryl group, phenyl or naphthyl, amino, mono(C₁-C₆)alkylamino, di(C₁-C₆)alkylamino, phenylamino, mono- or di-(C₁-C₆)alkyl substituted phenylamino, mono- or di-(C₁-C₆)alkoxy substituted phenylamino, diphenylamino, mono- or di(C₁-C₆)alkyl substituted diphenylamino, mono- or di(C₁-C₆)alkoxy substituted diphenylamino, morpholino or piperidino, R₁₄ being chosen from hydrogen, -C(O)R₁₁, C₁-C₆ alkyl, C₁-C₃ alkoxy(C₁-C₆)alkyl, phenyl(C₁-C₃)alkyl, mono(C₁-C₆)alkoxy substituted phenyl(C₁-C₃)alkyl or an unsubstituted, mono- or di-substituted aryl group, phenyl or naphthyl, each of said aryl group substituents being independently chosen from C₁-C₆ alkyl or C₁-C₆ alkoxy;

(vii) the group T represented by the formula:



wherein -Z being chosen from -C(O)- or -CH₂-, Z' being chosen from C₁-C₃ alkoxy or a polymerizable group, x, y and z each being independently chosen from a number between 0 and 50, and the sum of x, y and z being between 2 and 50; or

(viii) R₂ and R₃ together form an oxo group;

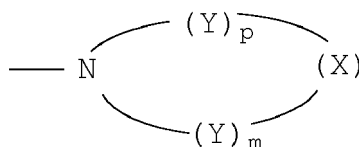
(d) R₄ is chosen from hydrogen, C₁-C₆ alkyl or the group R_a chosen from:

(i) -OR₈', R₈' being chosen from phenyl(C₁-C₃)alkyl, C₁-C₆ alkyl, mono(C₁-C₆)alkyl substituted phenyl(C₁-C₃)alkyl, mono(C₁-C₆)alkoxy substituted phenyl(C₁-C₃)alkyl, C₁-C₆ alkoxy(C₂-C₄)alkyl, C₃-C₇ cycloalkyl, mono(C₁-C₄)alkyl substituted C₃-C₇ cycloalkyl, C₁-C₆ chloroalkyl, C₁-C₆ fluoroalkyl, allyl or -CH(R₉)Q, R₉ being chosen from hydrogen or C₁-C₃ alkyl; or

(ii) a group chosen from:

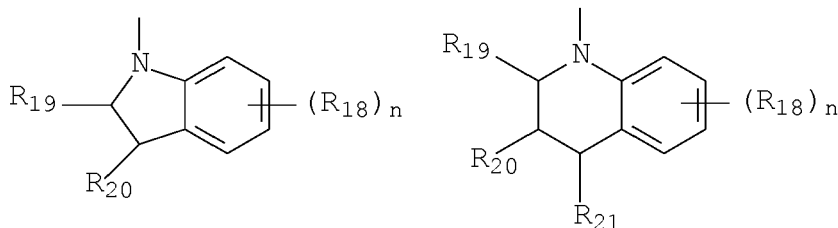
(1) -N(R₁₅)R₁₆ wherein R₁₅ and R₁₆ being the same as described hereinbefore in (a)(i);

(2) a nitrogen containing ring represented by the following graphic formula:



wherein Y, X, m and p being the same as described hereinbefore in (a)(ii); or

(3) a group represented by the following graphic formulae:

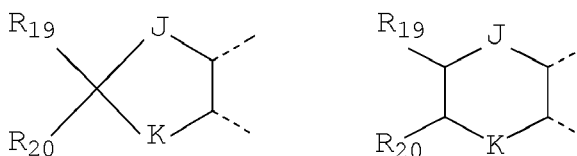


wherein R₁₈, R₁₉, R₂₀, R₂₁ and n being the same as described hereinbefore in (a)(iii);

(e) R₅ is chosen from hydrogen, C₁-C₆ alkyl or R_a, said R_a being the same as described hereinbefore in (d);

(f) R₆ is chosen from hydrogen, C₁-C₆ alkyl or R_a, said R_a being the same as described hereinbefore in (d); or

(g) R₅ and R₆ together form one of the following graphic formulae:



wherein J and K being independently chosen for each occurrence in each formula from oxygen or -N(R₁₅)-, R₁₅ being the same as described hereinbefore in (a)(i), R₁₉ and R₂₀ each being the same as described hereinbefore in (a)(iii);

(h) B and B' are each independently chosen from:

(i) mono-T-substituted phenyl;

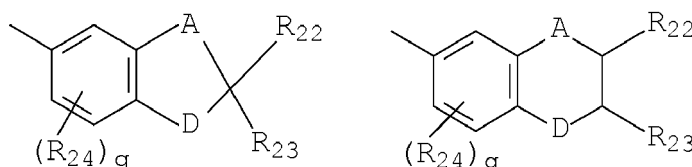
(ii) an unsubstituted, mono-, di-, or tri-substituted aryl group, phenyl or naphthyl;

(iii) 9-julolidinyl or the 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, each of said aryl and heteroaromatic substituents in (h) (ii) and (iii) being independently chosen from hydroxy, -C(O)W, described hereinbefore in (c)(i), aryl, mono(C₁-C₆)alkoxyaryl, di(C₁-C₆)alkoxyaryl, mono(C₁-C₆)alkylaryl, di(C₁-C₆)alkylaryl, chloroaryl, fluoroaryl, C₃-C₇ cycloalkylaryl, C₃-C₇ cycloalkyl, C₃-C₇ cycloalkyloxy, C₃-C₇ cycloalkyloxy(C₁-C₆)alkyl, C₃-C₇ cycloalkyloxy(C₁-C₆)alkoxy, aryl(C₁-C₆)alkyl, aryl(C₁-C₆)alkoxy, aryloxy, aryloxy(C₁-C₆)alkyl, aryloxy(C₁-C₆)alkoxy, mono- or di-(C₁-C₆)alkylaryl(C₁-C₆)alkyl, mono- or di-(C₁-C₆)alkoxyaryl(C₁-C₆)alkyl, mono- or di-(C₁-C₆)alkylaryl(C₁-C₆)alkoxy, mono- or di-(C₁-C₆)alkoxyaryl(C₁-C₆)alkoxy, amino, mono(C₁-C₆)alkylamino, di(C₁-C₆)alkylamino, diarylamino, piperazino, N-(C₁-C₆)alkylpiperazino, N-aryl piperazino, aziridino, indolino, piperidino, morpholino, thiomorpholino, tetrahydroquinolino, tetrahydroisoquinolino, pyrrolidyl, C₁-C₆ alkyl, C₁-C₆ chloroalkyl, C₁-C₆ fluoroalkyl, C₁-C₆ alkoxy, mono(C₁-C₆)alkoxy(C₁-C₄)alkyl, acryloxy, methacryloxy, bromo, chloro or fluoro, said aryl being chosen from phenyl or naphthyl;

(iv) an unsubstituted or mono-substituted group chosen from pyrazolyl, imidazolyl, pyrazolinyl, imidazolinyl, pyrrolinyl, phenothiazinyl, phenoxazinyl, phenazinyl or acridinyl, each of said substituents being independently chosen from C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, fluoro, chloro or bromo;

(v) mono-substituted phenyl, said phenyl having a substituent located at the para position as described hereinbefore in (c)(iii);

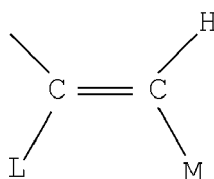
(vi) a group represented by one of the following graphic formulae:



wherein A being independently chosen in each formula from methylene or oxygen and D being independently chosen in each formula from oxygen or substituted nitrogen, provided that when D is substituted nitrogen, A is methylene; said nitrogen substituents being chosen from hydrogen, C₁-C₆ alkyl, or C₂-C₆ acyl; each R₂₄ being independently chosen for each occurrence in each formula from C₁-C₆ alkyl, C₁-C₆ alkoxy, hydroxy, chloro or fluoro; R₂₂ and R₂₃ each being independently chosen in each formula from hydrogen or C₁-C₆ alkyl; and q being chosen from the integer 0, 1 or 2;

(vii) C₁-C₆ alkyl, C₁-C₆ chloroalkyl, C₁-C₆ fluoroalkyl, C₁-C₆ alkoxy(C₁-C₄)alkyl, C₃-C₆ cycloalkyl, mono(C₁-C₆)alkoxy(C₃-C₆)cycloalkyl, mono(C₁-C₆)alkyl(C₃-C₆)cycloalkyl, chloro(C₃-C₆)cycloalkyl, fluoro(C₃-C₆)cycloalkyl or C₄-C₁₂ bicycloalkyl;

(viii) a group represented by the following graphic formula:



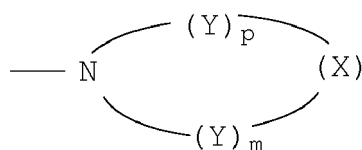
wherein L being chosen from hydrogen or C₁-C₄ alkyl and M being chosen from an unsubstituted, mono-, or di-substituted group chosen from naphthyl, phenyl, furanyl, or thienyl; each of said group substituents being independently chosen from C₁-C₄ alkyl, C₁-C₄ alkoxy, fluoro, or chloro; or

(i) B and B' taken together form fluoren-9-ylidene, mono-, or di-substituted fluoren-9-ylidene or a group being independently chosen from saturated C₃-C₁₂ spiro-monocyclic hydrocarbon rings, saturated C₇-C₁₂ spiro-bicyclic hydrocarbon rings or saturated C₇-C₁₂ spiro-tricyclic hydrocarbon rings; each of said fluoren-9-ylidene substituents being independently chosen from C₁-C₄ alkyl, C₁-C₄ alkoxy, fluoro or chloro.

5. The naphthopyran of claim 4 wherein:

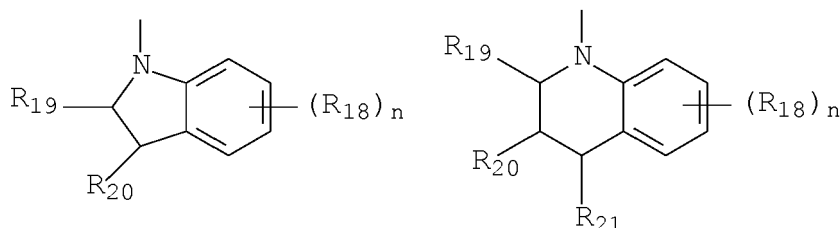
(a) R₁ is represented by:

(i) -N(R₁₅)R₁₆, R₁₅ and R₁₆ each being independently chosen from, C₁-C₆ alkyl, or C₃-C₂₀ cycloalkyl;
 (ii) a nitrogen containing ring represented by the following graphic formula:



wherein each Y being -CH₂- and X being independently chosen from -Y-, -O-, -S-, -N(R₁₇)- or -N(phenyl)-, R₁₇ being C₁-C₆ alkyl, m being chosen from the integer 1, 2 or 3, and p being chosen from the integer 0, 1, 2 or 3;

(iii) a group represented by one of the following graphic formulae:



wherein R₁₉, R₂₀ and R₂₁ each being independently chosen from hydrogen, C₁-C₅ alkyl or phenyl, R₁₈ being independently chosen from hydrogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, fluoro or chloro and n being chosen from the integer 0 or 1;

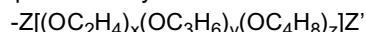
(iv) unsubstituted or mono-substituted C₅-C₁₈ spirobicyclic amine; or
 (v) unsubstituted or mono-substituted C₅-C₁₈ spirotricyclic amine;

(b) R₁' being independently chosen from C₁-C₄ alkyl or C₁-C₄ alkoxy and n being chosen from the integer 0 or 1;

(c) R₂ and R₃ each being independently chosen from:

(i) hydrogen, hydroxy, C₃-C₇ cycloalkyl, allyl, benzyl or the group, -C(O)W, wherein W being C₁-C₆ alkyl or C₁-C₆ alkoxy;
 (ii) an unsubstituted or mono-substituted phenyl, said substituent being chosen from chloro, fluoro, C₁-C₄ alkyl or C₁-C₄ alkoxy;
 (iii) a mono-substituted phenyl, having a substituent located at the para position that is -(CH₂)_t- or -O-(CH₂)_t-, wherein t being chosen from the integer 2 or 3, connected to an aryl group which is a member of another photochromic naphthopyran;
 (iv) -OR₈, R₈ being chosen from C₁-C₆ alkyl, C₁-C₆ acyl or phenyl(C₁-C₃)alkyl; or R₈ being the group -CH(R₉)Q, wherein R₉ being hydrogen and Q being -COOR₁₀, R₁₀ being C₁-C₃ alkyl, or R₈ being the group, -C(O)V, wherein V being C₁-C₆ alkoxy;
 (v) -CH(Q')₂, Q' being -COOR₁₁, wherein R₁₁ being C₁-C₆ alkyl;
 (vi) -CH(R₁₂)G, R₁₂ being hydrogen or C₁-C₆ alkyl; G being -COOR₁₁ or -CH₂OR₁₄, wherein R₁₄ being hydrogen, C₁-C₆ alkyl, or C₁-C₃ alkoxy(C₁-C₆)alkyl;

(vii) the group T represented by the formula:



wherein -Z being -CH₂-, Z' being C₁-C₃ alkoxy or a polymerizable group, x, y and z each being independently chosen from a number between 0 and 30, and the sum of x, y and z being between 2 and 30; or

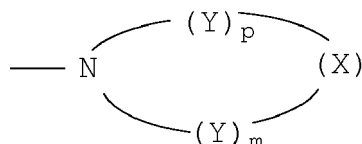
(viii) R₂ and R₃ together form an oxo group;

(d) R₄ being hydrogen, C₁-C₆ alkyl or R_a, said R_a being chosen from:

(i) -OR₈', R₈' being phenyl(C₁-C₃)alkyl or C₁-C₆ alkyl;

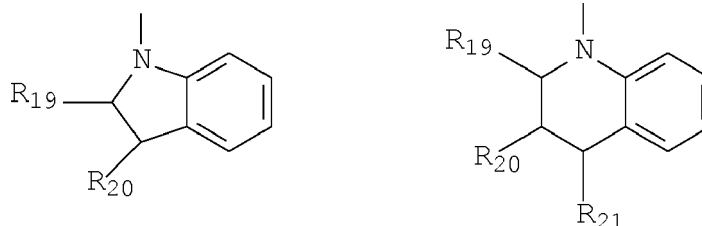
(ii) -N(R₁₅)R₁₆, R₁₅ and R₁₆ each being the same as described hereinbefore in (a)(i);

(iii) a nitrogen containing ring represented by the following graphic formula:



wherein each Y being -CH₂-, and X being independently chosen from -Y-, -O-, -S-, -NH-, -N(R₁₇)- or -N(aryl)-, wherein R₁₇ is C₁-C₆ alkyl, said aryl being chosen from phenyl or naphthyl, m being chosen from the integer 1, 2 or 3, and p being chosen from the integer 0, 1, 2 or 3 provided that when p is 0, X is Y; or

(iv) a group represented by one of the following graphic formulae:

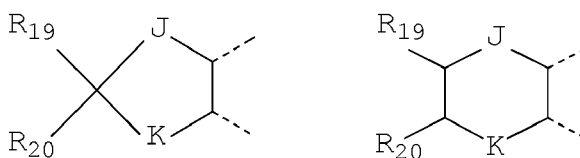


wherein R₁₉, R₂₀ and R₂₁ each being independently chosen from hydrogen, C₁-C₅ alkyl or phenyl;

(e) R₅ being chosen from hydrogen, C₁-C₄ alkyl or R_a, said R_a being described hereinbefore in (d);

(f) R₆ being chosen from hydrogen, C₁-C₄ alkyl or R_a, said R_a being described hereinbefore in (d); or

(g) R₅ and R₆ together form one of the following graphic formula:



wherein J and K each being oxygen; and R₁₉ and R₂₀ being the same as described hereinbefore in (d)(iv);

(h) B and B' each being independently chosen from:

(i) mono-T-substituted phenyl;

(ii) an unsubstituted, mono-, di-, or tri-substituted aryl group, said aryl being phenyl or naphthyl;

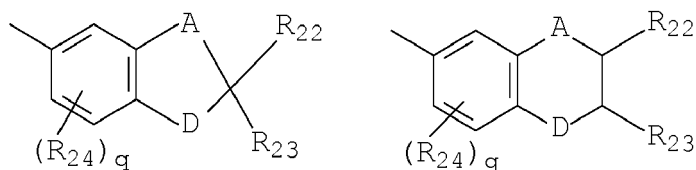
(iii) 9-julolidinyl or the unsubstituted, mono- or di-substituted heteroaromatic group chosen from pyridyl, benzofuran-2-yl, benzofuran-3-yl, thienyl, benzothien-2-yl, benzothien-3-yl, dibenzofuranyl, dibenzothienyl, or carbazoyl, each of said aryl and heteroaromatic substituents in (h) (ii) and (iii) being independently chosen from hydroxy, C₃-C₇ cycloalkyl, C₃-C₇ cycloalkyloxy, aryl(C₁-C₆)alkyl, aryloxy, aryloxy(C₁-C₆)alkoxy, amino, mono(C₁-C₆)alkylamino, di(C₁-C₆)alkylamino, diarylamino, piperazino, N-arylpiperazino, indolino, piperidino, morpholino, thiomorpholino, pyrrolidyl, C₁-C₆ alkyl, C₁-C₆ alkoxy or fluoro;

(iv) an unsubstituted or mono-substituted group chosen from phenothiazinyl or phenoxazinyl, each of said substituents being independently chosen from C₁-C₆ alkyl or C₁-C₆ alkoxy;

(v) a monosubstituted phenyl, said phenyl having a substituent at the para position as described hereinbefore

in (c)(iii);

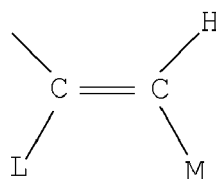
(vi) a group represented by one of the following graphic formulae:



wherein A being independently chosen in each formula from methylene or oxygen and D being independently chosen in each formula from oxygen or substituted nitrogen, provided that when D is substituted nitrogen, A is methylene, said nitrogen substituents being chosen from hydrogen or C₁-C₄ alkyl; each R₂₄ being C₁-C₄ alkyl; R₂₂ and R₂₃ each being hydrogen; and q being the integer 0, 1 or 2;

(vii) C₁-C₆ alkyl, C₃-C₆ cycloalkyl or C₄-C₁₂ bicycloalkyl;

(viii) a group represented by the following graphic formula:



wherein L being chosen from hydrogen or C₁-C₄ alkyl and M being chosen from an unsubstituted, mono-, or di-substituted phenyl; each of said phenyl substituents being independently chosen from C₁-C₄ alkyl or C₁-C₄ alkoxy; or

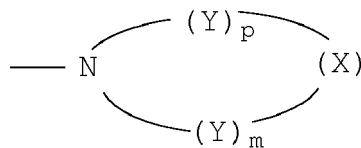
(i) B and B' taken together form fluoren-9-ylidene or mono-substituted fluoren-9-ylidene or a group being independently chosen from saturated C₃-C₁₂ spiro-monocyclic hydrocarbon rings, saturated C₇-C₁₂ spiro-bicyclic hydrocarbon rings or saturated C₇-C₁₂ spiro-tricyclic hydrocarbon rings; said fluoren-9-ylidene substituent being chosen from C₁-C₄ alkyl or C₁-C₄ alkoxy.

6. The naphthopyran of claim 5 wherein:

(a) R₁ is represented by:

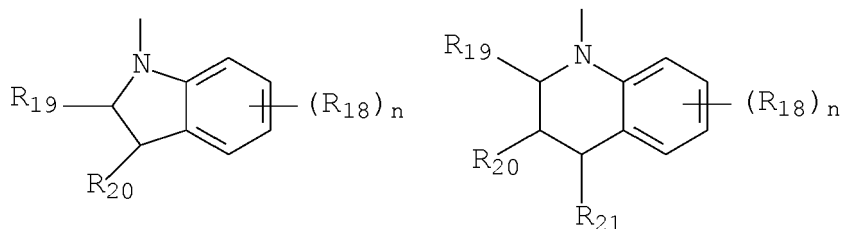
(i) -N(R₁₅)R₁₆, R₁₅ and R₁₆ each being independently chosen from C₁-C₄ alkyl;

(ii) a nitrogen containing ring represented by the following graphic formula:



wherein each Y for each occurrence being -CH₂- and X being independently chosen from -Y-, -O-, or --N(R₁₇)-, R₁₇ being C₁-C₄ alkyl, m being chosen from the integer 1 or 2, and p being chosen from the integer 0, 1 or 2; or

(iii) a group represented by the following graphic formulae:



wherein R_{19} , R_{20} , and R_{21} each being hydrogen and n is 0;

(b) R_1' being C_1 - C_2 alkyl or C_1 - C_3 alkoxy;

(c) R_2 and R_3 each being independently chosen from:

(i) hydrogen, hydroxy or C_3 - C_7 cycloalkyl;

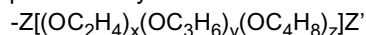
(ii) phenyl or mono- $(C_1$ - C_4 alkoxy) substituted phenyl;

(iii) a mono-substituted phenyl, having a substituent located at the para position being $-O-(CH_2)_t$, t being chosen from the integer 2 or 3, connected to an aryl group being a member of another photochromic naphthopyran;

(iv) $-OR_8$, R_8 being C_1 - C_6 alkyl or $-CH(R_9)Q$, R_9 being hydrogen, Q being $-COOR_{10}$, and R_{10} being C_1 - C_3 alkyl;

(v) $-CH(R_{12})G$, R_{12} being hydrogen; G being $-COOR_{11}$, wherein R_{11} being C_1 - C_6 alkyl or C_1 - C_3 alkoxy(C_1 - C_6)alkyl; or

(vi) the group T represented by the formula:



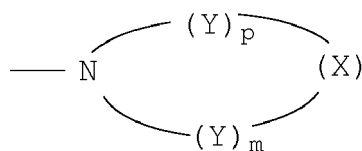
wherein $-Z$ being $-CH_2-$, Z' being C_1 - C_3 alkoxy, x , y and z each being independently chosen from a number between 0 and 20, and the sum of x , y and z being between 2 and 20;

(d) R_4 being hydrogen, C_1 - C_6 alkyl or R_a , said R_a being chosen from:

(i) $-OR_8'$, R_8' being C_1 - C_4 alkyl;

(ii) $-N(R_{15})R_{16}$, R_{15} and R_{16} each being the same as described hereinbefore in (a)(i); or

(iii) a nitrogen containing ring represented by the following graphic formula:



wherein each Y being $-CH_2-$, and X being independently chosen from $-Y-$, $-O-$, $-S-$, or $-N(R_{17})-$, R_{17} being C_1 - C_4 alkyl, m being chosen from the integer 1, 2 or 3, and p being chosen from the integer 0, 1, 2 or 3;

(e) R_5 being hydrogen or C_1 - C_4 alkyl;

(f) R_6 being hydrogen;

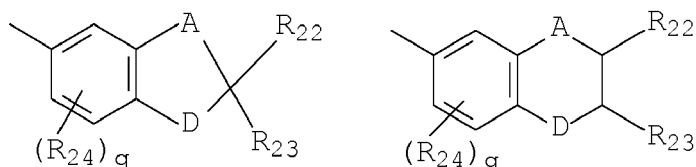
(g) B and B' each being independently chosen from:

(i) mono-, di-, and tri-substituted phenyl;

(ii) an unsubstituted, mono- or di-substituted heteroaromatic group chosen from benzofuran-2-yl or dibenzofuranyl, each of said aryl and heteroaromatic substituents in (g) (i) and (ii) being independently chosen from C_3 - C_7 cycloalkyl, aryloxy, aryloxy(C_1 - C_6)alkoxy, di(C_1 - C_6)alkylamino, piperazino, indolino, piperidino, morpholino, pyrrolidyl, C_1 - C_6 alkyl, C_1 - C_6 alkoxy or fluoro;

(iii) a monosubstituted phenyl, said phenyl having a substituent at the para position as described hereinbefore in (c)(iii);

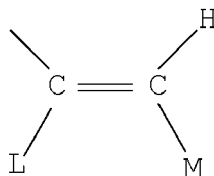
(iv) a group represented by one of the following graphic formulae:



wherein A being methylene and D being independently chosen in each formula from oxygen or substituted nitrogen, said nitrogen substituents being C₁-C₃ alkyl; each R₂₄ being C₁-C₃ alkyl; R₂₂ and R₂₃ each being hydrogen; and q being chosen from the integer 0, 1 or 2;

(v) C₁-C₄ alkyl or C₃-C₅ cycloalkyl;

(vi) the group represented by the following graphic formula:



wherein L being hydrogen and M being chosen from an unsubstituted, mono-, or di-substituted phenyl, each of said phenyl substituents being C₁-C₄ alkoxy; or

(i) B and B' taken together form fluoren-9-ylidene, mono-substituted fluoren-9-ylidene or a saturated C₇-C₁₂ spiro-bicyclic hydrocarbon ring, each of said fluoren-9-ylidene substituents being C₁-C₄ alkoxy.

7. The naphthopyran of claim 4 wherein said naphthopyran is chosen from:

- (a) 3,3-di(4-methoxyphenyl)-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
- (b) 3-phenyl-3-(4-morpholino-phenyl)-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho-[1,2-b]pyran;
- (c) 3,3-di(4-(2-methoxyethoxyphenyl))-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
- (d) 3,3-di(4-methoxyphenyl)-11-morpholino-13-hydroxy-13-ethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
- (e) 3,3-di(4-methoxyphenyl)-10-methoxy-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
- (f) 3-(4-methoxyphenyl)-3-(4-morpholinophenyl)-10-methoxy-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
- (g) 3-(3,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
- (h) 3-(4-methoxyphenyl)-3-(4-morpholinophenyl)-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; or
- (i) mixtures thereof.

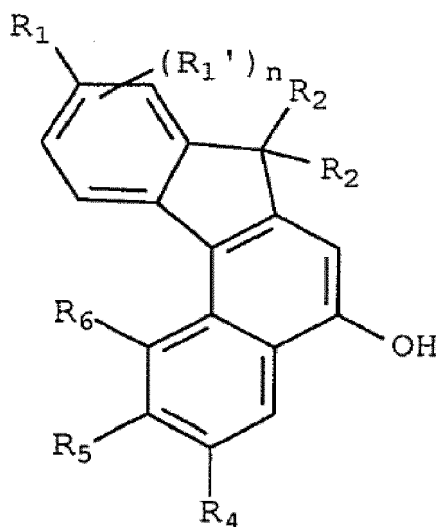
8. The photochromic material of any of the preceding claims wherein said photochromic material is chosen from:

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

9. A photochromic article comprising an at least partially cured polymer and at least a photochromic amount of at least one photochromic material according to any of claims 1-7.

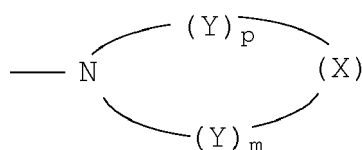
10. The photochromic article of claim 9 further comprising at least one other photochromic material comprising at least one activated absorption maxima within the range of from 400 to 700 nanometers.
- 5 11. The photochromic article of claim 10 wherein the at least one other photochromic material is chosen from chromenes, spiropyrans, oxazines, organo-metal dithiozonates, fulgides, fulgimides or a mixture thereof.
12. The photochromic article of claim 9 wherein the at least partially cured polymer is chosen from thermosetting or thermoplastic organic polymeric materials.
- 10 13. The photochromic article of claim 12 wherein the at least partially cured polymer is a thermosetting or thermoplastic organic polymeric material which is chosen from poly(C₁-C₁₂ alkyl methacrylates), poly(oxyalkylene dimethacrylates), 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), thermoplastic polycarbonates, polyesters, polyurethanes, polythiourethanes, poly(urea-urethane), poly(ethylene terephthalate), polystyrene, poly(alpha methylstyrene), copoly(styrene-methylmethacrylate), copoly(styrene-acrylonitrile), polyvinylbutyral or is polymerized from monomers chosen from bis(allyl carbonate) monomers, polyfunctional acrylate monomers, polyfunctional methacrylate monomers, diethylene glycol dimethacrylate monomers, diisopropenyl benzene monomers, ethoxylated bisphenol A dimethacrylate monomers, ethylene glycol bismethacrylate monomers, poly(ethylene glycol) bismethacrylate monomers, ethoxylated phenol bis methacrylate monomers, alkoxylated polyhydric alcohol polyacrylate monomers, styrene monomers, urethane acrylate monomers, glycidyl acrylate monomers, glycidyl methacrylate monomers, diallylidene pentaerythritol monomers or mixtures thereof.
- 15 14. The photochromic article of claim 9 further comprising a superstrate connected to at least a portion of the at least partially cured polymer, said superstrate comprising at least one organic polymeric material.
- 20 15. The photochromic article of claim 14 wherein the superstrate is adheringly bonded to at least a portion of the at least partially cured polymer.
- 25 16. The photochromic article of any of claims 14 and 15 wherein the superstrate is an organic polymeric material and is chosen from thermosetting or thermoplastic materials.
- 30 17. The photochromic article of claim 16 wherein the superstrate is a thermoplastic material and is polyurethane.
- 35 18. The photochromic article of claim 14 further comprising an at least partially abrasion resistant film superposed on at least a portion of the superstrate.
19. The photochromic article of claim 18 wherein the at least partially abrasion resistant film is an organic polymeric material chosen from thermoplastic or thermosetting materials.
- 40 20. The photochromic article of claim 19 wherein the at least partially abrasion resistant film is a thermoplastic material and is polycarbonate.
- 45 21. The photochromic article of claim 14 further comprising an at least partial coating of an at least partially antireflective coating applied to the at least partially abrasion resistant film superposed on at least a portion of the superstrate.
22. The photochromic article of any of claims 9-20 wherein the at least partially cured polymer is an optical element, preferably an ophthalmic lens.
- 50 23. A photochromic article comprising a substrate and an at least partial coating of a photochromic polymeric coating comprising a film forming polymer and at least a photochromic amount of at least one photochromic material according to any of claims 1-7.
- 55 24. The photochromic article of claim 23 wherein the photochromic polymeric coating further comprises at least one other photochromic material comprising at least one activated absorption maxima within the range of from 400 to 700 nanometers.
25. The photochromic article of claim 24 wherein the at least one other photochromic material is chosen from chromenes, spiropyrans, oxazines, organo-metal dithiozonates, fulgides, fulgimides or a mixture thereof.

26. The photochromic article of claim 23 wherein the substrate is paper, glass, ceramic, wood, masonry, textile, metal or polymeric organic material.
27. The photochromic article of claim 26 wherein the substrate is a polymeric organic material and is chosen from thermosetting or thermoplastic organic polymeric materials.
28. The photochromic article of claim 23 wherein the film-forming polymer is chosen from thermosetting or thermoplastic organic polymeric materials.
29. The photochromic article of claim 28 wherein the film forming polymer is thermosetting and is chosen from polyurethanes, aminoplast resins, polysilanes, polyanhydrides, polyacrylamides or epoxy resins.
30. The photochromic article of claim 23 further comprising a primer at least partially interposed between the substrate and the at least partial coating of a photochromic polymeric coating composition.
31. The photochromic article of claim 30 further comprising an at least partially abrasion resistant coating applied to at least a portion of the surface of the at least partial coating of a photochromic polymeric coating composition.
32. The photochromic article of claim 31 further comprising an at least partial coating of an at least partially antireflective coating applied to the at least partially abrasion resistant coating applied to at least a portion of the surface of the at least partial coating of a photochromic polymeric coating composition.
33. The photochromic article of any of claims 23-32 wherein the substrate is an optical element, preferably an ophthalmic lens.
34. A naphthol represented by the following graphic formula:



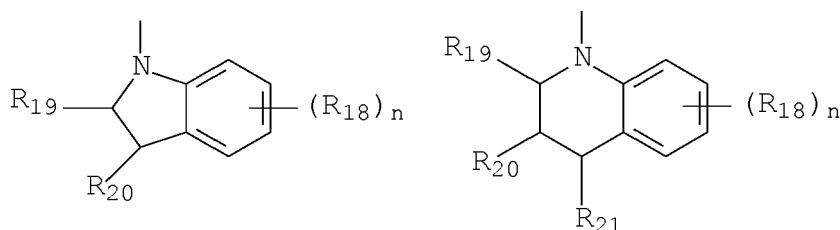
(a) R_1 is represented by:

- (i) $-N(R_{15})R_{16}$, R_{15} and R_{16} each being independently chosen from C_1 - C_8 alkyl, C_1 - C_8 alkylaryl, C_3 - C_{20} cycloalkyl, C_4 - C_{20} bicycloalkyl, C_5 - C_{20} tricycloalkyl or C_1 - C_{20} alkoxyalkyl and said aryl group being phenyl or naphthyl;
- (ii) a nitrogen containing ring represented by the following graphic formula:



wherein each Y being independently chosen for each occurrence from $-\text{CH}_2-$, $-\text{CH}(\text{R}_{17})-$, $-\text{C}(\text{R}_{17})(\text{R}_{17})-$, $-\text{CH}(\text{aryl})-$, $-\text{C}(\text{aryl})_2-$ or $-\text{C}(\text{R}_{17})(\text{aryl})-$; X being $-\text{Y}-$, $-\text{O}-$, $-\text{S}-$, $-\text{NH}-$, $-\text{N}(\text{R}_{17})-$ or $-\text{N}(\text{aryl})-$; R_{17} being C_1 - C_6 alkyl; said aryl group being phenyl or naphthyl, m being chosen from the integer 1, 2 or 3 and p being chosen from the integer 0, 1, 2 or 3; provided that when p is 0, X is Y;

(iii) a group represented by one of the following graphic formulae:



wherein each R_{19} , R_{20} and R_{21} being chosen independently for each occurrence in each formula from hydrogen, C_1 - C_5 alkyl, phenyl or naphthyl; or the groups R_{19} and R_{20} together form a ring of 5 to 8 carbon atoms; R_{18} being chosen independently for each occurrence from C_1 - C_6 alkyl, C_1 - C_6 alkoxy, fluoro or chloro and n being chosen from the integer 0, 1 or 2;

(iv) unsubstituted, mono- or di- substituted C_4 - C_{18} spirobicyclic amine; or

(v) unsubstituted, mono- or di- substituted C_4 - C_{18} spirotricyclic amine; said substituents for (v) and (iv) being independently chosen for each occurrence from aryl, C_1 - C_6 alkyl or C_1 - C_6 alkoxy or phenyl (C_1 - C_6) alkyl;

(b) R_1' is independently chosen for each occurrence from C_1 - C_6 alkyl or C_1 - C_6 alkoxy and n being chosen from the integer 0, 1 or 2;

(c) each R_2 or each R_3 is independently chosen for each occurrence from:

(i) hydrogen, hydroxy, amino, mono- or di-substituted amino, C_1 - C_{12} alkyl, C_3 - C_{12} alkylidene, C_2 - C_{12} alkylidyne, vinyl, C_3 - C_7 cycloalkyl, C_1 - C_6 haloalkyl, allyl, benzyl, mono-substituted benzyl, chloro, fluoro or $-\text{C}(\text{O})\text{W}$, wherein W being hydroxy, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, mono-substituted phenyl, amino, mono(C_1 - C_6)alkylamino, di(C_1 - C_6)alkylamino, morpholino, piperidino or pyrrolidyl; said amino substituents being C_1 - C_6 alkyl, phenyl, benzyl or naphthyl; each of said benzyl and phenyl substituents being C_1 - C_6 alkyl or C_1 - C_6 alkoxy;

(ii) an unsubstituted, mono- di- or tri-substituted group chosen from phenyl, naphthyl, phenanthryl, pyrenyl, quinolyl, isoquinolyl, benzofuranyl, thienyl, benzothienyl, dibenzofuranyl, dibenzothienyl, carbazolyl or indolyl; each of said group substituents in (c)(ii) being chosen independently for each occurrence from chloro, fluoro, C_1 - C_6 alkyl or C_1 - C_6 alkoxy;

(iii) a monosubstituted phenyl, said phenyl having a substituent located at the para position being $-(\text{CH}_2)_t-$ or $-\text{O}-(\text{CH}_2)_t-$, connected to an aryl group which is a member of another photochromic material, and t being chosen from the integer 1, 2, 3, 4, 5 or 6;

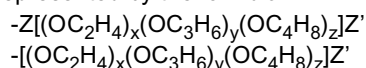
(iv) $-\text{OR}_8$, R_8 being chosen from C_1 - C_6 alkyl, C_1 - C_6 acyl, phenyl(C_1 - C_3)alkyl, mono(C_1 - C_6)alkyl substituted phenyl(C_1 - C_3)alkyl, mono(C_1 - C_6)alkoxy substituted phenyl(C_1 - C_3)alkyl, C_1 - C_6 alkoxy(C_2 - C_4)alkyl, C_3 - C_7 cycloalkyl, mono(C_1 - C_4)alkyl substituted C_3 - C_7 cycloalkyl, C_1 - C_6 chloroalkyl, C_1 - C_6 fluoroalkyl, allyl, tri(C_1 - C_6)alkylsilyl, tri(C_1 - C_6)alkoxysilyl, di(C_1 - C_6)alkyl (C_1 - C_6)alkoxysilyl, di(C_1 - C_6)alkoxy(C_1 - C_6)alkylsilyl, benzoyl, mono-substituted benzoyl, naphthoyl or mono-substituted naphthoyl; each of said benzoyl and naphthoyl substituents being independently chosen from C_1 - C_6 alkyl or C_1 - C_6 alkoxy; or R_8 being $-\text{CH}(\text{R}_9)\text{Q}$, wherein R_9 being chosen from hydrogen or C_1 - C_3 alkyl and Q being chosen from $-\text{CN}$, $-\text{CF}_3$,

or $-\text{COOR}_{10}$ and R_{10} being chosen from hydrogen or C_1 - C_3 alkyl; or R_8 being $-\text{C}(\text{O})\text{V}$, wherein V being chosen from hydrogen, C_1 - C_6 alkoxy, phenoxy, mono- or di-(C_1 - C_6)alkyl substituted phenoxy, mono- or di-(C_1 - C_6)alkoxy substituted phenoxy, an unsubstituted, mono- or di-substituted aryl group, phenyl or naphthyl, amino, mono(C_1 - C_6)alkylamino, di(C_1 - C_6)alkylamino, phenylamino, mono- or di-(C_1 - C_6)alkyl substituted phenylamino, or mono- or di-(C_1 - C_6)alkoxy substituted phenylamino; each of said aryl group substituents being independently chosen from C_1 - C_6 alkyl or C_1 - C_6 alkoxy;

(v) $-\text{CH}(\text{Q}')_2$, Q' being chosen from $-\text{CN}$ or $-\text{COOR}_{11}$ and R_{11} being chosen from hydrogen, C_1 - C_6 alkyl, phenyl(C_1 - C_3)alkyl, mono(C_1 - C_6)alkyl substituted phenyl(C_1 - C_3)alkyl, mono(C_1 - C_6)alkoxy substituted phenyl(C_1 - C_3)alkyl or an unsubstituted, mono- or di-substituted aryl group, phenyl or naphthyl; each of said aryl group substituents being independently chosen from C_1 - C_6 alkyl or C_1 - C_6 alkoxy;

(vi) $-\text{CH}(\text{R}_{12})\text{G}$, R_{12} being chosen from hydrogen, $\text{C}_1\text{-C}_6$ alkyl or an unsubstituted, mono- or di-substituted aryl group, phenyl or naphthyl, and G being chosen from $-\text{COOR}_{11}$, $-\text{COR}_{13}$ or $-\text{CH}_2\text{OR}_{14}$, wherein R_{13} being chosen from hydrogen, $\text{C}_1\text{-C}_6$ alkyl, an unsubstituted, mono- or di-substituted aryl group, phenyl or naphthyl, amino, mono($\text{C}_1\text{-C}_6$)alkylamino, di($\text{C}_1\text{-C}_6$)alkylamino, phenylamino, mono- or di-($\text{C}_1\text{-C}_6$)alkyl substituted phenylamino, mono- or di-($\text{C}_1\text{-C}_6$)alkoxy substituted phenylamino, diphenylamino, mono- or di($\text{C}_1\text{-C}_6$)alkyl substituted diphenylamino, mono- or di($\text{C}_1\text{-C}_6$)alkoxy substituted diphenylamino, morpholino or piperidino, R_{14} being chosen from hydrogen, $-\text{C}(\text{O})\text{R}_{11}$, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_3$ alkoxy($\text{C}_1\text{-C}_6$)alkyl, phenyl($\text{C}_1\text{-C}_3$)alkyl, mono($\text{C}_1\text{-C}_6$)alkoxy substituted phenyl($\text{C}_1\text{-C}_3$)alkyl or an unsubstituted, mono- or di-substituted aryl group, phenyl or naphthyl, each of said aryl group substituents being independently chosen from $\text{C}_1\text{-C}_6$ alkyl or $\text{C}_1\text{-C}_6$ alkoxy;

(vii) the group T represented by the formula:



wherein $-\text{Z}$ being chosen from $-\text{C}(\text{O})-$ or $-\text{CH}_2-$, Z' being chosen from $\text{C}_1\text{-C}_3$ alkoxy or a polymerizable group, x , y and z each being independently chosen from a number between 0 and 50, and the sum of x , y and z being between 2 and 50; or (viii) R_2 and R_2 or R_3 and R_3 together form an oxo group;

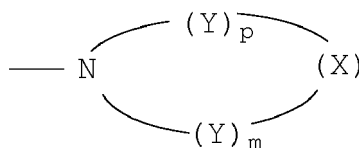
(d) R_4 is chosen from hydrogen, $\text{C}_1\text{-C}_6$ alkyl or the group R_a chosen from:

(i) $-\text{OR}_8'$, R_8' being chosen from phenyl($\text{C}_1\text{-C}_3$)alkyl, $\text{C}_1\text{-C}_6$ alkyl, mono($\text{C}_1\text{-C}_6$)alkyl substituted phenyl($\text{C}_1\text{-C}_3$)alkyl, mono($\text{C}_1\text{-C}_6$)alkoxy substituted phenyl($\text{C}_1\text{-C}_3$)alkyl, $\text{C}_1\text{-C}_6$ alkoxy($\text{C}_2\text{-C}_4$)alkyl, $\text{C}_3\text{-C}_7$ cycloalkyl, mono($\text{C}_1\text{-C}_4$)alkyl substituted $\text{C}_3\text{-C}_7$ cycloalkyl, $\text{C}_1\text{-C}_6$ chloroalkyl, $\text{C}_1\text{-C}_6$ fluoroalkyl, allyl or $-\text{CH}(\text{R}_9)\text{Q}$, R_9 being chosen from hydrogen or $\text{C}_1\text{-C}_3$ alkyl; or

(ii) a group chosen from:

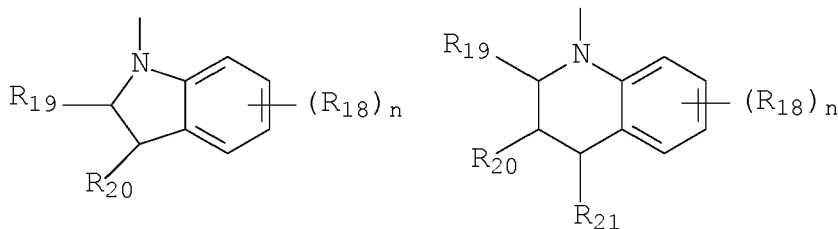
(1) $-\text{N}(\text{R}_{15})\text{R}_{16}$ wherein R_{15} and R_{16} being the same as described hereinbefore in (a)(i);

(2) a nitrogen containing ring represented by the following graphic formula:



wherein Y , X , m and p being the same as described hereinbefore in (a)(ii); or

(3) a group represented by the following graphic formulae:

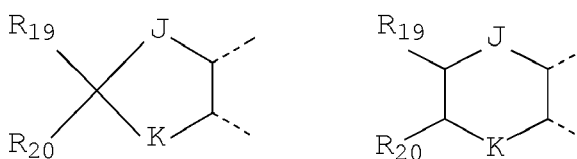


wherein R_{18} , R_{19} , R_{20} , R_{21} and n being the same as described herein before;

(e) R_5 is chosen from hydrogen, $\text{C}_1\text{-C}_6$ alkyl or R_a , said R_a being the same as described hereinbefore in (d);

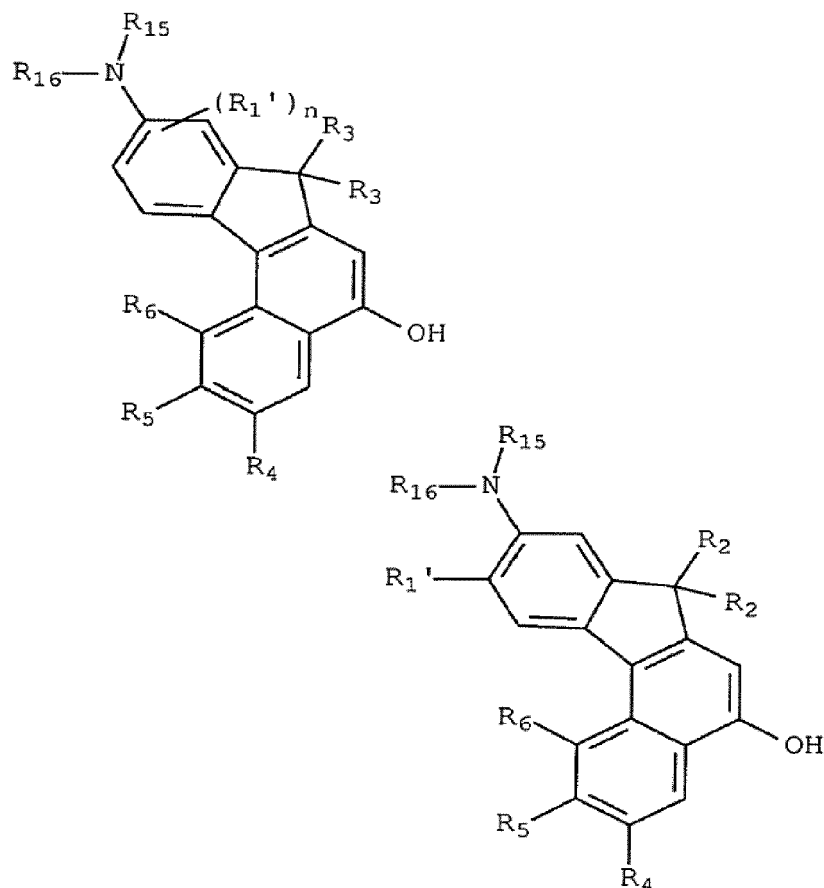
(f) R_6 is chosen from hydrogen, $\text{C}_1\text{-C}_6$ alkyl or R_a , said R_a being the same as described hereinbefore in (d); or

(g) R_5 and R_6 together form one of the following graphic formulae:



wherein J and K being independently chosen for each occurrence in each formula from oxygen or -N(R₁₅)-, R₁₅ being the same as described hereinbefore in (a)(i), R₁₉ and R₂₀ each being the same as described hereinbefore in (a)(iii).

35. The naphthol of claim 34 wherein said naphthol is represented by one of the following graphic formulae:



36. The naphthol of claim 34 wherein said naphthol is chosen from:

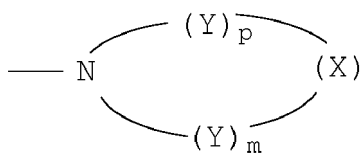
- (a) 7,7-dimethyl-5-hydroxy-9-morpholino-7H-benzo[C]fluorene;
- (b) 7,7-dimethyl-5-hydroxy-10-methoxy-9-morpholino-7H-benzo[C]fluorene;
- (c) 7-dimethyl-7-methoxy-5-hydroxy-9-dimethylamino-7H-benzo[C]fluorene;
- (d) 7-ethyl-7-methoxy-5-hydroxy-9-piperidino-7H-benzo[C]fluorene;
- (e) 7,7-dimethyl-5-hydroxy-9-piperidino-7H-benzo[C]fluorene;
- (f) 7,7-dimethyl-3-methoxy-5-hydroxy-9-morpholino-7H-benzo[C]fluorene;
- (g) 7,7-dimethyl-3,4-dimethoxy-5-hydroxy-9-morpholino-7H-benzo[C]fluorene;
- (h) 7,7-dimethyl-3-methoxy-4-methyl-5-hydroxy-9-morpholino-7H-benzo[C]fluorene;
- (i) 7-phenyl-7-hydroxy-3-methoxy-4-methyl-5-hydroxy-9-morpholino-7H-benzo[C]fluorene;
- (j) mixtures thereof.

Patentansprüche

1. Photochromes Material mit der Indeno [2',3':3,4]naphtho[1,2-b]pyran-struktur, **dadurch gekennzeichnet, dass es** einen stickstoffhaltigen Substituenten, ausgewählt aus

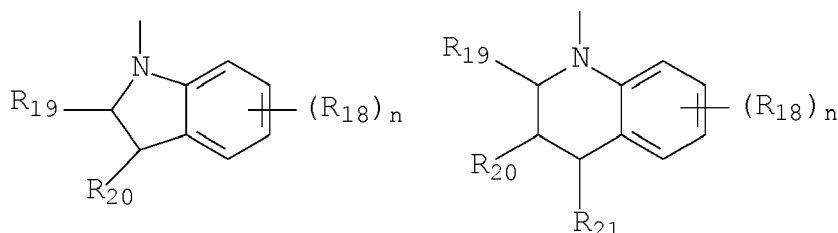
- (i) -N(R₁₅)R₁₆, wobei R₁₅ und R₁₆ jeweils unabhängig voneinander ausgewählt sind aus C₁-C₈-Alkyl, C₁-C₈-Aryl, C₃-C₂₀-Cycloalkyl, C₄-C₂₀-Bicycloalkyl, C₅-C₂₀-Tricycloalkyl oder C₁-C₂₀-Alkoxyalkyl und diese Arylgruppe Phenyl oder Naphthyl ist,

(ii) einem stickstoffhaltigen Ring, der durch die folgende graphische Formel wiedergegeben ist



worin jedes Y unabhängig voneinander bei jedem Auftreten ausgewählt ist aus $-\text{CH}_2-$, $-\text{CH}(\text{R}_{17})-$, $-\text{C}(\text{R}_{17})(\text{R}_{17})-$, $-\text{CH}(\text{Aryl})-$, $-\text{C}(\text{Aryl})_2-$ oder $-\text{C}(\text{R}_{17})(\text{Aryl})-$; worin X gleich $-\text{Y}-$, $-\text{O}-$, $-\text{S}-$, $-\text{NH}-$, $-\text{N}(\text{R}_{17})-$ oder $-\text{N}(\text{Aryl})-$ ist, R_{17} gleich C_1 - C_6 -Alkyl ist, diese Arylgruppe Phenyl oder Naphthyl ist, m ausgewählt ist aus den ganzen Zahlen 1, 2 oder 3 und p ausgewählt ist aus den ganzen Zahlen 0, 1, 2 oder 3; vorausgesetzt, dass, wenn p gleich 0 ist, X gleich Y ist,

(iii) eine Gruppe, die durch eine der folgenden graphischen Formeln wiedergegeben ist

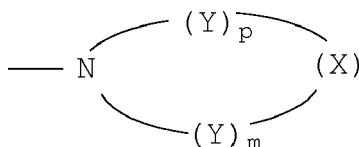


worin jedes R_{19} , R_{20} und R_{21} unabhängig voneinander bei jedem Auftreten in jeder Formel ausgewählt ist aus Wasserstoff, C_1 - C_5 -Alkyl, Phenyl oder Naphthyl oder die Gruppen R_{19} und R_{20} zusammen einen Ring mit 5 bis 8 Kohlenstoffatomen bilden, R_{18} bei jedem Auftreten unabhängig voneinander ausgewählt ist aus C_1 - C_6 -Alkyl, C_1 - C_6 -Alkoxy, Fluor oder Chlor und n ausgewählt ist aus den ganzen Zahlen 0, 1 oder 2,
 (iv) unsubstituiertem, mono- oder disubstituiertem C_4 - C_{18} -spirobicyclischem Amin oder
 (v) unsubstituiertem mono- oder disubstituiertem C_4 - C_{18} -spirotricyclischem Amin, wobei diese Substituenten für (iv) und (v) unabhängig voneinander bei jedem Auftreten ausgewählt sind aus Aryl, C_1 - C_6 -Alkyl, C_1 - C_6 -Alkoxy oder Phenyl(C_1 - C_6)alkyl,

an dem Ringatom in 11-Position enthält, wobei diese Ringatome gemäß den Nomenklaturregeln der International Union of Pure and Applied Chemistry nummeriert sind, beginnend mit der 1-Position, die das Kohlenstoffatom para zu dem Sauerstoffatom in dem Pyranring ist, und ausgehend davon die Nummerierung in Uhrzeigerrichtung, wobei dieses photochrome Material frei von Spirosubstituenten an der 13-Position ist.

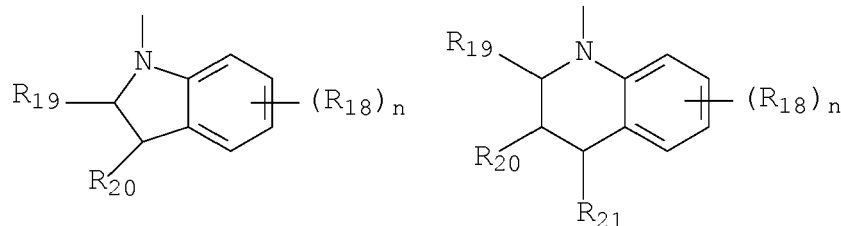
2. Photochromes Material nach Anspruch 1, wobei der stickstoffhaltige Substituent am Ringatom in 11-Position wiedergegeben ist durch:

- (i) $-\text{N}(\text{R}_{15})\text{R}_{16}$, wobei R_{15} und R_{16} jeweils unabhängig voneinander ausgewählt sind aus C_1 - C_6 -Alkyl,
 (ii) einen stickstoffhaltigen Ring, der durch die folgende graphische Formel wiedergegeben ist:



Worin jeder Y gleich $-\text{CH}_2-$ ist und X unabhängig voneinander ausgewählt ist aus $-\text{Y}-$, $-\text{O}-$, $-\text{S}-$, $-\text{N}(\text{R}_{17})-$ und $-\text{N}(\text{Phenyl})-$, wobei R_{17} gleich C_1 - C_6 -Alkyl ist, m ausgewählt ist aus den ganzen Zahlen 1, 2 oder 3 und p ausgewählt ist aus den ganzen Zahlen 0, 1, 2 oder 3

(iii) eine Gruppe, die durch die folgende graphische Formel wiedergegeben ist:



worin R_{19} , R_{20} und R_{21} jeweils unabhängig voneinander ausgewählt sind aus Wasserstoff oder C_1 - C_5 -Alkyl, R_{18} unabhängig voneinander ausgewählt ist aus C_1 - C_4 -Alkyl, C_1 - C_4 -Alkoxy, Fluor oder Chlor und n ausgewählt ist aus den ganzen Zahlen 0 oder 1,

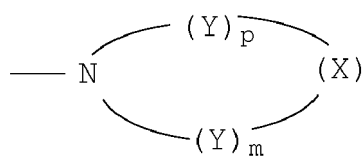
(iv) unsubstituiertes oder monosubstituiertes C_5 - C_{18} -spirobicyclisches Amin oder

(v) unsubstituiertes oder monosubstituiertes C_5 - C_{18} -spirotricyclisches Amin, wobei diese Substituenten für (iv) und (v) unabhängig voneinander bei jedem Auftreten ausgewählt sind aus Phenyl, C_1 - C_3 -Alkyl, C_1 - C_3 -Alkoxy oder Phenyl(C_1 - C_3)alkyl.

3. Photochromes Material nach Anspruch 2, wobei der stickstoffhaltige Substituent am Ringatom in der 11-Position wiedergegeben ist durch:

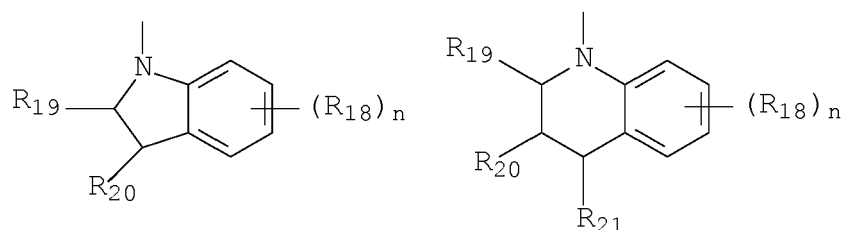
(i) $-N(R_{15})R_{16}$, wobei R_{15} und R_{16} jeweils C_1 - C_3 -Alkyl sind;

(ii) einen stickstoffhaltigen Ring, der durch die folgende graphische Formel wiedergegeben ist:



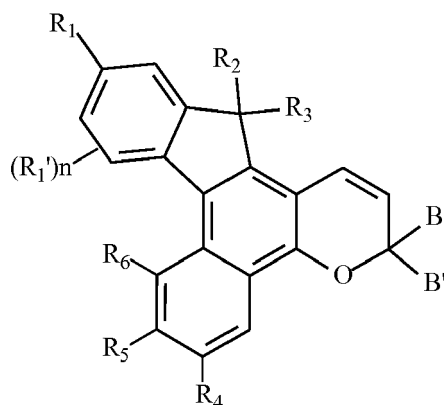
wobei jedes Y gleich $-CH_2-$ ist und X unabhängig voneinander ausgewählt ist aus $-Y-$, $-O-$ und $-N(R_{17})-$, R_{17} gleich C_1 - C_4 -Alkyl ist, m ausgewählt ist aus den ganzen Zahlen 1 oder 2 und p ausgewählt ist aus den ganzen Zahlen 0, 1 oder 2, oder

(iii) eine Gruppe, die durch die folgenden graphischen Formeln wiedergegeben ist,



worin R_{19} , R_{20} und R_{21} jeweils Wasserstoff sind n gleich 0 ist.

4. Naphthopyran nach Anspruch 1, wiedergegeben durch die folgende graphische Formel:

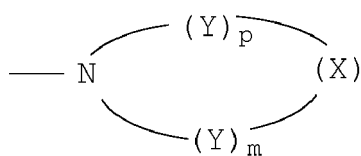


worin

(a) R_1 wiedergegeben ist durch

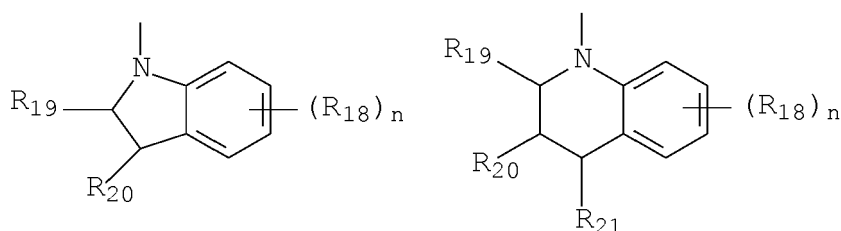
(i) $-N(R_{15})R_{16}$, wobei R_{15} und R_{16} jeweils unabhängig voneinander ausgewählt sind aus C_1 - C_8 -Alkyl, C_1 - C_8 -Alkylaryl, C_3 - C_{20} -Cycloalkyl, C_4 - C_{20} -Bicycloalkyl, C_5 - C_{20} -Tricycloalkyl oder C_1 - C_{20} -Alkoxyalkyl und diese Arylgruppe Phenyl oder Naphthyl ist,

(ii) einen stickstoffhaltigen Ring, wiedergegeben durch die folgende graphische Formel:



worin jedes Y bei jedem Auftreten unabhängig voneinander ausgewählt ist aus $-CH_2-$, $-CH(R_{17})-$, $-C(R_{17})(R_{17})-$, $-CH(Aryl)-$, $-C(Aryl)_2-$ oder $-C(R_{17})(Aryl)-$, X gleich $-Y-$, $-O-$, $-S-$, $-NH-$, $-N(R_{17})-$ oder $-N(Aryl)-$ ist, R_{17} gleich C_1 - C_6 -Alkyl ist, diese Arylgruppe Phenyl oder Naphthyl ist, m ausgewählt ist aus den ganzen Zahlen 1, 2 oder 3 und p ausgewählt ist aus den ganzen Zahlen 0, 1, 2 oder 3, vorausgesetzt, dass, wenn p gleich 0 ist, X gleich Y ist,

(iii) eine Gruppe, die durch die folgenden graphischen Formeln wiedergegeben ist,



worin jedes R_{19} , R_{20} und R_{21} bei jedem Auftreten in jeder Formel unabhängig voneinander ausgewählt ist aus Wasserstoff, C_1 - C_5 -Alkyl, Phenyl oder Naphthyl oder die Gruppen R_{19} und R_{20} zusammen einen Ring mit 5 bis 8 Kohlenstoffatomen bilden, R_{18} bei jedem Auftreten unabhängig voneinander ausgewählt ist aus C_1 - C_6 -Alkyl, C_1 - C_6 -Alkoxy, Fluor oder Chlor und n ausgewählt ist aus den ganzen Zahlen 0, 1 oder 2,

(iv) unsubstituiertes, mono- oder disubstituiertes C_4 - C_{18} -spirobicyclisches Amin oder

(v) unsubstituiertes, mono- oder disubstituiertes C_4 - C_{18} -spirotricyclisches Amin, wobei diese Substituenten für (v) und (iv) bei jedem Auftreten unabhängig voneinander ausgewählt sind aus Aryl, C_1 - C_6 -Alkyl, C_1 - C_6 -Alkoxy oder Phenyl(C_1 - C_6)alkyl,

(b) R_1' bei jedem Auftreten unabhängig voneinander ausgewählt ist aus C_1 - C_6 -Alkyl oder C_1 - C_6 -Alkoxy und n ausgewählt ist aus den ganzen Zahlen 0, 1 oder 2;

(c) R_2 und R_3 jeweils unabhängig voneinander ausgewählt sind aus:

(i) Wasserstoff, Hydroxy, Amino, mono- oder disubstituiertem Amino, C₁-C₁₂-Alkyl, C₃-C₁₂-Alkyliden, C₂-C₁₂-Alkylidin, Vinyl, C₃-C₇-Cycloalkyl, C₁-C₅-Halogenalkyl, Allyl, Benzyl, monosubstituiertem Benzyl, Chlor, Fluor oder -C(O)W, worin W gleich Hydroxy, C₁-C₆-Alkyl, C₁-C₆-Alkoxy, Phenyl, monosubstituiertes Phenyl, Amino, Mono(C₁-C₆)alkylamino, Di(C₁-C₆)alkylamino, Morpholino, Piperidin oder Pyrrolidyl ist, diese Substituenten des Amins C₁-C₆-Alkyl, Phenyl, Benzyl oder Naphthyl sind, jeder dieser Substituenten des Benzyls und Phenyls C₁-C₆-Alkyl oder C₁-C₆-Alkoxy ist,

(ii) einer unsubstituierten, mono-, di- oder trisubstituierten Gruppe, ausgewählt aus Phenyl, Naphthyl, Phenanthryl, Pyrenyl, Chinolyl, Isochinolyl, Benzofuranyl, Thienyl, Benzothienyl, Dibenzofuranyl, Dibenzothienyl, Carbazolyl oder Indolyl, wobei jeder dieser Substituenten der Gruppe in (c)(ii) bei jedem Auftreten unabhängig voneinander ausgewählt ist aus Chlor, Fluor, C₁-C₆-Alkyl oder C₁-C₆-Alkoxy;

(iii) einem monosubstituierten Phenyl, wobei das Phenyl einen Substituenten in der para-Position aufweist, der -(CH₂)_t- oder -O-(CH₂)_t-, verbunden mit einer Arylgruppe ist, die ein Teil eines anderen photochromen Materials ist, und t ausgewählt ist aus den ganzen Zahlen 1, 2, 3, 4, 5 oder 6,

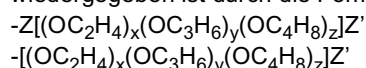
(iv) -OR₈, wobei R₈ ausgewählt ist aus C₁-C₆-Alkyl, C₁-C₆-Acyl, Phenyl(C₁-C₃)alkyl, mono(C₁-C₆)alkylsubstituiertem Phenyl(C₁-C₃)alkyl, mono(C₁-C₆)alkoxysubstituiertem Phenyl(C₁-C₃)alkyl, C₁-C₅-Alkoxy(C₂-C₄)alkyl, C₃-C₇-Cycloalkyl, mono(C₁-C₄)alkylsubstituiertem C₃-C₇-Cycloalkyl, C₁-C₆-Chloroalkyl, C₁-C₅-Fluoroalkyl, Allyl, Tri(C₁-C₆)alkyl-silyl, Tri(C₁-C₆)alkoxysilyl, Di(C₁-C₆)alkyl(C₁-C₆)alkoxysilyl, Di(C₁-C₆)alkoxy(C₁-C₆)alkylsilyl, Benzoyl, monosubstituiertem Benzoyl, Naphthoyl oder monosubstituiertem Naphthoyl, wobei jeder der Substituenten des Benzoyls und Naphthoyls unabhängig voneinander ausgewählt ist aus C₁-C₆-Alkyl oder C₁-C₆-Alkoxy oder R₈ gleich -CH(R₉)Q ist, worin R₉ ausgewählt ist aus Wasserstoff oder C₁-C₃-Alkyl und Q ausgewählt ist aus -CN, -CF₃ oder -COOR₁₀ und R₁₀ ausgewählt ist aus Wasserstoff oder C₁-C₃-Alkyl oder R₈ gleich -C(O)V ist, worin V ausgewählt ist aus Wasserstoff, C₁-C₆-Alkoxy, Phenoxy, mono- oder di(C₁-C₆)alkylsubstituiertem Phenoxy, mono- oder di(C₁-C₆)alkoxy-

substituiertem Phenoxy, einer unsubstituierten, mono- oder disubstituierten Arylgruppe, Phenyl oder Naphthyl, Amino, Mono(C₁-C₆)alkylamino, Di(C₁-C₆)alkylamino, Phenylamin, mono- oder di(C₁-C₆)alkylsubstituiertem Phenylamin oder mono- oder di(C₁-C₆)alkoxysubstituiertem Phenylamino, wobei jeder dieser Substituenten der Arylgruppen unabhängig voneinander ausgewählt ist aus C₁-C₆-Alkyl oder C₁-C₆-Alkoxy;

(v) -CH(Q')₂, wobei Q' ausgewählt ist aus -CN oder -COOR₁₁ und R₁₁ ausgewählt ist aus Wasserstoff, C₁-C₆-Alkyl, Phenyl(C₁-C₃)alkyl, mono(C₁-C₆)alkylsubstituiertem Phenyl(C₁-C₃)alkyl, mono(C₁-C₆)alkoxy-substituiertem Phenyl(C₁-C₃)alkyl oder einer unsubstituierten, mono- oder disubstituierten Arylgruppe, Phenyl oder Naphthyl, wobei jeder dieser Substituenten der Arylgruppe unabhängig voneinander ausgewählt ist aus C₁-C₆-Alkyl oder C₁-C₆-Alkoxy;

(vi) -CH(R₁₂)G, wobei R₁₂ ausgewählt ist aus Wasserstoff, C₁-C₆-Alkyl oder einer unsubstituierten, mono- oder disubstituierten Arylgruppe, Phenyl oder Naphthyl und G ausgewählt ist aus -COOR₁₃, -COR₁₃ oder -CH₂OR₁₄, worin R₁₃ ausgewählt ist aus Wasserstoff, C₁-C₆-Alkyl, einer unsubstituierten, mono- oder disubstituierten Arylgruppe, Phenyl oder Naphthyl, Amino, Mono(C₁-C₆)alkylamino, Di(C₁-C₆)alkylamino, Phenylamino, mono- oder di(C₁-C₆)alkylsubstituiertem Phenylamino, mono- oder di(C₁-C₆)alkoxysubstituiertem Phenylamino, Diphenylamino, mono- oder di(C₁-C₆)alkylsubstituiertem Diphenylamino, mono- oder di(C₁-C₆)alkoxysubstituiertem Diphenylamino, Morpholino oder Piperidino, R₁₄ ausgewählt ist aus Wasserstoff, -C(O)R₁₁, C₁-C₆-Alkyl, C₁-C₃-Alkoxy(C₁-C₆)alkyl, Phenyl(C₁-C₃)alkyl, mono(C₁-C₆)alkoxy-substituiertem Phenyl(C₁-C₃)alkyl oder einer unsubstituierten, mono- oder disubstituierten Arylgruppe, Phenyl oder Naphthyl, wobei jeder dieser Substituenten dieser Arylgruppe unabhängig voneinander ausgewählt ist aus C₁-C₆-Alkyl oder C₁-C₆-Alkoxy;

(vii) die Gruppe T wiedergegeben ist durch die Formel:



worin -Z ausgewählt ist aus -C(O)- oder -CH₂-, Z' ausgewählt ist aus C₁-C₃-Alkoxy oder einer polymerisierbaren Gruppe, x, y und z jeweils unabhängig voneinander ausgewählt sind aus einer Zahl zwischen 0 und 50 und die Summe von x, y und z zwischen 2 und 50 liegt, oder

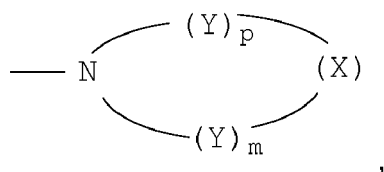
(viii) R₂ und R₃ zusammen eine Oxogruppe bilden;

(d) R₄ ausgewählt ist aus Wasserstoff, C₁-C₆-Alkyl oder der Gruppe R_a, die ausgewählt ist aus:

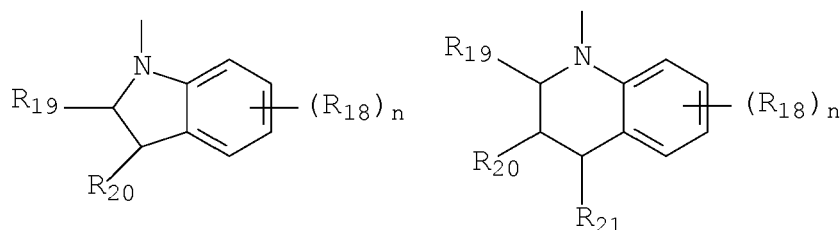
(i) -OR₈', wobei R₈' ausgewählt ist aus Phenyl(C₁-C₃)alkyl, C₁-C₆-Alkyl, mono(C₁-C₆)alkylsubstituiertem Phenyl(C₁-C₃)alkyl, mono(C₁-C₆)alkoxysubstituiertem Phenyl(C₁-C₃)alkyl, C₁-C₅-Alkoxy(C₂-C₄)alkyl, C₃-C₇-Cycloalkyl, mono(C₁-C₄)alkylsubstituiertem C₃-C₇-Cycloalkyl, C₁-C₅-Chloroalkyl, C₁-C₆-Fluoroalkyl, Allyl oder -CH(R₉)Q, wobei R₉ ausgewählt ist aus Wasserstoff oder C₁-C₃-Alkyl, oder

(ii) einer Gruppe, ausgewählt aus:

- (1) $-N(R_{15})R_{16}$, wobei R_{15} und R_{16} die gleichen sind, wie hierin vorstehend in (a)(i) beschrieben;
 (2) einem stickstoffhaltigen Ring, wiedergegeben durch die folgende graphische Formel:

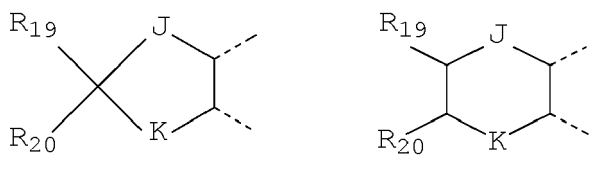


worin Y, X, m und p die gleichen sind wie hierin vorstehend in (a)(ii) beschrieben oder
 (3) einer Gruppe, die durch die folgenden graphischen Formeln wiedergegeben ist:



, worin R_{13} , R_{19} , R_{20} , R_{21} und n die gleichen sind, wie hierin vorstehend in (a)(iii) beschrieben;

- (e) R_5 ausgewählt ist aus Wasserstoff, C_1 - C_6 -Alkyl oder R_a , wobei R_a das gleiche ist, wie hierin vorstehend in (d) beschrieben,
 (f) R_6 ausgewählt ist aus Wasserstoff, C_1 - C_6 -Alkyl oder R_a , wobei R_a das gleiche ist, wie hierin vorstehend in (d) beschrieben, oder
 (g) R_5 und R_6 zusammen eine der folgenden graphischen Formeln bilden:



worin J und K bei jedem Auftreten unabhängig voneinander in jeder Formel ausgewählt sind aus Sauerstoff oder $-N(R_{15})-$, wobei R_{15} das gleiche ist, wie hierin vorstehend in (a)(i) beschrieben, R_{19} und R_{20} jeweils das gleiche sind, wie hierin vorstehend in (a)(iii) beschrieben,
 (h) B und B' unabhängig voneinander ausgewählt sind aus:

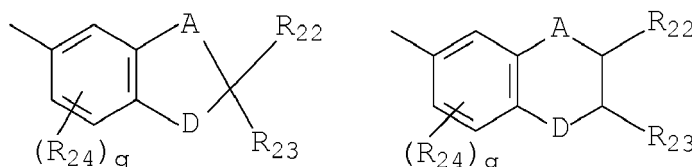
- (i) mono-T-substituiertem Phenyl;
 (ii) einer unsubstituierten, mono-, di- oder trisubstituierten Arylgruppe, Phenyl oder Naphthyl,
 (iii) 9-Julolidinyl oder der unsubstituierten, mono- oder disubstituierten heteroaromatischen Gruppe, ausgewählt aus Pyridyl, Furanyl, Benzofuran-2-yl, Benzofuran-3-yl, Thienyl, Benzothien-2-yl, Benzothien-3-yl, Dibenzofuranyl, Dibenzothienyl, Carbazoyl, Benzopyridyl, Indolinyl oder Fluorenyl, wobei jeder dieser Substituenten am Aryl- oder an der heteroaromatischen Verbindung in (h) (ii) und (iii) unabhängig voneinander ausgewählt ist aus Hydroxy, $-C(O)W$, wie hierin vorstehend beschrieben in (c)(i), Aryl, Mono(C_1 - C_6)alkoxyaryl, Di(C_1 - C_6)alkoxyaryl, Mono(C_1 - C_6)alkylaryl, Di(C_1 - C_6)alkylaryl, Chloraryl, Fluoraryl, C_3 - C_7 -Cycloalkylaryl, C_3 - C_7 -Cycloalkyl, C_3 - C_7 -Cycloalkyloxy, C_3 - C_7 -Cycloalkyloxy(C_1 - C_6)alkyl, C_3 - C_7 -Cycloalkyloxy(C_1 - C_6)alkoxy, Aryl(C_1 - C_6)alkyl, Aryl(C_1 - C_6)alkoxy, Aryloxy, Aryloxy(C_1 - C_6)-alkyl, Aryloxy(C_1 - C_6)alkoxy, Mono- oder Di(C_1 - C_6)alkyl-aryl(C_1 - C_5)alkyl, Mono- oder Di(C_1 - C_6)alkoxyaryl(C_1 - C_6)-alkyl, Mono- oder Di(C_1 - C_6)alkylaryl(C_1 - C_6)alkoxy, Mono- oder Di(C_1 - C_6)alkoxyaryl(C_1 - C_6)alkoxy, Amino, Mono-(C_1 - C_6)alkylamino, Di(C_1 - C_6)alkylamin, Diarylamino, Piperazino, N-(C_1 - C_6)Alkylpiperazino, N-Arylpiperazino, Aziridino, Indolino, Piperidino, Morpholino, Thiomorpholino, Tetrahydrochinolino, Tetrahydroisochinolino, Pyrrolidyl, C_1 - C_6 -Alkyl, C_1 - C_5 -Chloralkyl, C_1 - C_5 -Fluoralkyl, C_1 - C_6 -Alkoxy, Mono(C_1 - C_6)alkoxy(C_1 - C_4)alkyl, Acryloxy, Methacryloxy, Brom, Chlor oder Fluor, wobei jedes dieser Aryle ausgewählt ist aus Phenyl oder

Naphthyl,

(iv) einer unsubstituierten oder monosubstituierten Gruppe, ausgewählt aus Pyrazolyl, Imidazolyl, Pyrazolyl, Imidazolyl, Pyrrolinyl, Phenothiazinyl, Phenoxazinyl, Phenazinyl oder Acridinyl, wobei jeder dieser Substituenten unabhängig voneinander ausgewählt ist aus C₁-C₆-Alkyl, C₁-C₆-Alkoxy, Phenyl, Fluor, Chlor oder Brom,

(v) monosubstituiertem Phenyl, wobei dieses Phenyl einen Substituenten in der para-Position aufweist, wie hierin zuvor beschrieben in (c)(iii),

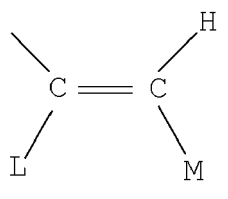
(vi) einer Gruppe, die durch die folgenden graphischen Formeln wiedergegeben ist:



worin A in jeder Formel unabhängig voneinander ausgewählt ist aus Methylen oder Sauerstoff und D in jeder Formel unabhängig voneinander ausgewählt ist aus Sauerstoff oder substituiertem Stickstoff, vorausgesetzt, dass, wenn D substituiertem Stickstoff ist, A Methylen ist; wobei diese Substituenten des Stickstoffs ausgewählt sind aus Wasserstoff, C₁-C₆-Alkyl oder C₂-C₆-Acyl, jedes R₂₄ in jeder Formel und bei jedem Auftreten unabhängig voneinander ausgewählt ist aus C₁-C₆-Alkyl, C₁-C₆-Alkoxy, Hydroxy, Chlor oder Fluor, R₂₂ und R₂₃ in jeder Formel unabhängig voneinander ausgewählt sind aus Wasserstoff oder C₁-C₆-Alkyl und q ausgewählt ist aus den ganzen Zahlen 0, 1 oder 2,

(vii) C₁-C₆-Alkyl, C₁-C₆-Chloralkyl, C₁-C₆-Fluoralkyl, C₁-C₆-Alkoxy(C₁-C₄)alkyl, C₃-C₆-Cycloalkyl, Mono(C₁-C₆)alkoxy(C₃-C₆)cycloalkyl, Mono(C₁-C₆)alkyl(C₃-C₆)cycloalkyl, Chlor(C₃-C₆)cycloalkyl, Fluor(C₃-C₆)cycloalkyl oder C₄-C₁₂-Bicycloalkyl,

(viii) einer Gruppe, wiedergegeben durch die folgende graphische Formel:



worin L ausgewählt ist aus Wasserstoff oder C₁-C₄-Alkyl, M ausgewählt ist aus einer unsubstituierten, mono- oder disubstituierten Gruppe, ausgewählt aus Naphthyl, Phenyl, Furanyl oder Thienyl, wobei jeder der Substituenten dieser Gruppe unabhängig voneinander ausgewählt ist aus C₁-C₄-Alkyl, C₁-C₄-Alkoxy, Fluor oder Chlor, oder

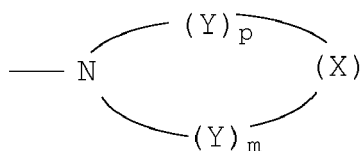
(i) B und B' zusammengekommen Fluoren-9-yliden, mono- oder disubstituiertes Fluoren-9-yliden oder eine Gruppe, die unabhängig voneinander ausgewählt sind aus gesättigten C₃-C₁₂-spiro-monocyclischen Kohlenwasserstoffringen, gesättigten C₇-C₁₂-spirobicyclischen Kohlenwasserstoffringen oder gesättigten C₇-C₁₂-spirotricyclischen Kohlenwasserstoffringen, bilden, wobei jeder dieser Substituenten des Fluoren-9-ylidens unabhängig voneinander ausgewählt ist aus C₁-C₄-Alkyl, C₁-C₄-Alkoxy, Fluor oder Chlor.

5. Naphthopyran nach Anspruch 4, wobei:

(a) R₁ wiedergegeben ist durch:

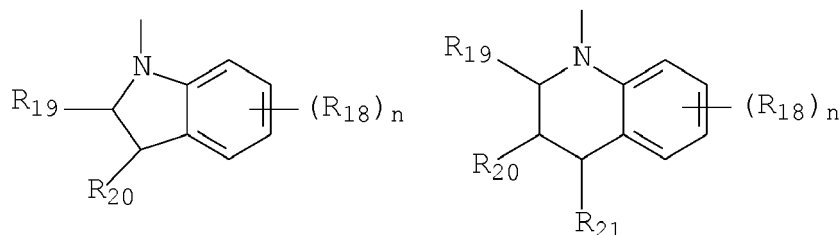
(i) -N(R₁₅)R₁₆, wobei R₁₅ und R₁₆ jeweils unabhängig voneinander ausgewählt sind aus C₁-C₆-Alkyl oder C₃-C₂₀-Cycloalkyl,

(ii) einen stickstoffhaltigen Ring, der durch die folgende graphische Formel wiedergegeben ist:



worin jedes Y gleich $-\text{CH}_2-$ ist und X unabhängig voneinander ausgewählt ist aus $-\text{Y}-$, $-\text{O}-$, $-\text{S}-$, $-\text{N}(\text{R}_{17})-$ oder $-\text{N}(\text{Phenyl})-$, R_{17} gleich C_1 - C_6 -Alkyl ist, m ausgewählt ist aus den ganzen Zahlen 1, 2 oder 3 und p ausgewählt ist aus den ganzen Zahlen 0, 1, 2 oder 3,

(iii) eine Gruppe, die durch eine der folgenden graphischen Formeln wiedergegeben ist:



worin R_{19} , R_{20} und R_{21} jeweils unabhängig voneinander ausgewählt sind aus Wasserstoff, C_1 - C_5 -Alkyl oder Phenyl, R_{18} unabhängig voneinander ausgewählt ist aus Wasserstoff, C_1 - C_4 -Alkyl, C_{1-4} -Alkoxy, Fluor oder Chlor und n ausgewählt ist aus den ganzen Zahlen 0 oder 1,

(iv) unsubstituiertes oder monosubstituiertes C_5 - C_{18} -spirobicyclisches Amin oder

(v) unsubstituiertes oder monosubstituiertes C_5 - C_{18} -spirotricyclisches Amin,

(b) R_1' unabhängig voneinander ausgewählt ist aus C_1 - C_4 -Alkyl oder C_1 - C_4 -Alkoxy und n ausgewählt ist aus den ganzen Zahlen 0 oder 1,

(c) R_2 und R_3 jeweils unabhängig voneinander ausgewählt sind aus:

(i) Wasserstoff, Hydroxy, C_3 - C_7 -Cycloalkyl, Allyl, Benzyl oder der Gruppe $-\text{C}(\text{O})\text{W}$, worin W gleich C_1 - C_6 -Alkyl oder C_1 - C_6 -Alkoxy ist,

(ii) einem unsubstituierten oder monosubstituierten Phenyl, wobei dieser Substituent ausgewählt ist aus Chlor, Fluor, C_1 - C_4 -Alkyl oder C_1 - C_4 -Alkoxy,

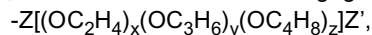
(iii) einem monosubstituierten Phenyl, mit einem Substituenten, der in der para-Position angeordnet ist und $-(\text{CH}_2)_t-$ oder $-\text{O}-(\text{CH}_2)_t-$ ist, wobei t ausgewählt ist aus den ganzen Zahlen 2 oder 3, verbunden mit einer Arylgruppe, die ein Teil eines anderen photochromen Naphthopyrans ist,

(iv) $-\text{OR}_8$, wobei R_8 ausgewählt ist aus C_1 - C_6 -Alkyl, C_1 - C_6 -Acyl oder Phenyl(C_1 - C_3)alkyl oder R_8 die Gruppe $-\text{CH}(\text{R}_9)\text{Q}$ ist, worin R_9 gleich Wasserstoff ist und Q gleich $-\text{COOR}_{10}$ ist, R_{10} gleich C_1 - C_3 -Alkyl ist oder R_8 die Gruppe $-\text{C}(\text{O})\text{V}$ ist, worin V gleich C_1 - C_6 -Alkoxy ist,

(v) $-\text{CH}(\text{Q}')_2$, wobei Q' gleich $-\text{COOR}_{11}$ ist, wobei R_{11} gleich C_1 - C_6 -Alkyl ist,

(vi) $-\text{CH}(\text{R}_{12})\text{G}$, wobei R_{12} gleich Wasserstoff oder C_1 - C_6 -Alkyl ist, G gleich $-\text{COOR}_{11}$ oder $-\text{CH}_2\text{OR}_{14}$ ist, worin R_{14} gleich Wasserstoff, C_1 - C_6 -Alkyl oder C_1 - C_3 -Alkoxy(C_1 - C_6)alkyl ist,

(vii) der Gruppe T, die durch die Formel wiedergegeben ist:



worin $-\text{Z}$ gleich $-\text{CH}_2-$ ist, Z' gleich C_1 - C_3 -Alkoxy oder eine polymerisierbare Gruppe ist, x, y und z jeweils unabhängig voneinander ausgewählt sind aus einer Zahl zwischen 0 und 30 und die Summe von x, y und z zwischen 2 und 30 liegt, oder

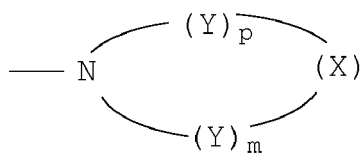
(viii) R_2 und R_3 zusammen eine Oxogruppe bilden;

(d) R_4 gleich Wasserstoff, C_1 - C_5 -Alkyl oder R_a ist, wobei R_a ausgewählt ist aus:

(i) $-\text{OR}_8'$, wobei R_8' gleich Phenyl(C_1 - C_3)alkyl oder C_1 - C_6 -Alkyl ist;

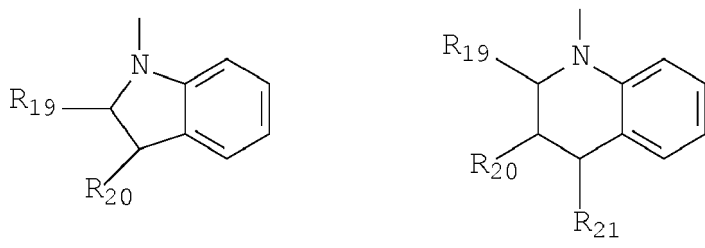
(ii) $-\text{N}(\text{R}_{15})\text{R}_{16}$, R_{15} und R_{16} dieselben sind wie hierin in (a)(i) beschrieben,

(iii) einem stickstoffhaltigen Ring, der durch die folgende graphische Formel wiedergegeben ist:



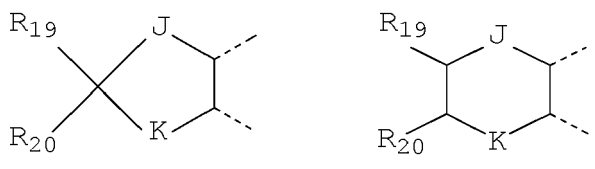
worin jedes Y gleich $-\text{CH}_2-$ ist und X unabhängig voneinander ausgewählt ist aus $-\text{Y}-$, $-\text{O}-$, $-\text{S}-$, $-\text{NH}-$, $-\text{N}(\text{R}_{17})-$ oder $-\text{N}(\text{Aryl})-$, worin R_{17} gleich C_1 - C_6 -Alkyl ist und dieses Aryl aus Phenyl oder Naphthyl ausgewählt ist, m ausgewählt ist aus den ganzen Zahlen 1, 2 oder 3 und p ausgewählt ist aus den ganzen Zahlen 0, 1, 2 oder 3, vorausgesetzt, dass, wenn p gleich 0 ist, X gleich Y ist, oder

(iv) einer Gruppe, die durch die folgenden graphischen Formeln wiedergegeben ist:



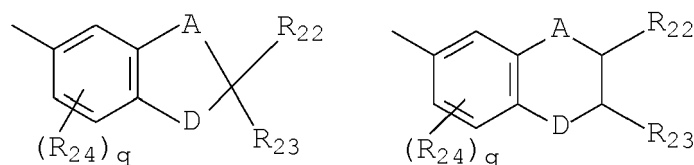
worin R_{19} , R_{20} und R_{21} jeweils unabhängig voneinander ausgewählt sind aus Wasserstoff, C_1 - C_5 -Alkyl oder Phenyl,

- (e) R_5 ausgewählt ist aus Wasserstoff, C_1 - C_4 -Alkyl oder R_a , wobei R_a wie hierin zuvor in (d) beschrieben ist,
 (f) R_6 ausgewählt ist aus Wasserstoff, C_1 - C_4 -Alkyl oder R_a , wobei R_a wie hierin zuvor in (d) beschrieben ist, oder
 (g) R_5 und R_6 zusammen eine der folgenden graphischen Formeln bilden:

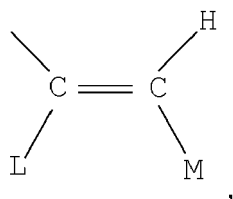


worin J und K jeweils Sauerstoff sind und R_{19} und R_{20} dieselben sind, wie hierin zuvor in (d)(iv) beschrieben,
 (h) B und B' jeweils unabhängig voneinander ausgewählt sind aus:

- (i) mono-T-substituiertem Phenyl;
 (ii) einer unsubstituierten, mono-, di- oder trisubstituierten Arylgruppe, wobei dieses Aryl gleich Phenyl oder Naphthyl ist,
 (iii) 9-Julolidinyl oder den unsubstituierten, mono- oder disubstituierten heteroaromatischen Gruppen ausgewählt aus Pyridyl, Benzofuran-2-yl, Benzofuran-3-yl, Thienyl, Benzothien-2-yl, Benzothien-3-yl, Dibenzofuranyl, Dibenzothienyl oder Carbazoyl, wobei jeder dieser Substituenten des Aryls und der heteroaromatischen Gruppe in (h) (ii) und (iii) unabhängig voneinander ausgewählt ist aus Hydroxy, C_3 - C_7 -Cycloalkyl, C_3 - C_7 -Cycloalkyloxy, Aryl(C_1 - C_6)alkyl, Aryloxy, Aryloxy(C_1 - C_6)alkoxy, Amino, Mono(C_1 - C_6)alkylamino, Di(C_1 - C_6)alkylamino, Diarylamino, Piperazino, N-Arylpiperazino, Indolino, Piperidino, Morpholino, Thiomorpholino, Pyrrolidyl, C_1 - C_6 -Alkyl, C_1 - C_6 -Alkoxy oder Fluor,
 (iv) einer unsubstituierten oder monosubstituierten Gruppe, ausgewählt aus Phenothiazinyl oder Phenoxyzinyl, wobei jeder dieser Substituenten unabhängig voneinander ausgewählt ist aus C_1 - C_6 -Alkyl oder C_1 - C_6 -Alkoxy;
 (v) einem monosubstituierten Phenyl, wobei dieses Phenyl einen Substituenten in der para-Position aufweist wie hierin zuvor in (c)(iii) beschrieben,
 (vi) einer Gruppe, die durch eine der folgenden graphischen Formeln wiedergegeben ist:



worin A unabhängig voneinander in jeder Formel ausgewählt ist aus Methylen oder Sauerstoff und D unabhängig voneinander in jeder Formel ausgewählt ist aus Sauerstoff oder substituiertem Stickstoff, vorausgesetzt, dass, wenn D substituiertem Stickstoff ist, A gleich Methylen ist, wobei dieses Substituenten des Stickstoffs aus Wasserstoff oder C₁-C₄-Alkyl ausgewählt sind, jedes R₂₄ gleich C₁-C₄-Alkyl ist, R₂₂ und R₂₃ jeweils Wasserstoff sind und q die ganze Zahl 0, 1 oder 2 ist,
 (vii) C₁-C₆-Alkyl, C₃-C₆-Cycloalkyl oder C₄-C₁₂-Bicycloalkyl,
 (viii) einer Gruppe, die durch die folgende graphische Formel wiedergegeben ist:



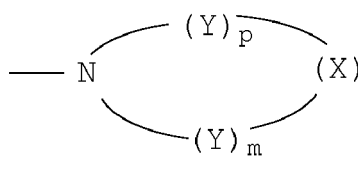
worin L aus Wasserstoff oder C₁-C₄-Alkyl ausgewählt ist und M ausgewählt ist aus einem unsubstituierten, mono- oder disubstituierten Phenyl, wobei jeder dieser Substituenten des Phenyls unabhängig voneinander ausgewählt ist aus C₁-C₄-Alkyl oder C₁-C₄-Alkoxy, oder

(i) B und B' zusammengekommen Fluoren-9-yliden oder monosubstituiertes Fluoren-9-yliden oder eine Gruppe, die unabhängig voneinander aus gesättigten C₃-C₁₂-spiromonocyclischen Kohlenwasserstoffringen, gesättigten C₇-C₁₂-spirobicyclischen Kohlenwasserstoffringen oder gesättigten C₇-C₁₂-spirotricyclischen Kohlenwasserstoffringen ausgewählt sind, bilden, wobei dieser Substituent des Fluoren-9-ylidens aus C₁-C₄-Alkyl oder C₁-C₄-Alkoxy ausgewählt ist.

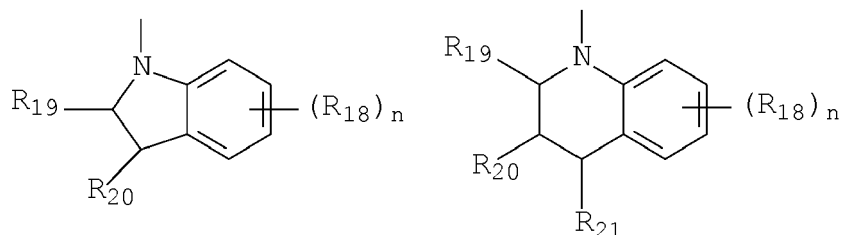
6. Naphthopyran nach Anspruch 5, worin:

(a) R₁ wiedergegeben ist durch:

- (i) -N(R₁₅)R₁₆, wobei R₁₅ und R₁₆ jeweils unabhängig voneinander ausgewählt sind aus C₁-C₄-Alkyl;
- (ii) einen stickstoffhaltigen Ring, der durch die folgende graphische Formel wiedergegeben ist:



worin jedes Y bei jedem Auftreten -CH₂- ist und X unabhängig voneinander ausgewählt ist aus -Y-, -O-, oder -N(R₁₇)-, wobei R₁₇ gleich C₁-C₄-Alkyl ist, m ausgewählt ist aus den ganzen Zahlen 1 oder 2 und p ausgewählt ist aus den ganzen Zahlen 0, 1 oder 2, oder
 (iii) eine Gruppe, die durch folgenden graphischen Formeln wiedergegeben ist:



worin R_{19} , R_{20} und R_{21} jeweils Wasserstoff sind und n gleich 0 ist,

(b) R_1' gleich C_1 - C_2 -Alkyl oder C_1 - C_3 -Alkoxy ist,

(c) R_2 und R_3 jeweils unabhängig voneinander ausgewählt sind aus:

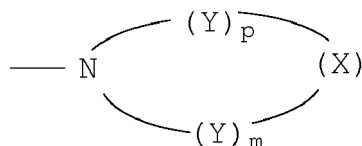
- (i) Wasserstoff, Hydroxy oder C_3 - C_7 -Cycloalkyl,
- (ii) Phenyl oder mono- $(C_1$ - C_4 alkoxy)substituiertem Phenyl,
- (iii) einem monosubstituierten Phenyl mit einem Substituenten, der in der para-Position angeordnet ist und $-O-(CH_2)_t$ ist, wobei t aus den ganzen Zahlen 2 oder 3 ausgewählt ist, gebunden an eine Arylgruppe, die ein Teil eines anderen photochromen Naphthopyrans ist,
- (iv) $-OR_8$, wobei R_8 gleich C_1 - C_6 -Alkyl oder $-CH(R_9)Q$ ist, wobei R_9 gleich Wasserstoff ist, Q $-COOR_{10}$ ist und R_{10} gleich C_1 - C_3 -Alkyl ist,
- (v) $-CH(R_{12})G$, wobei R_{12} gleich Wasserstoff ist, G gleich $-COOR_{11}$ ist, wobei R_{11} gleich C_1 - C_6 -Alkyl oder C_1 - C_3 -Alkoxy(C_1 - C_6)alkyl ist, oder
- (vi) der Gruppe T, wiedergegeben durch die Formel:

$$-Z[(OC_2H_4)_x(OC_3H_6)_y(OC_4H_8)_z]Z'-$$

worin $-Z$ gleich $-CH_2-$ ist, Z' gleich C_1 - C_3 -Alkoxy ist, x , y und z jeweils unabhängig voneinander ausgewählt sind aus einer Zahl zwischen 0 und 20 und die Summe von x , y und z zwischen 2 und 20 liegt,

(d) R_4 gleich Wasserstoff, C_1 - C_5 -Alkyl oder R_a ist, wobei R_a ausgewählt ist aus:

- (i) $-OR_8'$, wobei R_8' gleich C_1 - C_4 -Alkyl;
- (ii) $-N(R_{15})R_{16}$, wobei R_{15} und R_{16} jeweils dieselben sind wie zuvor in (a)(i) beschrieben, oder
- (iii) einem stickstoffhaltigen Ring, der durch die folgende graphische Formel wiedergegeben ist:



worin jedes Y gleich $-CH_2-$ ist und X unabhängig voneinander ausgewählt ist aus $-Y-$, $-O-$, $-S-$ oder $-N(R_{17})-$, wobei R_{17} gleich C_1 - C_4 -Alkyl ist, m ausgewählt ist aus den ganzen Zahlen 1, 2 oder 3 und p ausgewählt ist aus den ganzen Zahlen 0, 1, 2 oder 3,

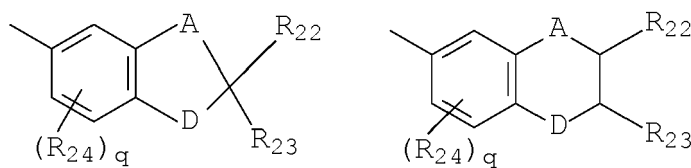
(e) R_5 gleich Wasserstoff oder C_1 - C_4 -Alkyl ist,

(f) R_6 gleich Wasserstoff ist,

(g) B und B' jeweils unabhängig voneinander ausgewählt sind aus:

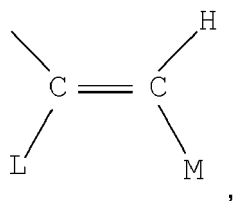
- (i) mono-, di- und trisubstituiertem Phenyl,
- (ii) einer unsubstituierten, mono- oder disubstituierten heteroaromatischen Gruppe, ausgewählt aus Benzo-furan-2-yl oder Dibenzofuranyl, wobei jeder dieser Substituenten der Arylgruppe und der heteroaromatischen Gruppe in (g) (i) und (ii) unabhängig voneinander ausgewählt sind aus C_3 - C_7 -Cycloalkyl, Aryloxy, Aryloxy(C_1 - C_6)alkoxy, Di(C_1 - C_6)alkylamino, Piperazino, Indolino, Piperidino, Morpholino, Pyrrolidyl, C_1 - C_6 -Alkyl, C_1 - C_6 -Alkoxy oder Fluor,
- (iii) einem monosubstituierten Phenyl, wobei dieses Phenyl einen Substituenten in der para-Position aufweist wie hierin zuvor in (c)(iii) beschrieben,

(iv) einer Gruppe, die durch eine der folgenden graphischen Formeln wiedergegeben ist:



worin A gleich Methylen ist und D in jeder Formel unabhängig voneinander ausgewählt ist aus Sauerstoff oder substituiertem Stickstoff, wobei diese Substituenten des Stickstoffs C₁-C₃-Alkyl sind, jedes R₂₄ gleich C₁-C₃-Alkyl ist, R₂₂ und R₂₃ jeweils Wasserstoff sind und q ausgewählt ist aus den ganzen Zahlen 0, 1 oder 2, (v) C₁-C₄-Alkyl oder C₃-C₅-Cycloalkyl;

(vi) der Gruppe, wiedergegeben durch die folgende graphische Formel:



worin L gleich Wasserstoff ist und M ausgewählt ist aus unsubstituiertem, mono- oder disubstituiertem Phenyl, wobei jeder dieser Substituenten des Phenyls C₁-C₄-Alkoxy ist, oder

(i) B und B' zusammengekommen Fluoren-9-yliden, monosubstituiertes Fluoren-9-yliden oder einen gesättigten C₇-C₁₂-spirobicyclischen Kohlenwasserstoff bilden, wobei jeder dieser Substituenten des Fluoren-9-ylidens C₁-C₄-Alkoxy ist.

7. Naphthopyran nach Anspruch 4, wobei dieses Naphthopyran ausgewählt ist aus:

- (a) 3,3-Di(4-methoxyphenyl)-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
- (b) 3-Phenyl-3-(4-morpholino-phenyl)-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
- (c) 3,3-Di(4-(2-methoxyethoxyphenyl))-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
- (d) 3,3-Di(4-methoxyphenyl)-11-morpholino-13-hydroxy-13-ethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
- (e) 3,3-Di(4-methoxyphenyl)-10-methoxy-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
- (f) 3-(4-Methoxyphenyl)-3-(4-morpholinophenyl)-10-methoxy-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
- (g) 3-(3,4-Dimethoxyphenyl)-3-(4-methoxyphenyl)-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran;
- (h) 3-(4-Methoxyphenyl)-3-(4-morpholinophenyl)-11-morpholino-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran oder
- (i) Mischungen derselben.

8. Photochromes Material nach einem der vorstehenden Ansprüche, wobei dieses photochrome Material ausgewählt ist aus:

- (a) einer einzelnen photochromen Verbindung,
- (b) einer Mischung von photochromen Verbindungen,
- (c) einem Material, das wenigstens eine photochrome Verbindung enthält,
- (d) einem Material, an das wenigstens eine photochrome Verbindung chemisch gebunden ist,
- (e) Material (c) oder (d), das zusätzlich eine Beschichtung enthält, um im Wesentlichen den Kontakt der wenigstens einen photochromen Verbindung mit externen Stoffen zu verhindern,

- (f) einem photochromen Polymer oder
- (g) Mischungen davon.

- 5 9. Photochromer Gegenstand, enthaltend ein wenigstens teilweise gehärtetes Polymer und wenigstens eine photochrome Menge wenigstens eines photochromen Materials gemäß einem der Ansprüche 1 bis 7.
10. Photochromer Gegenstand nach Anspruch 9, der zusätzlich wenigstens ein anderes photochromes Material enthält, das wenigstens ein aktiviertes Absorptionsmaximum im Bereich von 400 bis 700 Nanometern aufweist.
- 10 11. Photochromer Gegenstand nach Anspruch 10, wobei das wenigstens eine andere photochrome Material ausgewählt ist aus Chromenen, Spiropyranen, Oxazinen, Organometalldithiozonaten, Fulgiden, Fulgimiden oder einer Mischung davon.
- 15 12. Photochromer Gegenstand nach Anspruch 9, wobei das wenigstens teilweise gehärtete Polymer ausgewählt ist aus wärmehärtenden oder thermoplastischen organischen polymeren Materialien.
- 20 13. Photochromer Gegenstand nach Anspruch 12, wobei das wenigstens teilweise gehärtete Polymer ein wärmehärtendes oder thermoplastisches organisches polymeres Material ist, das ausgewählt ist aus Poly(C₁-C₁₂-alkylmethacrylaten), Poly(oxyalkylendimethacrylaten), Poly(alkoxylierten Phenolmethacrylaten), Celluloseacetat, Celluloseacetat, Celluloseacetatpropionat, Celluloseacetatbutyrat, Poly(vinylacetat), Poly(vinylalkohol), Poly(vinylchlorid), Poly(vinylidenchlorid), thermoplastischen Polycarbonaten, Polyestern, Polyurethanen, Polythiourethanen, Poly(harnstoffurethan), Poly(ethylenterephthalat), Polystyrol, Poly(a-methylstyrol), Copoly-(styrol-methylmethacrylat), Copoly(styrol-acrylnitril), Polyvinylbutyral oder aus Monomeren polymerisiert ist, die ausgewählt sind aus Bis(allylcarbonat)monomeren, polyfunktionellen Acrylatmonomeren, polyfunktionellen Methacrylatmonomeren, Diethylenglykoldimethacrylatmonomeren, Diisopropenylbenzolmonomeren, ethoxylierten Bisphenol-A-Dimethacrylatmonomeren, Ethylenglykolbismethacrylatmonomeren, Poly(ethylenglykol)bis-methacrylatmonomeren, ethoxylierten Phenolbismethacrylatmonomeren, alkoxylierten Polyalkoholpolyacrylatmonomeren, Styrolmonomeren, Urethana-
25 crylatmonomeren, Glycidylacrylatmonomeren, Glycidylmethacrylatmonomer, Diallylidenpentaerythritmonomeren oder Mischungen davon.
- 30 14. Photochromer Gegenstand nach Anspruch 9, der zusätzlich ein Superstrat enthält, das mit wenigstens einem Teil des wenigstens teilweise gehärteten Polymers verbunden ist, wobei dieses Superstrat wenigstens ein organisches polymeres Material enthält.
- 35 15. Photochromer Gegenstand nach Anspruch 14, wobei das Superstrat haftend mit wenigstens einem Teil des wenigstens teilweise gehärteten Polymers verbunden ist.
- 40 16. Photochromer Gegenstand nach einem der Ansprüche 14 und 15, wobei das Superstrat ein organisches polymeres Material ist und ausgewählt ist aus duroplastischen oder thermoplastischen Materialien.
17. Photochromer Gegenstand nach Anspruch 16, wobei das Superstrat ein thermoplastisches Material ist und Polyurethan ist.
- 45 18. Photochromer Gegenstand nach Anspruch 14, enthaltend wenigstens einen zum Teil abriebbeständigen Film, der auf wenigstens einem Teil des Superstrats angeordnet ist.
19. Photochromer Gegenstand nach Anspruch 18, wobei der wenigstens teilweise abriebbeständige Film ein organisches Polymermaterial, ausgewählt aus thermoplastischen oder duroplastischen Materialien ist.
- 50 20. Photochromer Gegenstand nach Anspruch 19, wobei der wenigstens teilweise abriebbeständige Film ein thermoplastisches Material ist und Polycarbonat ist.
21. Photochromer Gegenstand nach Anspruch 14, der zusätzlich eine zumindest teilweise Beschichtung einer zumindest teilweise antireflektierenden Beschichtung, aufgebracht auf den zumindest teilweise abriebbeständigen Film auf
55 wenigstens einem Teil des Superstrats, enthält.
22. Photochromer Gegenstand nach einem der Ansprüche 9 bis 20, wobei das zumindest teilweise gehärtete Polymer ein optisches Element, vorzugsweise eine ophthalmische Linse, ist.

23. Photochromer Gegenstand, enthaltend ein Substrat und wenigstens eine teilweise Beschichtung einer photochromen polymeren Beschichtung, die ein filmbildendes Polymer und wenigstens eine photochrome Menge wenigstens eines photochromen Materials gemäß einem der Ansprüche 1 bis 7 enthält.

24. Photochromer Gegenstand nach Anspruch 23, wobei die photochrome polymere Beschichtung zusätzlich wenigstens ein anderes photochromes Material enthält, das wenigstens ein aktiviertes Absorptionsmaximum innerhalb des Bereichs von 400 bis 700 Nanometer aufweist.

25. Photochromer Gegenstand nach Anspruch 24, wobei das wenigstens eine andere photochrome Material ausgewählt ist aus Chromenen, Spiropyranen, Oxazinen, Organometalldithiozonaten, Fulgiden, Fulgimiden oder einer Mischung davon.

26. Photochromer Gegenstand nach Anspruch 23, wobei das Substrat Papier, Glas, Keramik, Holz, ein Baustoff, Textil, Metall oder ein polymeres organisches Material ist.

27. Photochromer Gegenstand nach Anspruch 26, wobei das Substrat ein polymeres organisches Material ist und ausgewählt ist aus duroplastischen oder thermoplastischen organischen polymeren Materialien.

28. Photochromer Gegenstand nach Anspruch 23, wobei das filmbildende Polymer ausgewählt ist wärmehärtenden oder thermoplastischen organischen polymeren Materialien.

29. Photochromer Gegenstand nach Anspruch 28, wobei das filmbildende Polymer wärmehärtend ist und ausgewählt ist aus Polyurethanen, Aminoplastharzen, Polysilanen, Polyanhydriden, Polyacrylamiden oder Epoxyharzen.

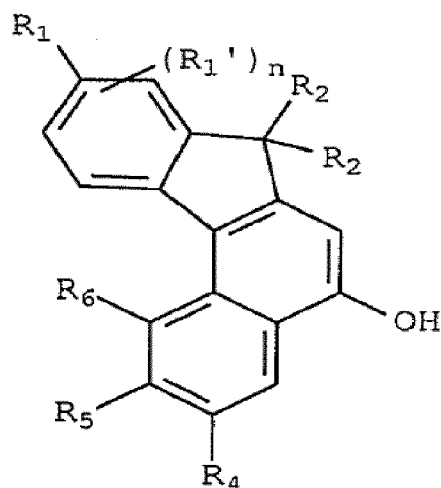
30. Photochromer Gegenstand nach Anspruch 23, der zusätzlich eine Grundierung enthält, die zumindest teilweise zwischen dem Substrat und der zumindest teilweisen Beschichtung einer photochromen polymeren Beschichtungszusammensetzung angeordnet ist.

31. Photochromer Gegenstand nach Anspruch 30, der zusätzlich wenigstens eine teilweise abriebbeständige Beschichtung enthält, die auf wenigstens einem Teil der Oberfläche der zumindest teilweisen Beschichtung einer photochromen polymeren Beschichtungszusammensetzung aufgebracht ist.

32. Photochromer Gegenstand nach Anspruch 31, der zusätzlich eine wenigstens teilweise Beschichtung einer wenigstens teilweise antireflektierenden Beschichtung enthält, die auf die zumindest teilweise abriebbeständige Beschichtung aufgebracht ist, die auf wenigstens einem Teil der Oberfläche der wenigstens teilweisen Beschichtung einer photochromen polymeren Beschichtungszusammensetzung aufgebracht ist.

33. Photochromer Gegenstand nach einem der Ansprüche 23 bis 32, wobei das Substrat ein optisches Element, vorzugsweise eine ophthalmische Linse, ist.

34. Naphthol, wiedergegeben durch die folgende graphische Formel:

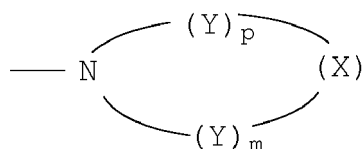


worin

(a) R_1 wiedergegeben ist durch:

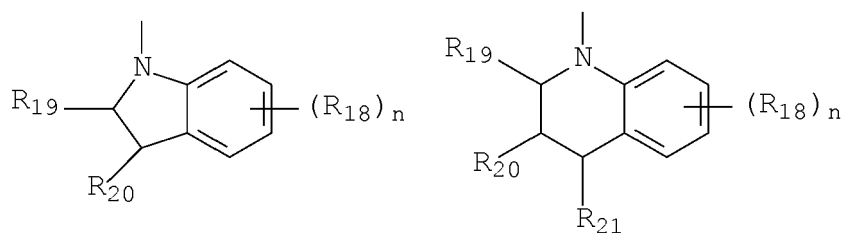
(i) $-N(R_{15})R_{16}$, wobei R_{15} und R_{16} jeweils unabhängig voneinander ausgewählt sind aus C_1 - C_8 -Alkyl, C_1 - C_8 -Alkylaryl, C_3 - C_{20} -Cycloalkyl, C_4 - C_{20} -Bicycloalkyl, C_5 - C_{20} -Tricycloalkyl oder C_1 - C_{20} -Alkoxyalkyl und diese Arylgruppe Phenyl oder Naphthyl ist,

(ii) einen stickstoffhaltigen Ring, wiedergegeben durch die folgende graphische Formel:



worin jedes Y bei jedem Auftreten unabhängig voneinander ausgewählt ist aus $-CH_2-$, $-CH(R_{17})-$, $-C(R_{17})(R_{17})-$, $-CH(Aryl)-$, $-C(Aryl)_2-$ oder $-C(R_{17})(Aryl)-$, X gleich $-Y-$, $-O-$, $-S-$, $-NH-$, $-N(R_{17})-$ oder $-N(Aryl)-$ ist, R_{17} gleich C_1 - C_6 -Alkyl ist, wobei diese Arylgruppe Phenyl oder Naphthyl ist, m ausgewählt ist aus einer der ganzen Zahlen 1, 2 oder 3 und p ausgewählt ist aus den ganzen Zahlen 0, 1, 2 oder 3, vorausgesetzt, dass wenn p gleich 0 ist, X gleich Y ist,

(iii) eine Gruppe, wiedergegeben durch eine der folgenden graphischen Formeln:



worin jedes R_{19} , R_{20} und R_{21} jeweils unabhängig voneinander bei jedem Auftreten in jeder Formel ausgewählt ist aus Wasserstoff, C_1 - C_5 -Alkyl, Phenyl oder Naphthyl, oder die Gruppen R_{19} und R_{20} zusammen einen Ring mit 5 bis 8 Kohlenstoffatomen bilden, R_{18} bei jedem Auftreten unabhängig voneinander ausgewählt ist aus C_1 - C_6 -Alkyl, C_1 - C_6 -Alkoxy, Fluor oder Chlor ist und n aus den ganzen Zahlen 0, 1 oder 2 ausgewählt ist,

(iv) unsubstituiertes, mono- oder disubstituiertes C_4 - C_{18} -spirobicyclisches Amin oder

(v) unsubstituiertes, mono- oder disubstituiertes C_4 - C_{18} -spirotricyclisches Amin, wobei diese Substituenten für (v) und (iv) unabhängig voneinander bei jedem Auftreten ausgewählt sind aus Aryl, C_1 - C_6 -Alkyl oder

C₁-C₆-Alkoxy oder Phenyl(C₁-C₆)-alkyl,

(b) R₁' unabhängig voneinander bei jedem Auftreten ausgewählt ist aus C₁-C₆-Alkyl oder C₁-C₆-Alkoxy und n ausgewählt ist aus den ganzen Zahlen 0, 1 oder 2,

(c) jedes R₂ oder jedes R₃ bei jedem Auftreten unabhängig ausgewählt ist aus:

(i) Wasserstoff, Hydroxy, Amino, mono- oder disubstituiertem Amino, C₁-C₁₂-Alkyl, C₃-C₁₂-Alkyliden, C₂-C₁₂-Alkylidin, Vinyl, C₃-C₇-Cycloalkyl, C₁-C₆-Halogenalkyl, Allyl, Benzyl, monosubstituiertem Benzyl, Chlor, Fluor oder -C(O)W, worin W gleich Hydroxy, C₁-C₆-Alkyl, C₁-C₆-Alkoxy, Phenyl, monosubstituiertes Phenyl, Amino, Mono(C₁-C₆)alkylamin, Di(C₁-C₆)alkylamino, Morpholino, Piperidino oder Pyrrolidyl ist, diese Substituenten der Aminogruppen C₁-C₆-Alkyl, Phenyl, Benzyl oder Naphthyl sind, jeder dieser Substituenten des Benzyls und Phenyls C₁-C₆-Alkyl oder C₁-C₆-Alkoxy ist,

(ii) einer unsubstituierten, mono-, di- oder trisubstituierten Gruppe, ausgewählt aus Phenyl, Naphthyl, Phenanthryl, Pyrenyl, Chinolyl, Isochinolyl, Benzofuranyl, Thienyl, Benzothienyl, Dibenzofuranyl, Dibenzothienyl, Carbazolyl oder Indolyl, wobei jeder dieser Substituenten dieser Gruppen in (c)(ii) unabhängig voneinander bei jedem Auftreten ausgewählt ist aus Chlor, Fluor, C₁-C₆-Alkyl oder C₁-C₆-Alkoxy,

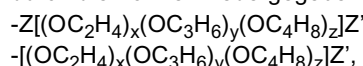
(iii) einem monosubstituierten Phenyl, wobei dieses Phenyl einen Substituenten in der para-Position aufweist, der -(CH₂)_t- oder -O-(CH₂)_t- ist und an eine Arylgruppe gebunden ist, die ein Teil eines anderen photochromen Materials ist und t ausgewählt ist aus den ganzen Zahlen 1, 2, 3, 4, 5 oder 6,

(iv) -OR₈, wobei R₈ ausgewählt ist aus C₁-C₆-Alkyl, C₁-C₆-Acy, Phenyl(C₁-C₃)alkyl, mono(C₁-C₆)alkylsubstituiertem Phenyl(C₁-C₃)alkyl, mono(C₁-C₆)alkoxysubstituiertem Phenyl(C₁-C₃)alkyl, C₁-C₅-Alkoxy(C₂-C₄)alkyl, C₃-C₇-Cycloalkyl, mono(C₁-C₄)alkylsubstituiertem C₃-C₇-Cycloalkyl, C₁-C₆-Chloroalkyl, C₁-C₅-Fluoroalkyl, Allyl, Tri(C₁-C₆)alkylsilyl, Tri(C₁-C₆)alkoxysilyl, Di(C₁-C₆)alkyl(C₁-C₆)alkoxysilyl, Di(C₁-C₆)alkoxy(C₁-C₆)alkylsilyl, Benzoyl, monosubstituiertem Benzoyl, Naphthoyl oder monosubstituiertem Naphthoyl, wobei jeder dieser Substituenten des Benzoyls und Naphthoyls unabhängig voneinander ausgewählt sind aus C₁-C₆-Alkyl oder C₁-C₆-Alkoxy, oder R₈ gleich -CH(R₉)Q ist, worin R₉ ausgewählt ist aus Wasserstoff oder C₁-C₃-Alkyl und Q ausgewählt ist aus -CN, -CF₃ oder -COOR₁₀ und R₁₀ ausgewählt ist aus Wasserstoff oder C₁-C₃-Alkyl, oder R₈ gleich -C(O)V ist, wobei V ausgewählt ist aus Wasserstoff, C₁-C₆-Alkoxy, Phenoxy, mono- oder di-(C₁-C₆)alkylsubstituiertem Phenoxy, mono- oder di-(C₁-C₆)alkoxysubstituiertem Phenoxy, einer unsubstituierten, mono- oder disubstituierten Arylgruppe, Phenyl oder Naphthyl, Amino, Mono(C₁-C₆)alkylamino, Di(C₁-C₆)alkylamino, Phenylamino, mono- oder di-(C₁-C₆)alkylsubstituiertem Phenylamino, oder mono- oder di-(C₁-C₆)alkoxysubstituiertem Phenylamino; wobei jeder dieser Substituenten der Arylgruppe unabhängig voneinander ausgewählt ist aus C₁-C₆-Alkyl oder C₁-C₆-Alkoxy,

(v) -CH(Q')₂, wobei Q' ausgewählt ist aus -CN oder -COOR₁₁ und R₁₁ ausgewählt ist aus Wasserstoff, C₁-C₆-Alkyl, Phenyl(C₁-C₃)alkyl, mono(C₁-C₆)alkylsubstituiertem Phenyl(C₁-C₃)alkyl, mono(C₁-C₆)alkoxysubstituiertem Phenyl(C₁-C₃)alkyl oder einer unsubstituierten, mono- oder disubstituierten Arylgruppe, Phenyl oder Naphthyl; wobei jeder dieser Substituenten der Arylgruppe unabhängig voneinander ausgewählt ist aus C₁-C₆-Alkyl oder C₁-C₆-Alkoxy,

(vi) -CH(R₁₂)G, wobei R₁₂ ausgewählt ist aus Wasserstoff, C₁-C₆-Alkyl oder einer unsubstituierten, mono- oder disubstituierten Arylgruppe, Phenyl oder Naphthyl und G ausgewählt ist aus -COOR₁₃, -COR₁₃ oder -CH₂OR₁₄, worin R₁₃ ausgewählt ist aus Wasserstoff, C₁-C₆-Alkyl, einer unsubstituierten, mono- oder disubstituierten Arylgruppe, Phenyl oder Naphthyl, Amino, Mono(C₁-C₆)alkylamino, Di(C₁-C₆)alkylamino, Phenylamino, mono- oder di-(C₁-C₆)alkylsubstituiertem Phenylamino, mono- oder di-(C₁-C₆)alkoxysubstituiertem Phenylamino, Diphenylamino, mono- oder di-(C₁-C₆)alkylsubstituiertem Diphenylamino, mono- oder di-(C₁-C₆)alkoxysubstituiertem Diphenylamino, Morpholino oder Piperidino, R₁₄ ausgewählt ist aus Wasserstoff, -C(O)R₁₁, C₁-C₆-Alkyl, C₁-C₃-Alkoxy(C₁-C₆)alkyl, Phenyl(C₁-C₃)alkyl, mono(C₁-C₆)alkoxysubstituiertem Phenyl(C₁-C₃)alkyl oder einer unsubstituierten, mono- oder disubstituierten Arylgruppe, Phenyl oder Naphthyl, wobei jeder dieser Substituenten der Arylgruppe unabhängig voneinander ausgewählt ist aus C₁-C₆-Alkyl oder C₁-C₆-Alkoxy,

(vii) die Gruppe T durch die Formel wiedergegeben ist:



worin -Z ausgewählt ist aus -C(O)- oder -CH₂-, Z' ausgewählt ist aus C₁-C₃-Alkoxy oder einer polymerisierbaren Gruppe, x, y und z jeweils unabhängig voneinander ausgewählt sind aus einer Zahl zwischen 0 und 50 und die Summe von x, y und z zwischen 2 und 50 liegt, oder

(viii) R₂ und R₂ oder R₃ und R₃ zusammen eine Oxogruppe bilden,

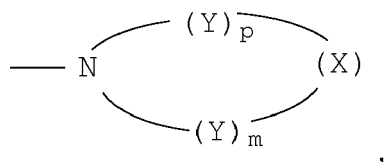
(d) R₄ ausgewählt ist aus Wasserstoff, C₁-C₆-Alkyl oder der Gruppe R_a, ausgewählt aus:

(i) $-OR_8'$, wobei R_8' ausgewählt ist aus Phenyl(C_1 - C_3)alkyl, C_1 - C_6 -Alkyl, mono(C_1 - C_6)alkylsubstituiertem Phenyl(C_1 - C_3)-alkyl, mono(C_1 - C_6)alkoxysubstituiertem Phenyl(C_1 - C_3)alkyl, C_1 - C_5 -Alkoxy(C_2 - C_4)alkyl, C_3 - C_7 -Cycloalkyl, mono(C_1 - C_4)-alkylsubstituiertem C_3 - C_7 -Cycloalkyl, C_1 - C_6 -Chloralkyl, C_1 - C_6 -Fluoralkyl, Allyl oder $-CH(R_9)Q$, wobei R_9 ausgewählt ist aus Wasserstoff oder C_1 - C_3 -Alkyl, oder

(ii) einer Gruppe, ausgewählt aus:

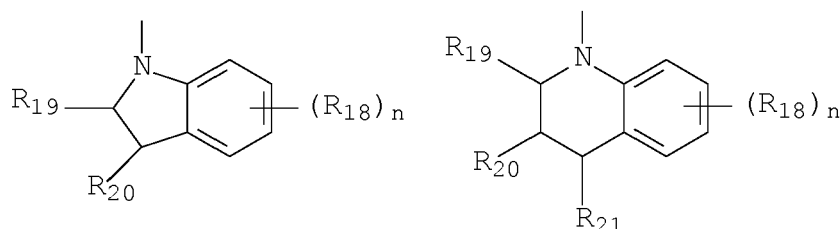
(1) $-N(R_{15})R_{16}$ wobei R_{15} und R_{16} dieselben sind, wie zuvor in (a)(i) beschrieben,

(2) einem stickstoffhaltigen Ring, der durch die folgende graphische Formel wiedergegeben ist:



worin Y, X, m und p dieselben sind wie vorhergehend in (a)(ii) beschrieben oder

(3) einer Gruppe, die durch die folgenden graphischen Formeln wiedergegeben ist:

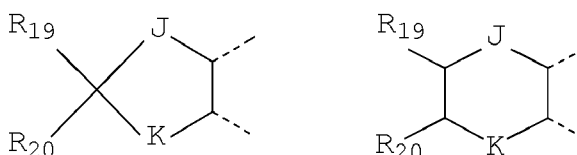


worin R_{18} , R_{19} , R_{20} , R_{21} und n dieselben sind, wie zuvor beschrieben,

(e) R_5 ausgewählt ist aus Wasserstoff, C_1 - C_6 -Alkyl oder R_a , wobei dieses R_a dasselbe ist wie hierin zuvor in (d) beschrieben,

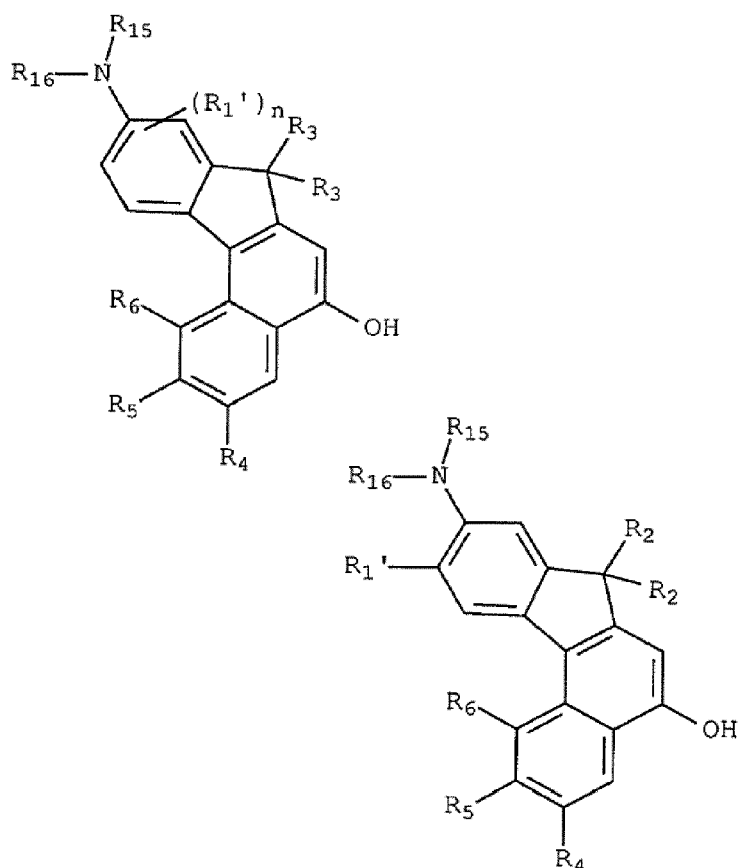
(f) R_6 ausgewählt ist aus Wasserstoff, C_1 - C_6 -Alkyl oder R_a , wobei dieses R_a dasselbe ist wie hierin zuvor in (d) beschrieben oder

(g) R_5 und R_6 zusammen eine der folgenden graphischen Formeln bilden,



worin J und K bei jedem Auftreten in jeder Formel unabhängig voneinander ausgewählt sind aus Sauerstoff oder $-N(R_{15})-$, wobei R_{15} dasselbe ist wie hierin zuvor in (a)(i) beschrieben, R_{19} und R_{20} jeweils dieselben sind wie hierin zuvor in (a)(iii) beschrieben.

35. Naphthol nach Anspruch 34, wobei dieses Naphthol durch die folgenden graphischen Formeln wiedergegeben ist



36. Naphthol nach Anspruch 34, wobei dieses Naphthol ausgewählt ist aus:

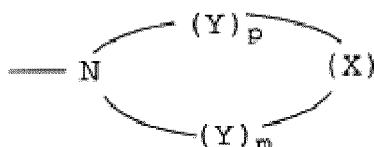
- (a) 7,7-Dimethyl-5-hydroxy-9-morpholino-7H-benzo[C]fluoren,
- (b) 7,7-Dimethyl-5-hydroxy-10-methoxy-9-morpholino-7H-benzo[C]fluoren,
- (c) 7-Dimethyl-7-methoxy-5-hydroxy-9-dimethylamino-7H-benzo[C]fluoren,
- (d) 7-Ethyl-7-methoxy-5-hydroxy-9-piperidino-7H-benzo[C]fluoren,
- (e) 7,7-Dimethyl-5-hydroxy-9-piperidino-7H-benzo[C]fluoren,
- (f) 7,7-Dimethyl-3-methoxy-5-hydroxy-9-morpholino-7H-benzo[C]fluoren,
- (g) 7,7-Dimethyl-3,4-dimethoxy-5-hydroxy-9-morpholino-7H-benzo[C]fluoren,
- (h) 7,7-Dimethyl-3-methoxy-4-methyl-5-hydroxy-9-morpholino-7H-benzo[C]fluoren,
- (i) 7-Phenyl-7-hydroxy-3-methoxy-4-methyl-5-hydroxy-9-morpholino-7H-benzo[C]fluoren,
- (j) Mischungen davon.

Revendications

1. Matériau photochromique de structure indéno [2',3':3,4]naphto[1,2-b]pyrane, **caractérisé en ce qu'il** comprend :

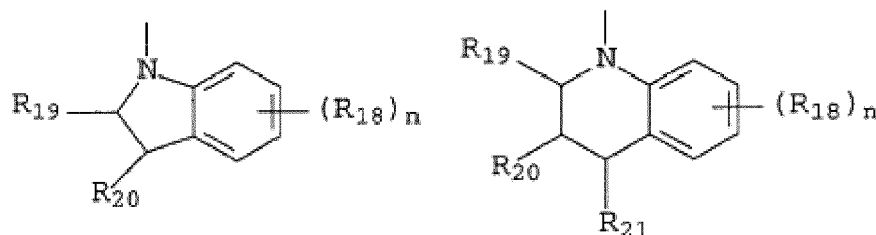
- un substituant contenant de l'azote choisi parmi

- (i) -N(R₁₅)R₁₆, R₁₅ et R₁₆ étant chacun indépendamment choisis parmi C₁-C₈ alkyle, C₁-C₈ alkylaryle, C₃-C₂₀ cycloalkyle, C₄-C₂₀ bicycloalkyle, C₅-C₂₀ tricycloalkyle ou C₁-C₂₀ alcoxyalkyle et ledit groupe aryle étant un phényle ou naphthyle ;
- (ii) un cycle contenant de l'azote représenté par la formule graphique suivante :



dans laquelle chaque Y est indépendamment choisi pour chaque occurrence parmi $-\text{CH}_2-$, $-\text{CH}(\text{R}_{17})-$, $-\text{C}(\text{R}_{17})(\text{R}_{17})-$, $-\text{CH}(\text{aryle})-$, $-\text{C}(\text{aryle})_2-$ ou $-\text{C}(\text{R}_{17})(\text{aryle})-$; X étant $-\text{Y}-$, $-\text{O}-$, $-\text{S}-$, $-\text{NH}-$, $-\text{N}(\text{R}_{17})-$ ou $-\text{N}(\text{aryle})-$; R_{17} étant C_1 - C_6 alkyle; ledit groupe aryle étant un phényle ou naphtyle, m étant choisi parmi les entiers 1, 2 ou 3 et p étant choisi parmi les entiers 0, 1, 2 ou 3; à condition que lorsque p vaut 0, X soit Y;

(iii) un groupe représenté par l'une des formules graphiques suivantes :



dans lesquelles chaque R_{19} , R_{20} et R_{21} est indépendamment choisi pour chaque occurrence dans chaque formule parmi hydrogène, C_1 - C_5 alkyle, phényle ou naphtyle; ou les groupes R_{19} et R_{20} forment ensemble un cycle de 5 à 8 atomes de carbone; R_{18} étant choisi indépendamment pour chaque occurrence parmi C_1 - C_6 alkyle, C_1 - C_6 alcoxy, fluoro ou chloro et n étant choisi parmi les entiers 0, 1 ou 2;

(iv) une amine C_4 - C_{18} spirobicyclique non substituée, mono- ou di-substituée; ou

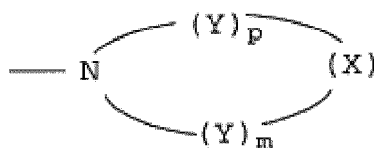
(v) une amine C_4 - C_{18} spirobicyclique non substituée, mono- ou di-substituée; lesdits substituants pour (iv) et (v) étant indépendamment choisis pour chaque occurrence parmi aryle, C_1 - C_6 alkyle, C_1 - C_6 alcoxy ou phényl(C_1 - C_6)alkyle;

au niveau de l'atome de cycle en position 11, lesdits atomes de cycle étant numérotés selon les règles de la nomenclature l'Union internationale de chimie pure et appliquée en commençant par l'atome de cycle en position 1 qui est l'atome de carbone en para par rapport à l'atome d'oxygène du cycle pyrane et en numérotant dans le sens horaire à partir de celui-ci, ledit matériau photochromique étant exempt de substituants spiro en position 13.

2. Matériau photochromique selon la revendication 1, dans lequel le substituant contenant de l'azote au niveau de l'atome de cycle en position 11 est représenté par :

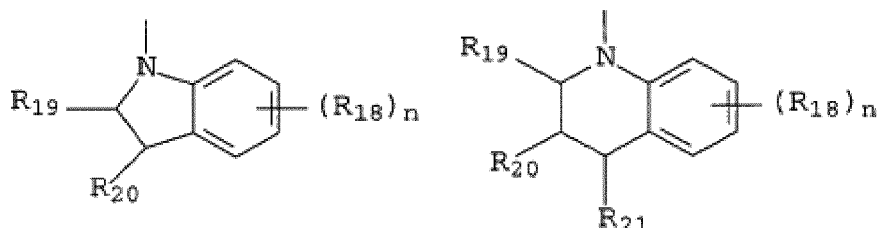
(i) $-\text{N}(\text{R}_{15})\text{R}_{16}$, R_{15} et R_{16} étant chacun indépendamment choisis parmi C_1 - C_6 alkyle;

(ii) un cycle contenant de l'azote représenté par la formule graphique suivante :



dans laquelle chaque Y est $-\text{CH}_2-$ et X étant indépendamment choisi parmi $-\text{Y}-$, $-\text{O}-$, $-\text{S}-$, $-\text{N}(\text{R}_{17})-$ et $\text{N}(\text{phényle})-$, R_{17} étant C_1 - C_6 alkyle; m étant choisi parmi les entiers 1, 2 ou 3, et p étant choisi parmi les entiers 0, 1, 2 ou 3;

(iii) un groupe représenté par l'une des formules graphiques suivantes :



dans lesquelles R_{19} , R_{20} et R_{21} sont chacun indépendamment choisis parmi hydrogène, C_1 - C_5 alkyle, R_{15} étant indépendamment choisi parmi hydrogène, C_1 - C_4 alkyle, C_1 - C_4 alcoxy, fluoro ou chloro et n étant choisi parmi les entiers 0 ou 1 ;

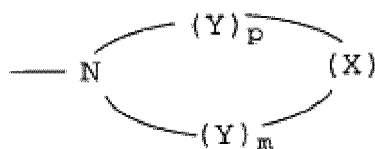
(iv) une amine C_5 - C_{18} spirobicyclique non substituée ou mono-substituée ; ou

(v) une amine C_5 - C_{18} spirobicyclique non substituée, mono-substituée ; lesdits substituants pour (iv) et (v) étant indépendamment choisis pour chaque occurrence parmi phényle, C_1 - C_3 alkyle, C_1 - C_3 alcoxy ou phényle (C_1 - C_3)alkyle.

3. Matériau photochromique selon la revendication 2, dans lequel le substituant contenant de l'azote au niveau de l'atome de cycle en position 11 est représenté par :

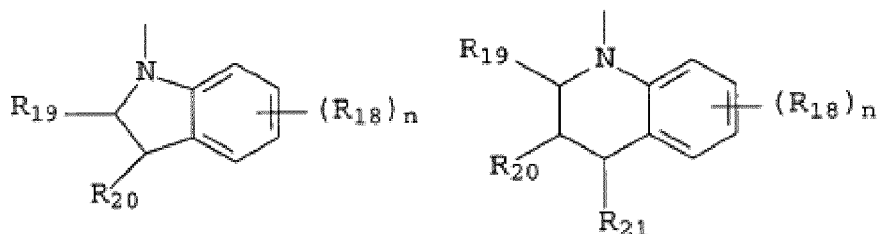
(i) $-N(R_{15})R_{16}$, R_{15} et R_{16} étant chacun en C_1 - C_3 alkyle;

(ii) un cycle contenant de l'azote représenté par la formule graphique suivante :



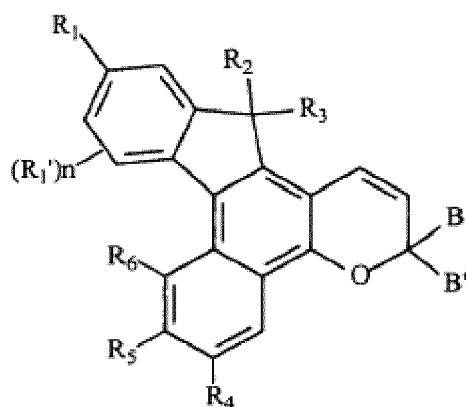
dans laquelle chaque Y est $-CH_2-$ et X étant indépendamment choisi parmi $-Y-$, $-O-$, et $-N(R_{17})-$, R_{17} étant C_1 - C_4 alkyle ; m étant choisi parmi les entiers 1 ou 2, et p étant choisi parmi les entiers 0, 1 ou 2 ; ou

(iii) un groupe représenté par les formules graphiques suivantes :



dans lesquelles R_{19} , R_{20} et R_{21} sont chacun hydrogène et n vaut 0 ;

4. Naphtopyrane selon la revendication 1, représenté par la formule graphique suivante :

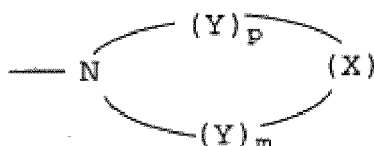


dans laquelle,

(a) R_1 est représenté par :

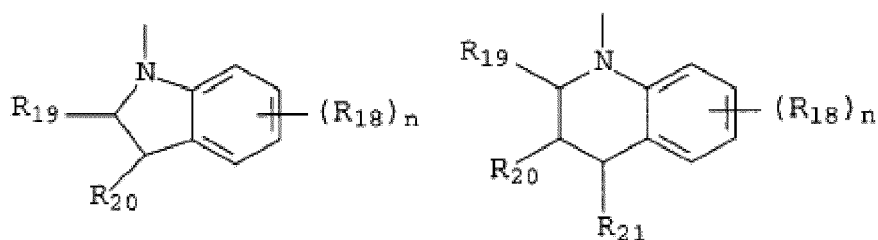
(i) $-N(R_{15})R_{16}$, R_{15} et R_{16} étant chacun indépendamment choisi parmi C_1 - C_8 alkyle, C_1 - C_8 alkylaryle, C_3 - C_{20} cycloalkyle, C_4 - C_{20} bicycloalkyle, C_5 - C_{20} tricycloalkyle ou C_1 - C_{20} alcoxyalkyle et ledit groupe aryle étant phényle ou naphthyle ;

(ii) un cycle contenant de l'azote représenté par la formule graphique suivante :



dans laquelle chaque Y est indépendamment choisi pour chaque occurrence parmi $-CH_2-$, $-CH(R_{17})-$, $-C(R_{17})(R_{17})-$, $-CH(aryle)-$, $-C(aryle)_2-$ ou $-C(R_{17})(aryle)-$; X étant $-Y-$, $-O-$, $-S-$, $-NH-$, $-N(R_{17})-$ ou $-N(aryle)-$; R_{17} est C_1 - C_6 alkyle ; ledit groupe aryle étant phényle ou naphthyle, m étant choisi parmi les entiers 1, 2 ou 3 et p étant choisi parmi les entiers 0, 1, 2 ou 3 ; à condition que lorsque p vaut 0, X soit Y ;

(iii) un groupe représenté par l'une des formules graphiques suivantes :



dans lesquelles chaque R_{19} , R_{20} et R_{21} sont indépendamment choisis pour chaque occurrence dans chaque formule parmi hydrogène, C_1 - C_5 alkyle, phényle ou naphthyle ; ou les groupes R_{19} et R_{20} forment conjointement un cycle de 5 à 8 atomes de carbone ; R_{15} étant choisi indépendamment pour chaque occurrence parmi C_1 - C_6 alkyle, C_1 - C_6 alcoxy, fluoro ou chloro et n étant choisi parmi les entiers 0, 1 ou 2 ;

(iv) une amine C_4 - C_{18} spirobicyclique non substituée, mono- ou di-substituée ; ou

(v) une amine C_4 - C_{18} spirobicyclique non substituée, mono- ou di-substituée ; lesdits substituants de (iv) et (v) étant indépendamment choisis pour chaque occurrence parmi aryle, C_1 - C_6 alkyle, C_1 - C_6 alcoxy ou phényl(C_1 - C_6) alkyle ;

(b) R_1' est indépendamment choisi pour chaque occurrence parmi C_1 - C_6 alkyle ou C_1 - C_6 alcoxy et n étant choisi parmi les entiers 0, 1 ou 2 ;

(c) R_2 et R_3 sont chacun indépendamment choisis parmi :

(i) hydrogène, hydroxy, amino, amino mono- ou di-substitué, C_1 - C_{12} alkyle, C_3 - C_{12} alkylidène, C_2 - C_{12}

alkylidyne, vinyle, C₃-C₇ cycloalkyle, C₁-C₆ halogénoalkyle, allyle, benzyle, benzyle mono-substitué, chloro, fluoro ou -C(O)W, dans lequel W est hydroxy, C₁-C₆ alkyle, C₁-C₆ alcoxy, phényle, phényle mono-substitué, amino, mono(C₁-C₆)alkylamino, di(C₁-C₆)alkylamino, morpholino, pipéridino ou pyrrolidyle ; lesdits substituants d' amino étant C₁-C₆ alkyle, phényle, benzyle ou naphthyle ; chacun desdits substituants de benzyle et de phényle étant C₁-C₆ alkyle ou C₁-C₆ alcoxy ;

(ii) un groupe non substitué, mono-, di- ou tri-substitué choisi parmi phényle, naphthyle, phénanthryle, pyrényle, quinoléyle, isoquinoléyle, benzofuranyle, thiényl, benzothiényl, dibenzofuranyl, dibenzothiényl, carbazolyle ou indolyle ; chacun desdits groupes substituants dans (c)(ii) étant choisi indépendamment pour chaque occurrence parmi chloro, fluoro, C₁-C₆ alkyle ou C₁-C₆ alcoxy ;

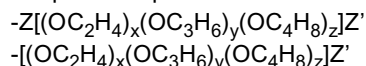
(iii) un phényle monosubstitué, ledit phényle ayant un substituant situé en position para étant -(CH₂)_t- ou -O-(CH₂)_t-, relié à un groupe aryle qui est un élément d'un autre matériau photochromique, et t étant choisi parmi les entiers 1, 2, 3, 4, 5 ou 6 ;

(iv) -OR₈, R₈ étant choisi parmi C₁-C₆ alkyle, C₁-C₆ acyle, phényl(C₁-C₃)alkyle, phényl(C₁-C₃)alkyle substitué par mono(C₁-C₆)alkyle, phényl(C₁-C₃)alkyle substitué par mono(C₁-C₆)alcoxy, C₁-C₆alcoxy(C₂-C₄)alkyle, C₃-C₇ cycloalkyle, C₃-C₇ cycloalkyle substitué par mono(C₁-C₄)alkyle, C₁-C₆ chloroalkyle, C₁-C₆ fluoroalkyle, allyle, tri(C₁-C₆)alkylsilyle, tri(C₁-C₆)alcoxysilyle, di(C₁-C₆)alkyl(C₁-C₆)alcoxysilyle, di(C₁-C₆)alcoxy(C₁-C₆)alkylsilyle, benzoyl, benzoyl mono-substitué, naphthoyl ou naphthoyl mono-substitué ; chacun desdits substituants de benzoyl et de naphthoyl étant indépendamment choisi parmi C₁-C₆ alkyle ou C₁-C₆ alcoxy ; ou R₈ étant -CH(R₉)Q, dans lequel R₉ est choisi parmi hydrogène ou C₁-C₃ alkyle et Q étant choisi parmi -CN, -CF₃, ou -COOR₁₀ et R₁₀ étant choisi parmi hydrogène ou C₁-C₃ alkyle ; ou R₈ étant -C(O)V, dans lequel V est choisi parmi hydrogène, C₁-C₆ alcoxy, phénoxy, phénoxy substitué par mono- ou di-(C₁-C₆)alkyle, phénoxy substitué par mono- ou di-(C₁-C₆)alcoxy, un groupe aryle non substitué, mono- ou di-substitué, phényle ou naphthyle, amino, mono (C₁-C₆)alkylamino, di(C₁-C₆)alkylamino, phénylamino, phénylamino substitué par mono- ou di-(C₁-C₆)alkyle, ou phénylamino substitué par mono- ou di-(C₁-C₆)alcoxy ; chacun desdits substituants du groupe aryle étant indépendamment choisi parmi C₁-C₆ alkyle ou C₁-C₆ alcoxy ;

(v) -CH(Q')₂, Q' étant choisi parmi -CN ou -COOR₁₁ et R₁₁ étant choisi parmi hydrogène, C₁-C₆ alkyle, phényl (C₁-C₃)alkyle, phényl (C₁-C₃) alkyle substitué par mono(C₁-C₆)alkyle, phényl(C₁-C₃)alkyle substitué par mono(C₁-C₆)alcoxy ou un groupe aryle non substitué, mono- ou di-substitué, phényle ou naphthyle ; chacun desdits substituants du groupe aryle étant indépendamment choisi parmi C₁-C₆ alkyle ou C₁-C₆ alcoxy ;

(vi) -CH(R₁₂)G, R₁₂ étant choisi parmi hydrogène, C₁-C₆ alkyle ou un groupe aryle non substitué, mono- ou di-substitué, phényle ou naphthyle, et G étant choisi parmi -COOR₁₁, -COR₁₃ ou -CH₂OR₁₄, dans lequel R₁₃ est choisi parmi hydrogène, C₁-C₆ alkyle, un groupe aryle non substitué, mono- ou di-substitué, phényle ou naphthyle, amino, mono(C₁-C₆)alkylamino, di(C₁-C₆)alkylamino, phénylamino, phénylamino substitué par mono- ou di-(C₁-C₆)alkyle, phénylamino substitué par mono- ou di-(C₁-C₆)alcoxy, diphenylamino, diphenylamino substitué par mono- ou di-(C₁-C₆)alkyle, diphenylamino substitué par mono- ou di-(C₁-C₆)alcoxy, morpholino ou pipéridino, R₁₄ étant choisi parmi hydrogène, -C(O)R₁₁, C₁-C₆ alkyle, C₁-C₃ alcoxy(C₁-C₆)alkyle, phényl(C₁-C₃)alkyle, phényl(C₁-C₃)alkyle substitué par mono(C₁-C₆)alcoxy ou un groupe aryle non substitué, mono- ou di-substitué, phényle ou naphthyle, chacun desdits substituants du groupe aryle étant indépendamment choisi parmi C₁-C₆ alkyle ou C₁-C₆ alcoxy ;

(vii) le groupe T est représenté par la formule :



dans laquelle -Z est choisi parmi -C(O)- ou -CH₂-, Z' étant choisi parmi C₁-C₃ alcoxy ou un groupe polymérisable ; x, y et z étant chacun indépendamment choisi parmi un nombre entre 0 et 50, et la somme de x, y et z étant comprise entre 2 et 50 ; ou

(viii) R₂ et R₃ forment ensemble un groupe oxo ;

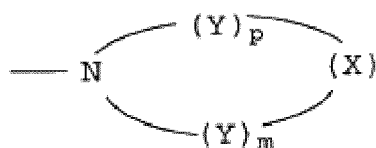
(d) R₄ est choisi parmi hydrogène, C₁-C₆ alkyle ou le groupe R_a est choisi parmi :

(i) -OR₈', R₈' étant choisi parmi phényl(C₁-C₃)alkyle, C₁-C₆ alkyle, phényl(C₁-C₃)alkyle substitué par mono(C₁-C₆)alkyle, phényl(C₁-C₃)alkyle substitué par mono(C₁-C₆)alcoxy, C₁-C₆ alcoxy(C₂-C₄)alkyle, C₃-C₇ cycloalkyle, C₃-C₇ cycloalkyle substitué par mono(C₁-C₄)alkyle, C₁-C₆ chloroalkyle, C₁-C₆ fluoroalkyle, allyle ou -CH(R₉)Q, R₉ étant choisi parmi hydrogène ou C₁-C₃ alkyle ; ou

(ii) un groupe choisi parmi :

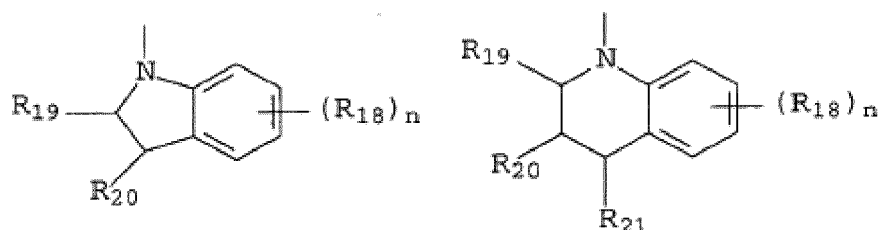
(1) -N(R₁₅)R₁₆ dans lequel R₁₅ et R₁₆ sont identiques comme décrit ci-avant dans (a)(i) ;

(2) un cycle contenant de l'azote représenté par la formule graphique suivante :



dans laquelle Y, X, m et p sont identiques comme décrit ci-avant dans (a)(ii) ; ou

(3) un groupe représenté par les formules graphiques suivantes :

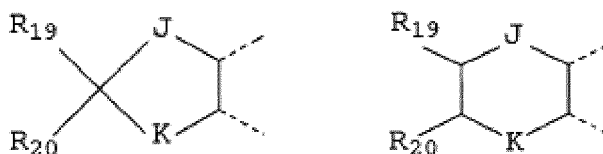


dans lesquelles R₁₈, R₁₉, R₂₀, R₂₁ et n sont identiques comme décrit ci-avant dans (a)(iii) ;

(e) R₅ est choisi parmi hydrogène, C₁-C₆ alkyle ou R_a, ledit R_a étant identique comme décrit ci-avant dans (d) ;

(f) R₆ est choisi parmi hydrogène, C₁-C₆ alkyle ou R_a, ledit R_a étant identique comme décrit ci-avant dans (d) ; ou

(g) R₅ et R₆ forment ensemble l'une des formules graphiques suivantes :



dans lesquelles J et K sont indépendamment choisis pour chaque occurrence dans chaque formule parmi oxygène ou -N(R₁₅)-, R₁₅ étant identique comme décrit ci-avant dans (a)(i), R₁₉ et R₂₀ étant chacun identique comme décrit ci-avant dans (a)(iii) ;

(h) B et B' sont chacun indépendamment choisis parmi :

(i) phényle mono-T-substitué ;

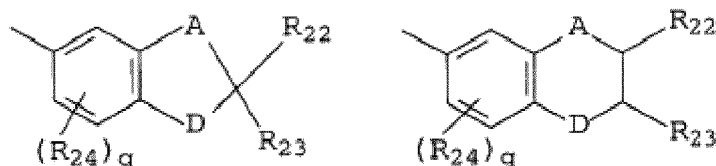
(ii) un groupe aryle non substitué, mono, di- ou tri-substitué, phényle ou naphthyle ;

(iii) 9-julolidinyle ou le groupe hétéroaromatique non substitué, mono- ou di-substitué choisi parmi pyridyle, furanyle, benzofuran-2-yle, benzofuran-3-yle, thiényl, benzothiényl-2-yle, benzothiényl-3-yle, dibenzofuranyl, dibenzothiényl, carbazole, benzopyridyle, indolinyle ou fluorényl, chacun desdits substituants des groupes aryle et hétéroaromatique dans (h) (ii) et (iii) étant indépendamment choisis parmi hydroxy, -C(O)W, décrit ci-avant dans (c)(i), aryle, mono(C₁-C₆)alcoxyaryle, di(C₁-C₆)alcoxyaryle, mono(C₁-C₆)alkylaryle, di(C₁-C₆)alkylaryle, chloroaryle, fluoroaryle, C₃-C₇ cycloalkylaryle, C₃-C₇ cycloalkyle, C₃-C₇ cycloalkyloxy, C₃-C₇ cycloalkyloxy(C₁-C₆)alkyle, C₃-C₇cycloalkyloxy(C₁-C₆)alcoxy, aryl(C₁-C₆)alkyle, aryl(C₁-C₆)alcoxy, aryloxy, aryloxy(C₁-C₆)alkyle, aryloxy(C₁-C₆)alcoxy, mono- ou di-(C₁-C₆)alkylaryl(C₁-C₆)alkyle, mono- ou di-(C₁-C₆)alcoxyaryl(C₁-C₆)alkyle, mono- ou di-(C₁-C₆)alkylaryl(C₁-C₆)alcoxy, mono- ou di-(C₁-C₆)alcoxyaryl(C₁-C₆)alcoxy, amino, mono(C₁-C₆)alkylamino, di(C₁-C₆)alkylamino, diarylamino, pipérazino, N-(C₁-C₆)alkylpipérazino, N-arylpipérazino, aziridino, indolino, pipéridino, morpholino, thiomorpholino, tétrahydroquinoléino, tétrahydroisoquinoléino, pyrrolidyle, C₁-C₆ alkyle, C₁-C₆ chloroalkyle, C₁-C₆ fluoroalkyle, C₁-C₆ alcoxy, mono(C₁-C₆)alcoxy(C₁-C₄)alkyle, acryloxy, méthacryloxy, bromo, chloro ou fluoro, ledit aryle étant choisi parmi phényle ou naphthyle ;

(iv) un groupe non substitué ou mono-substitué choisi parmi pyrazolyle, imidazolyle, pyrazolinyle, imidazolinyle, pyrrolinyle, phénothiazinyle, phénoxazinyle, phénazinyle ou acridinyle, chacun desdits substituants étant indépendamment choisi parmi C₁-C₆ alkyle, C₁-C₆ alcoxy, phényle, fluoro, chloro ou bromo ;

(v) phényle mono-substitué, ledit phényle ayant un substituant situé en position para comme décrit ci-avant dans (c)(iii) ;

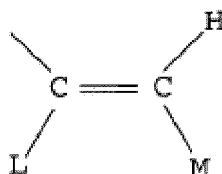
(vi) un groupe représenté par l'une des formules graphiques suivantes :



dans lesquelles A est indépendamment choisi dans chaque formule parmi méthylène ou oxygène et D étant indépendamment choisi dans chaque formule parmi oxygène ou azote substitué, à condition que lorsque D est un azote substitué, A soit un méthylène ; lesdits substituants de l'azote étant choisis parmi hydrogène, C₁-C₆ alkyle, ou C₂-C₆ acyle ; chaque R₂₄ étant indépendamment choisi pour chaque occurrence pour chaque formule parmi C₁-C₆ alkyle, C₁-C₆ alcoxy, hydroxy, chloro ou fluoro ; R₂₂ et R₂₃ étant chacun indépendamment choisis dans chaque formule parmi hydrogène ou C₁-C₆ alkyle ; et q étant choisi parmi les entiers 0, 1 ou 2 :

(vii) C₁-C₆ alkyle, C₁-C₆ chloroalkyle, C₁-C₆ fluoroalkyle, C₁-C₆ alkoxy(C₁-C₄)alkyle, C₃-C₆ cycloalkyle, mono(C₁-C₆)alkoxy(C₃-C₆)cycloalkyle, mono(C₁-C₆)alkyl(C₃-C₆)cycloalkyle, chloro(C₃-C₆)cycloalkyle, fluoro(C₃-C₆)cycloalkyle ou C₄-C₁₂ bicycloalkyle ;

(viii) un groupe représenté par la formule graphique suivante :



dans laquelle L est choisi parmi hydrogène ou C₁-C₄ alkyle et M étant choisi parmi un groupe non substitué, mono-, ou di-substitué choisi parmi naphtyle, phényle, furanyle, ou thiényle ; chacun desdits substituants du groupe étant indépendamment choisi parmi C₁-C₄ alkyle, C₁-C₄ alcoxy, fluoro ou chloro ; ou

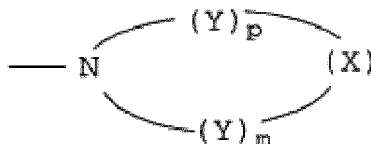
(i) B et B' pris ensemble forment un fluorén-9-ylidène, un fluorén-9-ylidène mono- ou di-substitué ou un groupe indépendamment choisi parmi des cycles hydrocarbure C₃-C₁₂ spiro-monocyclique saturé, des cycles hydrocarbure C₇-C₁₂ spiro-bicyclique saturé ou cycles hydrocarbure C₇-C₁₂ spiro-tricyclique saturé ; chacun desdits substituants du fluorén-9-ylidène étant indépendamment choisi parmi C₁-C₄ alkyle, C₁-C₄ alcoxy, fluoro ou chloro.

5. Naphthopyrane selon la revendication 4, dans lequel :

(a) R_1 est représenté par :

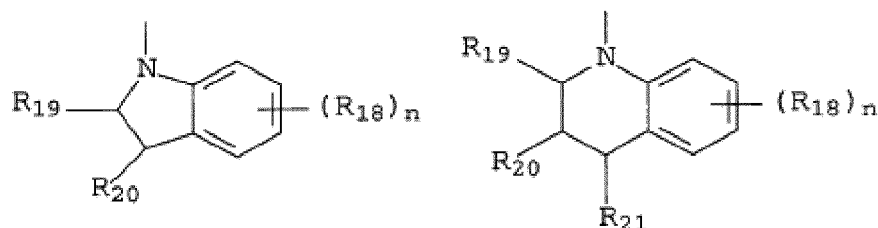
(i) -N(R₁₅)R₁₆, R₁₅ et R₁₆ étant chacun indépendamment choisis parmi C₁-C₆ alkyle ou C₃-C₂₀ cycloalkyle ;

(ii) un cycle contenant de l'azote représenté par la formule graphique suivante :



dans laquelle chaque Y est $-CH_2-$ et X étant chacun indépendamment choisi parmi $-Y-$, $-O-$, $-S-$, $-N(R_{17})-$ ou $-N(\text{phényle})-$; R_{17} étant C_1-C_6 alkyle; m étant choisi parmi les entiers 1, 2 ou 3, et p étant choisi parmi les entiers 0, 1, 2 ou 3;

(iii) un groupe représenté par l'une des formules graphiques suivantes :



dans lesquelles R_{19} , R_{20} et R_{21} sont indépendamment choisis parmi hydrogène, C_1 - C_5 alkyle ou phényle ; R_{18} étant indépendamment choisi parmi hydrogène, C_1 - C_4 alkyle, C_1 - C_4 alcoxy, fluoro ou chloro et n étant choisi parmi les entiers 0 ou 1 ;

(iv) une amine C_5 - C_{18} spirobicyclique non substituée ou mono-substituée ; ou

(v) une amine C_5 - C_{18} spirotricyclique non substituée ou mono-substituée ;

(b) R_1' étant indépendamment choisi parmi C_1 - C_4 alkyle ou C_1 - C_4 alcoxy et n étant choisi parmi les entiers 0 ou 1 ;
(c) R_2 et R_3 étant chacun indépendamment choisis parmi :

(i) hydrogène, hydroxy, C_3 - C_7 cycloalkyle, allyle, benzyle ou le groupe $-C(O)W$, dans lequel W est C_1 - C_6 alkyle ou C_1 - C_6 alcoxy ;

(ii) un phényle non substitué ou mono-substitué, ledit substituant étant choisi parmi chloro, fluoro, C_1 - C_4 alkyle ou C_1 - C_4 alcoxy ;

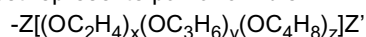
(iii) un phényle mono-substitué, ayant un substituant situé en position para qui est $-(CH_2)_t-$ ou $-O-(CH_2)_t-$, dans lequel t est choisi parmi les entiers 2 ou 3, relié à un groupe aryle qui est un élément d'un autre naphthopyrane photochromique ;

(iv) $-OR_8$, R_8 étant choisi parmi C_1 - C_6 alkyle, C_1 - C_6 acyle ou phényl(C_1 - C_3)alkyle ; ou R_8 étant le groupe $-CH(R_9)Q$, dans lequel R_9 est hydrogène et Q étant $-COOR_{10}$, R_{10} étant C_1 - C_3 alkyle ; ou R_8 est le groupe $-C(O)V$, dans lequel V est C_1 - C_6 alcoxy ;

(v) $-CH(Q')_2$, Q' étant $-COOR_{11}$, dans lequel R_{11} est C_1 - C_6 alkyle ;

(vi) $-CH(R_{12})G$, R_{12} étant hydrogène ou C_1 - C_6 alkyle ; G étant $-COOR_{11}$ ou $-CH_2OR_{14}$, dans lequel R_{14} est hydrogène, C_1 - C_6 alkyle ou C_1 - C_3 alcoxy(C_1 - C_6)alkyle ;

(vii) le groupe T est représenté par la formule :



dans laquelle $-Z$ est $-CH_2-$, Z' étant C_1 - C_3 alcoxy ou un groupe polymérisable, x , y et z étant chacun indépendamment choisi parmi un nombre compris entre 0 et 30, et la somme de x , y et z étant comprise entre 2 et 30 ; ou

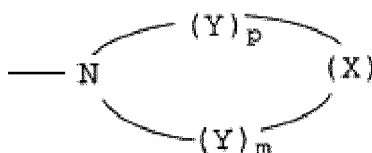
(viii) R_2 et R_3 forment ensemble un groupe oxo ;

(d) R_4 est hydrogène, C_1 - C_6 alkyle ou R_a , ledit R_a étant choisi parmi :

(i) $-OR_8'$, R_8' étant phényl(C_1 - C_3)alkyle ou C_1 - C_6 alkyle ;

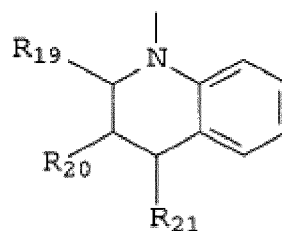
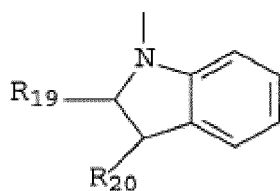
(ii) $-N(R_{15})R_{16}$, R_{15} et R_{16} étant identiques comme décrit ci-avant dans (a)(i) ;

(iii) un cycle contenant de l'azote représenté par la formule graphique suivante :



dans laquelle chaque Y est $-CH_2-$, et X étant indépendamment choisi parmi $-Y-$, $-O-$, $-S-$, $-NH-$, $-N(R_{17})-$ ou $-N(\text{aryle})-$, dans lequel R_{17} est C_1 - C_6 alkyle, ledit aryle étant choisi parmi phényle ou naphthyle ; m étant choisi parmi les entiers 1, 2 ou 3, et p étant choisi parmi les entiers 0, 1, 2 ou 3 à condition que lorsque p vaut 0, X soit Y ; ou

(iv) un groupe représenté par l'une des formules graphiques suivantes :

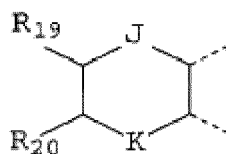
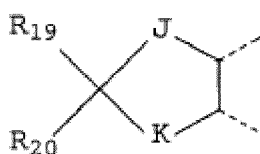


dans lesquelles R_{19} , R_{20} et R_{21} sont chacun indépendamment choisis parmi hydrogène, C_1 - C_5 alkyle ou phényle ;

(e) R_5 étant choisi parmi hydrogène, C_1 - C_4 alkyle ou R_a , ledit R_a étant décrit ci-avant dans (d) ;

(f) R_6 est choisi parmi hydrogène, C_1 - C_4 alkyle ou R_a , ledit R_a étant décrit ci-avant dans (d) ; ou

(g) R_5 et R_6 forment ensemble l'une des formules graphiques suivantes :



dans laquelle J et K sont chacun oxygène ; et R_{19} et R_{20} étant comme décrits ci-avant dans (d)(iv) ;

(h) B et B' étant chacun indépendamment choisis parmi :

(i) un phényle mono-T-substitué ;

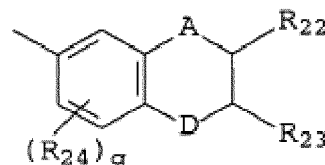
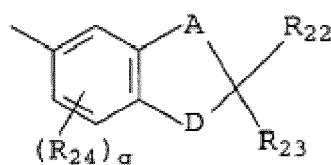
(ii) un groupe aryle non substitué, mono, di- ou tri-substitué, ledit aryle étant phényle ou naphtyle ;

(iii) 9-julolidinyle ou le groupe hétéroaromatique non substitué, mono- ou di-substitué choisi parmi pyridyle, benzofuran-2-yle, benzofuran-3-yle, thiényl, benzothiényl-2-yle, benzothiényl-3-yle, dibenzofuranyl, dibenzothiényl ou carbazoyl, chacun desdits substituants des groupes aryle et hétéroaromatique dans (h)(ii) et (iii) étant indépendamment choisi parmi hydroxy, C_3 - C_7 cycloalkyle, C_3 - C_7 cycloalkyloxy, aryl(C_1 - C_6)alkyle, aryloxy, aryloxy(C_1 - C_6)alcoxy, amino, mono(C_1 - C_6)alkylamino, di(C_1 - C_6)alkylamino, diarylamino, pipérazino, N-arylpipérazino, indolino, pipéridino, morpholino, thiomorpholino, pyrrolidyle, C_1 - C_6 alkyle, C_1 - C_6 alcoxy ou fluoro ;

(iv) un groupe non substitué ou mono-substitué choisi parmi phénothiazinyle ou phénoxazinyle, chacun desdits substituants étant indépendamment choisi parmi C_1 - C_6 alkyle ou C_1 - C_6 alcoxy ;

(v) un phényle mono-substitué, ledit phényle ayant un substituant en position para comme décrit ci-avant dans (c) (iii) ;

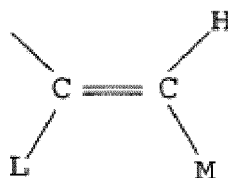
(vi) un groupe représenté par l'une des formules graphiques suivantes :



dans lesquelles A est indépendamment choisi dans chaque formule parmi méthylène ou oxygène et D est indépendamment choisi dans chaque formule parmi oxygène ou azote substitué, à condition que lorsque D est un azote substitué, A soit un méthylène ; lesdits substituants d'azote étant choisis parmi hydrogène ou C_1 - C_4 alkyle ; chaque R_{24} étant C_1 - C_4 alkyle ; R_{22} et R_{23} étant chacun hydrogène ; et q étant l'entier 0, 1 ou 2 ;

(vii) C_1 - C_6 alkyle, C_3 - C_6 cycloalkyle ou C_4 - C_{12} bicycloalkyle ;

(viii) un groupe représenté par la formule graphique suivante :



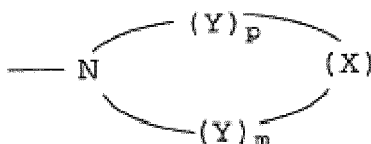
dans laquelle L est choisi parmi hydrogène ou C₁-C₄ alkyle et M étant choisi parmi un phényle non substitué, mono-, ou di-substitué ; chacun desdits substituants de phényle étant indépendamment choisi parmi C₁-C₄ alkyle ou C₁-C₄ alcoxy ; ou

(i) B et B' pris ensemble forment un fluorén-9-ylidène ou un fluorén-9-ylidène mono-substitué ou un groupe étant indépendamment choisi parmi les cycles hydrocarbure C₃-C₁₂ spiro-monocyclique saturé, les cycles hydrocarbure C₇-C₁₂ spiro-bicyclique saturé ou les cycles hydrocarbure C₇-C₁₂ spiro-tricyclique saturé ; ledit substituant de fluorén-9-ylidène étant choisi parmi C₁-C₄ alkyle ou C₁-C₄ alcoxy.

6. Naphtopyrane selon la revendication 5, dans lequel :

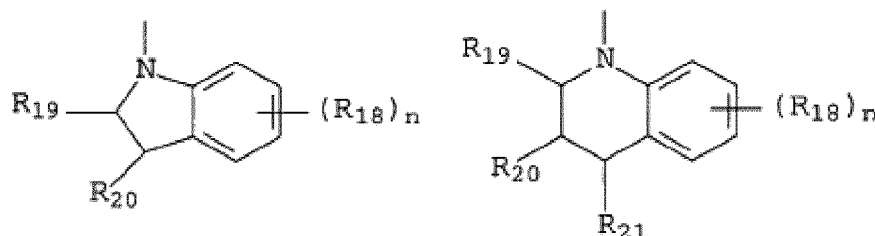
(a) R₁ est représenté par :

- (i) -N(R₁₅)R₁₆, R₁₅ et R₁₆ étant chacun indépendamment choisis parmi C₁-C₄ alkyle ;
- (ii) un cycle contenant de l'azote représenté par la formule graphique suivante :



dans laquelle chaque Y pour chaque occurrence est -CH₂- et X étant indépendamment choisi parmi -Y-, -O- ou -N(R₁₇)- ; R₁₇ étant C₁-C₄ alkyle ; m étant choisi parmi les entiers 1 ou 2, et p étant choisi parmi les entiers 0, 1 ou 2 ; ou

(iii) un groupe représenté par les formules graphiques suivantes :

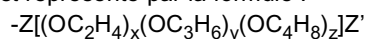


dans lesquelles R₁₉, R₂₀ et R₂₁ sont chacun hydrogène et n vaut 0 ;

(b) R₁' est C₁-C₂ alkyle ou C₁-C₃ alcoxy ;

(c) R₂ et R₃ sont chacun indépendamment choisis parmi :

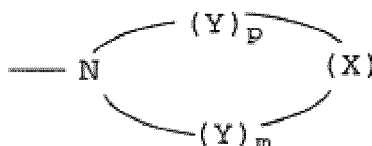
- (i) hydrogène, hydroxy ou C₃-C₇ cycloalkyle ;
- (ii) phényle ou phényle substitué par mono-(C₁-C₄ alcoxy) ;
- (iii) un phényle mono-substitué, ayant un substituant situé en position para étant -O-(CH₂)_t, t étant choisi parmi les entiers 2 ou 3, relié à un groupe aryle étant un élément d'un autre naphthopyrane photochromique ;
- (iv) -OR₈, R₈ étant C₁-C₆ alkyle ou -CH(R₉)Q, R₉ étant hydrogène, Q étant -COOR₁₀ et R₁₀ étant C₁-C₃ alkyle ;
- (v) -CH(R₁₂)G, R₁₂ étant hydrogène, G étant -COOR₁₁, dans lequel R₁₁ est C₁-C₆ alkyle ou C₁-C₃ alcoxy(C₁-C₆)alkyle ; ou
- (vi) le groupe T est représenté par la formule :



dans laquelle -Z est -CH₂-, Z' étant C₁-C₃ alcoxy, x, y et z étant chacun indépendamment choisis parmi un nombre compris entre 0 et 20, et la somme de x, y et z étant comprise entre 2 et 20 ;

(d) R₄ est hydrogène, C₁-C₆ alkyle ou R_a, ledit R_a est choisi parmi :

- (i) -OR₈', R₈' étant C₁-C₄ ;
- (ii) -N(R₁₅)R₁₆, R₁₅ et R₁₆ étant chacun comme décrit ci-avant dans (a)(i) ; ou
- (iii) un cycle contenant de l'azote représenté par la formule graphique suivante :



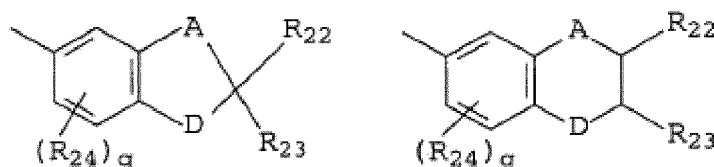
dans laquelle Y est -CH₂-, et X étant indépendamment choisi parmi -Y-, -O-, -S-, ou -N(R₁₇)- ; R₁₇ étant C₁-C₄ alkyle, m étant choisi parmi les entiers 1, 2 ou 3, et p étant choisi parmi les entiers 0, 1, 2 ou 3 ;

(e) R₅ étant hydrogène ou C₁-C₄ alkyle ;

(f) R₆ étant hydrogène ;

(g) B et B' étant chacun indépendamment choisis parmi :

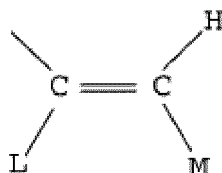
- (i) un phényle mono-, di- et tri-substitué ;
- (ii) un groupe hétéroaromatique non substitué, mono- ou di-substitué choisi parmi benzofuran-2-yle ou dibenzofuranyle, chacun desdits substituants des groupes aryle et hétéroaromatiques dans (g) (i) et (ii) étant indépendamment choisi parmi C₃-C₇ cycloalkyle, aryloxy, aryloxy(C₁-C₆)alcoxy, di(C₁-C₆)alkylamino, pipérazino, indolino, pipéridino, morpholino, pyrrolidyle, C₁-C₆ alkyle, C₁-C₆ alcoxy ou fluoro ;
- (iii) un phényle non substitué, ledit phényle ayant un substituant en position para comme décrit ci-avant dans (c) (iii) ;
- (iv) un groupe représenté par l'une des formules graphiques suivantes :



dans laquelle A est méthylène et D étant indépendamment choisi dans chaque formule parmi oxygène ou l'azote substitué, lesdits substituants d'azote étant C₁-C₃ alkyle ; chaque R₂₄ est C₁-C₃alkyle ; R₂₂ et R₂₃ étant chacun hydrogène ; et q étant choisi parmi les entiers 0, 1 ou 2 ;

(v) C₁-C₄ alkyle ou C₁-C₃ cycloalkyle ;

(vi) un groupe représenté par la formule graphique suivante :



dans laquelle L est choisi parmi hydrogène et M étant choisi parmi un phényle non substitué, mono-, ou di-substitué, chacun desdits substituants de phényle étant C₁-C₄ alcoxy ; ou

(i) B et B' pris ensemble forment un fluorén-9-ylidène, un fluorén-9-ylidène mono-substitué ou un cycle hydrocarbure C₇-C₁₂ spiro-bicyclique saturé, chacun desdits substituants de fluorén-9-ylidène étant C₁-C₄ alcoxy.

7. Naphtopyrane selon la revendication 4, dans lequel ledit naphtopyrane est choisi parmi :

- (a) le 3,3-di(4-méthoxyphényl)-11-morpholino-13,13-diméthyl-3H,13H-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
- (b) le 3-phényl-3-(4-morpholino-phényl)-11-morpholino-13,13-diméthyl-3H,13H-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
- (c) le 3,3-di(4-(2-méthoxyéthoxyphényl))-11-morpholino-13,13-diméthyl-3H,13H-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
- (d) le 3,3-di(4-méthoxyphényl)-11-morpholino-13-hydroxy-13-éthyl-3H,13H-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
- (e) le 3,3-di(4-méthoxyphényl)-10-méthoxy-11-morpholino-13,13-diméthyl-3H,13H-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
- (f) le 3-(4-méthoxyphényl)-3-(4-morpholinophényl)-10-méthoxy-11-morpholino-13,13-diméthyl-3H,13H-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
- (g) le 3-(3,4-diméthoxyphényl)-3-(4-méthoxyphényl)-11-morpholino-13,13-diméthyl-3H,13H-indéno[2',3':3,4]naphto[1,2-b]pyrane ;
- (h) le 3-(4-méthoxyphényl)-3-(4-morpholinophényl)-11-morpholino-13,13-diméthyl-3H,13H-indéno[2',3':3,4]naphto[1,2-b]pyrane ; ou
- (i) des mélanges de ceux-ci.

8. Matériau photochromique selon l'une quelconque des revendications précédentes, dans lequel ledit matériau photochromique est choisi parmi :

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

9. Article photochromique comprenant un polymère au moins partiellement durci et au moins une quantité photochromique d'au moins un matériau photochromique selon l'une quelconque des revendications 1 à 7.

10. Article photochromique selon la revendication 9, comprenant en outre au moins un autre matériau photochromique comprenant au moins un maximum d'absorption activé dans la plage de 400 à 700 nanomètres.

11. Article photochromique selon la revendication 10, dans lequel l'au moins un autre matériau photochromique est choisi parmi les chromènes, les spiropyranes, les oxazines, les dithiozonates organométalliques, les fulgides, les fulgimides ou l'un de leur mélange.

12. Article photochromique selon la revendication 9, dans lequel le polymère au moins partiellement durci est choisi parmi les matériaux polymériques organiques thermodurcissables ou thermoplastiques.

13. Article photochromique selon la revendication 12, dans lequel le polymère au moins partiellement durci est un matériau polymérique organique thermodurcissable ou thermoplastique qui est choisi parmi les poly(méthacrylates C₁-C₁₂ alkyle), les poly(diméthacrylates d'oxyalkylène), les poly(méthacrylates de phénol alcoxylés), l'acétate de cellulose, le triacétate de cellulose, l'acétopropionate de cellulose, l'acétobutyrate de cellulose, le poly(acétate de vinyle), le poly(alcool vinylique), le poly(chlorure de vinyle), le poly(chlorure de vinylidène), les polycarbonates thermoplastiques, les polyesters, les polyuréthanes, les polythiouréthanes, le poly(urée uréthane), le poly(téréphthalate d'éthylène), le polystyrène, le poly(alpha méthylstyrène), le copoly(styrène-méthacrylate de méthyle), le copoly(styrène-acrylonitrile), le polyvinylbutyral ou est polymérisé à partir de monomères choisis parmi les monomères de bis (carbonate d'allyle), les monomères d'acrylate polyfonctionnel, les monomères de méthacrylate polyfonctionnel, les monomères de diméthacrylate de diéthylèneglycol, les monomères de diisopropénylbenzène, les monomères de diméthacrylate de bisphénol A éthoxylés, les monomères de bisméthacrylate d'éthylèneglycol, les monomères de bisméthacrylate de poly(éthylène glycol), les monomères de bisméthacrylate de phénol éthoxylé, les monomères de polyacrylate d'alcool polyhydrique alcoxylé, les monomères de styrène, les monomères d'acrylate d'uréthane, les monomères d'acrylate de glycidyle, les monomères de méthacrylate de glycidyle, les monomères de pentaérythritol diallylidène ou leurs mélanges.

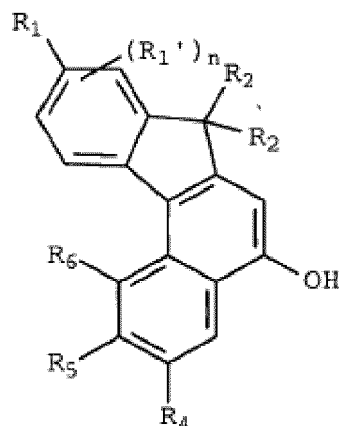
14. Article photochromique selon la revendication 9, comprenant en outre un superstrat relié à au moins une portion d'au moins un polymère au moins partiellement durci, ledit superstrat comprenant au moins un matériau polymérique organique.
- 5 15. Article photochromique selon la revendication 14, dans lequel le superstrat est lié par adhérence à au moins une portion du polymère au moins partiellement durci.
16. Article photochromique selon l'une quelconque des revendications 14 et 15, dans lequel le superstrat est un matériau polymérique organique choisi parmi les matériaux thermodurcissables ou thermoplastiques.
- 10 17. Article photochromique selon la revendication 16, dans lequel le superstrat est un matériau thermoplastique et est du polyuréthane.
18. Article photochromique selon la revendication 14, comprenant en outre un film au moins partiellement résistant à l'abrasion superposé sur au moins une portion du superstrat.
- 15 19. Article photochromique selon la revendication 18, dans lequel le film au moins partiellement résistant à l'abrasion est un matériau polymérique organique choisi parmi les matériaux thermoplastiques ou thermodurcissables.
- 20 20. Article photochromique selon la revendication 19, dans lequel le film au moins partiellement résistant à l'abrasion est un matériau thermoplastique et est un polycarbonate.
21. Article photochromique selon la revendication 14, comprenant en outre un revêtement au moins partiel sur au moins un revêtement au moins partiellement antireflet appliqué au film au moins partiellement résistant à l'abrasion, superposé sur au moins une portion du superstrat.
- 25 22. Article photochromique selon l'une quelconque des revendications 9 à 20, dans lequel le polymère au moins partiellement durci est un élément optique, de préférence une lentille ophtalmique.
- 30 23. Article photochromique comprenant un substrat et un revêtement au moins partiel d'un revêtement polymérique photochromique comprenant un polymère filmogène et au moins une quantité photochromique d'au moins un matériau photochromique selon l'une quelconque des revendications 1 à 7.
- 35 24. Article photochromique selon la revendication 23, dans lequel le revêtement polymérique photochromique comprend en outre au moins un autre matériau photochromique comprenant au moins un maximum d'absorption activé dans la plage de 400 à 700 nanomètres.
- 40 25. Article photochromique selon la revendication 24, dans lequel l'au moins un autre matériau photochromique est choisi parmi les chromènes, les spiropyranes, les oxazines, les dithiozonates organométalliques, les fulgides, les fulgimides ou l'un de leur mélange.
- 45 26. Article photochromique selon la revendication 23, dans lequel le substrat est du papier, du verre, de la céramique, du bois, une maçonnerie, un textile, un métal ou un matériau organique polymérique.
- 50 27. Article photochromique selon la revendication 26, dans lequel le substrat est un matériau organique polymérique et est choisi parmi les matériaux polymériques organiques thermodurcissables ou thermoplastiques.
28. Article photochromique selon la revendication 23, dans lequel le polymère filmogène est choisi parmi les matériaux polymériques organiques thermodurcissables ou thermoplastiques.
- 55 29. Article photochromique selon la revendication 28, dans lequel le polymère filmogène est thermodurcissable et est choisi parmi les polyuréthanes, les résines aminoplaste, les polysilanes, les polyanhydrides, les polyacrylamides ou les résines époxy.
30. Article photochromique selon la revendication 23, comprenant en outre un apprêt au moins partiellement interposé entre le substrat et le revêtement au moins partiel d'une composition de revêtement polymérique photochromique.
31. Article photochromique selon la revendication 30, comprenant en outre un revêtement au moins partiellement

résistant à l'abrasion appliqué à au moins une portion de la surface du revêtement au moins partiel d'une composition de revêtement polymérique photochromique.

32. Article photochromique selon la revendication 31, comprenant en outre un revêtement au moins partiel sur un revêtement antireflet d'un revêtement au moins partiellement antireflet appliqué au revêtement au moins partiellement résistant à l'abrasion appliqué à au moins une portion de la surface du revêtement au moins partiel d'une composition de revêtement polymérique photochromique.

33. Article photochromique selon l'une quelconque des revendications 23 à 32, dans lequel le substrat est un élément optique, de préférence une lentille ophtalmique.

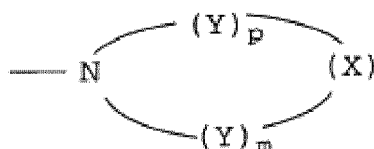
34. Naphtol représenté par la formule graphique suivante :



(a) R_1 est représenté par :

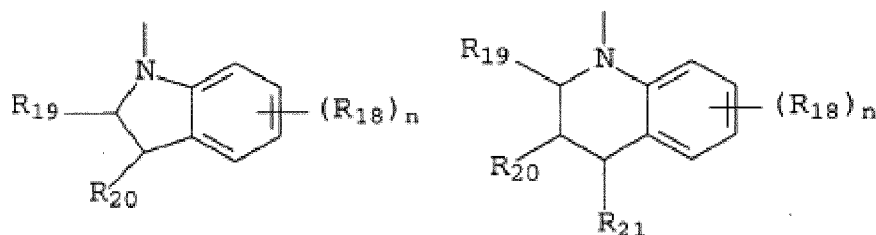
(i) $-N(R_{15})R_{16}$, R_{15} et R_{16} étant chacun indépendamment choisis parmi C_1 - C_8 alkyle, C_1 - C_8 alkylaryle, C_3 - C_{20} cycloalkyle, C_4 - C_{20} bicycloalkyle, C_5 - C_{20} tricycloalkyle ou C_1 - C_{20} alcoxyalkyle et ledit groupe aryle étant phényle ou naphtyle ;

(ii) un cycle contenant de l'azote représenté par la formule graphique suivante :



dans laquelle chaque Y est indépendamment choisi pour chaque occurrence parmi $-CH_2-$, $-CH(R_{17})-$, $-C(R_{17})(R_{17})-$, $-CH(aryle)-$, $-C(aryle)_2-$ ou $-C(R_{17})(aryle)-$; X étant $-Y-$, $-O-$, $-S-$, $-NH-$, $-N(R_{17})-$ ou $-N(aryle)-$; R_{17} est C_1 - C_6 alkyle ; ledit groupe aryle étant phényle ou naphtyle, m étant choisi parmi les entiers 1, 2 ou 3 et p étant choisi parmi les entiers 0, 1, 2 ou 3 ; à condition que lorsque p vaut 0, X soit Y ;

(iii) un groupe représenté par l'une des formules graphiques suivantes :



dans lesquelles chaque R_{19} , R_{20} et R_{21} sont indépendamment choisis pour chaque occurrence dans chaque formule parmi hydrogène, C_1 - C_5 alkyle, phényle ou naphtyle ; ou les groupes R_{19} et R_{20} forment conjoint-

tement un cycle de 5 à 8 atomes de carbone ; R_{18} étant choisi indépendamment pour chaque occurrence parmi C_1-C_6 alkyle, C_1-C_6 alcoxy, fluoro ou chloro et n étant choisi parmi les entiers 0, 1 ou 2 ;

(iv) une amine C_4-C_{18} spirobicyclique non substituée, mono- ou di-substituée ; ou

(v) une amine C_4-C_{18} spirobicyclique non substituée, mono- ou di-substituée ; lesdits substituants de (iv) et (v) étant indépendamment choisis pour chaque occurrence parmi aryle, C_1-C_6 alkyle, C_1-C_6 alcoxy ou phényl(C_1-C_6)alkyle ;

(b) R_1' est indépendamment choisi pour chaque occurrence parmi C_1-C_6 alkyle ou C_1-C_6 alcoxy et n étant choisi parmi les entiers 0, 1 ou 2 ;

(c) chaque R_2 ou chaque R_3 est indépendamment choisi pour chaque occurrence parmi :

(i) hydrogène, hydroxy, amino, amino mono- ou di-substitué, C_1-C_{12} alkyle, C_3-C_{12} alkylidène, C_2-C_{12} alkylidyne, vinyne, C_3-C_7 cycloalkyle, C_1-C_6 halogénoalkyle, allyle, benzyle, benzyle mono-substitué, chloro, fluoro ou -C(O)W, dans lequel W est hydroxy, C_1-C_6 alkyle, C_1-C_6 alcoxy, phényle, phényle mono-substitué, amino, mono(C_1-C_6)alkylamino, di(C_1-C_6)alkylamino, morpholino, pipéridino ou pyrrolidyle ; lesdits substituants d'amino étant C_1-C_6 alkyle, phényle, benzyle ou naphthyle ; chacun desdits substituants benzyle et phényle étant C_1-C_6 alkyle ou C_1-C_6 alcoxy ;

(ii) un groupe non substitué, mono-, di- ou tri-substitué choisi parmi phényle, naphthyle, phénanthryle, pyrényle, quinoléyle, isoquinoléyle, benzofuranyle, thiényne, benzothiényne, dibenzofuranyle, dibenzothiényne, carbazolyne ou indolyne ; chacun desdits groupes substituants dans (c) (ii) étant choisi indépendamment pour chaque occurrence parmi chloro, fluoro, C_1-C_6 alkyle ou C_1-C_6 alcoxy ;

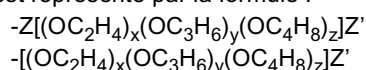
(iii) un phényle monosubstitué, ledit phényle ayant un substituant situé en position para étant $-(CH_2)_t-$ ou $-O-(CH_2)_t-$, relié à un groupe aryle qui est un élément d'un autre matériau photochromique, et t étant choisi parmi les entiers 1, 2, 3, 4, 5 ou 6 ;

(iv) $-OR_8$, R_8 étant choisi parmi C_1-C_6 alkyle, C_1-C_6 acyle, phényl(C_1-C_3)alkyle, phényl(C_1-C_3)alkyle substitué par mono(C_1-C_6)alkyle, phényl(C_1-C_3)alkyle substitué par mono(C_1-C_6)alcoxy, C_1-C_6 alcoxy(C_2-C_4)alkyle, C_3-C_7 cycloalkyle, C_3-C_7 cycloalkyle substitué par mono(C_1-C_4)alkyle, C_1-C_6 chloroalkyle, C_1-C_6 fluoroalkyle, allyle, tri(C_1-C_6)alkylsilyle, tri(C_1-C_6)alcoxsilyle, di(C_1-C_6)alkyl(C_1-C_6)alcoxsilyle, (C_1-C_6)alcoxy(C_1-C_6)alkylsilyle, benzoyle, benzoyle mono-substitué, naphthoyle ou naphthoyle mono-substitué ; chacun desdits substituants de benzoyle et naphthoyle étant indépendamment choisis parmi C_1-C_6 alkyle ou C_1-C_6 alcoxy ; ou R_8 étant $-CH(R_9)Q$, dans lequel R_9 est choisi parmi hydrogène ou C_1-C_3 alkyle et Q étant choisi parmi $-CN$, $-CF_3$, ou $-COOR_{10}$ et R_{10} étant choisi parmi hydrogène ou C_1-C_3 alkyle ; ou R_8 étant $-C(O)V$, dans lequel V est choisi parmi hydrogène, C_1-C_6 alcoxy, phénoxy, phénoxy substitué par mono- ou di-(C_1-C_6)alkyle, phénoxy substitué par mono- ou di-(C_1-C_6)alcoxy, un groupe aryle non substitué, mono- ou di-substitué, phényle ou naphthyle, amino, mono(C_1-C_6)alkylamino, di(C_1-C_6)alkylamino, phénylamino, phénylamino substitué par mono- ou di-(C_1-C_6)alkyle, ou phénylamino substitué par mono- ou di-(C_1-C_6)alcoxy ; chacun desdits substituants du groupe aryle étant indépendamment choisi parmi C_1-C_6 alkyle ou C_1-C_6 alcoxy ;

(v) $-CH(Q')_2$, Q' étant choisi parmi $-CN$ ou $-COOR_{11}$ et R_{11} étant choisi parmi hydrogène, C_1-C_6 alkyle, phényl(C_1-C_3)alkyle, phényl(C_1-C_3)alkyle substitué par mono(C_1-C_6)alkyle, phényl(C_1-C_3)alkyle substitué par mono(C_1-C_6)alcoxy ou un groupe aryle non substitué, mono- ou di-substitué, phényle ou naphthyle ; chacun desdits substituants du groupe aryle étant indépendamment choisi par C_1-C_6 alkyle ou C_1-C_6 alcoxy ;

(vi) $-CH(R_{12})G$, R_{12} étant choisi parmi hydrogène, C_1-C_6 alkyle ou un groupe aryle non substitué, mono- ou di-substitué, phényle ou naphthyle, et G étant choisi parmi $-COOR_{11}$, $-COR_{13}$ ou $-CH_2OR_{14}$, dans lequel R_{13} est choisi parmi hydrogène, C_1-C_6 alkyle, un groupe aryle non substitué, mono- ou di-substitué, phényle ou naphthyle, amino, mono(C_1-C_6)alkylamino, di(C_1-C_6)alkylamino, phénylamino, phénylamino substitué par mono- ou di-(C_1-C_6)alkyle, phénylamino substitué par mono- ou di-(C_1-C_6)alcoxy, diphenylamino, diphenylamino substitué par mono- ou di-(C_1-C_6)alkyle, diphenylamino substitué par mono- ou di-(C_1-C_6)alcoxy, morpholino ou pipéridino, R_{14} étant choisi parmi hydrogène, $-C(O)R_{11}$, C_1-C_6 alkyle, C_1-C_3 alcoxy(C_1-C_6)alkyle, phényl(C_1-C_3)alkyle, phényl(C_1-C_3)alkyle substitué par mono(C_1-C_6) alcoxy ou un groupe aryle non substitué, mono- ou di-substitué, phényle ou naphthyle, chacun desdits substituants du groupe aryle étant indépendamment choisi parmi C_1-C_6 alkyle ou C_1-C_6 alcoxy ;

(vii) le groupe T est représenté par la formule :



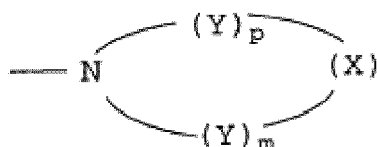
dans laquelle $-Z$ est choisi parmi $-C(O)-$ ou $-CH_2-$, Z' étant choisi parmi C_1-C_3 alcoxy ou un groupe polymérisable ; x , y et z étant chacun indépendamment choisis parmi un nombre entre 0 et 50, et la somme de x , y et z étant comprise entre 2 et 50 ; ou

(viii) R_2 et R_2 ou R_3 et R_3 forment ensemble un groupe oxo ;

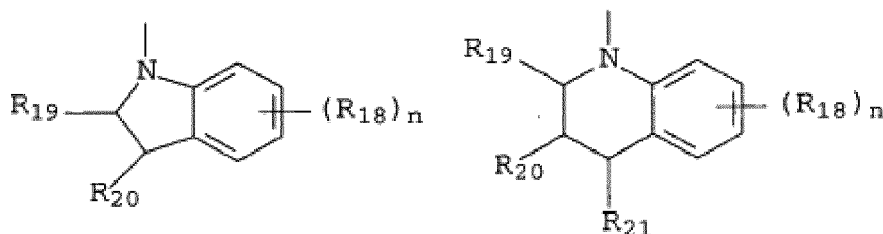
(d) R_4 est choisi parmi hydrogène, C_1 - C_6 alkyle ou le groupe R_a est choisi parmi :

- (i) $-OR_8'$, R_8' étant choisi parmi phényl(C_1 - C_3)alkyle, C_1 - C_6 alkyle, phényl(C_1 - C_3)alkyle substitué mono(C_1 - C_6)alkyle, phényl(C_1 - C_3)alkyle substitué par mono(C_1 - C_6)alcoxy, C_1 - C_6 alcoxy(C_2 - C_4)alkyle, C_3 - C_7 cycloalkyle, C_3 - C_7 cycloalkyle substitué par mono(C_1 - C_4)alkyle, C_1 - C_6 chloroalkyle, C_1 - C_6 fluoroalkyle, allyle ou $-CH(R_9)Q$, R_9 étant choisi parmi hydrogène ou C_1 - C_3 alkyle ; ou
- (ii) un groupe choisi parmi :

- (1) $-N(R_{15})R_{16}$ dans lequel R_{15} et R_{16} sont identiques comme décrit ci-avant dans (a)(i) ;
- (2) un cycle contenant de l'azote représenté par la formule graphique suivante :

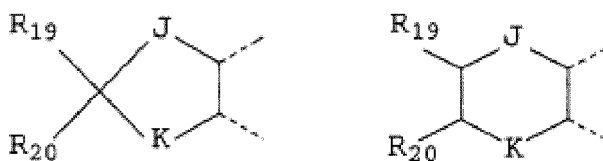


- dans laquelle Y, X, m et p sont identiques comme décrit ci-avant dans (a)(ii) ;
- (3) un groupe représenté par les formules graphiques suivantes :



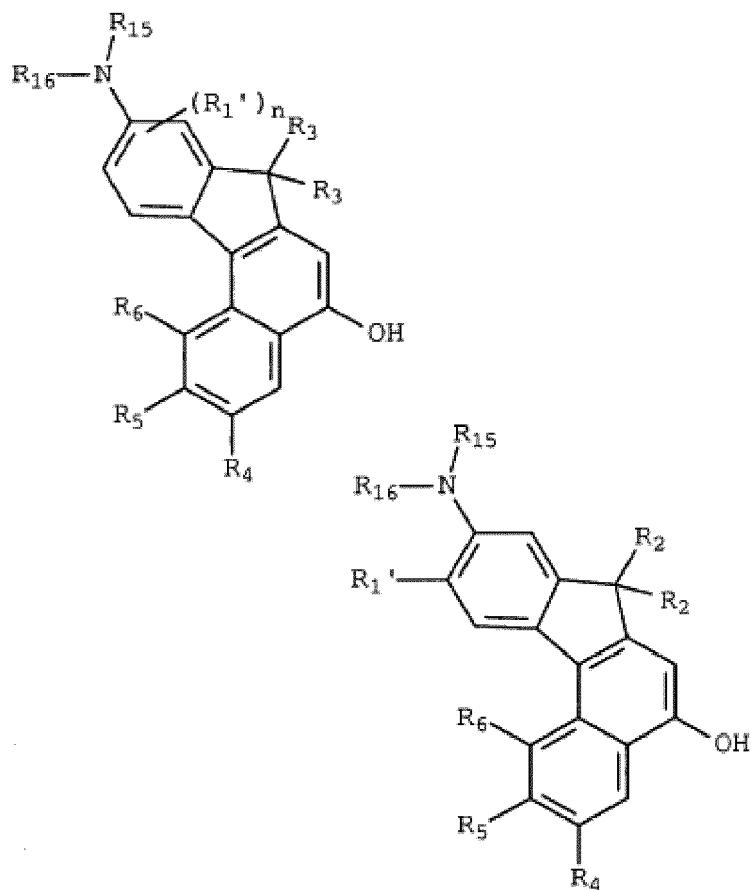
dans lesquelles R_{18} , R_{19} , R_{20} , R_{21} et n sont identiques comme décrit ci-avant ;

- (e) R_5 est choisi parmi hydrogène, C_1 - C_6 alkyle ou R_a , ledit R_a étant identique comme décrit ci-avant dans (d) ;
- (f) R_6 est choisi parmi hydrogène, C_1 - C_6 alkyle ou R_a , ledit R_a étant identique comme décrit ci-avant dans (d) ; ou
- (g) R_5 et R_6 forment ensemble l'une des formules graphiques suivantes :



dans lesquelles J et K sont indépendamment choisis pour chaque occurrence dans chaque formule parmi oxygène ou $-N(R_{15})-$, R_{15} étant identique comme décrit ci-avant dans (a)(i), R_{19} et R_{20} étant chacun identique comme décrit ci-avant dans (a)(iii).

35. Naphtol selon la revendication 34, dans lequel ledit naphtol est représenté par l'une des formules graphiques suivantes :



36. Naphtol selon la revendication 34, dans lequel ledit naphtol est choisi parmi :

- (a) le 7,7-diméthyl-5-hydroxy-9-morpholino-7H-benzo[C]fluorène ;
- (b) le 7,7-diméthyl-5-hydroxy-10-méthoxy-9-morpholino-7H-benzo[C]fluorène ;
- (c) le 7-diméthyl-7-méthoxy-5-hydroxy-9-diméthylamino-7H-benzo[C]fluorène ;
- (d) le 7-éthyl-7-méthoxy-5-hydroxy-9-pipéridino-7H-benzo[C]fluorène ;
- (e) le 7,7-diméthyl-5-hydroxy-9-pipéridino-7H-benzo [C]fluorène ;
- (f) le 7,7-diméthyl-3-méthoxy-5-hydroxy-9-morpholino-7H-benzo[C]fluorène ;
- (g) le 7,7-diméthyl-3,4-diméthoxy-5-hydroxy-9-morpholino-7H-benzo[C]fluorène ;
- (h) le 7,7-diméthyl-3-méthoxy-4-méthyl-5-hydroxy-9-morpholino-7H-benzo[C]fluorène ;
- (i) le 7-phényl-7-hydroxy-3-méthoxy-4-méthyl-5-hydroxy-9-morpholino-7H-benzo[C]fluorène ;
- (j) des mélanges de ceux-ci.

REFERENCES CITED IN THE DESCRIPTION

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