

OPHTHALMIC DEVICES COMPRISING PHOTOCHROMIC MATERIALS HAVING EXTENDED PI-CONJUGATED SYSTEMS

BACKGROUND

[001] Various non-limiting embodiments disclosed herein relate to certain ophthalmic devices comprising photochromic materials having an extended pi-conjugated system.

[002] Many conventional photochromic materials, such as indeno-fused naphthopyrans, can undergo a transformation in response to certain wavelengths of electromagnetic radiation (or “actinic radiation”) from one form (or state) to another, with each form having a characteristic absorption spectrum. As used herein the term “actinic radiation” refers to electromagnetic radiation that is capable of causing a photochromic material to transform from one form or state to another. For example, many conventional photochromic materials are capable of transforming from a closed-form, corresponding to a “bleached” or “unactivated” state of the photochromic material, to an open-form, corresponding to a “colored” or “activated” state of the photochromic material, in response to actinic radiation, and reverting back to the closed-form in the absence of the actinic radiation in response to thermal energy. Photochromic compositions and articles that contain one or more photochromic materials, for example photochromic lenses for eyewear applications, may display clear and colored states that generally correspond to the states of the photochromic material(s) that they contain.

[003] Typically, the amount of a photochromic material needed to achieve a desired optical effect when incorporated into a composition or article will depend, in part, on the amount of actinic radiation that the photochromic material absorbs on a per molecule basis. That is, the more actinic radiation that the photochromic material absorbs on a per molecule basis, the more likely (i.e., the higher the probability) the photochromic material will transform from the closed-form to the open-form. Photochromic compositions and articles that are made using photochromic materials having a relatively high molar absorption coefficient (or “extinction coefficient”) for actinic radiation may generally be used in lower

concentrations than photochromic materials having lower molar absorption coefficients, while still achieving the desired optical effect.

[004] For some applications, such as ophthalmic devices which reside in or on the eye, the amount of photochromic material that can be incorporated into the article may be limited due to the physical dimensions of the article. Accordingly, the use of conventional photochromic materials that have a relatively low molar absorption coefficient in such articles may be impractical because the amount photochromic material needed to achieve the desired optical effects cannot be physically accommodated in the article. Further, in other applications, the size or solubility of the photochromic material itself may limit the amount of the photochromic material that can be incorporated into the article.

[005] Accordingly, for ophthalmic devices which reside in or on the eye, it may be advantageous to develop photochromic materials that can display hyperchromic absorption of actinic radiation, which may enable the use of lower concentrations of the photochromic material while still achieving the desired optical effects. As used herein, the term “hyperchromic absorption” refers to an increase in the absorption of electromagnetic radiation by a photochromic material having an extended pi-conjugated system on a per molecule basis as compared to a comparable photochromic material that does not have an extended pi-conjugated system.

[006] Additionally, as mentioned above, typically the transformation between the closed-form and the open-form requires that the photochromic material be exposed to certain wavelengths of electromagnetic radiation. For many conventional photochromic materials, the wavelengths of electromagnetic radiation that may cause this transformation typically range from 320 nanometers (“nm”) to 390 nm. Accordingly, conventional photochromic materials may not be optimal for use in applications that are shielded from a substantial amount of electromagnetic radiation in the range of 320 nm to 390 nm. For example, lenses for eyewear applications that are made using conventional photochromic materials may not reach their fully-colored state when used in an automobile. This is because a large portion of electromagnetic radiation in the range of 320 nm to 390 nm can be absorbed by the

windshield of the automobile before it can be absorbed by the photochromic material(s) in the lenses. Therefore, for ophthalmic devices which reside in or on the eye, it may be advantageous to develop photochromic materials that can have a closed-form absorption spectrum for electromagnetic radiation that is shifted to longer wavelengths, that is "bathochromically shifted." As used herein the term "closed-form absorption spectrum" refers to the absorption spectrum of the photochromic material in the closed-form or unactivated state. For example, in applications involving behind the windshield use of photochromic materials, it may be advantageous if the closed-form absorption spectrum of the photochromic material were shifted such that the photochromic material may absorb sufficient electromagnetic radiation having a wavelength greater than 390 nm to permit the photochromic material to transform from the closed-form to an open-form.

BRIEF SUMMARY OF THE DISCLOSURE

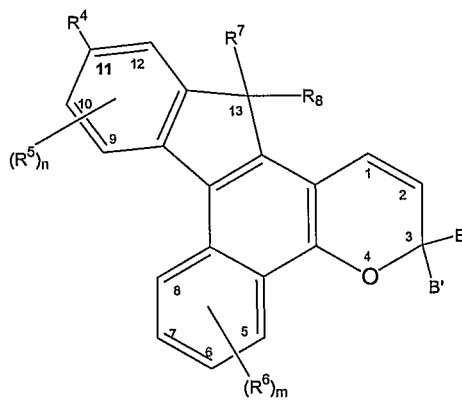
[007] Various non-limiting embodiments disclosed herein relate to ophthalmic devices comprising photochromic materials comprising: (i) an indeno-fused naphthopyran; and (ii) a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position of thereof, provided that if the group bonded at the 11-position of the indeno-fused naphthopyran and a group bonded at the 10-position or 12-position of the indeno-fused naphthopyran together form a fused group, said fused group is not a benzo-fused group; and wherein the 13-position of the indeno-fused naphthopyran is unsubstituted, mono-substituted or di-substituted, provided that if the 13-position of the indeno-fused naphthopyran is di-substituted, the substituents do not together form norbornyl.

[008] Other non-limiting embodiments relate to ophthalmic devices comprising photochromic materials comprising an indeno-fused naphthopyran, wherein the 13-position of the indeno-fused naphthopyran is unsubstituted, mono-substituted or di-substituted, provided that if the 13-position of the indeno-fused naphthopyran is di-substituted, the substituents do not together form norbornyl, and wherein the photochromic material has an integrated extinction coefficient greater than 1.0×10^6 nm x mol⁻¹ x cm⁻¹ as determined by integration of a plot of extinction coefficient of

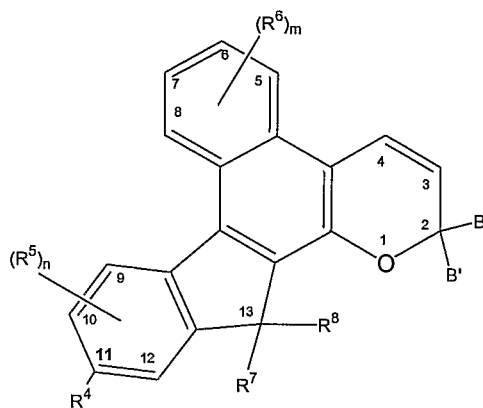
the photochromic material vs. wavelength over a range of wavelengths ranging from 320 nm to 420 nm, inclusive.

[009] Still other non-limiting embodiments relate to ophthalmic devices comprising photochromic materials comprising: an indeno-fused naphthopyran chosen from an indeno[2',3':3,4]naphtho[1,2-b]pyran, an indeno[1',2':4,3]naphtho[2,1-b]pyran, and mixtures thereof, wherein the 13-position of the indeno-fused naphthopyran is unsubstituted, mono-substituted or di-substituted, provided that if the 13-position of the indeno-fused naphthopyran is di-substituted, the substituent groups do not together form norbornyl; and a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof, where said group is a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, or a group represented by $-X=Y$ or $-X\equiv Y$, wherein X, X', Y and Y' are as described herein below and as set forth in the claims; or the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position of the indeno-fused naphthopyrans together with a group bonded at the 12-position of the indeno-fused naphthopyran or together with a group bonded at the 10-position of the indeno-fused naphthopyran form a fused group, said fused group being indeno, dihydronaphthalene, indole, benzofuran, benzopyran or thianaphthene.

[010] Yet other non-limiting embodiments relate to ophthalmic devices comprising



photochromic materials represented by:



or a mixture thereof, wherein R^4 , R^5 , R^6 , R^7 , R^8 , B and B' represent groups as described herein below and as set forth in the claims.

[011] Still other non-limiting embodiments relate to methods of making ophthalmic devices comprising photochromic materials according to various non-limiting embodiments disclosed herein. For example, one specific non-limiting embodiment relates to an ophthalmic device adapted for use behind a substrate that blocks a substantial portion of electromagnetic radiation in the range of 320 nm to 390 nm, the ophthalmic device comprising a photochromic material comprising an indeno-fused naphthopyran and a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof connected to at least a portion of the ophthalmic device, wherein the at least a portion of the ophthalmic device absorbs a sufficient amount of electromagnetic radiation having a wavelength greater than 390 nm passing through the substrate that blocks a substantial portion of electromagnetic radiation in the range of 320 nm to 390 nm such that the at least a portion of the ophthalmic device transforms from a first state to a second state.

BRIEF DESCRIPTION OF THE DRAWING(S)

[012] Various non-limiting embodiments disclosed herein may be better understood when read in conjunction with the drawings, in which:

Fig. 1 shows the absorption spectra obtained for a photochromic material according to one non-limiting embodiment disclosed herein at two different concentrations and the absorption spectra of a conventional photochromic material;

Figs. 2a, 2b, 3a and 3b are representations of photochromic materials according to various non-limiting embodiments disclosed herein;

Fig. 4 is a schematic diagram of a reaction scheme for making an intermediate material that may be used in forming photochromic materials according to various non-limiting embodiments disclosed herein; and

Figs. 5-8 are schematic diagrams of reaction schemes that may be used in making photochromic materials according to various non-limiting embodiments disclosed herein.

DETAILED DESCRIPTION

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

[014] Additionally, for the purposes of this specification, unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and other properties or parameters used in the specification are to be understood as being modified in all instances by the term "about." Accordingly, unless otherwise indicated, it should be understood that the numerical parameters set forth in the following specification and attached claims are approximations. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, numerical parameters should be read in light of the number of reported significant digits and the application of ordinary rounding techniques. Further, while the numerical ranges and parameters setting forth the broad scope of the invention are approximations as discussed above, the numerical values set forth in the Examples section are reported as precisely as possible. It should be understood, however, that such numerical values inherently contain certain errors resulting from the measurement equipment and/or measurement technique.

[015] As used herein in the terms "lens" and "ophthalmic device" refer to devices that reside in or on the eye. These devices can provide optical correction, wound care, drug delivery, diagnostic functionality, cosmetic enhancement or effect or a combination of these properties. The terms lens and ophthalmic device include but

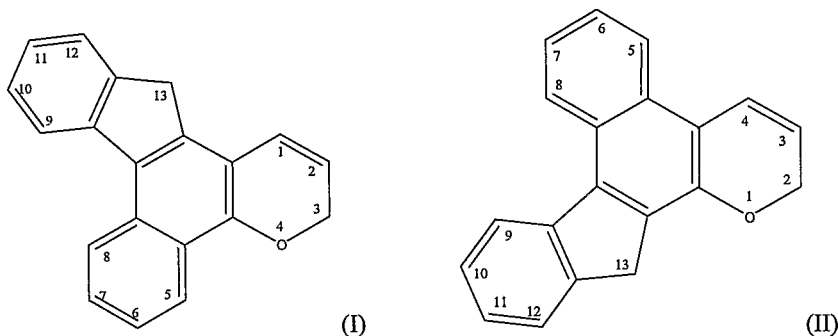
are not limited to soft contact lenses, hard contact lenses, intraocular lenses, overlay lenses, ocular inserts, and optical inserts.

[016] Photochromic materials suitable for use in the ophthalmic devices according to various non-limiting embodiments of the invention will now be discussed. As used herein, the term “photochromic” means having an absorption spectrum for at least visible radiation that varies in response to absorption of at least actinic radiation. Further, as used herein the term “photochromic material” means any substance that is adapted to display photochromic properties, i.e. adapted to have an absorption spectrum for at least visible radiation that varies in response to absorption of at least actinic radiation. As previously discussed, as used herein the term “actinic radiation” refers to electromagnetic radiation that is capable of causing a photochromic material transform from one form or state to another.

[017] Various non-limiting embodiments disclosed herein relate to ophthalmic devices comprising photochromic materials comprising: (i) an indeno-fused naphthopyran; and (ii) a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position of thereof, provided that if the group bonded at the 11-position of the indeno-fused naphthopyran and a group bonded at the 10-position or 12-position of the indeno-fused naphthopyran together form a fused group, said fused group is not a benzo-fused group; and wherein the 13-position of the indeno-fused naphthopyran is unsubstituted, mono-substituted or di-substituted, provided that if the 13-position of the indeno-fused naphthopyran is di-substituted, the substituent groups do not together form norbornyl (also known as bicyclo[2.2.1]heptyl or 8,9,10-trinorbornyl). As used herein the term “fused” means covalently bonded in at least two positions.

[018] As used herein, the terms “10-position,” “11-position,” “12-position,” “13-position,” etc. refer to the 10-, 11-, 12- and 13- position, etc. of the ring atoms of the indeno-fused naphthopyran, respectively. For example, according to one non-limiting embodiment, wherein the indeno-fused naphthopyran is an indeno[2',3':3,4]naphtho[1,2-b]pyran, the ring atoms of the indeno-fused naphthopyran are numbered as shown below in (I). According to another non-

limiting embodiment, wherein the indeno-fused naphthopyran is an indeno[1',2':4,3]naphtho[2,1-b]pyran, the ring atoms of the indeno-fused naphthopyran are numbered shown below in (II).



[019] Further, according to various non-limiting embodiments disclosed herein, the indeno-fused naphthopyrans may have group(s) that can stabilize the open-form of the indeno-fused naphthopyran bonded to the pyran ring at an available position adjacent the oxygen atom (i.e., the 3-position in (I) above, or the 2-position in (II) above). For example, according to one non-limiting embodiment, the indeno-fused naphthopyrans may have a group that can extend the pi-conjugated system of the open-form of the indeno-fused naphthopyran bonded to the pyran ring adjacent the oxygen atom. Non-limiting examples of groups that may be bonded to the pyran ring as discussed above are described in more detail herein below with reference to B and B'.

[020] Further, as discussed in more detail herein below, in addition to the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position of the indeno-fused naphthopyran, the photochromic materials according to various non-limiting embodiments disclosed may include additional groups bonded or fused at various positions on the indeno-fused naphthopyran other than the 11-position.

[021] As used herein the terms "group" or "groups" mean an arrangement of one or more atoms. As used herein, the phrase "group that extends the pi-conjugated system of the indeno-fused naphthopyran" means a group having at least one pi-bond (π -bond) in conjugation with the pi-conjugated system of the indeno-fused naphthopyran. It will be appreciated by those skilled in the art that in such system,

the pi-electrons in the pi-conjugated system of the indeno-fused naphthopyran can be de-localized over the combined pi-system of the indeno-fused naphthopyran and the group having at least one pi-bond in conjugation with the pi-conjugated system of the indeno-fused naphthopyran. Conjugated bond systems may be represented by an arrangement of at least two double or triple bonds separated by one single bond, that is a system containing alternating double (or triple) bonds and single bonds, wherein the system contains at least two double (or triple) bonds. Non-limiting examples of groups that may extend the pi-conjugated system of the indeno-fused naphthopyran according to various non-limiting embodiments disclosed herein are set forth below in detail.

[022] As previously discussed, the more actinic radiation that a photochromic material absorbs on a per molecule basis, the more likely the photochromic material will be to make the transformation from the closed-form to the open-form. Further, as previously discussed, photochromic materials that absorb more actinic radiation on a per molecule basis may generally be used in lower concentrations than those that absorb less actinic radiation on a per molecule basis while still achieving the desired optical effects.

[023] Although not meant to be limiting herein, it has been observed by the inventors that the indeno-fused naphthopyrans that comprise a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof according to certain non-limiting embodiments disclosed herein may absorb more actinic radiation on a per molecule basis than a comparable indeno-fused naphthopyran without a group that extends the pi-conjugated system of the comparable indeno-fused naphthopyran bonded at the 11-position thereof. That is, the indeno-fused naphthopyrans according to certain non-limiting embodiments disclosed herein may display hyperchromic absorption of actinic radiation. As discussed above, as used herein the term "hyperchromic absorption" refers to an increase in the absorption of electromagnetic radiation by a photochromic material having an extended pi-conjugated system on a per molecule basis as compared to a comparable photochromic material that does not have an extended pi-conjugated

system. Thus, while not meant to be limiting herein, it is contemplated that the indeno-fused naphthopyrans according to certain non-limiting embodiments disclosed herein may be advantageously employed in ophthalmic devices wherein it may be necessary or desirable to limit the amount of the photochromic material employed.

[024] The amount of radiation absorbed by a material (or the “absorbance” of the material) can be determined using a spectrophotometer by exposing the material to incident radiation having a particular wavelength and intensity and comparing the intensity of radiation transmitted by the material to that of the incident radiation. For each wavelength tested, the absorbance (“A”) of the material is given by the following equation:

$$A = \log I_0/I$$

wherein “ I_0 ” is the intensity of the incident radiation and “ I ” is the intensity of the transmitted radiation. An absorption spectrum for the material can be obtained by plotting the absorbance of a material vs. wavelength. By comparing the absorption spectrum of photochromic materials that were tested under the same conditions, that is using the same concentration and path length for electromagnetic radiation passing through the sample (e.g., the same cell length or sample thickness), an increase in the absorbance of one of the materials at a given wavelength can be seen as an increase in the intensity of the spectral peak for that material at that wavelength.

[025] Referring now to Fig. 1, there is shown the absorption spectra for two different photochromic materials. Absorption spectra **1a** and **1b** were obtained from .22 cm x 15.24 cm x 15.24 cm acrylic chips that were made by adding 0.0015 molal (m) solutions of a photochromic material to be tested to a monomer blend, and subsequently casting the mixture to form the acrylic chips. Absorption spectrum **1c** was obtained from a .22 cm x 15.24 cm x 15.24 cm acrylic chip that was obtained by adding 0.00075 m solution of the same photochromic material used to obtain spectrum **1a** to the above-mentioned monomer blend and casting. The preparation of acrylic test chips is described in more detail in the Examples.

[026] More particularly, absorption spectrum **1a** is the absorption spectrum at “full concentration” (i.e., 0.0015 m) for an indeno-fused naphthopyran according to one non-limiting embodiment disclosed herein comprising a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof. Specifically, absorption spectrum **1a** is the absorption spectrum for a 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(4-(phenyl)phenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran. Since the absorbance of this photochromic material exceeded the maximum detection limit over the range of wavelengths tested, a plateau in absorbance is observed in absorption spectrum **1a**. Absorption spectrum **1b** is the absorption spectrum at “full concentration” (i.e., 0.0015 m) for a comparable indeno-fused naphthopyran without a group that extends the pi-conjugated system of the comparable indeno-fused naphthopyran bonded at the 11-position thereof. Specifically, absorption spectrum **1b** is the absorption spectrum for a 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

[027] As can be seen from absorption spectra **1a** and **1b** in Fig. 1, the indeno-fused naphthopyran comprising the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof (spectrum **1a**) according to one non-limiting embodiment disclosed herein displays an increase in absorption of electromagnetic radiation having a wavelength ranging from 320 nm to 420 nm (i.e., displays hyperchromic absorption of electromagnetic radiation) as compared to a comparable indeno-fused naphthopyran without the group that extends the pi-conjugated system of the comparable indeno-fused naphthopyran bonded at the 11-position thereof (spectrum **1b**).

[028] Referring again to Fig. 1, as previously discussed, absorption spectrum **1c** is the absorption spectrum for the same indeno-fused naphthopyran as spectrum **1a**, but was obtained from a sample having one-half of the full-concentration used to obtain absorption spectrum **1a**. As can be seen by comparing spectra **1c** and **1b** in Fig. 1, at one-half the concentration of the comparable photochromic material, the indeno-fused naphthopyran comprising the group that extends the pi-conjugated

system of the indeno-fused naphthopyran bonded at the 11-position thereof according to one non-limiting embodiment disclosed herein displays hyperchromic absorption of electromagnetic radiation having a wavelength from 320 nm to 420 nm as compared to the comparable indeno-fused naphthopyran without the group that extends the pi-conjugated system of the comparable indeno-fused naphthopyran at the 11-position thereof at full concentration.

[029] Another indication of the amount of radiation a material can absorb is the extinction coefficient of the material. The extinction coefficient (“ ϵ ”) of a material is related to the absorbance of the material by the following equation:

$$\epsilon = A / (c \times l)$$

wherein “A” is the absorbance of the material at a particular wavelength, “c” is the concentration of the material in moles per liter (mol/L) and “l” is the path length (or cell thickness) in centimeters. Further, by plotting the extinction coefficient vs. wavelength and integrating over a range of wavelengths (e.g., $\int \epsilon(\lambda) d\lambda$) it is possible to obtain an “integrated extinction coefficient” for the material. Generally speaking, the higher the integrated extinction coefficient of a material, the more radiation the material will absorb on a per molecule basis.

[030] The photochromic materials according to various non-limiting embodiments disclosed herein may have an integrated extinction coefficient greater than 1.0×10^6 nm/(mol x cm) or ($\text{nm} \times \text{mol}^{-1} \times \text{cm}^{-1}$) as determined by integration of a plot of extinction coefficient of the photochromic material vs. wavelength over a range of wavelengths ranging from 320 nm to 420 nm, inclusive. Further, the photochromic materials according to various non-limiting embodiments disclosed herein may have an integrated extinction coefficient of at least $1.1 \times 10^6 \text{ nm} \times \text{mol}^{-1} \times \text{cm}^{-1}$, or at least $1.3 \times 10^6 \text{ nm} \times \text{mol}^{-1} \times \text{cm}^{-1}$ as determined by integration of a plot of extinction coefficient of the photochromic material vs. wavelength over a range of wavelengths ranging from 320 nm to 420 nm, inclusive. For example, according to various non-limiting embodiments, the photochromic material may have an integrated extinction coefficient ranging from 1.1×10^6 to $4.0 \times 10^6 \text{ nm} \times \text{mol}^{-1} \times \text{cm}^{-1}$ (or greater) as determined by integration of a plot of extinction coefficient of the photochromic

material vs. wavelength over a range of wavelengths ranging from 320 nm to 420 nm, inclusive. However, as indicated above, generally speaking the higher the integrated extinction coefficient of a photochromic material, the more radiation the photochromic material will absorb on a per molecule basis. Accordingly, other non-limiting embodiments disclosed herein contemplate photochromic materials having an integrated extinction coefficient greater than $4.0 \times 10^6 \text{ nm} \times \text{mol}^{-1} \times \text{cm}^{-1}$.

[031] As previously discussed, for many conventional photochromic materials, the wavelengths of electromagnetic radiation required to cause the material to transformation from a closed-form (or unactivated state) to an open-form (or activated state) may range from 320 nm to 390 nm. Thus, conventional photochromic materials may not achieve their fully-colored state when used in applications that are shielded from a substantial amount of electromagnetic radiation in the range of 320 nm to 390 nm. Although not meant to be limiting herein, it has been observed by the inventors that indeno-fused naphthopyrans comprising a group that extends the pi-conjugated system of the indeno-fused naphthopyran at the 11-position thereof according to certain non-limiting embodiments disclosed herein may have a closed-form absorption spectrum for electromagnetic radiation that is bathochromically shifted as compared to a closed-form absorption spectrum for electromagnetic radiation of a comparable indeno-fused naphthopyran without the group that extends the pi-conjugated system of the comparable indeno-fused naphthopyran bonded at the 11-position thereof. As discussed above, as used herein the term "closed-form absorption spectrum" refers to the absorption spectrum of the photochromic material in the closed-form or unactivated state.

[032] For example, referring again to Fig. 1, absorption spectrum **1a**, which is the absorption spectrum for an indeno-fused naphthopyran according to one non-limiting embodiment disclosed herein, is bathochromically shifted- that is, the absorption spectrum is displaced toward longer wavelengths- as compared to absorption spectrum **1b**. Since absorption spectrum **1a** has an increased absorption in the 390 nm to 420 nm range as compared to absorption spectrum **1b**, it is contemplated the photochromic material from which absorption spectrum **1a** was

obtained may be advantageously employed in applications wherein a substantial amount of electromagnetic radiation in the range of 320 nm to 390 nm is shielded or blocked- for example, in applications involving use behind a windshield.

[033] As discussed above, the photochromic materials according to various non-limiting embodiments disclosed herein comprise an indeno-fused naphthopyran and a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof. Non-limiting examples of groups that may extend the pi-conjugated system of the indeno-fused naphthopyran according to various non-limiting embodiments disclosed herein, include a substituted or unsubstituted aryl group, such as, but not limited to, phenyl, naphthyl, fluorenyl, anthracenyl and phenanthracenyl; a substituted or unsubstituted heteroaryl group, such as, but not limited to, pyridyl, quinoliny, isoquinoliny, bipyridyl, pyridazinyl, cinnoliny, phthalazinyl, pyrimidinyl, quinazolinyl, pyrazinyl, quinoxalinyl, phenanthrolyl, triazinyl, pyrrolyl, indolyl, furfuryl, benzofurfuryl, thienyl, benzothienyl, pyrazolyl, indazolyl, imidazolyl, benzimidazolyl, triazolyl, benzotriazolyl, tetrazolyl, oxazolyl, benzoxazolyl, isoxazolyl, benzisoxazolyl, thiazolyl, benzothiazolyl, isothiazolyl, benzisothiazolyl, thiadiazolyl, benzothiadiazolyl, thiatriazolyl, purinyl, carbazolyl and azaindolyl; and a group represented by (III) or (IV) (below).



[034] With reference to (III) above, non-limiting examples of groups that X may represent according to various non-limiting embodiments disclosed herein include -CR¹, -N, -NO, -SR¹, -S(=O)R¹ and -P(=O)R¹. Further according to various non-limiting embodiments disclosed herein, if X represents -CR¹ or -N, Y may represent a group such as, but not limited to, C(R²)₂, NR², O and S. Still further, according to various non-limiting embodiments disclosed herein, if X represents -NO, -SR¹, -S(=O)R¹ or -P(=O)R¹, Y may represent a group such as, but not limited to, O. Non-limiting examples of groups that R¹ may represent include amino, dialkyl amino, diaryl amino, acyloxy, acylamino, a substituted or unsubstituted C₂-C₂₀ alkyl, a substituted or unsubstituted C₂-C₂₀ alkenyl, a substituted or unsubstituted C₂-C₂₀ alkynyl, halogen, hydrogen, hydroxy, oxygen, a polyol residue (such as, but

not limited to, those discussed herein below with respect to -G-), a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, alkylamino, mercapto, alkylthio, a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heterocyclic group (e.g., piperazino, piperidino, morpholino, pyrrolidino etc.), a reactive substituent, a compatibilizing substituent, and a photochromic material. Non-limiting examples of groups from which each R^2 group discussed above may be independently chosen include those groups discussed above with respect to R^1 .

[035] With reference to (IV) above, according to various non-limiting embodiments disclosed herein, X' may represent a group including, but not limited to, -C or $-N^+$, and Y' may represent a group including, but not limited to, CR^3 or N. Non-limiting examples of groups that R^3 may represent include those groups discussed above with respect to R^1 .

[036] Alternatively, as discussed above, according to various non-limiting embodiments disclosed herein, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position of the indeno-fused naphthopyran together with a group bonded at the 12-position of the indeno-fused naphthopyran or together with a group bonded at the 10-position of the indeno-fused naphthopyran may form a fused group, provided that the fused group is not a benzo-fused group. According to other non-limiting embodiments, the group bonded at the 11-position together with a group bonded at the 12-position or the 10-position may form a fused group, provided that the fused group extends the pi-conjugated system of the indeno-fused naphthopyran at the 11-position, but does not extend the pi-conjugated system of the indeno-fused naphthopyran at the 10-position or the 12-position. For example, according to various non-limiting embodiments disclosed herein, if the group bonded at the 11-position of the indeno-fused naphthopyran together with a group bonded at the 10-position or 12-position of the indeno-fused naphthopyran forms a fused group, the fused group may be indeno, dihydronaphthalene, indole, benzofuran, benzopyran or thianaphthene.

[037] According to various non-limiting embodiments disclosed herein, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof may be a substituted or unsubstituted C₂-C₂₀ alkenyl; a substituted or unsubstituted C₂-C₂₀ alkynyl; a substituted or unsubstituted aryl; a substituted or unsubstituted heteroaryl; -C(=O)R¹, wherein R¹ may represent a group as set forth above; or -N(=Y) or -N⁺(≡Y'), wherein Y may represent a group such as, but not limited to, C(R²)₂, NR², O and S, and Y' may represent a group such as, but not limited to, CR³ and N, wherein R² and R³ may represent groups such as those discussed above. Substituents that may be bonded to the substituted C₂-C₂₀ alkenyl, substituted C₂-C₂₀ alkynyl, substituted aryl, and substituted heteroaryl groups according to these and other non-limiting embodiments disclosed herein include groups, which may be substituted or unsubstituted, such as, but not limited to, alkyl, alkoxy, oxyalkoxy, amide, amino, aryl, heteroaryl, azide, carbonyl, carboxy, ester, ether, halogen, hydroxy, oxygen, a polyol residue, phenoxy, benzyloxy, cyano, nitro, sulfonyl, thiol, a heterocyclic group, a reactive substituent, a compatibilizing substituent, and a photochromic material. Further, according to various non-limiting embodiments disclosed herein wherein the group that extends the pi-conjugated system of the indeno-fused naphthopyran comprises more than one substituent, each substituent may be independently chosen from those groups discussed above.

[038] For example, according to one non-limiting embodiment, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof may be an aryl group or a heteroaryl group that is unsubstituted or substituted with at least one of a substituted or unsubstituted alkyl, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, amide, a substituted or unsubstituted amino, a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, azide, carbonyl, carboxy, ester, ether, halogen, hydroxy, a polyol residue, a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, cyano, nitro, sulfonyl, thiol, a substituted or unsubstituted heterocyclic group, a reactive substituent, a compatibilizing substituent or a photochromic material. Further, if the aryl group or the heteroaryl group comprises

more than one substituent, each substituent may be the same as or different from one or more of the remaining substituents.

[039] According to another non-limiting embodiment, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof may be $-C(=O)R^1$, and R^1 may represent acylamino, acyloxy, a substituted or unsubstituted C_1 - C_{20} alkyl, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, amino, dialkyl amino, diaryl amino, a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heterocyclic group, halogen, hydrogen, hydroxy, oxygen, a polyol residue, a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, a reactive substituent or a photochromic material.

[040] Further, the photochromic materials comprising a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position according to various non-limiting embodiments disclosed herein may further comprise another photochromic material that is linked, directly or indirectly, to the group that extends the pi-conjugated system or another position on the photochromic material. For example, although not limiting herein, as shown in Fig. 2a, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof may be represented by $-X=Y$, wherein X represents $-CR^1$ and Y represents O (i.e., $-C(=O)R^1$), wherein R^1 represents a heterocyclic group (e.g., a piperazino group as shown in Fig. 2a) that is substituted with a photochromic material (e.g., a 3,3-diphenyl-6,11-dimethoxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran as shown in Fig. 2a). According to another non-limiting embodiment shown in Fig. 2b, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof may be represented by $-X=Y$, wherein X represents $-CR^1$ and Y represents O (i.e., $-C(=O)R^1$), wherein R^1 represents an oxyalkoxy (e.g., an oxyethoxy as shown in Fig. 2b) that is substituted with a photochromic material (e.g., a 3,3-diphenyl-6,11-dimethoxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran as shown in Fig. 2b).

[041] Although not limiting herein, according to various non-limiting embodiments wherein the photochromic material comprising the group that extends the pi-conjugated system bonded at the 11-position thereof comprises an additional photochromic material that is linked thereto, the additional photochromic material may be linked to the photochromic material comprising the group that extends the pi-conjugated system bonded at the 11-position thereof by an insulating group. As used herein, the term “insulating group” means a group having at least two consecutive sigma (σ) bonds that separate the pi-conjugated systems of the photochromic materials. For example, and without limitation herein, as shown in Figs. 2a and 2b, the additional photochromic material may be linked to the photochromic material comprising the group that extends the pi-conjugated system bonded at the 11-position thereof by one or more insulating group(s). Specifically, although not limiting herein, as shown in Fig. 2a, the insulating group may be the alkyl portion of a piperazino group, and, as shown in Fig. 2b, the insulating group may be the alkyl portion of an oxyalkoxy group.

[042] Still further, and as discussed in more detail below, according to various non-limiting embodiments, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position may comprise a reactive substituent or a compatibilizing substituent. As used herein the term “reactive substituent” means an arrangement of atoms, wherein a portion of the arrangement comprises a reactive moiety or a residue thereof. As used herein, the term “moiety” means a part or portion of an organic molecule that has a characteristic chemical property. As used herein, the term “reactive moiety” means a part or portion of an organic molecule that may react to form one or more covalent bond(s) with an intermediate in a polymerization reaction, or with a polymer into which it has been incorporated. As used herein the term “intermediate in a polymerization reaction” means any combination of two or more monomer units that are capable of reacting to form one or more bond(s) to additional monomer unit(s) to continue a polymerization reaction or, alternatively, reacting with a reactive moiety of the reactive substituent on the photochromic material. For example, although not

limiting herein, the reactive moiety may react with an intermediate in a polymerization reaction of a monomer or oligomer as a co-monomer in the polymerization reaction or may react as, for example and without limitation, a nucleophile or electrophile, that adds into the intermediate. Alternatively, the reactive moiety may react with a group (such as, but not limited to a hydroxyl group) on a polymer.

[043] As used herein the term “residue of a reactive moiety” means that which remains after a reactive moiety has been reacted with a protecting group or an intermediate in a polymerization reaction. As used herein the term “protecting group” means a group that is removably bonded to a reactive moiety that prevents the reactive moiety from participating in a reaction until the group is removed. Optionally, the reactive substituents according to various non-limiting embodiments disclosed herein may further comprise a linking group. As used herein the term “linking group” means one or more group(s) or chain(s) of atoms that connect the reactive moiety to the photochromic material.

[044] As used herein the term “compatibilizing substituent” means an arrangement of atoms that can facilitate integration of the photochromic material into another material or solvent. For example, according to various non-limiting embodiments disclosed herein, the compatibilizing substituent may facilitate integration of the photochromic material into a hydrophilic material by increasing the miscibility of the photochromic material in water or a hydrophilic polymeric, oligomeric, or monomeric material. According to other non-limiting embodiments, the compatibilizing substituent may facilitate integration of the photochromic material into a lipophilic material. Although not limiting herein, photochromic materials according to various non-limiting embodiments disclosed herein that comprise a compatibilizing substituent that facilitates integration into a hydrophilic material may be miscible in hydrophilic material at least to the extent of one gram per liter. Non-limiting examples of compatibilizing substituents include those substituents comprising the group $-J$, where $-J$ represents the group $-K$ or hydrogen, which are discussed herein below. When the ophthalmic device of the present invention is

formed from a hydrogel, non-limiting examples of suitable compatibilizing groups include, but are not limited to $-\text{SO}_3^-$, $-\text{Cl}$, $-\text{OH}$, aniline groups, morpholino groups and combinations thereof, which may be in any position, so long as the Pi conjugated system of the indeno-fused naphthopyran bonded at the 11 position is retained.

[045] Further, it should be appreciated that some substituents may be both compatibilizing and reactive. For example, a substituent that comprises hydrophilic linking group(s) that connects a reactive moiety to the photochromic material may be both a reactive substituent and a compatibilizing substituent. As used herein, such substituents may be termed as either a reactive substituent or a compatibilizing substituent. It should also be appreciated that the photochromic material may contain a plurality of reactive substituents, compatibilizing substituents or both.

[046] As discussed above, various non-limiting embodiments disclosed herein relate to photochromic materials comprising an indeno-fused naphthopyran and a group that extends the pi -conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof, provided that if the group bonded at the 11-position of the indeno-fused naphthopyran together with a group bonded at the 10-position or 12-position of the indeno-fused naphthopyran forms a fused group, said fused group is not a benzo-fused group; and wherein the 13-position of the indeno-fused naphthopyran is unsubstituted, mono-substituted or di-substituted, provided that if the 13-position of the indeno-fused naphthopyran is di-substituted, the substituent groups do not together form norbornyl. Further, according to other non-limiting embodiments, the indeno-fused naphthopyran may be free of spiro-cyclic groups at the 13-position of the indeno-fused naphthopyran. As used herein the phrase "free of spiro-cyclic groups at the 13-position" means that if the 13-position of the indeno-fused naphthopyran is di-substituted, the substituent groups do not together form a spiro-cyclic group. Non-limiting examples of suitable groups that may be bonded at the 13-position are set forth with respect to R^7 and R^8 in (XIV) and (XV) herein below.

[047] Further, various non-limiting embodiments disclosed herein relate to photochromic materials comprising an indeno-fused naphthopyran and a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof (as discussed above), wherein the indeno-fused naphthopyran is an indeno[2',3':3,4]naphtho[1,2-b]pyran, and wherein the 6-position and/or the 7-position of the indeno-fused naphthopyran may each independently be substituted with a nitrogen containing group or an oxygen containing group; and the 13-position of the indeno-fused naphthopyran may be di-substituted. Non-limiting examples of substituents that may be bonded at the 13-position according to this non-limiting embodiment include hydrogen, C₁-C₆ alkyl, C₃-C₇ cycloalkyl, allyl, a substituted or unsubstituted phenyl, a substituted or unsubstituted benzyl, a substituted or unsubstituted amino and -C(O)R³⁰. Non-limiting examples of groups that R³⁰ may represent include hydrogen, hydroxy, C₁-C₆ alkyl, C₁-C₆ alkoxy, the unsubstituted, mono- or di-substituted aryl groups phenyl or naphthyl, phenoxy, mono- or di-(C₁-C₆) alkyl substituted phenoxy or mono- and di-(C₁-C₆)alkoxy substituted phenoxy. Suitable non-limiting examples of nitrogen containing groups and oxygen containing groups that may be present at the 6-position and/or the 7-position of the indeno-fused naphthopyran according to these and other non-limiting embodiments disclosed herein include those that are set forth with respect to R⁶ in (XIV) and (XV) herein below.

[048] Other non-limiting embodiments disclosed herein relate to photochromic materials comprising an indeno-fused naphthopyran, wherein the 13-position of the indeno-fused naphthopyran is unsubstituted, mono-substituted or di-substituted, provided that if the 13-position of the indeno-fused naphthopyran is di-substituted, the substituent groups do not together form norbornyl, and wherein the photochromic material has an integrated extinction coefficient greater than $1.0 \times 10^6 \text{ nm} \times \text{mol}^{-1} \times \text{cm}^{-1}$ as determined by integration of a plot of extinction coefficient of the photochromic material vs. wavelength over a range of wavelengths ranging from 320 nm to 420 nm, inclusive. Further, according to these non-limiting embodiments the integrated extinction coefficient may range from 1.1×10^6 to $4.0 \times 10^6 \text{ nm} \times \text{mol}^{-1}$

$^1 \times \text{cm}^{-1}$ as determined by integration of a plot of extinction coefficient of the photochromic material vs. wavelength over a range of wavelengths ranging from 320 nm to 420 nm, inclusive. Still further, the photochromic materials according to these non-limiting embodiments may comprise a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof. Non-limiting examples of groups bonded at the 11-position of the indeno-fused naphthopyran that extend the pi-conjugated system of the indeno-fused naphthopyran include those discussed above.

[049] One specific non-limiting embodiment disclosed herein provides a photochromic material comprising: (i) an indeno-fused naphthopyran chosen from an indeno[2',3':3,4]naphtho[1,2-b]pyran and an indeno[1',2':4,3]naphtho[2,1-b]pyran, and mixtures thereof, wherein the 13-position of the indeno-fused naphthopyran is unsubstituted, mono-substituted or di-substituted, provided that if the 13-position of the indeno-fused naphthopyran is di-substituted, the substituent groups do not together form norbornyl; and (ii) a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof, wherein said group may be a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, or a group represented by $-X=Y$ or $-X' \equiv Y'$. Non-limiting examples of groups that X, X', Y and Y' may represent are as set forth above.

[050] Alternatively, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position of the indeno-fused naphthopyran together with a group bonded at the 12-position of the indeno-fused naphthopyran or together with a group bonded at the 10-position of the indeno-fused naphthopyran form a fused group, said fused group being indeno, dihydronaphthalene, indole, benzofuran, benzopyran or thianaphthene. Further, according to this non-limiting embodiment, the indeno-fused naphthopyran may be free of spiro-cyclic groups at the 13-position thereof.

[051] As previously discussed, the photochromic materials according to various non-limiting embodiments disclosed herein may comprise at least one of a reactive

substituent and/or a compatibilizing substituent. Further, according to various non-limiting embodiments disclosed herein wherein the photochromic material comprises multiple reactive substituents and/or multiple compatibilizing substituents, each reactive substituent and each compatibilizing substituent may be independently chosen. Non-limiting examples of reactive and/or compatibilizing substituents that may be used in conjunction with the various non-limiting embodiments disclosed herein may be represented by one of:

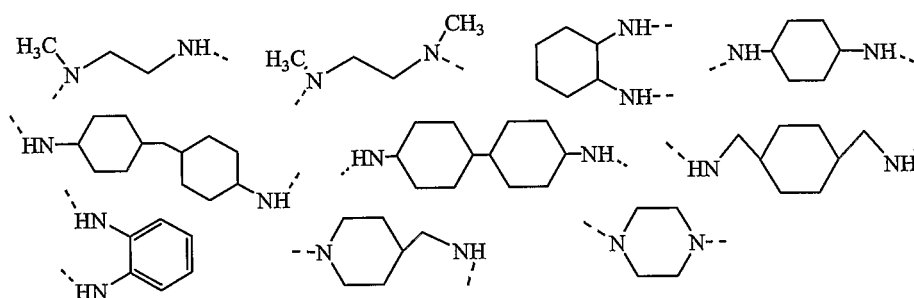
-A'-D-E-G-J (V);	-G-E-G-J (VI);	-D-E-G-J (VII);
-A'-D-J (VIII);	-D-G-J (IX);	-D-J (X);
-A'-G-J (XI);	-G-J (XII); and	-A'-J (XIII).

[052] With reference to (V)-(XIII) above, non-limiting examples of groups that -A'- may represent according to various non-limiting embodiments disclosed herein include -O-, -C(=O)-, -CH₂-, -OC(=O)- and -NHC(=O)-, provided that if -A'- represents -O-, -A'- forms at least one bond with -J.

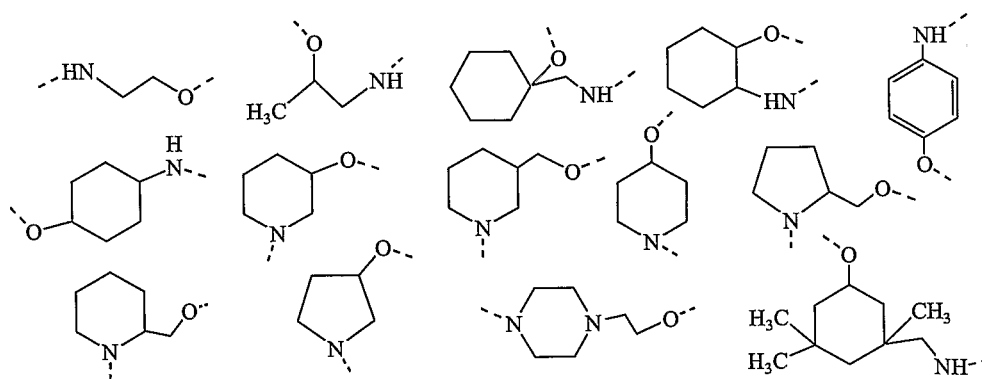
[053] Non-limiting examples of groups that -D- may represent according to various non-limiting embodiments include a diamine residue or a derivative thereof, wherein a first amino nitrogen of said diamine residue may form a bond with -A'-, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof, or a substituent or an available position on the indeno-fused naphthopyran, and a second amino nitrogen of said diamine residue may form a bond with -E-, -G- or -J; and an amino alcohol residue or a derivative thereof, wherein an amino nitrogen of said amino alcohol residue may form a bond with -A'-, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof, or a substituent or an available position on the indeno-fused naphthopyran, and an alcohol oxygen of said amino alcohol residue may form a bond with -E-, -G- or -J. Alternatively, according to various non-limiting embodiments disclosed herein the amino nitrogen of said amino alcohol residue may form a bond with -E-, -G- or -J, and said alcohol oxygen of said amino alcohol residue may form a bond with -A'-, the group that extends the pi-conjugated

system of the indeno-fused naphthopyran bonded at the 11-position thereof, or a substituent or an available position on the indeno-fused naphthopyran.

[054] Non-limiting examples of suitable diamine residues that -D- may represent include an aliphatic diamine residue, a cyclo aliphatic diamine residue, a diazacycloalkane residue, an azacyclo aliphatic amine residue, a diazacrown ether residue, and an aromatic diamine residue. Specific non-limiting examples diamine residues that may be used in conjunction with various non-limiting embodiments disclosed herein include the following:

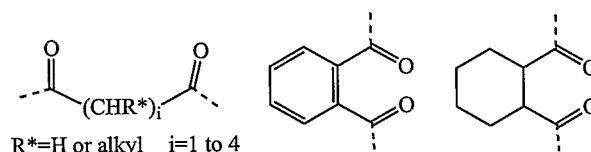


[055] Non-limiting examples of suitable amino alcohol residues that -D- may represent include an aliphatic amino alcohol residue, a cyclo aliphatic amino alcohol residue, an azacyclo aliphatic alcohol residue, a diazacyclo aliphatic alcohol residue and an aromatic amino alcohol residue. Specific non-limiting examples amino alcohol residues that may be used in conjunction with various non-limiting embodiments disclosed herein include the following:



[056] With continued reference to (V)-(XIII) above, according to various non-limiting embodiments disclosed herein, -E- may represent a dicarboxylic acid residue or a derivative thereof, wherein a first carbonyl group of said dicarboxylic

acid residue may form a bond with -G- or -D-, and a second carbonyl group of said dicarboxylic acid residue may form a bond with -G-. Non-limiting examples of suitable dicarboxylic acid residues that -E- may represent include an aliphatic dicarboxylic acid residue, a cycloaliphatic dicarboxylic acid residue and an aromatic dicarboxylic acid residue. Specific non-limiting examples of dicarboxylic acid residues that may be used in conjunction with various non-limiting embodiments disclosed herein include the following:



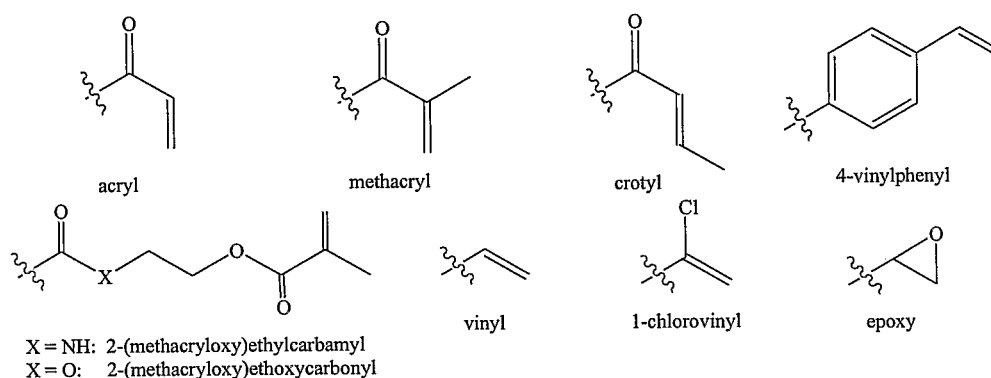
[057] According to various non-limiting embodiments disclosed herein, -G- may represent a group $-\text{[(OC}_2\text{H}_4)_x(\text{OC}_3\text{H}_6)_y(\text{OC}_4\text{H}_8)_z]-\text{O}-$, wherein x, y and z are each independently chosen and range from 0 to 50, and a sum of x, y, and z ranges from 1 to 50; a polyol residue or a derivative thereof, wherein a first polyol oxygen of said polyol residue may form a bond with -A'-, -D-, -E-, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof, or a substituent or an available position on the indeno-fused naphthopyran, and a second polyol oxygen of said polyol may form a bond with -E- or -J; or a combination thereof, wherein the first polyol oxygen of the polyol residue forms a bond with a group $-\text{[(OC}_2\text{H}_4)_x(\text{OC}_3\text{H}_6)_y(\text{OC}_4\text{H}_8)_z]-$ (i.e., to form the group $-\text{[(OC}_2\text{H}_4)_x(\text{OC}_3\text{H}_6)_y(\text{OC}_4\text{H}_8)_z]-\text{O}-$), and the second polyol oxygen forms a bond with -E- or -J. Non-limiting examples of suitable polyol residues that -G- may represent include an aliphatic polyol residue, a cyclo aliphatic polyol residue, and an aromatic polyol residue.

[058] Specific non-limiting examples of polyols from which the polyol residues that -G- may represent may be formed according to various non-limiting embodiments disclosed herein include (a) low molecular weight polyols having an average molecular weight less than 500, such as, but not limited to, those set forth in U.S. Patent No. 6,555,028 at col. 4, lines 48-50, and col. 4, line 55 to col. 6, line 5, which disclosure is hereby specifically incorporated by reference herein; (b)

polyester polyols, such as, but not limited to, those set forth in U.S. Patent No. 6,555,028 at col. 5, lines 7-33, which disclosure is hereby specifically incorporated by reference herein; (c) polyether polyols, such as but not limited to those set forth in U.S. Patent No. 6,555,028 at col. 5, lines 34-50, which disclosure is hereby specifically incorporated by reference herein; (d) amide-containing polyols, such as, but not limited to, those set forth in U.S. Patent No. 6,555,028 at col. 5, lines 51-62, which disclosure is hereby specifically incorporated by reference; (e) epoxy polyols, such as, but not limited to, those set forth in U.S. Patent No. 6,555,028 at col. 5 line 63 to col. 6, line 3, which disclosure is hereby specifically incorporated by reference herein; (f) polyhydric polyvinyl alcohols, such as, but not limited to, those set forth in U.S. Patent No. 6,555,028 at col. 6, lines 4-12, which disclosure is hereby specifically incorporated by reference herein; (g) urethane polyols, such as, but not limited to those set forth in U.S. Patent No. 6,555,028 at col. 6, lines 13-43, which disclosure is hereby specifically incorporated by reference herein; (h) polyacrylic polyols, such as, but not limited to those set forth in U.S. Patent No. 6,555,028 at col. 6, lines 43 to col. 7, line 40, which disclosure is hereby specifically incorporated by reference herein; (i) polycarbonate polyols, such as, but not limited to, those set forth in U.S. Patent No. 6,555,028 at col. 7, lines 41-55, which disclosure is hereby specifically incorporated by reference herein; and (j) mixtures of such polyols.

[059] Referring again to (V)-(XIII) above, according to various non-limiting embodiments disclosed herein, -J may represent a group -K, wherein -K represents a group such as, but not limited to, $-\text{CH}_2\text{COOH}$, $-\text{CH}(\text{CH}_3)\text{COOH}$, $-\text{C}(\text{O})(\text{CH}_2)_w\text{COOH}$, $-\text{C}_6\text{H}_4\text{SO}_3\text{H}$, $-\text{C}_5\text{H}_{10}\text{SO}_3\text{H}$, $-\text{C}_4\text{H}_8\text{SO}_3\text{H}$, $-\text{C}_3\text{H}_6\text{SO}_3\text{H}$, $-\text{C}_2\text{H}_4\text{SO}_3\text{H}$ and $-\text{SO}_3\text{H}$ wherein "w" ranges from 1 to 18. According to other non-limiting embodiments -J may represent hydrogen that forms a bond with an oxygen or a nitrogen of linking group to form a reactive moiety such as $-\text{OH}$ or $-\text{NH}$. For example, according to various non-limiting embodiments disclosed herein, -J may represent hydrogen, provided that if -J represents hydrogen, -J is bonded to an oxygen of -D- or -G-, or a nitrogen of -D-.

[060] According to still other non-limiting embodiments, -J may represent a group -L or residue thereof, wherein -L may represent a reactive moiety. For example, according to various non-limiting embodiments disclosed herein -L may represent a group such as, but not limited to, acryl, methacryl, crotyl, 2-(methacryloxy)ethylcarbamyl, 2-(methacryloxy)ethoxycarbonyl, 4-vinylphenyl, vinyl, 1-chlorovinyl or epoxy. As used herein, the terms acryl, methacryl, crotyl, 2-(methacryloxy)ethylcarbamyl, 2-(methacryloxy)ethoxycarbonyl, 4-vinylphenyl, vinyl, 1-chlorovinyl, and epoxy refer to the following structures:



[061] As previously discussed, -G- may represent a residue of a polyol, which is defined herein to include hydroxy-containing carbohydrates, such as those set forth in U.S. Patent No. 6,555,028 at col. 7, line 56 to col. 8, line 17, which disclosure is hereby specifically incorporated by reference herein. The polyol residue may be formed, for example and without limitation herein, by the reaction of one or more of the polyol hydroxyl groups with a precursor of -A'-, such as a carboxylic acid or a methylene halide, a precursor of polyalkoxylated group, such as polyalkylene glycol, or a hydroxyl substituent of the indeno-fused naphthopyran. The polyol may be represented by $q-(OH)_a$ and the residue of the polyol may be represented by the formula $-O-q-(OH)_{a-1}$, wherein q is the backbone or main chain of the polyhydroxy compound and "a" is at least 2.

[062] Further, as discussed above, one or more of the polyol oxygens of -G- may form a bond with -J (i.e., forming the group -G-J). For example, although not limiting herein, wherein the reactive and/or compatibilizing substituent comprises the group -G-J, if -G- represents a polyol residue and -J represents a group -K that

contains a carboxyl terminating group, -G-J may be produced by reacting one or more polyol hydroxyl groups to form the group -K (for example as discussed with respect to Reactions B and C at col. 13, line 22 to col. 16, line 15 of U.S. Patent No. 6,555,028, which disclosure is hereby specifically incorporated by reference herein) to produce a carboxylated polyol residue. Alternatively, if -J represents a group -K that contains a sulfo or sulfono terminating group, although not limiting herein, -G-J may be produced by acidic condensation of one or more of the polyol hydroxyl groups with $\text{HOC}_6\text{H}_4\text{SO}_3\text{H}$; $\text{HOC}_5\text{H}_{10}\text{SO}_3\text{H}$; $\text{HOC}_4\text{H}_8\text{SO}_3\text{H}$; $\text{HOC}_3\text{H}_6\text{SO}_3\text{H}$; $\text{HOC}_2\text{H}_4\text{SO}_3\text{H}$; or H_2SO_4 , respectively. Further, although not limiting herein, if -G- represents a polyol residue and -J represents a group -L chosen from acryl, methacryl, 2-(methacryloxy)ethylcarbamyl and epoxy, -L may be added by condensation of the polyol residue with acryloyl chloride, methacryloyl chloride, 2-isocyanatoethyl methacrylate or epichlorohydrin, respectively.

[063] As discussed above, according to various non-limiting embodiments disclosed herein, a reactive substituent and/or a compatibilizing substituent may be bonded to group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position of the indeno-fused naphthopyran. For example, as discussed above, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof may be an aryl or heteroaryl that is substituted with the reactive and/or compatibilizing substituent, or may be a group represented by $-\text{X}=\text{Y}$ or $-\text{X}'\equiv\text{Y}'$, wherein the groups X, X', Y and Y' may comprise the reactive and/or compatibilizing substituent as discussed above. For example, according to one non-limiting embodiment as shown in Fig. 3a, the group that extends the pi-conjugated system may be an aryl group (e.g., a phenyl group as shown in Fig. 3a) that is substituted with a reactive substituent (e.g., a (2-methacryloxyethoxy)carbonyl as shown in Fig. 3a), which may be represented by $-\text{A}'-\text{G}-\text{J}$ (as discussed above), wherein $-\text{A}'-$ represents $-\text{C}(=\text{O})-$, -G- represents $-\text{[OC}_2\text{H}_4\text{]O}-$, and -J represents methacryl.

[064] Additionally or alternatively, a reactive and/or compatibilizing substituent may be bonded at a substituent or an available position on the indeno-fused

naphthopyran ring other than at the 11-position. For example, although not limiting herein, in addition to or instead of having a reactive and/or compatibilizing substituent bonded to the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position of the indeno-fused naphthopyran, the 13-position of the indeno-fused naphthopyran may be mono- or di-substituted with a reactive and/or compatibilizing substituent. Further, if the 13-position is di-substituted, each substituent may be the same or different. In another non-limiting example, in addition to or instead of having a reactive and/or compatibilizing substituent bonded to the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position of the indeno-fused naphthopyran, a reactive and/or compatibilizing substituent may be substituted at the 3-position of an indeno[2',3':3,4]naphtho[1,2-b]pyran, the 2-position of an indeno[1',2':4,3]naphtho[2,1-b]pyran, and /or the 6- or 7- positions of these indeno-fused naphthopyrans. Further, if the photochromic material comprises more than one reactive and/or compatibilizing substituent, each reactive and/or compatibilizing substituent may be the same as or different from one or more of the remaining reactive and/or compatibilizing substituents.

[065] For example, referring now to Fig. 3b, according to one non-limiting embodiment, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof is a substituted aryl group (e.g., a (4-phenyl)-phenyl group as shown in Fig. 3b), and the photochromic material further comprises a reactive substituent (e.g., a 3-(2-methacryloxyethyl)carbamyloxymethylenepiperidino-1-yl) group as shown in Fig. 3b), which may be represented by -D-J (as discussed above), wherein -D- represents an azacyclo aliphatic alcohol residue, wherein the nitrogen of the azacyclo aliphatic alcohol residue forms a bond with the indeno-fused naphthopyran at the 7-position, and the alcohol oxygen of the azacyclo aliphatic alcohol residue forms a bond with -J, wherein -J represents 2-(methacryloxy)ethylcarbamyl. Another non-limiting example of a photochromic material according to various non-limiting embodiments disclosed herein that has a reactive substituent at the 7-position thereof is a 3-(4-

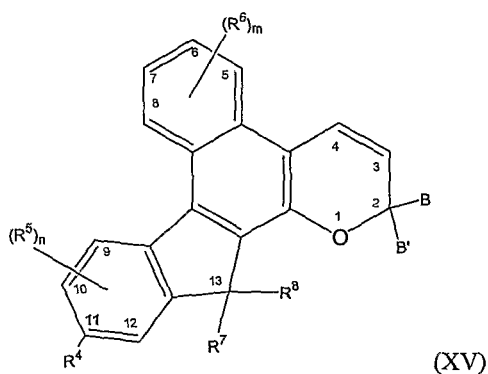
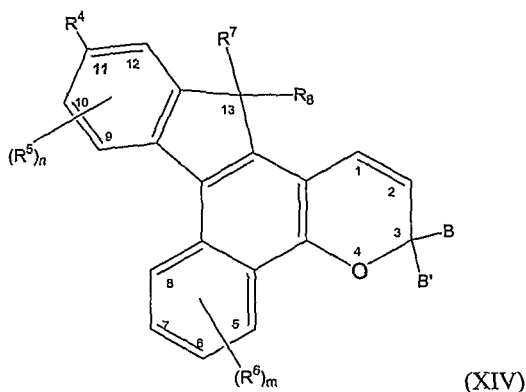
morpholinophenyl)-3-phenyl-6-methoxy-7-(3-(2-methacryloxyethyl)carbamylloxymethylenepiperidino-1-yl)-11-phenyl-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

[066] One non-limiting example of a photochromic material according to various non-limiting embodiments disclosed herein that has a reactive substituent at the 3-position thereof is a 3-(4-(2-(2-methacryloxyethyl)carbamylethoxy) phenyl)-3-phenyl-6,7-dimethoxy-11-phenyl-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

[067] Additional description of reactive substituents that may be used in connection with the photochromic materials described herein is set forth in U.S. Patent Application No. 11/_____, entitled OPHTHALMIC DEVICES COMPRISING PHOTOCHROMIC MATERIALS WITH REACTIVE SUBSTITUENTS, filed on a date even herewith, which lists Wenjing Xiao, Barry Van Gemert, Shivkumar Mahadevan and Frank Molock as inventors.

[068] which are hereby specifically incorporated by reference herein. Still other non-limiting examples of reactive and/or compatibilizing substituents are set forth in U.S. Patent No. 6,555,028, at col. 3, line 45 to col. 4, line 26, and U.S. Patent No. 6,113,814 at col. 3, lines 30-64, which disclosures are hereby specifically incorporated by reference herein.

[069] Other non-limiting embodiments disclosed herein provide a photochromic material represented by (XIV), (XV) (shown below) or a mixture thereof.



[070] With reference to (XIV) and (XV) above, according to various non-limiting embodiments disclosed herein R^4 may represent a substituted or unsubstituted aryl; a substituted or unsubstituted heteroaryl; or a group represented by $-X=Y$ or $-X'\equiv Y'$. Non-limiting examples of groups that X, X', Y and Y' may represent are set forth above. Suitable non-limiting examples of aryl and heteroaryl substituents are set forth above in detail.

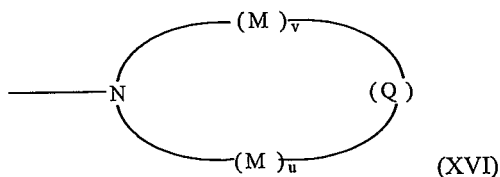
[071] Alternatively, according to various non-limiting embodiments disclosed herein, the group represented by R^4 together with a group represented by an R^5 bonded at the 12-position of the indeno-fused naphthopyran or together with a group represented by an R^5 group bonded at the 10-position of the indeno-fused naphthopyran may form a fused group. Examples of suitable fused groups include, without limitation, indeno, dihydronaphthalene, indole, benzofuran, benzopyran and thianaphthlene.

[072] With continued reference to (XIV) and (XV), according to various non-limiting embodiments disclosed herein, "n" may range from 0 to 3, and "m" may

range from 0 to 4. According to various non-limiting embodiments disclosed herein, where n is at least one and/or m is at least one, the groups represented by each R⁵ and/or each R⁶ may be independently chosen. Non-limiting examples of groups that R⁵ and/or R⁶ may represent include a reactive substituent; a compatibilizing substituent; hydrogen; C₁-C₆ alkyl; chloro; fluoro; C₃-C₇ cycloalkyl; a substituted or unsubstituted phenyl, said phenyl substituents being C₁-C₆ alkyl or C₁-C₆; -OR¹⁰ or -OC(=O)R¹⁰, wherein R¹⁰ may represent a group such as, but not limited to, S, hydrogen, amine, 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, (C₁-C₆)alkoxy(C₂-C₄)alkyl, C₃-C₇ cycloalkyl and mono(C₁-C₄)alkyl substituted C₃-C₇ cycloalkyl, a mono-substituted phenyl, said phenyl having a substituent located at the para position, the substituent being a dicarboxylic acid residue or derivative thereof, a diamine residue or derivative thereof, an amino alcohol residue or derivative thereof, a polyol residue or derivative thereof, -(CH₂)_t-, -(CH₂)_t- or -[O-(CH₂)_t]_k-, wherein "t" may range from 2 to 6, and "k" may range from 1 to 50, and wherein the substituent may be connected to an aryl group on another photochromic material; and a nitrogen-containing group.

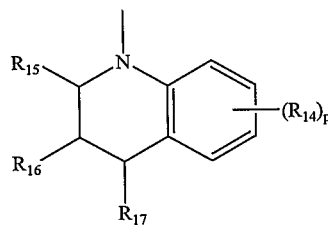
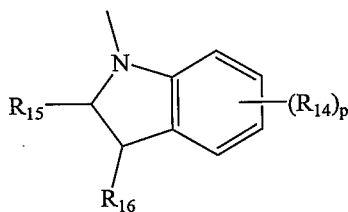
[073] Non-limiting examples of nitrogen-containing groups that R⁵ and/or R⁶ may represent include -N(R¹¹)R¹², wherein the groups represented by R¹¹ and R¹² may be the same or different. Examples of groups that R¹¹ and R¹² may represent according to various non-limiting embodiments disclosed herein include, without limitation, hydrogen, C₁-C₈ alkyl, phenyl, naphthyl, furanyl, benzofuran-2-yl, benzofuran-3-yl, thienyl, benzothien-2-yl, benzothien-3-yl, dibenzofuranyl, dibenzothienyl, benzopyridyl, fluorenyl, C₁-C₈ alkylaryl, C₃-C₂₀ cycloalkyl, C₄-C₂₀ bicycloalkyl, C₅-C₂₀ tricycloalkyl and C₁-C₂₀ alkoxyalkyl. Alternatively, according to various non-limiting embodiments, R¹¹ and R¹² may represent groups that come together with the nitrogen atom to form a C₃-C₂₀ hetero-bicycloalkyl ring or a C₄-C₂₀ hetero-tricycloalkyl ring.

[074] Other non-limiting examples of a nitrogen containing groups that R⁵ and/or R⁶ may represent include nitrogen containing rings represented by (XVI) below.



[075] With reference to (XVI), non-limiting examples of groups that -M- may represent according to various non-limiting embodiments disclosed herein include -CH₂-, -CH(R¹³)-, -C(R¹³)₂-, -CH(aryl)-, -C(aryl)₂- and -C(R¹³)(aryl)-. Non-limiting examples of groups that -Q- may represent according to various non-limiting embodiments disclosed herein include those discussed above for -M-, -O-, -S-, -S(O)-, -SO₂-, -NH-, -N(R¹³)- and -N(aryl). According to various non-limiting embodiments disclosed herein, each R¹³ may independently represent C₁-C₆ alkyl, and the group designated “(aryl)” may independently represent phenyl or naphthyl. Further, according to various non-limiting embodiments disclosed herein, “u” may range from 1 to 3 and “v” may range from 0 to 3, provided that if v is 0, -Q- represents a group discussed above with respect to -M-.

[076] Still other non-limiting examples of a suitable nitrogen containing groups that R⁵ and/or R⁶ may represent include groups represented by (XVIIA) or (XVIIB) below.

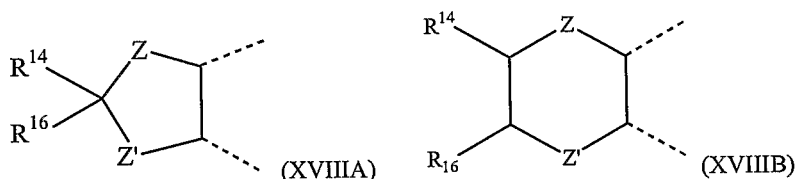


[077] According to various non-limiting embodiments disclosed herein, the groups represented by R¹⁵, R¹⁶ and R¹⁷ respectively in (XVIIA) and (XVIIB) above may be the same as or different from each one another. Non-limiting examples of groups that R¹⁵, R¹⁶ and R¹⁷ may independently represent according to various non-limiting embodiments disclosed herein include hydrogen, C₁-C₆ alkyl, phenyl, and naphthyl. Alternatively, according to various non-limiting embodiments, R¹⁵ and R¹⁶ may represent groups that together form a ring of 5 to 8 carbon atoms. Further, according

to various non-limiting embodiments disclosed herein, "p" may range from 0 to 3, and if p is greater than one, each group represented by R^{14} may be the same as or different from one or more other R^{14} groups. Non-limiting examples of groups that R^{14} may represent according to various non-limiting embodiments disclosed herein include C_1 - C_6 alkyl, C_1 - C_6 alkoxy, fluoro, and chloro.

[078] Yet other non-limiting examples of a nitrogen containing groups that R^5 and/or R^6 may represent include substituted or unsubstituted C_4 - C_{18} spirobicyclic amines and substituted or unsubstituted C_4 - C_{18} spirotricyclic amines. Non-limiting examples of spirobicyclic and spirotricyclic amine substituents include aryl, C_1 - C_6 alkyl, C_1 - C_6 alkoxy or phenyl(C_1 - C_6)alkyl.

[079] Alternatively, according to various non-limiting embodiments disclosed herein, a group represented by an R^6 in the 6-position and a group represented by an R^6 in the 7-position may together form a group represented by (XVIII A) or (XVIII B) below.



[080] In (XVIII A) or (XVIII B), the groups Z and Z' may be the same as or different from each other. Non-limiting examples of groups that Z and Z' may represent according to various non-limiting embodiments disclosed herein include oxygen and $-NR^{11}-$. Non-limiting examples of groups that R^{11} , R^{14} and R^{16} may represent according to various non-limiting embodiments disclosed herein include those discussed above.

[081] Referring again to (XIV) and (XV), according to various non-limiting embodiments disclosed herein the groups represented by R^7 and R^8 , respectively, may be the same or different. Non-limiting examples of groups that R^7 and R^8 may represent according to various non-limiting embodiments disclosed herein include a reactive substituent; a compatibilizing substituent; hydrogen; hydroxy; C_1 - C_6 alkyl; C_3 - C_7 cycloalkyl; allyl; a substituted or unsubstituted phenyl or benzyl, wherein each of said phenyl and benzyl group substituents is independently C_1 - C_6 alkyl or

C₁-C₆ alkoxy; chloro; fluoro; a substituted or unsubstituted amino; -C(O)R⁹, wherein R⁹ may represent groups such as, but not limited to, hydrogen, hydroxy, C₁-C₆ alkyl, C₁-C₆ alkoxy, the unsubstituted, mono- or di-substituted phenyl or naphthyl wherein each of said substituents is independently C₁-C₆ alkyl or C₁-C₆ alkoxy, phenoxy, mono- or di-(C₁-C₆)alkylsubstituted phenoxy, mono- or di-(C₁-C₆)alkoxy substituted phenoxy, amino, mono- or di-(C₁-C₆)alkylamino, phenylamino, mono- or di-(C₁-C₆)alkyl substituted phenylamino and mono- or di-(C₁-C₆)alkoxy substituted phenylamino; -OR¹⁸, wherein R¹⁸ may represent groups such as, but not limited to, 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, C₁-C₆ alkoxy(C₂-C₄)alkyl, C₃-C₇ cycloalkyl, mono(C₁-C₄)alkyl substituted C₃-C₇ cycloalkyl, C₁-C₆ chloroalkyl, C₁-C₆ fluoroalkyl, allyl and -CH(R¹⁹)T, wherein R¹⁹ may represent hydrogen or C₁-C₃ alkyl, T may represent CN, CF₃ or COOR²⁰, wherein R²⁰ may represent hydrogen or C₁-C₃ alkyl, or wherein R¹⁸ may be represented by -C(=O)U, wherein U may represents groups such as, but not limited to, hydrogen, C₁-C₆ alkyl, C₁-C₆ alkoxy, an unsubstituted, mono- or di-substituted phenyl or naphthyl wherein each of said substituents is independently C₁-C₆ alkyl or C₁-C₆ alkoxy, phenoxy, mono- or di-(C₁-C₆)alkyl substituted phenoxy, mono- or di-(C₁-C₆)alkoxy substituted phenoxy, amino, mono- or di-(C₁-C₆)alkylamino, phenylamino, mono- or di-(C₁-C₆)alkyl substituted phenylamino or mono- and di-(C₁-C₆)alkoxy substituted phenylamino; and a mono-substituted phenyl, said phenyl having a substituent located at the para position, the substituent being a dicarboxylic acid residue or derivative thereof, a diamine residue or derivative thereof, an amino alcohol residue or derivative thereof, a polyol residue or derivative thereof, -(CH₂)_t-, -(CH₂)_t- or -[O-(CH₂)_t]_k-, wherein "t" may range from 2 to 6 and "k" may range from 1 to 50, and wherein the substituent may be connected to an aryl group on another photochromic material.

[082] Alternatively, R⁷ and R⁸ may represent groups that may together form an oxo group; a spiro-carbocyclic group, containing 3 to 6 carbon atoms (provided that the spiro-carbocyclic group is not norbornyl); or a spiro-heterocyclic group containing 1 to 2 oxygen atoms and 3 to 6 carbon atoms including the spirocarbon atom. Further,

the spiro-carboxylic and spiro-heterocyclic groups may be annellated with 0, 1, or 2 benzene rings.

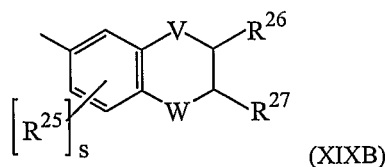
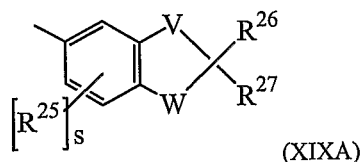
[083] Further according to various non-limiting embodiments, the groups represented by B and B' in (XIV) and (XV) may be the same or different. One non-limiting example of a group that B and/or B' may represent according to various non-limiting embodiments disclosed herein include an aryl group (for example, although not limiting herein, a phenyl group or a naphthyl group) that is mono-substituted with a reactive substituent and/or a compatibilizing substituent.

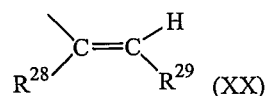
[084] Other non-limiting examples of groups that B and B' may represent according to various non-limiting embodiments disclosed herein include an unsubstituted, mono-, di- or tri-substituted aryl group (such as, but not limited to, phenyl or naphthyl); 9-julolidinyl; an unsubstituted, mono- or di-substituted heteroaromatic group chosen from pyridyl, furanyl, benzofuran-2-yl, benzofuran-3-yl, thienyl, benzothien-2-yl, benzothien-3-yl, dibenzofuranyl, dibenzothienyl, carbazoyl, benzopyridyl, indolinyl and fluorenyl. Examples of suitable aryl and heteroaromatic substituent include, without limitation, hydroxy, aryl, mono- or di-(C₁-C₁₂)alkoxyaryl, mono- or di-(C₁-C₁₂)alkylaryl, haloaryl, C₃-C₇ cycloalkylaryl, C₃-C₇ cycloalkyl, C₃-C₇ cycloalkyloxy, C₃-C₇ cycloalkyloxy(C₁-C₁₂)alkyl, C₃-C₇ cycloalkyloxy(C₁-C₁₂)alkoxy, aryl(C₁-C₁₂)alkyl, aryl(C₁-C₁₂)alkoxy, aryloxy, aryloxy(C₁-C₁₂)alkyl, aryloxy(C₁-C₁₂)alkoxy, mono- or di(C₁-C₁₂)alkylaryl(C₁-C₁₂)alkyl, mono- or di-(C₁-C₁₂)alkoxyaryl(C₁-C₁₂)alkyl, mono- or di-(C₁-C₁₂)alkylaryl(C₁-C₁₂)alkoxy, mono- or di-(C₁-C₁₂)alkoxyaryl(C₁-C₁₂)alkoxy, amino, mono- or di-(C₁-C₁₂)alkylamino, diarylamino, piperazino, N-(C₁-C₁₂)alkylpiperazino, N-aryl piperazino, aziridino, indolino, piperidino, morpholino, thiomorpholino, tetrahydroquinolino, tetrahydroisoquinolino, pyrrolidyl, C₁-C₁₂ alkyl, C₁-C₁₂ haloalkyl, C₁-C₁₂ alkoxy, mono(C₁-C₁₂)alkoxy(C₁-C₁₂)alkyl, acryloxy, methacryloxy, and halogen. Non-limiting examples of suitable halogen substituents include bromo, chloro and fluoro. Non-limiting examples of suitable aryl groups include phenyl and naphthyl.

[085] Other non-limiting examples of suitable aryl and heteroaromatic substituents include those represented by $-C(=O)R^{21}$, wherein R^{21} may represent groups such as, but not limited to, piperidino or morpholino, or R^{21} may be represented by $-OR^{22}$ or $-N(R^{23})R^{24}$, wherein R^{22} may represent groups, such as but not limited to allyl, C_1 - C_6 alkyl, phenyl, mono(C_1 - C_6)alkyl substituted phenyl, mono(C_1 - C_6)alkoxy substituted phenyl, 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 and C_1 - C_6 haloalkyl. Further, the groups represented by R^{23} and R^{24} may be the same or different and may include, without limitation C_1 - C_6 alkyl, C_5 - C_7 cycloalkyl and a substituted or unsubstituted phenyl, wherein said phenyl substituents may include C_1 - C_6 alkyl and C_1 - C_6 alkoxy. Non-limiting examples of suitable halogen substituents include bromo, chloro and fluoro.

[086] Still other non-limiting examples of groups that B and B' may represent according to various non-limiting embodiments disclosed herein include an unsubstituted or mono-substituted group chosen from pyrazolyl, imidazolyl, pyrazolinyl, imidazolinyl, pyrrolinyl, phenothiazinyl, phenoxazinyl, phenazinyl and acridinyl, wherein said substituents may be C_1 - C_{12} alkyl, C_1 - C_{12} alkoxy, phenyl or halogen; and a mono-substituted phenyl, said phenyl having a substituent located at the para position, the substituent being a dicarboxylic acid residue or derivative thereof, a diamine residue or derivative thereof, an amino alcohol residue or derivative thereof, a polyol residue or derivative thereof, $-(CH_2)_t$ -, $-(CH_2)_t$ - or $-[O-(CH_2)_t]_k$ -, wherein "t" may range from 2 to 6 and "k" may range from 1 to 50, wherein the substituent may be connected to an aryl group on another photochromic material.

[087] Yet other non-limiting examples of groups that B and B' may represent according to various non-limiting embodiments disclosed herein include groups represented by (XIXA), (XIXB) or (XX) below.





[088] With reference to (XIXA) and (XIXB) above, non-limiting examples of groups that V may represent according to various non-limiting embodiments disclosed herein include represent -CH₂- and -O-. Non-limiting examples of groups that W may represent according to various non-limiting embodiments disclosed herein include oxygen and substituted nitrogen, provided that if W is substituted nitrogen, V is -CH₂-. Suitable non-limiting examples of nitrogen substituents include hydrogen, C₁-C₁₂ alkyl and C₁-C₁₂ acyl. Further, according to various non-limiting embodiments disclosed herein, “s” may range from 0 to 2, and, if s is greater than one, each group represented by R²⁵ may be the same as or different from one or more other R²⁵ groups. Non-limiting examples of groups that R²⁵ may represent include: C₁-C₁₂ alkyl, C₁-C₁₂ alkoxy, hydroxy and halogen. Non-limiting examples of groups that R²⁶ and R²⁷ may represent according to various non-limiting embodiments disclosed herein include hydrogen and C₁-C₁₂ alkyl.

[089] With reference to (XX) above, non-limiting examples of groups that R²⁸ may represent according to various non-limiting embodiments disclosed herein include hydrogen and C₁-C₁₂ alkyl. Non-limiting examples of groups that R²⁹ may represent according to various non-limiting embodiments disclosed herein include an unsubstituted, mono- or di-substituted naphthyl, phenyl, furanyl, or thienyl, said substituents being C₁-C₁₂ alkyl, C₁-C₁₂ alkoxy or halogen.

[090] Alternatively, B and B' may represent groups that, taken together, may form a fluoren-9-ylidene or mono- or di- substituted fluoren-9-ylidene, each of said fluoren-9-ylidene substituents independently being C₁-C₁₂ alkyl, C₁-C₁₂ alkoxy or halogen.

[091] As previously discussed, the photochromic materials comprising a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof may be further linked to another photochromic material and may further comprise a reactive and/or compatibilizing substituent, such as, but not

limited to those set forth above. For example, referring again to Fig. 2a, there is shown a photochromic material according to various non-limiting embodiments disclosed herein, wherein the indeno-fused naphthopyran is an indeno[2',3':3,4]naphtho[1,2-b]pyran (for example, as represented by (XIV) above), wherein the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof (e.g., a group represented by R^4) may be represented by $-X=Y$, wherein X represents $-CR^1$ and Y is O (i.e., $-C(=O)R^1$), wherein R^1 represents a heterocyclic group (e.g., a piperazino as shown in Fig. 2a) that is substituted with a photochromic material (e.g., a 3,3-diphenyl-6,11-dimethoxy-13,13 dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran as shown in Fig. 2a). Further, although not limiting herein, as shown in Fig. 2a, the group represented by B (on the indeno-fused naphthopyran comprising the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof) may comprise a reactive substituent that may be represented by $-A'-D-J$. That is, according to this non-limiting embodiment, the group represented by B may be an aryl group (e.g., a phenyl group as shown in Fig. 2a) that is mono-substituted with a reactive substituent (e.g., (2-methacryloxyethyl)carbamyloxy as shown in Fig. 2a) that may be represented by $-A'-D-J$, wherein A' is $(-OC=O)-$, $-D-$ is the residue of an amino alcohol wherein an amino nitrogen is bonded to $-A'-$ and an alcohol oxygen is bonded to $-J$, and $-J$ is methacryl.

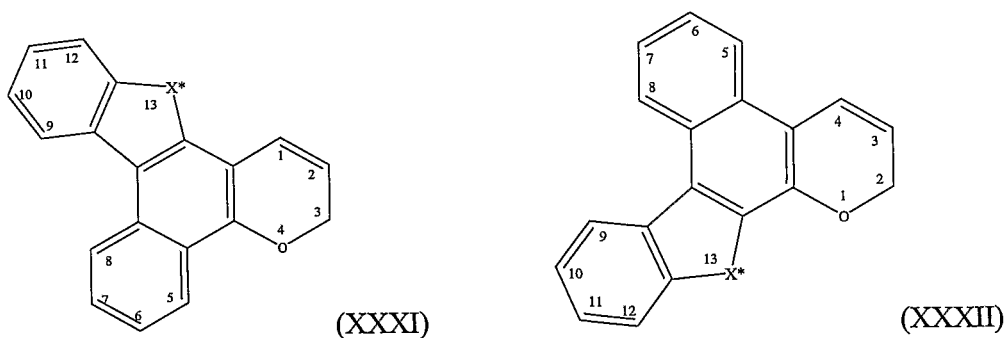
[092] According to another non-limiting embodiment wherein the photochromic material is represented by (XIV) or (XV) above, or a mixture thereof, at least one of a group represented by an R^6 at the 6-position, an R^6 group at the 7-position, B, B' , R^7 , R^8 or R^4 may comprise a reactive and/or compatibilizing substituent.

[093] According to still another non-limiting embodiment wherein the photochromic material is an [2',3':3,4]naphtho[1,2-b]pyran represented by (XIV) above, each of a group represented by an R^6 group at the 7-position and an R^6 group at the 6-position of the indeno[2',3':3,4]naphtho[1,2-b]pyran may be independently an oxygen containing group represented by $-OR^{10}$, wherein R^{10} may represent

groups including C₁-C₆ alkyl, a substituted or unsubstituted phenyl wherein said phenyl substituents may be C₁-C₆ alkyl or C₁-C₆ alkoxy, phenyl(C₁-C₃)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 and mono(C₁-C₄)alkyl substituted C₃-C₇ cycloalkyl; a nitrogen-containing group represented by -N(R¹¹)R¹², wherein R¹¹ and R¹² may represent the same or different groups, which may include, without limitation hydrogen, C₁-C₈ alkyl, C₁-C₈ alkylaryl, C₃-C₂₀ cycloalkyl, C₄-C₂₀ bicycloalkyl, C₅-C₂₀ tricycloalkyl and C₁-C₂₀ alkoxyalkyl, wherein said aryl group may be phenyl or naphthyl; the nitrogen containing ring represented by (XVI) above, wherein each -M- may represent a group such as -CH₂-, -CH(R₁₃)-, -C(R₁₃)₂-, -CH(aryl)-, -C(aryl)₂- or -C(R₁₃)(aryl)-, and -Q- may represent a group such as those set forth above for -M-, -O-, -S-, -NH-, -N(R¹³)- or -N(aryl)-, wherein each R¹³ may independently represent C₁-C₆ alkyl and each group designated (aryl) independently may represent phenyl or naphthyl, u ranges from 1 to 3, and v ranges from 0 to 3, provided that when v is 0, -Q- represents a group set forth above for -M-; or a reactive substituent, provided that the reactive substituent comprises a linking group comprising an aliphatic amino alcohol residue, a cyclo aliphatic amino alcohol residue, an azacyclo aliphatic alcohol residue, a diazacyclo aliphatic alcohol residue, a diamine residue, an aliphatic diamine residue, a cyclo aliphatic diamine residue, a diazacycloalkane residue, an azacyclo aliphatic amine residue, an oxyalkoxy group, an aliphatic polyol residue, or a cyclo aliphatic polyol residue that forms a bond with the indeno[2',3':3,4]naphtho[1,2-b]pyran at the 6-position or the 7-position. Alternatively, according to this non-limiting embodiment, a group represented by an R⁶ group in the 6-position and a group represented by an R⁶ group in the 7-position of the indeno[2',3':3,4]naphtho[1,2-b]pyran may together form a group represented (XVIII A) or (XVIII B) above, wherein the groups represented by Z and Z' may be the same or different, and may include oxygen and the group -NR¹¹-, where R¹¹ represents a group as set forth above.

[094] Further, according various non-limiting embodiments disclosed herein, the groups represented by R^7 and R^8 may each independently be hydrogen, C_1 - C_6 alkyl, C_3 - C_7 cycloalkyl, allyl, a substituted or unsubstituted phenyl or benzyl, a substituted or unsubstituted amino, and a group $-C(O)R^9$, wherein R^9 may represent groups including, without limitation, hydrogen, hydroxy, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, the unsubstituted, mono- or di-substituted aryl groups phenyl or naphthyl, phenoxy, mono- or di- (C_1-C_6) alkoxy substituted phenoxy, and mono- or di- (C_1-C_6) alkoxy substituted phenoxy.

[095] Still other non-limiting embodiments disclosed herein relate to photochromic materials comprising: (i) a naphthopyran, said a naphthopyran being at least one of a benzofurano-fused naphthopyran, an indolo-fused naphthopyran or a benzothieno-fused naphthopyran; and (ii) a group that extends the pi-conjugated system of the naphthopyran bonded at the 11-position thereof. Although not limiting herein, the naphthopyrans according to these non-limiting embodiments may be generally represented by structures (XXXI) and (XXXII) below, wherein X^* is O, N, or S.



[096] Non-limiting examples of 11-position groups that may extend the pi-conjugated system of the benzofurano-fused naphthopyrans, the indolo-fused naphthopyrans and the benzothieno-fused naphthopyrans according to various non-limiting embodiments disclosed herein include those 11-position groups that may extend the pi-conjugated system of the indeno-fused naphthopyrans discussed above. For example, according to various non-limiting embodiments disclosed herein, the group that extends the pi-conjugated system of the naphthopyran bonded at the 11-position thereof may be a substituted or unsubstituted aryl group (non-

limiting examples of which are set forth above), a substituted or unsubstituted heteroaryl group (non-limiting examples of which are set forth above), or a group represented by $-X=Y$ or $X' \equiv Y'$, wherein X, Y, X' and Y' may represent groups as set forth above in detail.

[097] Alternatively, according to various non-limiting embodiments disclosed herein, the group that extends the pi-conjugated system of the benzofurano-fused naphthopyran, the indolo-fused naphthopyran or the benzothieno-fused naphthopyran bonded at the 11-position thereof together with a group bonded at the 12-position of said naphthopyran or together with a group bonded at the 10-position of said naphthopyran may form a fused group. Although not required, according to one non-limiting embodiment wherein the group bonded at the 11-position together with a group bonded at the 12-position or the 10-position forms a fused group, the fused group may extend the pi-conjugated system of the benzofurano-fused naphthopyran, the indolo-fused naphthopyran or the benzothieno-fused naphthopyran at the 11-position, but not the 10-position or the 12-position thereof. Suitable non-limiting examples of such fused groups include indeno, dihydronaphthalene, indole, benzofuran, benzopyran and thianaphthene.

[098] Further, according to various non-limiting embodiments, the 13-position of the indolo-fused naphthopyran may be unsubstituted or mono-substituted. Non-limiting examples of suitable 13-position substituents include those discussed with respect to R^7 and R^8 in structures (XIV) and (XV) above.

[099] Suitable non-limiting examples of groups that may be bonded at the 4-, 5-, 6-, 7-, 8-, 9-, 10-, and 12-positions of the benzofurano-fused naphthopyran, the indolo-fused naphthopyran or the benzothieno-fused naphthopyran according to various non-limiting embodiments include those groups discussed with respect to R^5 and R^6 in structures (XIV) and (XV) above. Suitable non-limiting examples of groups that may be bonded at the 3-position of the benzofurano-fused naphthopyran, the indolo-fused naphthopyran or the benzothieno-fused naphthopyran represented by (XXXI) or the 2-position of the benzofurano-fused naphthopyran, the indolo-fused

naphthopyran or the benzothieno-fused naphthopyran represented by (XXXII) according to various non-limiting embodiments include those groups discussed with respect to B and B' in structures (XIV) and (XV) above.

[100] Methods of making photochromic materials comprising indeno-fused naphthopyrans according to various non-limiting embodiments disclosed herein will now be discussed with reference to the general reaction schemes presented in Figs. 4-8. Fig. 4 depicts a reaction scheme for making substituted 7H-benzo[C]fluoren-5-ol compounds that may be further reacted as shown in Figs. 5-8 to form photochromic materials comprising an indeno-fused naphthopyran and a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof according to various non-limiting embodiments disclosed herein. It should be appreciated that these reaction schemes are presented for illustration only and are not intended to be limiting herein. Additional examples of methods of making photochromic materials according to various non-limiting embodiments disclosed herein are set forth in the Examples.

[101] Referring now to Fig. 4, a solution of a γ -substituted benzoyl chloride, represented by structure (a) in Fig. 4, and benzene, represented by structure (b) in Fig. 4, which may have one or more substituents γ^1 , in methylene chloride are added to a reaction flask. Suitable γ -substituents include, for example and without limitation, halogen. Suitable γ^1 substituents include, for example and without limitation, those groups set forth above for R⁶. Anhydrous aluminum chloride catalyzes the Friedel Crafts acylation to give a substituted benzophenone represented by structure (c) in Fig. 4. This material is then reacted in a Stobbe reaction with dimethyl succinate to produce a mixture of half-esters, one of which is represented by structure (d) in Fig. 4. Thereafter the half-esters are reacted in acetic anhydride and toluene at an elevated temperature to produce, after recrystallization, a mixture of substituted naphthalene compounds, one of which is represented by structure (e) in Fig. 4. The mixture of substituted naphthalene compounds is then reacted with methyl magnesium chloride to produce a mixture of substituted naphthalene compounds, one of which is represented by structure (f) in Fig. 4. The mixture of

substituted naphthalene compounds is then cyclized with dodecylbenzene sulfonic acid to afford a mixture of 7H-benzo[C]fluoren-5-ol compounds, one of which is represented by structure (g) in Fig. 4.

[102] Referring now to Fig. 5, the 7H-benzo[C]fluoren-5-ol compound represented by structure (g) is refluxed with copper cyanide in anhydrous 1-methyl-2-pyrrolidinone to give, upon workup, a 9-cyano-7H-benzo[C]fluoren-5-ol compound represented by structure (h). As further indicated in PATH A of Fig. 5, the compound represented by structure (h) may be further reacted with a propargyl alcohol represented by structure (i) to produce the indeno-fused naphthopyran (represented by structure (j) in Fig. 5) according to one non-limiting embodiment disclosed herein, wherein a cyano group that extends the pi-conjugated system of the indeno-fused naphthopyran is bonded at the 11-position thereof. Suitable non-limiting examples of groups that B and B' may represent are discussed above.

[103] Alternatively, as shown in PATH B of Fig. 5, the compound represented by structure (h) may be hydrolyzed with aqueous sodium hydroxide under reflux conditions produce the 9-carboxy-7H-benzo[C]fluoren-5-ol compound represented by structure (k) in Fig. 5. As further indicated in Fig. 5, the compound represented by structure (k) may be further reacted with a propargyl alcohol represented by structure (i) to produce the indeno-fused naphthopyran (represented by structure (l) in Fig. 5) according to one non-limiting embodiment disclosed herein, wherein a carboxy group that extends the pi-conjugated system of the indeno-fused naphthopyran is bonded at the 11-position thereof.

[104] Alternatively, as shown in PATH C of Fig. 5, the compound represented by structure (k) may be esterified with an alcohol (represented by the formula $\gamma^2\text{OH}$ in Fig. 5) in aqueous hydrochloric acid to produce the 9- γ^2 carboxyl-7H-benzo[C]fluoren-5-ol compound represented by structure (m) in Fig. 5. Examples of suitable alcohols include, without limitation, methanol, diethylene glycol, alkyl alcohol, substituted and unsubstituted phenols, substituted and unsubstituted benzyl alcohols, polyols and polyol residues, such as, but not limited to those discussed above with respect to -G-. The compound represented by structure (m) may be

further reacted with a propargyl alcohol represented by structure (i) to produce the indeno-fused naphthopyran (represented by structure (n) in Fig. 5) according to one non-limiting embodiment disclosed herein, wherein a carbonyl group that extends the pi-conjugated system of the indeno-fused naphthopyran is bonded at the 11-position thereof. Non-limiting examples of carbonyl groups that may be bonded at the 11-position according to various non-limiting embodiments disclosed herein include: methoxycarbonyl, 2-(2-hydroxyethoxy)ethoxycarbonyl, alkoxycarbonyl, substituted and unsubstituted phenoxycarbonyl, substituted and unsubstituted benzyloxycarbonyl and esters of polyols.

[105] Referring now to Fig. 6, the 7H-benzo[C]fluoren-5-ol compound represented by structure (g) may be reacted with a phenyl boronic acid represented by structure (o), which may be substituted with a group represented by γ^3 as shown in Fig. 6, to form the 9-(4- γ^3 -phenyl)-7H-benzo[C]fluoren-5-ol compound represented by structure (p) in Fig. 6. Examples of suitable boronic acids include, without limitation, substituted and unsubstituted phenylboronic acids, 4-fluorophenylboronic acid, (4-hydroxymethyl)phenylboronic acid, biphenylboronic acid, and substituted and unsubstituted arylboronic acids. The compound represented by structure (p) may be further reacted with a propargyl alcohol represented by structure (i) to produce the indeno-fused naphthopyran (represented by structure (q) in Fig. 6), wherein a phenyl group that extends the pi-conjugated system of the indeno-fused naphthopyran is bonded at the 11-position thereof. Although not required, according to various non-limiting embodiments disclosed herein and as shown in Fig. 6, the phenyl group bonded at the 11-position may be substituted. Non-limiting examples of substituted phenyl groups that may be bonded at the 11-position according to various non-limiting embodiments disclosed herein include 4-fluorophenyl, 4-(hydroxymethyl)phenyl, 4-(phenyl)phenyl group, alkylphenyl, alkoxyphenyl, halophenyl, and alkoxycarbonylphenyl. Further, the substituted phenyl at the 11-position may have up to five substituents, and those substituents may be a variety of different substituents at any of the positions ortho, meta or para to the indeno-fused naphthopyran.

[106] Referring now to Fig. 7, the 7H-benzo[C]fluoren-5-ol compound represented by structure (g) may be coupled under palladium catalysis with a terminal alkyne group represented by structure (r), which may be substituted with a group represented by γ^4 as shown in Fig. 7, to form the 9-alkynyl-7H-benzo[C]fluoren-5-ol compound represented by structure '(s)' in Fig. 7. Examples of suitable terminal alkynes include, without limitation: acetylene, 2-methyl-3-butyne-2-ol, phenylacetylene, and alkylacetylene. The compound represented by structure '(s)' may be further reacted with a propargyl alcohol represented by structure (i) to produce the indeno-fused naphthopyran (represented by structure (t) in Fig. 7) having an alkynyl group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof. Although not required, as shown in Fig. 7, the alkynyl group bonded at the 11-position may be substituted with a group represented by γ^4 . Non-limiting examples of alkynyl groups that may be bonded at the 11-position according to various non-limiting embodiments disclosed herein include ethynyl, 3-hydroxy-3-methylbutynyl, 2-phenylethynyl and alkyl acetylenes.

[107] Referring now to Fig. 8, the 7H-benzo[C]fluoren-5-ol compound represented by structure (g) may be reacted with an alkene represented by structure (u), which may be substituted with a group represented by γ^5 as shown in Fig. 8, to form the 9-alkenyl-7H-benzo[C]fluoren-5-ol compound represented by structure (v) in Fig. 8. Examples of suitable alkenes include, without limitation 1-hexene, styrenes, and vinyl chlorides. The compound represented by structure (v) may be further reacted with a propargyl alcohol represented by structure (i) to produce the indeno-fused naphthopyran (represented by structure (w) in Fig. 8) having an alkenyl group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof. Although not required, as shown in Fig. 8, the alkenyl group bonded at the 11-position may be substituted with up to three γ^5 groups. Non-limiting examples of alkenyl groups that may be bonded at the 11-position according to various non-limiting embodiments disclosed herein include substituted and unsubstituted ethylenes, 2-phenyl ethylenes, and 2-chloroethylenes.

[108] Further, non-limiting examples of methods of forming benzofurano-fused naphthopyrans, indolo-fused naphthopyrans, and/or benzothieno-fused naphthopyrans that may be useful (with appropriate modifications that will be recognized by those skilled) in forming the benzofurano-fused naphthopyrans, indolo-fused naphthopyrans and/or benzothieno-fused naphthopyrans according to various non-limiting embodiments disclosed herein are set forth in U.S. Patent No. 5,651,923 at col. 6, line 43 to col. 13, line 48, which disclosure is hereby specifically incorporated by reference herein; International Patent Application Publication No. WO98/28289A1 at page 7, line 12 to page 9, line 10, which disclosure is specifically incorporated by reference herein; and International Patent Application Publication No. WO99/23071A1 at page 9, lines 1 to page 14, line 3, which disclosure is specifically incorporated by reference herein.

[109] As discussed above, the photochromic materials according to various non-limiting embodiments disclosed herein may be incorporated into at least a portion of an organic material, such as a polymeric, oligomeric or monomeric material, to form a photochromic composition which may be used to form ophthalmic devices and coating compositions that may be applied to said ophthalmic devices. As used herein the terms “polymer” and “polymeric material” refer to homopolymers and copolymers (e.g., random copolymers, block copolymers, and alternating copolymers), as well as blends and other combinations thereof. As used herein the terms “oligomer” and “oligomeric material” refer to a combination of two or more monomer units that is capable of reacting with additional monomer unit(s). As used herein the term “incorporated into” means physically and/or chemically combined with. For example, the photochromic materials according to various non-limiting embodiments disclosed herein may be physically combined with at least a portion of an organic material, for example and without limitation, by mixing or imbibing the photochromic material into the organic material; and/or chemically combined with at least a portion of an organic material, for example and without limitation, by copolymerization or otherwise bonding the photochromic material to the organic material.

[110] Further, it is contemplated that the photochromic materials according to various non-limiting embodiments disclosed herein may each be used alone, in combination with other photochromic materials according to various non-limiting embodiments disclosed herein, or in combination with an appropriate complementary conventional photochromic material. For example, the photochromic materials according to various non-limiting embodiments disclosed herein may be used in conjunction with conventional photochromic materials having activated absorption maxima within the range of 300 to 1000 nanometers. Further, the photochromic materials according to various non-limiting embodiments disclosed herein may be used in conjunction with a complementary conventional polymerizable or a compatibilized photochromic material, such as for example, those disclosed in U.S. Patent Nos. 6,113,814 (at col. 2, line 39 to col. 8, line 41), and 6,555,028 (at col. 2, line 65 to col. 12, line 56), which disclosures are hereby specifically incorporated by reference herein.

[111] As discussed above, according to various non-limiting embodiments disclosed herein, the photochromic compositions may contain a mixture of photochromic materials. For example, although not limiting herein, mixtures of photochromic materials may be used to attain certain activated colors such as a near neutral gray or near neutral brown. See, for example, U.S. Patent No. 5,645,767, col. 12, line 66 to col. 13, line 19, which describes the parameters that define neutral gray and brown colors and which disclosure is specifically incorporated by reference herein.

[112] Various non-limiting embodiments disclosed herein provide an ophthalmic device formed from an organic material, said organic material being at least one of polymeric material, an oligomeric material and a monomeric material, and a photochromic material according to any of the non-limiting embodiments of set forth above incorporated into at least a portion of the organic material. According to various non-limiting embodiments disclosed herein, the photochromic material may be incorporated into a portion of the organic material by at least one of blending and bonding the photochromic material with the organic material or a

precursor thereof. As used herein with reference to the incorporation of photochromic materials into an organic material, the terms “blending” and “blended” mean that the photochromic material is intermixed or intermingled with the at least a portion of the organic material, but not bonded to the organic material. Further, as used herein with reference to the incorporation of photochromic materials into an organic material, the terms “bonding” or “bonded” mean that the photochromic material is linked to a portion of the organic material or a precursor thereof. For example, although not limiting herein, the photochromic material may be linked to the organic material through a reactive substituent.

[113] According to one non-limiting embodiment wherein the ophthalmic device is formed from a polymeric material, the photochromic material may be incorporated into at least a portion of the polymeric material or at least a portion of the monomeric material or oligomeric material from which the polymeric material is formed. For example, photochromic materials according to various non-limiting embodiments disclosed herein that have a reactive substituent may be bonded to an organic material such as a monomer, oligomer, or polymer having a group with which a reactive moiety may be reacted, or the reactive moiety may be reacted as a co-monomer in the polymerization reaction from which the organic material is formed, for example, in a co-polymerization process.

[114] Further, according to various non-limiting embodiments at least a portion of the ophthalmic device is transparent. For example, according to various non-limiting embodiments, the ophthalmic device may be formed from an optically clear polymeric material. According to one specific non-limiting embodiment, the polymeric material is formed from a mixture comprising polymerizable and optionally non-polymerizable ophthalmic device forming components which are known in the art to be useful for forming ophthalmic devices, such as contact lenses. More specifically, suitable components include polymerizable monomers, prepolymers and macromers, wetting agents, UV absorbing compounds, compatibilizing components, colorants and tints, mold release agents, processing aids, mixtures thereof and the like.

[115] According to one specific non-limiting embodiment, the ophthalmic device forming components preferably form a hydrogel upon polymerization and hydration. A hydrogel is a hydrated, crosslinked polymeric system that contains water in an equilibrium state. Hydrogels typically are oxygen permeable and biocompatible, making them preferred materials for producing ophthalmic devices and in particular contact and intraocular lenses.

[116] Ophthalmic device forming components are known in the art and include polymerizable monomers, prepolymers and macromers which contain polymerizable group(s) and performance groups which provide the resulting polymeric material with desirable properties. Suitable performance groups include, but are not limited to, hydrophilic groups, oxygen permeability enhancing groups, UV or visible light absorbing groups, compatibilizing components, combinations thereof and the like.

[117] The term "monomer" used herein refers to low molecular weight compounds (i.e. typically having number average molecular weights less than about 700). Prepolymers are medium to high molecular weight compounds or polymers (having repeating structural units and a number average molecular weight greater than about 700) containing functional groups capable of further polymerization. Macromers are uncrosslinked polymers which are capable of cross-linking or further polymerization.

[118] One suitable class of ophthalmic device forming components includes hydrophilic components, which are capable of providing at least about 20% and preferably at least about 25% water content to the resulting lens when combined with the remaining components. The hydrophilic components that may be used to make the polymers of this invention are monomers having at least one polymerizable double bond and at least one hydrophilic functional group. Examples of polymerizable double bonds include acrylic, methacrylic, acrylamido, methacrylamido, fumaric, maleic, styryl, isopropenylphenyl, O-vinylcarbonate, O-vinylcarbamate, allylic, O-vinylacetyl and N-vinyl lactam and N-vinylamido double bonds. Non-limiting examples of hydrophilic monomers having acrylic and methacrylic polymerizable double bonds include N,N-dimethylacrylamide (DMA),

2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, glycerol methacrylate, 2-hydroxyethyl methacrylamide, polyethyleneglycol monomethacrylate, methacrylic acid, acrylic acid and mixtures thereof.

[119] Non-limiting examples of hydrophilic monomers having N-vinyl lactam and N-vinylamide polymerizable double bonds include N-vinyl pyrrolidone (NVP), N-vinyl-N-methyl acetamide, N-vinyl-N-ethyl acetamide, N-vinyl-N-ethyl formamide, N-vinyl formamide, N-2-hydroxyethyl vinyl carbamate, N-carboxy- β -alanine N-vinyl ester, with NVP and N-vinyl-N-methyl acetamide being preferred. Polymers formed from these monomers may also be included.

[120] Other hydrophilic monomers that can be employed in the invention include polyoxyethylene polyols having one or more of the terminal hydroxyl groups replaced with a functional group containing a polymerizable double bond.

[121] Still further examples are the hydrophilic vinyl carbonate or vinyl carbamate monomers disclosed in U.S. Pat. No. 5,070,215, and the hydrophilic oxazolone monomers disclosed in U.S. Pat. No. 4,190,277. Other suitable hydrophilic monomers will be apparent to one skilled in the art.

[122] Preferred hydrophilic monomers which may be incorporated into the polymerizable mixture of the present invention include hydrophilic monomers such as N,N-dimethyl acrylamide (DMA), 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate (HEMA), glycerol methacrylate, 2-hydroxyethyl methacrylamide, N-vinylpyrrolidone (NVP), N-vinyl-N-methyl acetamide, polyethyleneglycol monomethacrylate and mixtures thereof.

[123] Most preferred hydrophilic monomers include HEMA, DMA, NVP, N-vinyl-N-methyl acetamide and mixtures thereof.

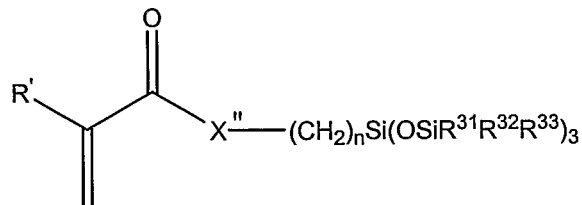
[124] The above references hydrophilic monomers are suitable for the production of conventional contact lenses such as those made from etafilcon, polymacon, vifilcon, genfilcon A and lenefilcon A and the like. For a conventional contact lens the amount of hydrophilic monomer incorporated into the polymerizable mixture is at least about 70 weight % and preferably at least about 80 weight %, based upon the weight of all the components in the polymerizable mixture.

[125] In another non-limiting embodiment, suitable contact lenses may be made from polymeric materials having increased permeability to oxygen, such as galyfilcon A, senofilcon A, balafilcon, lotrafilcon A and B and the like. The polymerization mixtures used to form these and other materials having increased permeability to oxygen, generally include one or more of the hydrophilic monomers listed above, with at least one silicone containing component.

[126] A silicone-containing component is one that contains at least one $[-Si-O-Si-]$ group, in a monomer, macromer or prepolymer. Preferably, the Si and attached O are present in the silicone-containing component in an amount greater than 20 weight percent, and more preferably greater than 30 weight percent of the total molecular weight of the silicone-containing component. Useful silicone-containing components preferably comprise polymerizable functional groups such as acrylate, methacrylate, acrylamide, methacrylamide, N-vinyl lactam, N-vinylamide, and styryl functional groups. Examples of silicone-containing components which are useful in this invention may be found in U.S. Pat. Nos. 3,808,178; 4,120,570; 4,136,250; 4,153,641; 4,740,533; 5,034,461 and 5,070,215, and EP080539. All of the patents cited herein are hereby incorporated in their entireties by reference. These references disclose many examples of olefinic silicone-containing components.

[127] Further examples of suitable silicone-containing monomers are polysiloxanylalkyl(meth)acrylic monomers represented by the following formula:

Formula XXI



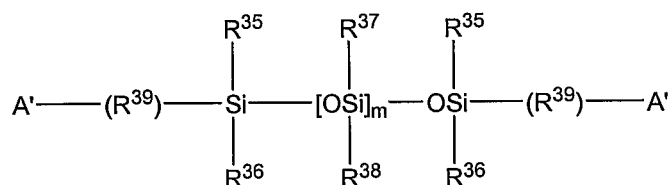
wherein: R' denotes H or lower alkyl; X'' denotes O or NR³⁴; each R³⁴ independently denotes hydrogen or methyl,

each R^{31} - R^{33} independently denotes a lower alkyl radical or a phenyl radical, and n is 1 or 3 to 10.

[128] Examples of these polysiloxanylalkyl (meth)acrylic monomers include methacryloxypropyl tris(trimethylsiloxy) silane, methacryloxymethylpentamethyldisiloxane, methacryloxypropylpentamethyldisiloxane, methyldi(trimethylsiloxy)methacryloxypropyl silane, and methyldi(trimethylsiloxy)methacryloxymethyl silane. Methacryloxypropyl tris(trimethylsiloxy)silane is the most preferred.

[129] One preferred class of silicone-containing components is a poly(organosiloxane) prepolymer represented by Formula XXII:

Formula XXII



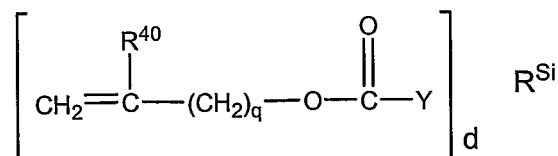
wherein each A' independently denotes an activated unsaturated group, such as an ester or amide of an acrylic or a methacrylic acid or an alkyl or aryl group (providing that at least one A' comprises an activated unsaturated group capable of undergoing radical polymerization); each of R^{35} , R^{36} , R^{37} and R^{38} are independently selected from the group consisting of a monovalent hydrocarbon radical or a halogen substituted monovalent hydrocarbon radical having 1 to 18 carbon atoms which may have ether linkages between carbon atoms;

R^{39} denotes a divalent hydrocarbon radical having from 1 to 22 carbon atoms, and

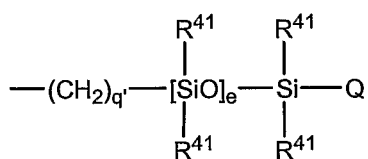
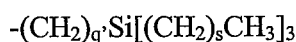
m is 0 or an integer greater than or equal to 1, and preferably 5 to 400, and more preferably 10 to 300. One specific example is α , ω -bismethacryloxypropyl poly-dimethylsiloxane. Another preferred example is mPDMS (monomethacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane).

[130] Another useful class of silicone containing components includes silicone-containing vinyl carbonate or vinyl carbamate monomers of the following formula:

Formula XXIII

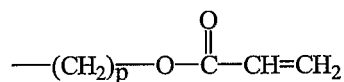


wherein: Y denotes O, S, or NH; R^{Si} denotes a silicone-containing organic radical; R^{40} denotes hydrogen or methyl; d is 1, 2, 3 or 4; and q is 0 or 1. Suitable silicone-containing organic radicals R^{Si} include the following:



wherein:

Q denotes



wherein p is 1 to 6; R^{41} denotes an alkyl radical or a fluoroalkyl radical having 1 to 6 carbon atoms; e is 1 to 200; q' is 1, 2, 3 or 4; and s is 0, 1, 2, 3, 4 or 5.

The silicone-containing vinyl carbonate or vinyl carbamate monomers specifically include: 1,3-bis[4-(vinylloxycarbonyloxy)but-1-yl]tetramethyldisiloxane; 3-(vinylloxycarbonylthio) propyl-[tris(trimethylsiloxy)silane]; 3-[tris(trimethylsiloxy)silyl] propyl allyl carbamate; 3-[tris(trimethylsiloxy)silyl]

propyl vinyl carbamate; trimethylsilylethyl vinyl carbonate; trimethylsilylmethyl vinyl carbonate, and

[131] The above description of silicone containing components is not an exhaustive list. Any other silicone components known in the art may be used. Further examples include, but are not limited to macromers made using group transfer polymerization, such as those disclosed in 6,367,929, polysiloxane containing polyurethane compounds such as those disclosed in US 6,858,218, polysiloxane containing macromers, such as those described as Materials A-D in US 5,760,100; macromers containing polysiloxane, polyalkylene ether, diisocyanate, polyfluorinated hydrocarbon, polyfluorinated ether and polysaccharide groups, such as those described is WO 96/31792; polysiloxanes with a polar fluorinated graft or side group(s) having a hydrogen atom attached to a terminal difluoro-substituted carbon atom, such as those described in U.S. Pat. Nos. 5,321,108; 5,387,662 and 5,539,016; hydrophilic siloxanyl methacrylate monomers and polysiloxane-dimethacrylate macromers such as those described in US 2004/0192872; combinations thereof and the like.

[132] The polymerizable mixture may contain additional components such as, but not limited to, wetting agents, such as those disclosed in US 6,822,016, US Serial No. 11/057,363, US Serial No. 10/954,560, US Serial No. 10/954,559 and US Serial No. 955,214; compatibilizing components, such as those disclosed in US 6,822,016 and WO03/022322; UV absorbers, medicinal agents, antimicrobial compounds, reactive tints, pigments, copolymerizable and nonpolymerizable dyes, release agents and combinations thereof.

[133] Also contemplated are copolymers of the aforementioned monomers, combinations, and blends of the aforementioned polymers and copolymers with other polymers, e.g., to form interpenetrating network products.

[134] The polymerizable mixture may optionally further comprise a diluent. Suitable diluents for polymerizable mixtures are well known in the art. Non-limiting examples for polymerizable mixtures for hydrophilic soft contact lenses include organic solvents or water or mixtures hereof. Preferred organic solvents include

alcohols, diols, triols, polyols and polyalkylene glycols. Examples include but are not limited to glycerin, diols such as ethylene glycol or diethylene glycol; boris acid esters of polyols such as those described in US Patents 4,680,336; 4,889,664 and 5,039,459; polyvinylpyrrolidone; ethoxylated alkyl glucoside; ethoxylated bisphenol A; polyethylene glycol; mixtures of propoxylated and ethoxylated alkyl glucoside; single phase mixture of ethoxylated or propoxylated alkyl glucoside and C₂₋₁₂ dihydric alcohol; adducts of ϵ -caprolactone and C₂₋₆ alkanediols and triols; ethoxylated C₃₋₆ alkanetriol; and mixtures of these as described in US Patents 5,457,140; 5,490,059, 5,490,960; 5,498,379; 5,594,043; 5,684,058; 5,736,409; 5,910,519. Diluents can also be selected from the group having a combination of a defined viscosity and Hanson cohesion parameter as described in US Patent 4,680,336.

[135] Non-limiting examples of diluents suitable for polymerizable mixtures for silicone hydrogel soft contact lenses include alcohols such as those disclosed in US 6,020,445 and US Serial No. 10/794,399 for silicone hydrogel soft contact lenses. The disclosure of these and all other references cited within this application are hereby incorporated by reference. Many other suitable examples are known to those of skill in the art and are included within the scope of this invention.

[136] Hard contact lenses are made from polymers that include but are not limited to polymers of poly(methyl)methacrylate, silicon acrylates, fluoroacrylates, fluoroethers, polyacetylenes, and polyimides, where the preparation of representative examples may be found in US Patents 4,540,761; 4,508,884; 4,433,125 and 4,330,383. Intraocular lenses of the invention can be formed using known materials. For example, the lenses may be made from a rigid material including, without limitation, polymethyl methacrylate, polystyrene, polycarbonate, or the like, and combinations thereof. Additionally, flexible materials may be used including, without limitation, hydrogels, silicone materials, acrylic materials, fluorocarbon materials and the like, or combinations thereof. Typical intraocular lenses are described in WO 0026698, WO 0022460, WO 9929750, WO 9927978,

WO 0022459, and JP 2000107277. Other ophthalmic devices, such as punctal plugs may be made from collagen and silicone elastomers.

[137] As previously discussed, it has been observed by the inventors that the photochromic materials according to certain non-limiting embodiments disclosed herein may display hyperchromic absorption of electromagnetic radiation having a wavelength from 320 nm to 420 nm as compared to a photochromic materials comprising a comparable indeno-fused naphthopyran without the group that extends the pi-conjugated system of the comparable indeno-fused naphthopyran bonded at the 11-position thereof. Accordingly, ophthalmic devices comprising the photochromic materials according to various non-limiting embodiments disclosed herein may also display increased absorption of electromagnetic radiation having a wavelength from 320 nm to 420 nm as compared to an ophthalmic device comprising a comparable indeno-fused naphthopyran without the group that extends the pi-conjugated system of the comparable indeno-fused naphthopyran bonded at the 11-position thereof.

[138] Additionally, as previously discussed, since the photochromic materials according to certain non-limiting embodiments disclosed herein may display hyperchromic properties as discussed above, it is contemplated that the amount or concentration of the photochromic material present in ophthalmic devices according to various non-limiting embodiments disclosed herein may be reduced as compared to the amount or concentration of a conventional photochromic materials that is typically required to achieve a desired optical effect. Since it may be possible to use less of the photochromic materials according to certain non-limiting embodiments disclosed herein than conventional photochromic materials while still achieving the desired optical effects, it is contemplated that the photochromic materials according to various non-limiting embodiments disclosed herein may be advantageously employed in ophthalmic devices wherein it is necessary or desirable to limit the amount of photochromic material used.

[139] Further, as previously discussed, it has been observed by the inventors that the photochromic materials according to certain non-limiting embodiments

disclosed herein the may have a closed-form absorption spectrum for electromagnetic radiation having a wavelength ranging from 320 nm to 420 nm that is bathochromically shifted as compared to a closed-form absorption spectrum for electromagnetic radiation having a wavelength ranging from 320 nm to 420 nm of a photochromic material comprising a comparable indeno-fused naphthopyran without the group that extends the pi-conjugated system of the comparable indeno-fused naphthopyran bonded at the 11-position thereof. Accordingly, ophthalmic devices comprising the photochromic materials according to various non-limiting embodiments disclosed herein may also have an absorption spectrum for electromagnetic radiation having a wavelength ranging from 320 nm to 420 nm that is bathochromically shifted as compared to an absorption spectrum for electromagnetic radiation having a wavelength ranging from 320 nm to 420 nm of a photochromic composition comprising a comparable indeno-fused naphthopyran without the group that extends the pi-conjugated system of the comparable indeno-fused naphthopyran bonded at the 11-position thereof.

[140] Accordingly, another non-limiting embodiment provides an ophthalmic device adapted for use behind a substrate that blocks a substantial portion of electromagnetic radiation in the range of 320 nm to 390 nm, the ophthalmic device comprising a photochromic material comprising an indeno-fused naphthopyran and a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof connected to at least a portion of the ophthalmic device, wherein the at least a portion of the ophthalmic device absorbs a sufficient amount of electromagnetic radiation having a wavelength greater than 390 nm passing through the substrate that blocks a substantial portion of electromagnetic radiation in the range of 320 nm to 390 nm such that the at least a portion of the ophthalmic device transforms from a first state to a second state. For example, according to this non-limiting embodiment, the first state may be a bleached state and the second state may be a colored state that corresponds to the colored state of the photochromic material(s) incorporated therein.

[141] As previously discussed, many conventional photochromic materials require electromagnetic radiation having a wavelength ranging from 320 nm to 390 nm to cause the photochromic material to transformation from a closed-form to an open-form (e.g., from a bleached state to a colored state). Therefore, conventional photochromic materials may not achieve their fully-colored state when used in applications that are shielded from a substantial amount of electromagnetic radiation in the range of 320 nm to 390 nm. Further, as previous discussed, it has been observed by the inventors that photochromic material according to certain non-limiting embodiments disclosed herein may display both hyperchromic and bathochromic properties. That is, the indeno-fused naphthopyrans comprising a group that extends the pi-conjugated system of the indeno-fused naphthopyran at the 11-position thereof according to certain non-limiting embodiments disclosed herein may not only display hyperchromic absorption of electromagnetic radiation as discussed above, but may also have a closed-form absorption spectrum for electromagnetic radiation having a wavelength ranging from 320 nm to 420 nm that is bathochromically shifted as compared to a closed-form absorption spectrum for electromagnetic radiation having a wavelength ranging from 320 nm to 420 nm of a comparable indeno-fused naphthopyran without the group that extends the pi-conjugated system of the comparable indeno-fused naphthopyran bonded at the 11-position thereof. Accordingly, the ophthalmic devices according to certain non-limiting embodiments disclosed herein comprise photochromic materials which may absorb a sufficient amount of electromagnetic radiation passing through a substrate that blocks a substantial portion of electromagnetic radiation having a wavelength ranging from 320 to 390 nm such that the photochromic material may transform from a closed-form to an open-form. That is, the amount of electromagnetic radiation having a wavelength of greater than 390 nm that is absorbed by the photochromic materials according to various non-limiting embodiments disclosed herein may be sufficient to permit the photochromic materials to transform from a closed-form to an open-form, thereby enabling their use behind a substrate that

blocks a substantial portion of electromagnetic radiation having a wavelength ranging from 320 nm to 390 nm.

[142] As previously discussed, the present invention contemplates photochromic ophthalmic devices, made using the photochromic materials and compositions according to various non-limiting embodiments disclosed herein.

[143] Various non-limiting embodiments disclosed herein provide photochromic ophthalmic devices, comprising a substrate and a photochromic material according to any of the non-limiting embodiments discussed above connected to a portion of the substrate. As used herein, the term “connected to” means associated with, either directly or indirectly through another material or structure.

[144] According to various non-limiting embodiments disclosed herein the photochromic material may be connected to at least a portion of the ophthalmic device by incorporating the photochromic material into at least a portion of the polymeric material of the ophthalmic device, or by incorporating the photochromic material into at least a portion of the oligomeric or monomeric material from which the ophthalmic device is formed. Ophthalmic devices of the present invention may be formed by a number of processes including. By way of non-limiting example, when the ophthalmic device is a soft contact lens, the polymerization mixture may be placed in a mold, cured and subsequently hydrated. Various processes are known for molding the polymerization mixture in the production of contact lenses, including spincoating and static casting. Spincoating methods are disclosed in U.S. Pat. Nos. 3,408,429 and 3,660,545, and static casting methods are disclosed in U.S. Pat. Nos. 4,113,224 and 4,197,266.

[145] A lens-forming amount of a lens material is dispensed into the mold. By “lens-forming amount” is meant an amount sufficient to produce a lens of the size and thickness desired. Typically, about 10 to about 40 mg of lens material is used.

[146] The mold containing the lens material then is exposed to conditions suitable to form the lens. The precise conditions will depend upon the components of lens material selected and are within the skill of one of ordinary skill in the art to

determine. Once curing is completed, the lens is released from the mold and may be treated with a solvent to remove the diluent (if used) or any traces of unreacted components. The lens is then hydrated to form the hydrogel lens. Thus, in one embodiment, the photochromic material is included in the polymerization mixture and incorporated into the contact lens either via polymerization if the photochromic compound included a reactive substituent, or via entrapment.

[147] According to still other non-limiting embodiments, the photochromic material may be connected to at least a portion of the substrate of the ophthalmic device as part of at least partial coating that is connected to at least a portion of the ophthalmic device. According to this non-limiting embodiment, the photochromic material may be incorporated into at least a portion of a coating composition prior to application of the coating composition to the ophthalmic device, or alternatively, a coating composition may be applied to the ophthalmic device, at least partially set, and thereafter the photochromic material may be imbibed into at least a portion of the coating. As used herein, the terms “set” and “setting” include, without limitation, curing, polymerizing, cross-linking, cooling, and drying.

[148] The at least partial coating comprising the photochromic material may be connected to at least a portion of the ophthalmic device, for example, by applying a coating composition comprising the photochromic material to at least a portion of a surface of the ophthalmic device, and at least partially setting the coating composition. Additionally or alternatively, the at least partial coating comprising the photochromic material may be connected to the ophthalmic device, for example, through one or more additional at least partial coatings. For example, while not limiting herein, according to various non-limiting embodiments, an additional coating composition may be applied to a portion of the surface of the ophthalmic device, at least partially set, and thereafter the coating composition comprising the photochromic material may be applied over the additional coating and at least partially set. Non-limiting methods of applying coating compositions to substrates are discussed herein below.

[149] Non-limiting examples of additional coatings and films that may be used in conjunction with the ophthalmic devices disclosed herein include ophthalmically compatible coatings including clear coats, and hydrophilic coatings, conventional photochromic coating and films; and combinations thereof.

[150] As used herein the term “ophthalmically compatible coating” refers to coatings which enhance the compatibility of the resulting ophthalmic device with the ocular environment. Non-limiting examples of ophthalmically compatible coatings include coatings which improve the hydrophilicity or lubricity of the ophthalmic device, antimicrobial coatings, UV blocking coatings, combinations thereof and the like.

[151] Non-limiting examples of conventional photochromic coatings and films include, but are not limited to, coatings and films comprising conventional photochromic materials.

[152] As discussed above, according to various non-limiting embodiments, an additional at least partial coating or film may be formed on or applied to the ophthalmic device prior to applying the at least partial coating comprising the photochromic material according to various non-limiting embodiments disclosed herein. For example, according to certain non-limiting embodiments a primer coating may be formed on the ophthalmic device prior to applying the coating composition comprising the photochromic material. Alternatively or additionally, the additional at least partial coating or film may be applied to or formed on the ophthalmic device after applying to or forming on the ophthalmic device the at least partial coating comprising the photochromic material according to various non-limiting embodiments disclosed herein, for example, as an overcoating.

[153] Non-limiting methods of making photochromic compositions and photochromic ophthalmic devices according to various non-limiting embodiments disclosed herein will now be discussed. One non-limiting embodiment provides a method of making a photochromic composition, the method comprising incorporating a photochromic material into at least a portion of an organic material. Non-limiting methods of incorporating photochromic materials to an organic

material include, for example, mixing the photochromic material into a solution or melt of a polymeric, oligomeric, or monomeric material, and subsequently at least partially setting the polymeric, oligomeric, or monomeric material (with or without bonding the photochromic material to the organic material); and imbibing the photochromic material into the organic material (with or without bonding the photochromic material to the organic material).

[154] Another non-limiting embodiment provides a method of making a photochromic ophthalmic device comprising connecting a photochromic material according to various non-limiting embodiments discussed above, to at least a portion of a said ophthalmic device. For example, the photochromic material may be connected to at least a portion of the ophthalmic device by at least one of the cast-in-place method and by imbibition. For example, in the cast-in-place method, the photochromic material may be mixed with a polymerizable mixture, which is subsequently cast into a mold having a desired shape and cured to form the ophthalmic device. Optionally, according to this non-limiting embodiment, the photochromic material may be bonded to a portion of the polymeric material of the ophthalmic device, for example by co-polymerization with the components used to form the ophthalmic device. In the imbibition method, the photochromic material may be caused to diffuse into the polymeric material of the ophthalmic device after it is formed, for example, by immersing the ophthalmic device in a solution containing the photochromic material, with or without heating.

[155] Other non-limiting embodiments disclosed herein provide a method of making an ophthalmic device comprising connecting at least one photochromic material to at least a portion of said ophthalmic device by at least one of in-mold casting, coating and lamination. For example, according to one non-limiting embodiment, the photochromic material may be connected to at least a portion of an ophthalmic device by in-mold casting. According to this non-limiting embodiment, a coating composition comprising the photochromic material, which may be a liquid coating composition, is applied to the surface of a mold and at least partially set.

Thereafter, a polymerizable mixture is cast over the coating and cured. After curing, the coated ophthalmic device is removed from the mold.

[156] According to still another non-limiting embodiment, the photochromic material may be connected to at least a portion of an ophthalmic device by coating. Non-limiting examples of suitable coating methods include spin coating, spray coating (e.g., using a liquid or powder coating), curtain coating, tampon printing, roll coating, spin and spray coating, over-molding, and combinations thereof. For example, according to one non-limiting embodiment, the photochromic material may be connected to the substrate by over-molding. According to this non-limiting embodiment, a coating composition comprising the photochromic material (which may be a liquid coating composition) may be applied to a mold and then the ophthalmic device may be placed into the mold such that the ophthalmic device contacts the coating causing it to spread over at least a portion of the surface of the ophthalmic device. Thereafter, the coating composition may be at least partially set and the coated ophthalmic device may be removed from the mold.

[157] Additionally or alternatively, a coating composition (with or without a photochromic material) may be applied to an ophthalmic device (for example, by any of the foregoing methods), the coating composition may be at least partially set, and thereafter, a photochromic material may be imbibed (as previously discussed) into the coating composition.

[158] Further, various non-limiting embodiments disclosed herein contemplate the use of various combinations of the foregoing methods to form photochromic articles according to various non-limiting embodiments disclosed herein. For example, and without limitation herein, according to one non-limiting embodiment, a photochromic material may be connected to an ophthalmic device by incorporation into an organic material from which the ophthalmic device is formed (for example, using the cast-in-place method and/or imbibition), and thereafter a photochromic material (which may be the same or different from the aforementioned photochromic material) may be connected to a portion of the substrate using the in-mold casting, coating methods described above.

[159] Further, it will be appreciated by those skilled in the art that the photochromic compositions and ophthalmic devices made therefrom according to various non-limiting embodiments disclosed herein may further comprise other additives that aid in the processing and/or performance of the composition or ophthalmic device. Non-limiting examples of such additives include from photoinitiators, thermal initiators, polymerization inhibitors, solvents, light stabilizers (such as, but not limited to, ultraviolet light absorbers and light stabilizers, such as hindered amine light stabilizers (HALS)), heat stabilizers, mold release agents, rheology control agents, leveling agents (such as, but not limited to, surfactants), free radical scavengers, adhesion promoters (such as hexanediol diacrylate and coupling agents), and combinations and mixtures thereof.

[160] According to various non-limiting embodiments, the photochromic materials described herein may be used in amounts (or ratios) such that the ophthalmic devices into which the photochromic materials are incorporated or otherwise connected to exhibit desired optical properties. For example, the amount and types of photochromic materials may be selected such that the ophthalmic device may be clear or colorless when the photochromic material is in the closed-form (i.e. in the bleached or unactivated state) and may exhibit a desired resultant color when the photochromic material is in the open-form (that is, when activated by actinic radiation). The precise amount of the photochromic material to be utilized in the various photochromic compositions and articles described herein is not critical provided that a sufficient amount is used to produce the desired effect. It should be appreciated that the particular amount of the photochromic material used may depend on a variety of factors, such as but not limited to, the absorption characteristics of the photochromic material, the color and intensity of the color desired upon activation, and the method used to incorporate or connect the photochromic material to the ophthalmic device. Although not limiting herein, according to various non-limiting embodiments disclosed herein, the amount of the photochromic material that is incorporated into an organic material may range from about 0.01 to about 40 weight percent, in some embodiments between about 0.1 to

about 30 weight %, and in other embodiments, between about 1% to about 20% weight percent, all based on the weight of the organic material.

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

EXAMPLES

[162] In Part 1 of the Examples, the synthesis procedures used to make photochromic materials according to various non-limiting embodiments disclosed herein are set forth in Examples 1-15, and the procedures used to make four comparative photochromic materials are described in Comparative Examples (CE) 1-4. In Part 2 the test procedures and results are described. In Part 3, the absorption properties of modeled photochromic materials are described.

PART 1: SYNTHESIS PROCEDURES

Example 1

Step 1

[163] 1,2-Dimethoxybenzene (31.4 g) and a solution of 4-bromobenzoyl chloride (50.0 g) in 500 mL of methylene chloride were added to a reaction flask fitted with a solid addition funnel under a nitrogen atmosphere. Solid anhydrous aluminum chloride (60.0 g) was added to the reaction mixture with occasionally cooling of the reaction mixture in an ice/water bath. The reaction mixture was stirred at room temperature for 3 hours. The resulting mixture was poured into 300 mL of a 1:1 mixture of ice and 1N HCl and stirred vigorously for 15 minutes. The mixture was extracted twice with 100 mL methylene chloride. The organic extracts were combined and washed with 50 mL of 10 wt % NaOH followed by 50 mL of water. The methylene chloride solvent was removed by rotary evaporation to give 75.0 g of a yellow solid. Nuclear magnetic resonance ("NMR") spectra showed the product to have a structure consistent with 3,4-dimethoxy-4'-bromobenzophenone.

Step 2

[164] Potassium t-butoxide (30.1 g) and 70.0 g of 3,4-dimethoxy-4'-bromobenzophenone from Step 1 were added to a reaction flask containing 500 mL of toluene under a nitrogen atmosphere. The mixture was heated to reflux and dimethyl succinate (63.7 g) was added dropwise over 1 hour. The mixture was refluxed for 5 hours and cooled to room temperature. The resulting mixture was

poured into 300 mL of water and vigorously stirred for 20 minutes. The aqueous and organic phases were separated and the organic phase was extracted with 100 mL portions of water three times. The combined aqueous layers were washed with 150 mL portions of chloroform three times. The aqueous layer was acidified to pH 2 with 6N HCl and a precipitate formed. The aqueous layer was extracted with three 100 mL portions of chloroform. The organic extracts were combined and concentrated by rotary evaporation. NMR spectra of the resulting oil showed the product to have structures consistent with a mixture of (E and Z) 4-(3,4-dimethoxyphenyl)-4-(4-bromophenyl)-3-methoxycarbonyl-3-butenic acids.

Step 3

[165] The crude half-esters from Step 2 (100.0 g), 60 mL of acetic anhydride, and 300 mL of toluene were added to a reaction flask under a nitrogen atmosphere. The reaction mixture was heated to 110° C for 6 hours, cooled to room temperature, and the solvents (toluene and acetic anhydride) removed by rotary evaporation. The residue was dissolved in 300 mL of methylene chloride and 200 mL of water. Solid Na₂CO₃ was added to the biphasic mixture until bubbling ceased. The layers separated and the aqueous layer was extracted with 50 mL portions of methylene chloride. The organic extracts were combined and the solvent was removed by rotary evaporation to yield thick red oil. The oil was dissolved in warm methanol and chilled at 0° C for 2 hours. The resulting crystals were collected by vacuum filtration, washed with cold methanol to produce the mixtures of 1-(4-bromophenyl)-2-methoxycarbonyl-4-acetoxy-6,7-dimethoxynaphthalene and 1-(3,4-dimethoxyphenyl)-2-methoxycarbonyl-4-acetoxy-6-bromonaphthalene. The product mixture was used without further purification in subsequent reaction.

Step 4

[166] The mixture (50.0 g) from Step 3 was weighed into a reaction flask under a nitrogen atmosphere and 300 mL of anhydrous THF was added. Methyl magnesium chloride (200 mL of 3.0M in THF) was added to the reaction mixture over 1 hour. The reaction mixture was stirred overnight and then poured into 300 mL of a 1:1 mixture of ice and 1N HCl. The mixture was extracted with chloroform (three times with 300 mL). The organic extracts were combined, washed with saturated aqueous

NaCl solution (400 mL) and dried over anhydrous Na_2SO_4 . Removal of the solvent by rotary evaporation yielded 40.0 g of 1-(4-bromophenyl)-2-(dimethylhydroxymethyl)-4-hydroxy-6,7-dimethoxynaphthalene and 1-(3,4-dimethoxyphenyl)-2-(dimethylhydroxymethyl)-4-hydroxy-6-bromonaphthalene.

Step 5

[167] The products from Step 4 (30.0 g) were placed in a reaction flask equipped with a Dean-Stark trap and 150 mL of toluene was added. The reaction mixture was stirred under a nitrogen atmosphere and dodecylbenzene sulfonic acid (about 0.5 mL) was added. The reaction mixture was heated at reflux for 2 hours and cooled to room temperature. Upon cooling the mixture to room temperature for 24 hours, the white solid was precipitated. NMR spectra showed the product to have a structure consistent with 2,3-dimethoxy-7,7-dimethyl-9-bromo-7H-benzo[C]fluoren-5-ol. This material was not purified further but was used directly in the next step.

Step 6

[168] The product from Step 5 (10.0 g) was placed in a reaction flask under a nitrogen atmosphere and 100 mL of anhydrous 1-methyl-2-pyrrolidinone was added. CuCN (4.5 g) was added to the reaction mixture. The reaction mixture was heated at reflux for 4 hours and cooled to room temperature. To the resulting mixture was added 100 mL of 6N HCl and the mixture was stirred for 10 minutes. The mixture was washed with 150 ml portions of ethyl acetate three times. The organic extracts were combined and the solvent was removed by rotary evaporation to give 7.2 g of a gray solid. NMR spectra showed the product to have a structure consistent with 2,3-dimethoxy-7,7-dimethyl-9-cyano-7H-benzo[C]fluoren-5-ol.

Step 7

[169] 2,3-Dimethoxy-7,7-dimethyl-9-cyano-7H-benzo[C]fluoren-5-ol from Step 6 (10 g), 1,1-bis(4-methoxyphenyl)-2-propyn-1-ol, (8.0 g, the product of Example 1 Step 1 in U.S. patent 5,458,814, which example is hereby specifically incorporated by reference herein), dodecylbenzene sulfonic acid (0.5 g) and chloroform (preserved with pentene, 250 mL) were combined in a reaction flask and stirred at room temperature for 5 hours. The reaction mixture was washed with 50 % saturated aqueous NaHCO_3 (200 mL) and the organic layer was dried over

anhydrous Na₂SO₄. The solvent was removed by rotary evaporation. Hot methanol was added to the resulting residue and the solution cooled to room temperature. The resulting precipitate was collected by vacuum filtration and washed with cold methanol yielding 14.0 g of 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-cyano-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran, (i.e., an indeno-fused naphtho[1,2-b]pyran with a cyano group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof). The product was used without further purification in the subsequent reaction.

Example 2:

Step 1

[170] 2,3-Dimethoxy-7,7-dimethyl-9-cyano-7H-benzo[C]fluoren-5-ol from Step 6 of Example 1 (10.0 g) was placed in a flask under a nitrogen atmosphere and NaOH (20 g) was added. To the mixture, ethanol (100mL) and water (100 mL) were added. The reaction mixture was heated at reflux for 24 hours and cooled to room temperature. The resulting mixture was poured into 200 mL of a 1:1 mixture of ice and 6N HCl and stirred vigorously for 15 minutes. The mixture was washed with 150 mL portions of ethyl acetate three times. The organic extracts were combined and the solvent was removed by rotary evaporation to give 9.0 g of a white solid. NMR spectra showed the product to have a structure consistent with 2,3-dimethoxy-7,7-dimethyl-9-carboxy-7H-benzo[C]fluoren-5-ol.

Step 2

[171] The procedure of Step 7 of Example 1 was followed except that 2,3-dimethoxy-7,7-dimethyl-9-carboxy-7H-benzo[C]fluoren-5-ol of Step 1 was used in place of 2,3-dimethoxy-7,7-dimethyl-9-cyano-7H-benzo[C]fluoren-5-ol to produce 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-carboxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 3:

Step 1

[172] 2,3-Dimethoxy-7,7-dimethyl-9-carboxy-7H-benzo[C]fluoren-5-ol from Step 1 of Example 2 (5.0 g), 1.0 mL of aqueous HCl, and 100 mL of methanol were combined in a flask and heated at reflux for 24 hours. The reaction mixture was cooled and the resulting precipitate was collected by vacuum filtration and washed

with cold methanol yielding 4.9 g of a white solid. NMR spectra showed the product to have a structure consistent with 2,3-dimethoxy-7,7-dimethyl-9-methoxycarbonyl-7H-benzo[C]fluoren-5-ol.

Step 2

[173] The procedure of Step 7 of Example 1 was followed except that 2,3-dimethoxy-7,7-dimethyl-9-methoxycarbonyl-7H-benzo[C]fluoren-5-ol of Step 1 was used in place of 2,3-dimethoxy-7,7-dimethyl-9-cyano-7H-benzo[C]fluoren-5-ol to produce 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-methoxycarbonyl-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 4:

[174] 3,3-Di(4-methoxyphenyl)-6,7-dimethoxy-11-carboxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran from Step 2 of Example 2 (1.8 g), diethylene glycol (0.2 g), dicyclohexyl carbodiimide (1.2 g), 4-(dimethylamino)-pyridine (0.01 g) and dichloromethane (10 mL) were added to a flask and heated under reflux for 24 hours. The solid produced was removed by filtration and the remaining solvent was removed by rotary evaporation. Ether was added to the resulting residue and the solution cooled to room temperature. The precipitate obtained was collected by vacuum filtration and washed with diethyl ether yielding 2.1 g of 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(2-(2-hydroxyethoxy)ethoxycarbonyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 5:

Step 1

[175] 2,3-Dimethoxy-7,7-dimethyl-9-bromo-benzo[C]fluoren-5-ol from Step 5 of Example 1 (1.4 g), tetrakis(triphenylphosphine)palladium (0.12 g), 4-fluorophenylboronic acid (0.6 g), sodium carbonate (1.06 g), ethylene glycol dimethyl ether (50 mL), and water (50 mL) were combined in a reaction flask under a nitrogen atmosphere and stirred for 1 hour at room temperature. The mixture was then heated at reflux for 24 hours. After this time, the mixture was filtered and extracted with ethyl acetate (three times with 300 mL). The organic extracts were combined and the solvent was removed by rotary evaporation to give 1.2 g of a

white solid. NMR spectra showed the product to have a structure consistent with 2,3-dimethoxy-7,7-dimethyl-9-(4-fluorophenyl)-7H-benzo[C]fluoren-5-ol.

Step 2

[176] The procedure of Step 7 of Example 1 was followed except that 2,3-dimethoxy-7,7-dimethyl-9-(4-fluorophenyl)-7H-benzo[C]fluoren-5-ol of Step 1 was used in place of 2,3-dimethoxy-5-hydroxy-7,7-dimethyl-9-cyano-7H-benzo[C]fluoren-5-ol to produce 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(4-fluorophenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 6:

Step 1

[177] The procedure of Step 1 of Example 5 was followed except that 4-phenylphenylboronic acid was used in place of 4-fluorophenylboronic acid to produce 2,3-dimethoxy-7,7-dimethyl-9-(4-(phenyl)phenyl)-7H-benzo[C]fluoren-5-ol.

Step 2

[178] The procedure of Step 7 of Example 1 was followed except that 2,3-dimethoxy-7,7-dimethyl-9-(4-(phenyl)phenyl)-7H-benzo[C]fluoren-5-ol of Step 1 was used in place of 2,3-dimethoxy-7,7-dimethyl-9-cyano-7H-benzo[C]fluoren-5-ol to produce 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(4-(phenyl)phenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 7:

Step 1

[179] The procedure of Step 1 of Example 5 was followed except that 4-(hydroxymethyl)phenylboronic acid was used in place of 4-fluorophenylboronic acid to produce 2,3-dimethoxy-7,7-dimethyl-9-(4-(hydroxymethyl)phenyl)-7H-benzo[C]fluoren-5-ol.

Step 2

[180] The procedure of Step 7 of Example 1 was followed except that 2,3-dimethoxy-7,7-dimethyl-9-(4-(hydroxymethyl)phenyl)-7H-benzo[C]fluoren-5-ol of Step 1 was used in place of 2,3-dimethoxy-7,7-dimethyl-9-cyano-7H-benzo[C]fluoren-5-ol to produce 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(4-(hydroxymethyl)phenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 8:Step 1

[181] 2,3-Dimethoxy-7,7-dimethyl-9-bromo-7H-benzo[C]fluoren-5-ol from Step 5 of Example 1 (5.0 g), triphenylphosphine (0.16 g), dichlorobis(triphenylphosphine) palladium (0.12 g), copper iodide (0.06 g), 2-methyl-3-butyn-2-ol (1.56 g) and diisopropylamine (30 mL) were combined in a reaction flask under a nitrogen atmosphere and stirred for 1 hour at room temperature. The mixture was then heated at 80°C for 24 hours. After this time, the solid was filtered off over a short pad of silica gel and the solution was concentrated under vacuum. NMR spectra confirmed the resulting white solid to have the structure 2,3-dimethoxy-7,7-dimethyl-9-(3-hydroxy-3-methylbutyn)-7H-benzo[C]fluoren-5-ol.

Step 2

[182] The procedure of Step 7 of Example 1 was followed except that 2,3-dimethoxy-7,7-dimethyl-9-(3-hydroxy-3-methylbutyn)-7H-benzo[C]fluoren-5-ol of Step 1 was used in place of 2,3-dimethoxy-7,7-dimethyl-9-cyano-7H-benzo[C]fluoren-5-ol to produce 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(3-hydroxy-3-methylbutyn)-13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 9:Step 1

[183] The procedure of Step 1 of Example 8 was followed except that phenylacetylene was used in place of 2-methyl-3-butyn-2-ol to produce 2,3-dimethoxy-7,7-dimethyl-9-(2-phenylethynyl)-7H-benzo[C]fluoren-5-ol.

Step 2

[184] The procedure of Step 7 of Example 1 was followed except that 2,3-dimethoxy-7,7-dimethyl-9-(2-phenylethynyl)-7H-benzo[C]fluoren-5-ol of Step 1 was used in place of 2,3-dimethoxy-7,7-dimethyl-9-cyano-7H-benzo[C]fluoren-5-ol to produce 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(2-phenylethynyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 10:Step 1

[185] 4-Biphenylcarbonyl chloride (150 g), 1,2-dimethoxybenzene (88 mL), and dichloromethane (1.4 L) were combined in a reaction flask under a nitrogen

atmosphere. The reaction flask was cooled in an ice bath and aluminum chloride anhydrous (92.3 g) was added slowly over 30 minutes using a solid addition funnel. The ice bath was removed and the reaction mixture allowed to warm to room temperature. Additional 1,2-dimethoxybenzene (40 mL) and aluminum chloride (30 grams) were added to the reaction flask. After 1.5 hours the reaction mixture was slowly poured into a mixture of saturated aqueous NH_4Cl and ice (1.5 L). The layers were separated and the aqueous layer was extracted with two 750 mL portions of dichloromethane. The organic portions were combined and washed with 50 % saturated aqueous solution of NaHCO_3 (1 L). The organic layer was dried over anhydrous magnesium sulfate and concentrated by rotary evaporation. The resulting residue was dissolved in hot *t*-butyl methyl ether and allowed to cool to room temperature slowly. A white solid precipitated and was collected by vacuum filtration, washing with cold *t*-butyl methyl ether yielding 208 g of 3,4-dimethoxy-4'-phenylbenzophenone.

Step 2

[186] 3,4-Dimethoxy-4'-phenylbenzophenone from Step 1 (200 g), potassium *tert*-butoxide (141 g), and toluene (3 L) were combined in a flask under a nitrogen atmosphere and heating begun. To this was added dimethyl succinate (144 mL) dropwise over 45 minutes. Reaction mixture was heated to 70 °C for 1.5 hours and then cooled to room temperature. The reaction mixture was poured into a mixture of saturated aqueous NaCl and ice (3 L). The layers were separated and the aqueous layer was extracted with two 1 L portions of diethyl ether. The organic layers were discarded and the aqueous layer was acidified to pH 1 with conc. HCl. Dichloromethane (2 L) was added, the mixture extracted and the layers separated. The aqueous layer was extracted with two 1 L portions of dichloromethane. The organic layers were combined and washed with water (2 L). The organic layer was dried over anhydrous magnesium sulfate and concentrated by rotary evaporation to an orange colored oil yielding 287 g of a mixture of (E and Z) 3-methoxycarbonyl-4-(4-phenyl)phenyl,4-(3,4-dimethoxyphenyl)-3-butenic acid. The product was used without further purification in the subsequent reaction.

Step 3

[187] A mixture of (E and Z) 3-methoxycarbonyl-4-(4-phenyl)phenyl,4-(3,4-dimethoxyphenyl)-3-butenic acid from Step 2 (272 g) and acetic anhydride (815 mL) were combined in a reaction flask under a nitrogen atmosphere and heated to reflux for 13 hours. The reaction mixture was cooled to room temperature and then slowly poured into ice water (1 L). The mixture was stirred for 3 hours and then saturated aqueous NaHCO₃ (2 L) was slowly added. Additional sodium bicarbonate (750 grams) was slowly added portion wise. Dichloromethane (2.5 L) was added to the mixture, which was then filtered, and the filtrate phase separated. The aqueous layer was extracted with dichloromethane (1 L). The organic layers were combined, dried over anhydrous magnesium sulfate, and concentrated by rotary evaporation to a dark red solid. The red solid was slurried in hot ethanol, cooled to room temperature, collected by vacuum filtration, and washed with cold ethanol yielding 187.5 g of a mixture of 1-(4-phenyl)phenyl-2-methoxycarbonyl-4-acetoxy-6,7-dimethoxynaphthalene and 1-(3,4-dimethoxyphenyl)-2-methoxycarbonyl-4-acetoxy-6-phenylnaphthalene. The product was used without further purification in the subsequent reaction.

Step 4

[188] The mixture of 1-(4-phenyl)phenyl-2-methoxycarbonyl-4-acetoxy-6,7-dimethoxynaphthalene and 1-(3,4-dimethoxyphenyl)-2-methoxycarbonyl-4-acetoxy-6-phenylnaphthalene from Step 3 (172 g), water (1035 mL), methanol (225 mL), and sodium hydroxide (258 g) were combined in a reaction flask and heated to reflux for 5 hours. The reaction mixture was cooled to room temperature and was then slowly poured into mixture of water (1.5 L), conc. HCl (500 mL) and ice. A white solid precipitated and was filtered and washed with water. The solid was dissolved in a small amount of anhydrous tetrahydrofuran and then diluted with *t*-butyl methyl ether. This solution was washed with saturated aqueous NaCl and the organic layer was dried over anhydrous magnesium sulfate and concentrated by rotary evaporation to a light orange solid. The solid was slurried in hot toluene, cooled to room temperature, filtered, and washed with cold toluene yielding 127 g of a white solid (1-(4-phenyl)phenyl-2-carboxy-4-hydroxy-6,7-dimethoxynaphthalene). The product was used in the subsequent reaction without purification.

Step 5

[189] 1-(4-Phenyl)phenyl-2-carboxy-4-hydroxy-6,7-dimethoxynaphthalene from Step 4 (25 g), acetic anhydride (29 mL), 4-(dimethylamino)pyridine (115 mg), and 1,2,4-trimethylbenzene (500 mL) were combined in a reaction flask under a nitrogen atmosphere and heated to 50 °C for one hour. Dodecylbenzene sulfonic acid (10.3 g) was added to the reaction mixture and the temperature increased to 144 °C. After 28 hours the reaction mixture was slowly cooled to room temperature and a solid precipitated. The reaction mixture was filtered and washed with toluene yielding 23.0 g of a red solid (2,3-dimethoxy-5-acetoxy-11-phenyl-7H-benzo[C]fluoren-7-one). The product was used in the subsequent reaction without further purification.

Step 6

[190] 2,3-Dimethoxy-5-acetoxy-11-phenyl-7H-benzo[C]fluoren-7-one from Step 5 (4.22 g) and anhydrous tetrahydrofuran (85 mL) were combined in a reaction flask under a nitrogen atmosphere and cooled in an ice bath. To this was added 13.5 mL of an ethylmagnesium bromide solution (3.0 M in diethyl ether) dropwise over 20 minutes. The reaction mixture was allowed to warm to room temperature and was then poured into a mixture of saturated aqueous NH₄Cl and ice (100 mL). The mixture was diluted with ethyl acetate (40 mL) and then the layers were separated. The aqueous layer was extracted with two 70 mL portions of ethyl acetate. The organic layers were combined and washed saturated aqueous NaHCO₃ (100 mL), dried over NaSO₄, and concentrated by rotary evaporation to afford an orange solid. The solid was slurried in hot *t*-butyl methyl ether, cooled to room temperature, filtered, and washed with cold *t*-butyl methyl ether yielding 2.6 g of a light orange solid (2,3-dimethoxy-7-hydroxy-7-ethyl-11-phenyl-7H-benzo[C]fluoren-5-ol). The product was used in the subsequent reaction without further purification.

Step 7

[191] 2,3-Dimethoxy-7-hydroxy-7-ethyl-11-phenyl-7H-benzo[C]fluoren-5-ol from Step 6 (2.59 g), 1,1-bis(4-methoxyphenyl)-2-propyl-1-ol (2.19g, the product of Example 1, Step 1 of US Patent No. 5,458,814, the disclosure of which is hereby specifically incorporated by reference), and dichloromethane (52 mL) were

combined in a reaction flask under a nitrogen atmosphere. To this was added trifluoroacetic acid (41 mg). After 2 hours *p*-toluenesulfonic acid monohydrate (29 mg) was added to the reaction flask. After an additional 45 minutes the reaction mixture was diluted with dichloromethane (25 mL) and then washed with 50% saturated aqueous NaHCO₃ (50 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated by rotary evaporation. Hot acetonitrile was added to the resulting residue and a solid precipitated. The mixture was cooled to room temperature, vacuum filtered, and washed with cold acetonitrile yielding 3.43 g of a light green solid (3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-phenyl-13-ethyl-13-hydroxy-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran). The product was used in the subsequent reaction without further purification.

Step 8

[192] 3,3-Di(4-methoxyphenyl)-6,7-dimethoxy-11-phenyl-13-ethyl-13-hydroxy-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran from Step 7 (3.4 g), anhydrous methanol (35 mL), toluene (34 mL), and *p*-toluenesulfonic acid monohydrate (75 mg) were combined in a reaction flask under a nitrogen atmosphere and heated to reflux. After 4 hours the reaction mixture was cooled to room temperature and diluted with toluene (35 mL). The reaction mixture was washed with two 35 mL portions of 50% saturated aqueous NaHCO₃. The organic layer was dried over anhydrous magnesium sulfate and concentrated by rotary evaporation. Hot methanol was added to the resulting residue and a solid precipitated. The mixture was cooled to room temperature, vacuum filtered, and the solid washed with cold methanol yielding 3.06 g of a light yellow solid. Mass Spectroscopy ("MS") analysis and NMR spectra show the product to have a structure consistent with 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-phenyl-13-ethyl-13-methoxy-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 11:

Step 1

[193] 2,3-Dimethoxy-7,7-dimethyl-9-bromo-7H-benzo[C]fluoren-5-ol from Step 5 of Example 1 (5 g), tetrakis(triphenylphosphine)palladium (0) (0.43 g), 4-methoxycarbonyl phenylboronic acid (2.5 g), sodium carbonate (3 g), ethylene

glycol dimethyl ether (90 mL), and water (30 mL) were combined in a reaction flask under nitrogen atmosphere and stirred for 1 hour at room temperature. The mixture was then heated at reflux for 24 hours. Water (60 mL) and sodium hydroxide (1 g) were added, and the reaction mixture was heated at reflux for 20 hours. After this time, the mixture was cooled to room temperature, and aqueous HCl (10%) was added to the mixture under stirring, the mixture was filtered and extracted with ethyl acetate (three times with 100 mL) and dichloromethane (three times with 100 mL). The organic extracts were combined and the solvent was removed by rotary evaporation to give 5 g of a yellow solid (2,3-dimethoxy-7,7-dimethyl-9-(4-hydroxycarbonylphenyl)-7H-benzo[C]fluoren-5-ol). The product was used without further purification in the subsequent reaction.

Step 2

[194] 2,3-Dimethoxy-7,7-dimethyl-9-(4-hydroxycarbonylphenyl)-7H-benzo[C]fluoren-5-ol from Step 1 (7.5 g), 1-phenyl-1-(4-methoxyphenyl)-2-propyn-1-ol (4.0 g, made as described in Example 1 Step 1 of U.S. patent 5,458,814), dodecylbenzene sulfonic acid (0.2 g) and chloroform (preserved with pentene, 70 mL) were combined in a reaction flask and stirred at room temperature for 2 hours. The reaction mixture was concentrated, and acetone (100 mL) was added to the residue, and the slurry was filtered, yielding 6.5 g of a green solid. The product was used without further purification in the subsequent reaction.

Step 3

[195] 3-Phenyl-3-(4-methoxyphenyl)-6,7-dimethoxy-11-(4-hydroxycarbonylphenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran from Step 2 (0.2 g), 2-hydroxyethyl methacrylate (0.5 mL), dicyclohexyl carbodiimide (0.2 g), 4-(dimethylamino)-pyridine (0.04 g) and dimethylformamide (20 mL) were added to a flask and heated to 55-58°C for 3 hours. Water was added to the reaction mixture, the precipitation was filtered out, yielding 0.27 g of an off-green solid. Mass spectroscopy ("MS") analysis supports the molecular weight of 3-phenyl-3-(4-methoxyphenyl)-6,7-dimethoxy-11-(4-(2-methacryloxyethoxy)carbonylphenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 12:Step 1

[196] 2,3-Dimethoxy-7,7-dimethyl-9-bromo-7H-benzo[C]fluoren-5-ol from Step 5 of Example 1 (4.7 g), 1,1-bis(4-methoxyphenyl)-2-propyn-1-ol (3.5 g, the product of Example 1 Step 1 of U.S. patent 5,458,814), pyridinium p-toluenesulfonate (0.15 g), trimethyl orthoformate (3.5 mL) and chloroform (preserved with pentene, 100 mL) were combined in a reaction flask and stirred at reflux for half hour. The reaction mixture was concentrated. Acetone was added to the residue, the slurry was filtered, yielding 7.7 g of an off-white solid, MS analysis supports the molecular weight of 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-bromo-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran. The product was used without further purification in the subsequent reaction.

Step 2

[197] The procedure of Step 1 of Example 5 was followed except that 4-phenylphenylboronic acid was used in place of 4-fluorophenylboronic acid to produce 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(4-phenylphenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran. The product was used without further purification in the subsequent reaction.

Step 3

[198] 3,3-Di(4-methoxyphenyl)-6,7-dimethoxy-11-(4-(phenyl)phenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran from Step 2, above, (6 g), 3-piperidinemethanol (1.3 g) and tetrahydrofuran (60 mL) were combined in a dry reaction flask under nitrogen atmosphere, butyl lithium (10 mL, 2.5 M in hexane) was cannulated into the reaction flask under stirring. The mixture was stirred for 30 minutes at room temperature and then carefully poured into ice water. The mixture was extracted with ethyl acetate (three times with 100 mL). The extracts were combined and washed with saturated aqueous sodium chloride solution. The solution was dried over Na₂SO₄ and filtered. The solution was concentrated and the residue was purified by silica gel chromatography (ethyl acetate/hexanes (v/v): 1/1). The major fraction was collected from column and concentrated, yielding 5 g of purple foam. MS analysis supports the molecular weight of 3,3-di(4-

methoxyphenyl)-6-methoxy-7-((3-hydroxymethylenepiperidino)-1-yl)-11-(4-(phenyl)phenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran. The product was used without further purification in the subsequent reaction.

Step 4

[199] 3,3-Di(4-methoxyphenyl)-6-methoxy-7-((3-hydroxymethylenepiperidino)-1-yl)-11-(4-(phenyl)phenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran from Step 3 (5 g), 2-isocyanatoethylmethacrylate (1 mL), dibutyltin dilaurate (1 drop) and ethyl acetate (50 mL) were combined in a reaction flask with a condenser open to air. The mixture was heated at reflux for 20 minutes. Methanol (5 mL) was added to the mixture to quench excess 2-isocyanatoethylmethacrylate. The reaction mixture was concentrated and the residue was purified by silica gel chromatography (ethyl acetate/hexanes (v/v): 1/1). The major fraction was collected from the column and concentrated, yielding 6 g of a purple foam. MS analysis supports the molecular weight of 3,3-di(4-methoxyphenyl)-6-methoxy-7-((3-(2-methoxyacryloxyethyl)carbamyloxymethylene piperidino)-1-yl)-11-(4-(phenyl)phenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 13:

Step 1

[200] The procedures of Example 1 were followed except that 4-bromophenyl-4'-methoxybenzophenone was used in place of 3,4-dimethoxy-4'-bromobenzophenone to produce 3-methoxy-9-bromo-7,7-dimethyl-7H-benzo[C]fluoren-5-ol.

Step 2

[201] 4-Hydroxybenzophenone (100 g), 2-chloroethanol (50 g), sodium hydroxide (20 g) and water (500 mL) were combined in a reaction flask. The mixture was heated at reflux for 6 hours. The oily layer was separated and crystallized upon cooling, the crystalline material was washed with aqueous sodium hydroxide followed by fresh water and dried, yielding an off-white solid 85 g. The product was used without further purification in the subsequent reaction.

Step 3

[202] The product from Step 2 (30 g) was dissolved in anhydrous dimethylformamide (250 mL) in a reaction flask with overhead stirring. Sodium acetylide paste in toluene (15 g, ~9wt%) was added to the reaction flask under vigorous stirring. After the reaction is complete, the mixture was added to water (500 mL), and the solution was extracted with ethyl ether (twice with 500 mL). The extracts were combined and washed with saturated aqueous sodium chloride solution and dried over sodium sulfate. The solution was then filtered and concentrated, and the dark residue was purified by silica gel chromatography (ethyl acetate/hexanes (v/v): 1/1). The major fraction was collected from column and concentrated, yielding 33 g of a white solid (1-phenyl-1-(4-(2-hydroxyethoxy)phenyl)-2-propyn-1-ol).

Step 4

[203] 3-Methoxy-9-bromo-7,7-dimethyl-7H-benzo[C]fluoren-5-ol from Step 1 (5 g), 1-phenyl-1-(4-(2-hydroxyethoxy)phenyl)-2-propyn-1-ol from Step 3 (4 g), dodecylbenzene sulfonic acid (2 drops) and chloroform (40 mL) were combined in a reaction flask. The mixture was heated at reflux for an hour and then concentrated. The residue was purified by silica gel chromatography (ethyl acetate/hexanes (v/v): 1/1). The major fraction was collected from the column and concentrated to 7 g of an expanded green foam. MS analysis supports the molecular weight of 3-phenyl-3-(2-hydroxyethoxy)phenyl-6-methoxy-11-bromo-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Step 5

[204] 3-Phenyl-3-(4-(2-hydroxyethoxy)phenyl)-6-methoxy-11-bromo-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran from Step 4 (3.5 g), tetrakis(triphenylphosphine)palladium (0) (0.12 g), phenylboronic acid (1.05 g), sodium carbonate (1.33 g), ethylene glycol dimethyl ether (50 mL), and water (10 mL) were combined in a reaction flask under nitrogen atmosphere and stirred for 1 hour at room temperature. The mixture was then heated at reflux for 28 hours. After this time, water (30 mL) was added to the mixture. The mixture was extracted with ethyl acetate (200 mL), the extract was washed with water and saturated aqueous sodium chloride solution and dried over sodium sulfate. The solution was

filtered and concentrated. The residue was purified by silica gel chromatography (ethyl acetate/hexanes (v/v): 1/1.5). The major fraction was recrystallized in ethyl acetate/hexanes (v/v: 1/2), yielding 1.6 g of a yellow-green solid. NMR spectra supports the structure of 3-phenyl-3-(4-(2-hydroxyethoxy)phenyl)-6-methoxy-11-phenyl-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Step 6

[205] 3-Phenyl-3-((4-(2-hydroxyethoxy)phenyl)-6-methoxy-11-phenyl-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran from Step 5 (1 g), 2-isocyanatoethylmethacrylate (0.8 mL), dibutyltin dilaurate (1 drop) and ethyl acetate (20 mL) were combined in a reaction flask with a condenser open to air. The mixture was heated at reflux for 1 hour. Methanol (4 mL) was added to the mixture to quench excess 2-isocyanatoethylmethacrylate. The reaction mixture was concentrated and the residue was purified by silica gel chromatography (dichloromethane/ hexanes/acetone (v/v/v): 10/5/1). The major fraction was collected from column and concentrated to an expanded blue-green foam. MS analysis supports the molecular weight of 3-phenyl-3-(4-(2-(2-methacryloxyethyl)carbamyloxyethoxy)phenyl)-6-methoxy-11-phenyl-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 14:

Step 1

[206] The procedures of Example 1 were followed except that 4,4'-dimethoxybenzophenone was used in place of 3,4-dimethoxy-4'-bromobenzophenone to produce 3,9-dimethoxy-7,7-dimethyl-7H-benzo[C]-fluoren-5-ol.

Step 2

[207] 3,9-Dimethoxy-7,7-dimethyl-7H-benzo[C]fluoren-5-ol from Step 1 (3 g), the product of Example 13 Step 3 (1-phenyl-1-(4-(2-hydroxyethoxy)phenyl)-2-propyn-1-ol (5 g), p-toluenesulfonic acid (0.2 g) and chloroform (preserved with pentene, 10 mL) were combined in a reaction flask and stirred at room temperature for half hour. The reaction mixture was concentrated. The residue was purified by silica gel chromatography (ethyl acetate/hexanes (v/v): 1/1). The major fraction was collected from column and concentrated, methanol was added to the residue and the

precipitation was filtered, yielding 3 g of a yellow-green solid. MS analysis supports the molecular weight of 3-phenyl-3-4-(2-hydroxyethoxy)phenyl-6,11-dimethoxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Step 3

[208] The product of Example 2 Step 1 2,3-dimethoxy-7,7-dimethyl-9-carboxy-7H-benzo[C]fluoren-5-ol (0.77 g), 1-phenyl-1-(4-methoxyphenyl)-2-propyn-1-ol (1 g, made as described in Example 1 Step 1 in U.S. patent 5,458,814), pyridinium p-toluenesulfonate (0.04 g), trimethyl orthoformate (0.5 mL) and chloroform (preserved with pentene, 50 mL) were combined in a reaction flask and stirred at reflux for 22 hours. The reaction mixture was concentrated, and the residue was added to acetone and t-butyl methyl ether (v/v: 1:1), the slurry was filtered, yielding 1 g of a yellow-green solid. MS analysis supports the molecular weight of 3-phenyl-3-(4-methoxyphenyl)-6,7-dimethoxy-11-carboxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran. The product was used without further purification in the subsequent reaction.

Step 4

[209] 3-Phenyl-3-((4-(2-hydroxyethoxy)phenyl)-6,11-dimethoxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran from Step 2 (0.7g), 3-phenyl-3-(4-methoxyphenyl)-6,7-dimethoxy-11-carboxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran from Step 3 (0.5 g), dicyclohexyl carbodiimide (1 g), 4-(dimethylamino)-pyridine (0.17 g) and dichloromethane (50 mL) were added to a flask and heated at reflux for 27 hours. The reaction mixture was concentrated, and the residue was purified by silica gel chromatography (dichloromethane/hexanes/methanol (v/v/v): 10/10/1). The major fraction was collected from column and concentrated to 0.7 g of blue-green foam. MS analysis supports the molecular weight of 3-phenyl-3-(4-methoxyphenyl)-6,7-dimethoxy-13,13-dimethyl-11-(2-(4-(3-phenyl-6,11-dimethoxy-13,13 dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran-3-yl)phenoxy)ethoxycarbonyl)-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Example 15:

Step 1

[210] *p*-Hydroxybenzophenone (45 g), 3,4-dihydro-2H-pyran (30 mL), dodecylbenzenesulfonic acid (10 drops) and dichloromethane (450 mL) were combined to a reaction flask under nitrogen atmosphere. The mixture was stirred at room temperature for 2 hours and poured into saturated aqueous sodium bicarbonate solution. The dichloromethane phase was separated and dried over sodium sulfate. The solution was filtered and concentrated. The residue was used in subsequent reaction without further purification.

Step 2

[211] The product from Step 1 (80 g) was dissolved in anhydrous dimethylformamide (130 mL) in a reaction flask with overhead stirring, sodium acetylide in toluene (35 g, ~9wt%) was added to the reaction flask under vigorous stirring. After the reaction was complete, the mixture was poured into water (200 mL), and the solution was extracted with ethyl ether (three times with 200 mL). The extracts were combined and washed with saturated aqueous sodium chloride solution and dried over sodium sulfate. The solution was filtered and concentrated. The product was used in subsequent reaction without further purification.

Step 3

[212] The product from Step 2 (80 g), *p*-toluenesulfonic acid (0.14g) and anhydrous methanol (50 mL) were combined in a reaction flask. The mixture was stirred at room temperature for 30 minutes and poured into saturated aqueous sodium bicarbonate solution (15 mL)/ water (150 mL), the mixture was extracted with ethyl acetate (three times with 200 mL), and the extracts were combined and dried over sodium sulfate. The solution was filtered and concentrated. The product was used in subsequent reaction without further purification.

Step 4

[213] The product of Example 2 Step 1 2,3-dimethoxy-7,7-dimethyl-9-carboxy-7H-benzo[C]-fluoren-5-ol (1 g), the product from Step 3 (3 g), dodecylbenzenesulfonic acid (5 drops), tetrahydrofuran (5 mL), and chloroform (40 mL) were combined in a reaction flask, the mixture was heat at reflux for 2 hours, and then concentrated. Methanol was added to the residue and the slurry was filtered, yielding 0.7 g of an off-white solid. MS analysis supports the molecular

weight of 3-phenyl-3-(4-hydroxyphenyl)-6,7-dimethoxy-11-carboxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Step 5

[214] 4-Fluorobenzophenone (30 g), piperazine (23 g), triethyl amine (23 mL), potassium carbonate (22 g) and dimethyl sulfoxide (50 mL) were combined in a reaction flask, and the mixture was heated at reflux for 20 hours. After this time, the mixture was cooled and poured into water, the slurry was extracted with chloroform and the chloroform phase was washed with water twice and dried over sodium sulfate. The solution was concentrated to 45 g of orange oil. The product was used in subsequent reaction without further purification.

Step 6

[215] The procedure of Step 2 was followed except that the product from Step 5 was used in place of the product from Step 1. After the work-up, the residue was purified by silica gel chromatography (ethyl acetate/methanol (v/v): 1/1). The major fraction was collected from column and concentrated to 17 g of a yellowish solid.

Step 7

[216] 3,9-Dimethoxy-7,7-dimethyl-7H-benzo[C]fluoren-5-ol from Step 1 of Example 14 (1 g), the product from Step 6 above (3g), p-toluenesulfonic acid (0.2g) and chloroform (70 mL) were combined in a reaction flask, the mixture was stirred at room temperature for 20 minutes and then poured into saturated aqueous potassium carbonate solution (20 mL), the chloroform phase was separated and dried over sodium sulfate. The solution was filtered and concentrated. The residue was purified by silica gel chromatography (ethyl acetate/methanol (v/v): 1/1). The blue fraction was collected and concentrated, the residue was added to methanol, and the slurry was filtered, yielding 0.6 g of a green solid. MS analysis supports the molecular weight of 3-phenyl-3-(4-piperazinophenyl)-6,11-dimethoxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran. The product was used without further purification in the subsequent reaction.

Step 8

[217] 3-Phenyl-3-(4-hydroxyphenyl)-6,7-dimethoxy-11-carboxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran from Step 4 (0.45 g), 2-isocyanatoethylmethacrylate (1.5 mL), dibutyltin dilaurate (1 drop) and

dimethylformamide (3 mL) were combined in a reaction flask, the mixture was heated to 80°C for 2 hours. The mixture was poured into water and extracted with ethyl acetate. The extract was washed with water twice and dried over sodium sulfate. The solution was filtered and concentrated. The residue was added to acetone and methanol (v/v: 1/1), the slurry was filtered, yielding 0.6 g of a yellow solid.

Step 9

[218] 3-Phenyl-3-(4-piperazinophenyl)-6,11-dimethoxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran from Step 7 (0.5 g), 3-phenyl-3-(4-(2-methacryloxyethyl)carbamyloxyphenyl)-6,7-dimethoxy-11-carboxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran from Step 8 (0.7 g), dicyclohexyl carbodiimide (0.5 g), 4-(dimethylamino)-pyridine (0.08 g) and dimethylformamide (10 mL) were added to a flask and heated to 80 °C for 18 hours. The mixture was poured into water, the slurry was filtered, and the solid (0.5 g) was further purified by silica gel chromatography (ethyl acetate/ methanol (v/v): 1/1). The pure fraction was concentrated to yield 130 mg of an expanded blue-green foam. MS analysis supports the molecular weight of 3-phenyl-3-(4-(2-methacryloxyethyl)carbamyloxyphenyl)-6,7-dimethoxy-13,13-dimethyl-11-((4-(4-(3-phenyl-6,11-dimethoxy-13,13 dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran-3-yl)-phenyl)piperazino-4-yl)carbonyl) -3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Comparative Example CE1:

Step 1

[219] Potassium t-butoxide (50.0 g) and benzophenone (100.0 g) were added to a reaction flask containing 500 mL of toluene under a nitrogen atmosphere. To the mixture was added dimethyl succinate (150.0 g) dropwise over 1 hour. The mixture was stirred for 5 hours at room temperature. The resulting mixture was poured into 300 mL of water and vigorously stirred for 20 minutes. The aqueous and organic phases were separated and the organic phases were extracted with 100 mL portions of water three times. The combined aqueous layers were washed with 150 ml portions of chloroform three times. The aqueous layer was acidified to pH 2 with

6N HCl and a precipitate formed. The aqueous layer was extracted with three 100 mL portions of chloroform. The organic extracts were combined and concentrated by rotary evaporation. NMR spectra showed the product to have a structure of 4,4-diphenyl-3-methoxycarbonyl-3-butenic acid.

Step 2

[220] The crude half-ester from Step 1 (100.0 g), 60 mL of acetic anhydride, and 300 mL of toluene were added to a reaction flask under a nitrogen atmosphere. The reaction mixture was heated to 110° C for 6 hours, cooled to room temperature, and the solvents (toluene and acetic acid) removed by rotary evaporation. The residue was dissolved in 300 mL of methylene chloride and 200 mL of water. Solid Na₂CO₃ was added to the biphasic mixture until bubbling ceased. The layers separated and the aqueous layer was extracted with 50 mL portions of methylene chloride. The organic extracts were combined and the solvent removed by rotary evaporation to yield thick red oil. The oil was dissolved in warm methanol and chilled at 0° C for 2 hours. The resulting crystals were collected by vacuum filtration, washed with cold methanol to produce the 1-phenyl-2-methoxycarbonyl-4-acetoxy-naphthalene. The product mixture was used without further purification in subsequent reaction.

Step 3

[221] 1-Phenyl-2-methoxycarbonyl-4-acetoxy-naphthalene from Step 2 (100 g), water (100 mL), methanol (200 mL), and sodium hydroxide (100 g) were combined in a reaction flask and heated to reflux for 5 hours. The reaction mixture was cooled to room temperature and was then slowly poured into mixture of water (1.5 L), conc. HCl (500 mL) and ice. A white solid precipitated and was filtered and washed with water. The solid was dissolved in a small amount of anhydrous tetrahydrofuran and then diluted with *t*-butyl methyl ether. This solution was washed with saturated aqueous NaCl and the organic layer was dried over anhydrous magnesium sulfate and concentrated by rotary evaporation to a light orange solid. NMR spectra showed the product to have a structure of 1-phenyl-2-carboxy-4-hydroxy-naphthalene.

Step 4

[222] 1-Phenyl-2-carboxy-4-hydroxy-naphthalene from Step 3 (50 g), acetic anhydride (60 mL), 4-(dimethylamino)pyridine (200 mg), and 1,2,4-trimethylbenzene (500 mL) were combined in a reaction flask under a nitrogen atmosphere and heated to 50°C for one hour. Dodecylbenzene sulfonic acid (5.0 g) was added to the reaction mixture and the temperature increased to 144°C. After 28 hours the reaction mixture was slowly cooled to room temperature and a solid precipitated. The reaction mixture was filtered and washed with toluene yielding 40.0 g of a red solid 5-acetoxy-7H-benzo[C]fluoren-7-one. The product was used in the subsequent reaction without further purification.

Step 5

[223] 5-Acetoxy-7H-benzo[C]fluoren-7-one from Step 4 (10 g) and anhydrous tetrahydrofuran (150 mL) were combined in a reaction flask under a nitrogen atmosphere and cooled in an ice bath. To this was added 2 grams of NaH. The reaction mixture was allowed to warm to room temperature and was then poured into a mixture of saturated aqueous NH₄Cl and ice (100 mL). The mixture was diluted with ethyl acetate (100 mL) and then the layers were separated. The aqueous layer was extracted with two 50 mL portions of ethyl acetate. The organic layers were combined and washed with saturated aqueous NaHCO₃ (100 mL), dried over NaSO₄, and concentrated by rotary evaporation to afford 5-hydroxy-7H-benzo[C]fluoren-7-ol.

Step 6

[224] 5-Hydroxy-7H-benzo[C]fluoren-5-ol from Step 5 (2.40 g), 1,1-bis(4-methoxyphenyl)-2-propyn-1-ol, (2.19g, the product of Example 1, Step 1 of U.S. Patent No. 5,458,814), , dodecylbenzene sulfonic acid (0.12 g) and dichloromethane (52 mL) were combined in a reaction flask and stirred at room temperature for 5 hours. The reaction mixture was washed with 50% saturated aqueous NaHCO₃ (200 mL) and the organic layer was dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporation and the product was isolated by column chromatography (hexane/ethyl acetate: 2/1). NMR spectra showed the product to have a structure of 3,3-di(4-methoxyphenyl)-13-hydroxy-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Comparative Example CE2:

[225] The procedures of comparative Example CE1 were followed except that 4,4'-dimethylbenzophenone was used in place of benzophenone to produce 3,3-di(4-methoxyphenyl)-6,11-dimethyl-13-hydroxy-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Comparative Example CE3:Step1

[226] The procedures of steps 2-5 of Example 1 were followed except that naphthobenzophenone was used in place of 3,4-dimethoxy-4'-bromobenzophenone to produce 13,13-dimethyl-dibenzo[a,g]fluoren-11-ol.

Step2

[227] 13,13-Dimethyl-dibenzo[a,g]fluoren-11-ol from step 1 (2.50 g), 1,1-bis(4-methoxyphenyl)-2-propyn-1-ol, (2.19 g the product of Example 1, Step 1 of U.S. Patent No. 5,458,814)), dodecylbenzene sulfonic acid (0.12 g), and dichloromethane (52 mL) were combined in a reaction flask and stirred at room temperature for 5 hours. The reaction mixture was washed with 50 % saturated aqueous NaHCO₃ (200 mL) and the organic layer was dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporation and the product was isolated by column chromatography (hexane/ethyl acetate: 85/15, R_f=0.3). NMR spectra showed the product to have a structure of 3,3-di(4-methoxyphenyl)-13,13-dimethyl-3H,13H-benz[p]-indeno[2',3':3,4]naphtho[1,2-b]pyran.

Comparative Example CE4:Step 1

[228] The procedures of Steps 1-5 of Example 1 were followed except that benzoyl chloride was used in place of bromobenzoyl chloride to produce 2,3-dimethoxy-7,7-dimethyl-7H-benzo[C]fluoren-5-ol.

Step 2

[229] The procedure of Step 7 of Example 1 was followed except that 2,3-dimethoxy-7,7-dimethyl-7H-benzo[C]fluoren-5-ol of Step 1 was used in place of 2,3-dimethoxy-7,7-dimethyl-9-cyano-7H-benzo[C]fluoren-5-ol to produce 3,3-di(4-

methoxyphenyl)-6,7-dimethoxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran.

PART 2: TESTING

Absorption Testing

[230] The photochromic performance of the photochromic materials of Examples 1-15, Comparative Examples CE1-CE4, as well as eleven additional photochromic materials (Examples 16-26, listed below in Table 1) comprising a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof were tested using the following optical bench set-up. It will be appreciated by those skilled in the art that the photochromic materials of Examples 16-26 may be made in accordance with the teachings and examples disclosed herein with appropriate modifications, which will be readily apparent to those skilled in the art. Further, those skilled in the art will recognize that various modifications to the disclosed methods, as well as other methods, may be used in making the photochromic materials of Examples 1-26.

[231] Prior to testing the molar absorbance, a solution of each photochromic material in chloroform was made at a concentration as indicated in Table 1. Each solution was then placed in an individual test cell having a solution pathlength of 1 cm and the test cells were measured for ultraviolet absorbance over a range of wavelengths ranging from 300 nm to 440 nm using a Cary 4000 UV spectrophotometer and a plot of absorbance vs. wavelength was obtained. The integrated extinction coefficient for each material tested was then determined by converting the absorption measurements to extinction coefficient and integrating the resultant plot over 320-420 nm using Igor program (distributed by WaveMetrics, Inc.).

Table 1: Absorption Test Data

Example No.	Name	Conc. (m)	Area 320-420nm	Integrated Extinction Coeff. (nm x mol ⁻¹ x cm ⁻¹)
1	As set forth in Example 1	1.45 x 10 ⁻⁴	195.8	1.4 x 10 ⁶
2	As set forth in Example 2	1.30 x 10 ⁻⁴	173.9	1.3 x 10 ⁶
3	As set forth in Example 3	1.28 x 10 ⁻⁴	175.5	1.4 x 10 ⁶
4	As set forth in Example 4	1.36 x 10 ⁻⁴	193.8	1.4 x 10 ⁶
5	As set forth in Example 5	1.26 x 10 ⁻⁴	151.8	1.2 x 10 ⁶

6	As set forth in Example 6	1.16×10^{-4}	206.4	1.8×10^6
7	As set forth in Example 7	1.24×10^{-4}	166.5	1.3×10^6
8	As set forth in Example 8	1.28×10^{-4}	161.5	1.3×10^6
9	As set forth in Example 9	1.33×10^{-4}	272.6	2.0×10^6
10	As set forth in Example 10	1.23×10^{-4}	161.4	1.3×10^6
11	As set forth in Example 11	1.02×10^{-4}	162.9	1.6×10^6
12	As set forth in Example 12	7.52×10^{-5}	162.5	2.2×10^6
13	As set forth in Example 13	8.78×10^{-5}	108.5	1.2×10^6
14	As set forth in Example 14	1.25×10^{-4}	246.4	2.0×10^6
15	As set forth in Example 15	2.32×10^{-5}	38.4	1.7×10^6
16	3,3-di(4-methoxyphenyl)-11-methoxycarboxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4] naphtho[1,2-b]pyran	1.52×10^{-4}	177.4	1.2×10^6
17	3-(4-morpholinophenyl)-3-phenyl-6,7-dimethoxy-11-carboxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran	1.30×10^{-4}	187.2	1.4×10^6
18	3-(4-morpholinophenyl)-3-phenyl-6,7-dimethoxy-11-methoxycarbonyl-13,13-dimethyl-3H,13H-indeno[2',3':3,4] naphtho[1,2-b]pyran	1.36×10^{-4}	201.9	1.5×10^6
19	3-(4-morpholinophenyl)-3-(4-methoxyphenyl)-6,7-dimethoxy-11-(4-fluorophenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4] naphtho[1,2-b]pyran	1.24×10^{-4}	152.0	1.2×10^6
20	3-(4-fluorophenyl)-3-(4-methoxyphenyl)-6,7-dimethoxy-11-cyano-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran	1.46×10^{-4}	189.0	1.3×10^6
21	3-(4-morpholinophenyl)-3-(4-methoxyphenyl)-11-(2-phenylethynyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4] naphtho[1,2-b]pyran	1.29×10^{-4}	277.5	2.1×10^6
22	3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(4-dimethylaminophenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran	1.25×10^{-4}	275.9	2.2×10^6
23	3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(4-methoxyphenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran	1.26×10^{-4}	185.4	1.5×10^6
24	3,3-di(4-methoxyphenyl)-6-methoxy-7-morpholino-11-phenyl-13-butyl-13-(2-(2-hydroxyethoxy)ethoxy)-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran	1.03×10^{-4}	170.7	1.7×10^6
25	3-(4-fluorophenyl)-3-(4-methoxyphenyl)-6-methoxy-7-morpholino-11-phenyl-13-butyl-13-(2-(2-hydroxyethoxy)ethoxy)-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran	1.03×10^{-4}	168.2	1.6×10^6
26	3,3-di(4-fluorophenyl)-11-cyano-13-dimethyl-3H,13H-indeno[2',3':3,4] naphtho[1,2-b]pyran	1.62×10^{-4}	181.5	1.1×10^6
CE1	As set forth in Comparative Example 1	1.88×10^{-4}	109.8	5.8×10^5

CE2	As set forth in Comparative Example 2	1.63×10^{-4}	93.9	5.8×10^5
CE3	As set forth in Comparative Example 3	1.44×10^{-4}	144.1	1.0×10^6
CE4	As set forth in Comparative Example 4	1.64×10^{-4}	94.1	5.7×10^5

[232] As can be seen from the data in Table 1, the photochromic materials according to various non-limiting embodiments disclosed herein (Example Nos. 1-26) all had integrated extinction coefficients greater than 1.0×10^6 , $\text{nm} \times \text{mol}^{-1} \times \text{cm}^{-1}$, wherein as the photochromic materials of comparative examples CE1-CE4 did not.

Photochromic Performance Testing

[233] The photochromic performance of the photochromic materials of Examples 1-15, Comparative Examples CE1-CE4, as well as the eleven additional photochromic materials (Examples 16-26, listed above in Table 1) were tested as follows.

[234] A quantity of the photochromic material to be tested calculated to yield a 1.5×10^{-3} M 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 material was dissolved into the monomer blend by stirring and gentle heating. After a clear solution was obtained, it was vacuum degassed before being 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 and then lower it to 60°C for at least 2 hours. After the mold was opened, the polymer sheet was cut using a diamond blade saw into 2 inch (5.1 cm) test squares.

[235] The photochromic test squares prepared as described above 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 15 minutes to cause the photochromic material to transform from the unactivated (or bleached) state to an activated (or colored) state, and then placed in a 75°C oven for about 15 minutes to allow the photochromic material to revert back to the bleached

state. The test squares were then cooled to room temperature, exposed to fluorescent room lighting for at least 2 hours, and then kept covered (that is, in a dark environment) for at least 2 hours prior to testing on an optical bench maintained at 73°F. The bench was fitted with a 300-watt xenon arc lamp, a remote controlled shutter, a Melles Griot KG2 filter that modifies the UV and IR wavelengths and acts as a heat-sink, neutral density filter(s) and a sample holder, situated within a water bath, in which the square to be tested was inserted. A collimated beam of light from a tungsten lamp was passed through the square at a small angle (approximately 30°) normal to the square. After passing through the square, the light from the tungsten lamp was directed to a collection sphere, where the light was blended, and on to an Ocean Optics S2000 spectrometer where the spectrum of the measuring beam was collected and analyzed. The $\lambda_{\text{max-vis}}$ is the wavelength in the visible spectrum at which the maximum absorption of the activated (colored) form of the photochromic compound in a test square occurs. The $\lambda_{\text{max-vis}}$ wavelength was determined by testing the photochromic test squares in a Varian Cary 300 UV-Visible spectrophotometer; it may also be calculated from the spectrum obtained by the S2000 spectrometer on the optical bench.

[236] The saturated optical density ("Sat'd OD") for each test square was determined by opening the shutter from the xenon lamp and measuring the transmittance after exposing the test chip to UV radiation for 30 minutes. The $\lambda_{\text{max-vis}}$ at the sat'd OD was calculated from the activated data measured by the S2000 spectrometer on the optical bench. The First Fade Half Life ("T1/2") is the time interval in seconds for the absorbance of the activated form of the photochromic material in the test squares to reach one half the Sat'd OD absorbance value at room temperature (73°F), after removal of the source of activating light. Results for the photochromic materials tested are listed below in Table 2.

Table 2: Photochromic Test Data

Example No.	T1/2 (at $\lambda_{\text{max-vis}}$)	SAT. OD (at $\lambda_{\text{max-vis}}$)	$\lambda_{\text{max-vis}}$	Example No.	T1/2 (at $\lambda_{\text{max-vis}}$)	SAT. OD (at $\lambda_{\text{max-vis}}$)	$\lambda_{\text{max-vis}}$
1	66	0.58	459	16	50	0.42	560
2	121	0.80	455	17	220	0.85	603
3	116	0.79	457	18	199	0.81	603

4	112	0.37	456	19	180	0.57	607
5	238	1.09	452	20	134	0.86	449
6	242	1.01	452	21	41	0.48	605
7	245	1.15	451	22	415	0.87	451
8	197	0.93	457	23	325	0.64	451
9	183	0.89	453	24	91	0.79	476
10	94	0.60	458	25	123	1.08	469
11	480	0.97	448	26	130	0.69	530
12	593	0.67	475	CE1	99	0.68	569
13	921	0.65	580	CE2	*	*	*
14	896	0.86	589	CE3	129	0.81	572
15	866	0.69	602	CE4	*	*	*

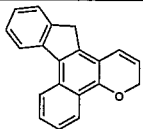
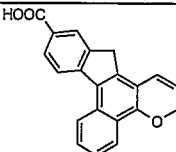
*Not tested

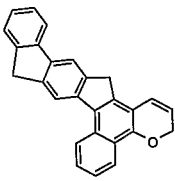
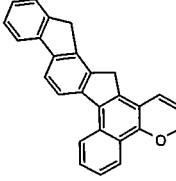
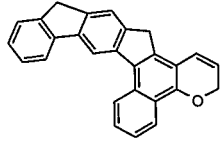
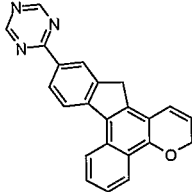
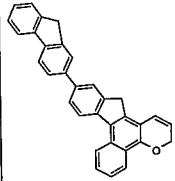
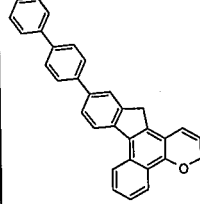
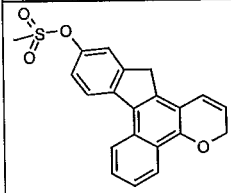
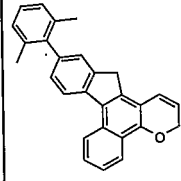
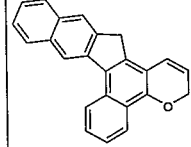
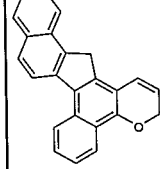
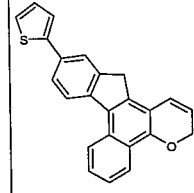
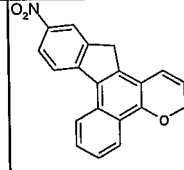
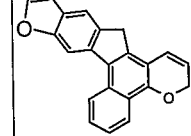
PART 3: MODELED SYSTEMS

Modeled 3H,13H-Indeno[2',3':3,4]naphtho[1,2-b]pyrans

[237] The substituent effect on UV absorption and intensity at the 11-position of the 3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyrans were calculated using density functional theory implemented in Gaussian98 software, which is purchased from Gaussian, Inc. of Wallingford, CT. Model systems were designed based on the 3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyrans with substitution at the 11-position of the indeno-fused naphthopyran (substituents at the 3-position were replaced with hydrogen atoms for ease of modeling). Geometry was first optimized using Becke's parameter functional in combination with the Lee, Yang, and Parr (LYP) correlation function and the 6-31G(d) basis set (B3LYP/6-31G(d)). The absorption spectra were calculated using time dependent density functional theory (TDDFT) with B3LYP functional and 6-31+G(d) basis set. The longest absorption and correspondent intensity calculated by TDDFT/6-31+G(d) are shown below in Table 3. All structures were optimized using B3LYP/6-31G(d).

Table 3: Modeled Intensity Data for Closed Form of Model Photochromic Materials

Modeled Photochromic Material	$\lambda_{\max 1}$ (nm)	Modeled Intensity at $\lambda_{\max 1}$	Modeled Photochromic Material	$\lambda_{\max 1}$ (nm)	Modeled Intensity at $\lambda_{\max 1}$
 MPM1	383	0.12	 MPM2	388	0.31

 MPM3	402	0.31	 MPM4	399	0.28
 MPM5	391	0.17	 MPM6	419	0.57
 MPM7	400	0.48	 MPM8	397	0.44
 MPM9	382	0.17	 MMP10	385	0.16
 MPM11	395	0.19	 MPM12	393	0.20
 MPM13	405	0.38	 MPM14	445	0.37
 MPM15	395	0.18			

[238] The modeling data indicates that groups that extend the pi-conjugated system of the 3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyrans bonded at the 11-position thereof have an increased modeled intensity and a bathochromic shift in $\lambda_{\max 1}$ as

compared to comparable photochromic materials without a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof (for example MPM1).

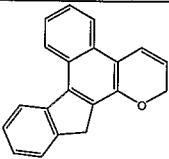
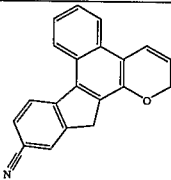
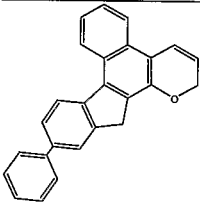
[239] Further, modeled photochromic materials having a group bonded at the 11-position but that does not extend the pi-conjugated system of the indeno-fused naphthopyran along the 11-position, for example MPM5, MPM9, and MPM10 do not appear to have a significant increase in modeled intensity as compared to MPM1. Modeled photochromic materials having a fused-group that is bonded at both the 11-position and the 10-position or the 11-position and 12-position of the indeno-fused naphthopyran, wherein the fused group extends the pi-conjugated system of the indeno-fused naphthopyran at both bonding positions (for example, MPM11 and MPM12) generally had a smaller increase in modeled intensity than those modeled photochromic materials that had a fused group that extends the pi-conjugated systems of the indeno-fused naphthopyran only at the 11-position (for example, MPM3 and MPM4) or indeno-fused naphthopyrans having a group that extends the pi-conjugated system of thereof bonded at the 11-position only. The modeled intensity data for MPM2, MPM8 and MPM12 is consistent with the integrated extinction coefficient measurements for similar compounds as described above.

Modeled 2H,13H-Indeno[1',2':4,3]naphtho[2,1-b]pyrans

[240] The substituent effect on UV absorption and intensity at the 11-position of the 2H,13H-indeno[1',2':4,3]naphtho[2,1-b]pyran was calculated using the same procedure as described for the 3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyrans. Model systems were designed based on the 2H,13H-indeno[1',2':4,3]naphtho[2,1-b]pyrans with substitution at the 11-position of the indeno-fused naphthopyran (substituents at the 2-position were replaced with hydrogen atoms for ease of modeling). The absorption spectra were calculated using time dependent density functional theory (TDDFT) with B3LYP functional and 6-31+G(d) basis set. The longest absorption and correspondent intensity calculated by TDDFT/6-31+G(d) are shown below in Table 4. All structures were optimized using B3LYP/6-31G(d). As

shown in Table 4, extending the conjugation at the 11-position increases the absorption intensity.

Table 4: Modeled Intensity Data for Closed Form of Model Photochromic Materials

Modeled Photochromic Material	$\lambda_{\max 1}$ (nm)	Modeled Intensity at $\lambda_{\max 1}$
 MPM16	383	0.33
 MPM17	402	0.42
 MPM18	396	0.57

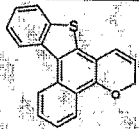
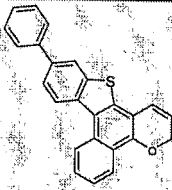
[241] As can be seen from Table 4, both MPM 17 and MPM 18 (which had a cyano- and a phenyl group, respectively, extending the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof) had higher modeled intensities and a bathochromically shifted $\lambda_{\max 1}$ as compared to MPM16, which did not have a group that extended the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof.

Molded 3H,13H-benzothieno[2',3':3,4]naphtho[1,2-b]pyrans

[242] The substituent effect on UV absorption and intensity at the 11-position of the 3H,13H-benzothieno[2',3':3,4]naphtho[1,2-b]pyran was calculated using the same procedure as described for the 3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyrans. Model systems were designed based on the 3H,13H-benzothieno[2',3':3,4]naphtho[1,2-b]pyrans with substitution at the 11-position of

the benzothieno-fused naphthopyran (substituents at the 3-position were replaced with hydrogen atoms for ease of modeling). The absorption spectra were calculated using time dependent density functional theory (TDDFT) with B3LYP functional and 6-31+G(d) basis set. The longest absorption and correspondent intensity calculated by TDDFT/6-31+G(d) are shown below in Table 5. All structures were optimized using B3LYP/6-31G(d). As shown in Table 5, extending the conjugation at the 11-position increases the absorption intensity.

Table 5: Modeled Intensity Data for Closed Form of Model Photochromic Materials

<u>Modeled Photochromic Material</u>	<u>λ_{max1} (nm)</u>	<u>Modeled Intensity at $\square_{max1}$</u>
 MPM19	373	0.10
 MPM20	383	0.22

[243] As can be seen from Table 5, MPM20 (which had a phenyl group, extending the pi-conjugated system of the benzothieno-fused naphthopyran bonded at the 11-position thereof) had a higher modeled intensity and a bathochromically shifted λ_{max1} as compared to MPM19, which did not have a group that extended the pi-conjugated system of the benzothieno-fused naphthopyran bonded at the 11-position thereof.

[244] It is to be understood that the present description illustrates aspects of the invention relevant to a clear understanding of the invention. Certain aspects of the invention that would be apparent to those of ordinary skill in the art and that, therefore, would not facilitate a better understanding of the invention have not been presented in order to simplify the present description. Although the present invention has been described in connection with certain embodiments, the present

invention is not limited to the particular embodiments disclosed, but is intended to cover modifications that are within the spirit and scope of the invention, as defined by the appended claims.

CLAIMS

We claim:

1. An ophthalmic device comprising at least one photochromic material comprising:
 - (i) an indeno-fused naphthopyran; and
 - (ii) a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position of thereof, provided that if the group bonded at the 11-position of the indeno-fused naphthopyran and a group bonded at the 10-position or 12-position of the indeno-fused naphthopyran together form a fused group, said fused group is not a benzo-fused group; andwherein the 13-position of the indeno-fused naphthopyran is unsubstituted, mono-substituted or di-substituted, provided that if the 13-position of the indeno-fused naphthopyran is di-substituted, the substituents do not together form norbornyl.
2. The ophthalmic device of claim 1 wherein the photochromic material comprises an indeno[2',3':3,4]naphtho[1,2-b]pyran, an indeno[1',2':4,3]naphtho[2,1-b]pyran or a mixture thereof.
3. The ophthalmic device of claim 1 wherein the photochromic material has an integrated extinction coefficient greater than $1.0 \times 10^6 \text{ nm} \times \text{mol}^{-1} \times \text{cm}^{-1}$ as determined by integration of a plot of extinction coefficient of the photochromic material vs. wavelength over a range of wavelengths ranging from 320 nm to 420 nm, inclusive.
4. The ophthalmic device of claim 3 wherein the integrated extinction coefficient is at least $1.3 \times 10^6 \text{ nm} \times \text{mol}^{-1} \times \text{cm}^{-1}$.
5. The ophthalmic device of claim 3 wherein the integrated extinction coefficient ranges from $1.1 \times 10^6 \text{ nm} \times \text{mol}^{-1} \times \text{cm}^{-1}$ to $4.0 \times 10^6 \text{ nm} \times \text{mol}^{-1} \times \text{cm}^{-1}$.

6. The ophthalmic device of claim 1 wherein the photochromic material displays hyperchromic absorption of electromagnetic radiation having a wavelength from 320 nm to 420 nm as compared to a photochromic material comprising a comparable indeno-fused naphthopyran without a group that extends the pi-conjugated system of the comparable indeno-fused naphthopyran bonded at the 11-position thereof.

7. The ophthalmic device of claim 1 wherein the photochromic material has a closed-form absorption spectrum for electromagnetic radiation that is bathochromically shifted as compared to a closed-form absorption spectrum for electromagnetic radiation of a photochromic material comprising a comparable indeno-fused naphthopyran without a group that extends the pi-conjugated system of the comparable indeno-fused naphthopyran bonded at the 11-position thereof.

8. The ophthalmic device of claim 1 wherein the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof is a substituted or unsubstituted aryl; a substituted or unsubstituted heteroaryl; or a group represented by $-X=Y$ or $-X'\equiv Y'$, wherein:

(i) X is $-CR^1$, $-N$, $-NO$, $-SR^1$, $-S(=O)R^1$ or $-P(=O)R^1$, wherein R^1 is amino, dialkyl amino, diaryl amino, acyloxy, acylamino, a substituted or unsubstituted C_1 - C_{20} alkyl, a substituted or unsubstituted C_2 - C_{20} alkenyl, a substituted or unsubstituted C_2 - C_{20} alkynyl, halogen, hydrogen, hydroxy, oxygen, a polyol residue, a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, alkylamino, mercapto, alkylthio, a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heterocyclic group, a reactive substituent, a compatibilizing substituent or a photochromic material, provided that:

(a) if X is $-CR^1$ or $-N$, Y is $C(R^2)_2$, NR^2 , O or S, wherein each R^2 is independently chosen for each occurrence from amino, dialkyl amino, diaryl amino, acyloxy, acylamino, a substituted or

unsubstituted C₁-C₂₀ alkyl, a substituted or unsubstituted C₂-C₂₀ alkenyl, a substituted or unsubstituted C₂-C₂₀ alkynyl, halogen, hydrogen, hydroxy, oxygen, a polyol residue, a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, alkylamino, mercapto, alkylthio, a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heterocyclic group, a reactive substituent, a compatibilizing substituent and a photochromic material; and

(b) if X is -NO, -SR¹, -S(=O)R¹ or -P(=O)R¹, Y is O; and

(ii) X' is -C or -N⁺, and Y' is CR³ or N; wherein R³ is amino, dialkyl amino, diaryl amino, acyloxy, acylamino, a substituted or unsubstituted C₂-C₂₀ alkyl, a substituted or unsubstituted C₂-C₂₀ alkenyl, a substituted or unsubstituted C₂-C₂₀ alkynyl, halogen, hydrogen, hydroxy, oxygen, a polyol residue, a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, alkylamino, mercapto, alkylthio, a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heterocyclic group, a reactive substituent, a compatibilizing substituent or a photochromic material; or

the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position of the indeno-fused naphthopyran together with a group bonded at the 12-position of the indeno-fused naphthopyran or together with a group bonded at the 10-position of the indeno-fused naphthopyran form a fused group, said fused group being indeno, dihydronaphthalene, indole, benzofuran, benzopyran or thianaphthene.

9. The ophthalmic device of claim 8 wherein the group that extends the pi-conjugated system of the indeno-fused naphthopyran is: a substituted or unsubstituted C₂-C₂₀ alkenyl; a substituted or unsubstituted C₂-C₂₀ alkynyl; a

substituted or unsubstituted aryl; a substituted or unsubstituted heteroaryl;
-C(=O)R¹; or -N(=Y) or -N⁺(≡Y'), wherein Y is C(R²)₂, NR², O or S, and Y' is CR³
or N.

10. The ophthalmic device of claim 9 wherein the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof is an aryl group or a heteroaryl group that is unsubstituted or substituted with at least one of a substituted or unsubstituted alkyl, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, amide, a substituted or unsubstituted amino, a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, azide, carbonyl, carboxy, ester, ether, halogen, hydroxy, a polyol residue, a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, cyano, nitro, sulfonyl, thiol, a substituted or unsubstituted heterocyclic group, a reactive substituent, a compatibilizing substituent or a photochromic material, provided that if the aryl group or the heteroaryl group comprises more than one substituent, each substituent may be independently chosen.

11. The ophthalmic device of claim 9 wherein the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof is -C(=O)R¹, wherein R¹ is acylamino, acyloxy, a substituted or unsubstituted C₁-C₂₀ alkyl, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, amino, dialkyl amino, diaryl amino, a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heterocyclic group, halogen, hydrogen, hydroxy, oxygen, a polyol residue, a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, a reactive substituent or a photochromic material.

12. The ophthalmic device of claim 1 wherein the photochromic material comprises at least one of a reactive substituent and a compatibilizing substituent, each of said reactive substituent or compatibilizing substituent each being independently represented by one of:

-A'-D-E-G-J;	-G-E-G-J;	-D-E-G-J;
-A'-D-J;	-D-G-J;	-D-J;
-A'-G-J;	-G-J; and	-A'-J

wherein:

- (i) each -A'- is independently -O-, -C(=O)-, -CH₂-, -OC(=O)- or -NHC(=O)-, provided that if -A'- is -O-, -A'- forms at least one bond with -J;
- (ii) each -D- is independently:
 - (a) a diamine residue or a derivative thereof, said diamine residue being an aliphatic diamine residue, a cyclo aliphatic diamine residue, a diazacycloalkane residue, an azacyclo aliphatic amine residue, a diazacrown ether residue or an aromatic diamine residue, wherein a first amino nitrogen of said diamine residue forms a bond with -A'-, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof, or a substituent or an available position on the indeno-fused naphthopyran, and a second amino nitrogen of said diamine residue forms a bond with -E-, -G- or -J; or
 - (b) an amino alcohol residue or a derivative thereof, said amino alcohol residue being an aliphatic amino alcohol residue, a cyclo aliphatic amino alcohol residue, an azacyclo aliphatic alcohol residue, a diazacyclo aliphatic alcohol residue or an aromatic amino alcohol residue, wherein an amino nitrogen of said amino alcohol residue forms a bond with -A'-, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof, or a substituent or an available position on the indeno-fused naphthopyran, and an alcohol oxygen of said amino alcohol residue forms a bond with -E-, -G- or -J, or said amino nitrogen of said amino alcohol residue forms a bond with -E-, -G- or -J, and said alcohol oxygen of said amino alcohol residue forms a bond with -A'-, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof, or a substituent or an available position on the indeno-fused naphthopyran;

- (iii) each -E- is independently a dicarboxylic acid residue or a derivative thereof, said dicarboxylic acid residue being an aliphatic dicarboxylic acid residue, a cycloaliphatic dicarboxylic acid residue or an aromatic dicarboxylic acid residue, wherein a first carbonyl group of said dicarboxylic acid residue forms a bond with -G- or -D- , and a second carbonyl group of said dicarboxylic acid residue forms a bond with -G-;
- (iv) each -G- is independently:
 - (a) $[(OC_2H_4)_x(OC_3H_6)_y(OC_4H_8)_z]-O-$, wherein x, y and z are each independently chosen and range from 0 to 50, and a sum of x, y, and z ranges from 1 to 50;
 - (b) a polyol residue or a derivative thereof, said polyol residue being an aliphatic polyol residue, a cyclo aliphatic polyol residue or an aromatic polyol residue, wherein a first polyol oxygen of said polyol residue forms a bond with -A'-, -D-, -E-, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof, or a substituent or an available position on the indeno-fused naphthopyran, and a second polyol oxygen of said polyol forms a bond with -E- or -J; or
 - (c) a combination thereof, wherein the first polyol oxygen of the polyol residue forms a bond with a group $[(OC_2H_4)_x(OC_3H_6)_y(OC_4H_8)_z]-$ and the second polyol oxygen forms a bond with -E- or -J; and
- (v) each -J is independently:
 - (a) a group -K, wherein -K is $-CH_2COOH$, $-CH(CH_3)COOH$, $-C(O)(CH_2)_wCOOH$, $-C_6H_4SO_3H$, $-C_5H_{10}SO_3H$, $-C_4H_8SO_3H$, $-C_3H_6SO_3H$, $-C_2H_4SO_3H$ or $-SO_3H$, wherein w ranges from 1 to 18;
 - (b) hydrogen, provided that if -J is hydrogen, -J is bonded to an oxygen of -D- or -G-, or a nitrogen of -D-; or
 - (c) a group -L or residue thereof, wherein -L is acryl, methacryl, crotyl, 2-(methacryloxy)ethylcarbamyl, 2-(methacryloxy)ethoxycarbonyl, 4-vinylphenyl, vinyl, 1-chlorovinyl or epoxy.

13. The ophthalmic device of claim 12 wherein the photochromic material comprises an indeno[2',3':3,4]naphtho[1,2-b]pyran and at least one of the 6-position, the 7-position, the 13-position, the 3-position, and the group that extends the pi-conjugated system of the indeno[2',3':3,4]naphtho[1,2-b]pyran bonded at the 11-position thereof comprises a reactive substituent.

14. The ophthalmic device of claim 1 wherein the indeno-fused naphthopyran is free of spiro-cyclic groups at the 13-position of the indeno-fused naphthopyran.

15. The ophthalmic device of claim 1 wherein the indeno-fused naphthopyran is an indeno[2',3':3,4]naphtho[1,2-b]pyran, and wherein:

- (i) the 6-position of the indeno[2',3':3,4]naphtho[1,2-b]pyran is substituted with a nitrogen containing group or an oxygen containing group;
- (ii) the 7-position of indeno[2',3':3,4]naphtho[1,2-b]pyran is substituted with a nitrogen containing group or an oxygen containing group; and
- (iii) the 13-position of the indeno[2',3':3,4]naphtho[1,2-b]pyran is di-substituted, provided that each of the substituents at the 13-position is independently hydrogen, C₁-C₆ alkyl, C₃-C₇ cycloalkyl, allyl, a substituted or unsubstituted phenyl, a substituted or unsubstituted benzyl, , a substituted or unsubstituted amino, or a group -C(O)R³⁰, wherein R³⁰ is hydrogen, hydroxy, C₁-C₆ alkyl, C₁-C₆ alkoxy, an unsubstituted, mono-or di-substituted phenyl or naphthyl, phenoxy, a mono- or di-(C₁-C₆)alkoxy substituted phenoxy or a mono- or di-(C₁-C₆)alkyl substituted phenoxy.

16. A ophthalmic device comprising the photochromic material of claim 1 incorporated into at least a portion of an organic material, said organic material being a polymeric material, an oligomeric material, a monomeric material or a mixture or combination thereof.

17. The ophthalmic device of claim 16 wherein the organic material is a polymeric material, said polymeric material being a copolymer of ethylene and vinyl acetate; a copolymer of ethylene and vinyl alcohol; a copolymer of ethylene, vinyl acetate and

vinyl alcohol; cellulose acetate butyrate; poly(urethane); poly(acrylate); poly(methacrylate); epoxy; an aminoplast functional polymer; poly(anhydride); poly(urea urethane); a N-alkoxymethyl(meth)acrylamide functional polymer; poly(siloxane); poly(silane); or a mixture or combination thereof.

18. The ophthalmic device of claim 16 wherein the photochromic composition displays an increased absorption of electromagnetic radiation having a wavelength from 320 nm to 420 nm as compared to a photochromic composition comprising a comparable indeno-fused naphthopyran without a group that extends the pi-conjugated system of the comparable indeno-fused naphthopyran bonded at the 11-position thereof.

19. The ophthalmic device of claim 16 wherein the photochromic composition has an absorption spectrum for electromagnetic radiation that is bathochromically shifted as compared to an absorption spectrum for electromagnetic radiation of a photochromic composition comprising a comparable indeno-fused naphthopyran without a group that extends the pi-conjugated system of the comparable indeno-fused naphthopyran bonded at the 11-position thereof.

20. The ophthalmic device of claim 16 wherein the photochromic composition comprises at least one of a complementary photochromic material, a photoinitiator, a thermal initiator, a polymerization inhibitor, a solvent, a light stabilizer, a heat stabilizer, a mold release agent, a rheology control agent, a leveling agent, a free radical scavenger, an adhesion promoter, a wetting agent, a compatibilizing component, a medicinal agent, an antimicrobial compound, a reactive tint, a pigment, a copolymerizable and nonpolymerizable dye and mixtures thereof.

21. The ophthalmic device of claim 1 wherein said photochromic material is connected to at least a portion of said ophthalmic device.

22. The ophthalmic device of claim 1, wherein the ophthalmic device is selected from the group consisting of soft contact lenses, hard contact lenses, intraocular lenses, overlay lenses, ocular inserts, and optical inserts.
23. The ophthalmic device of claim 22 wherein the ophthalmic device is a contact lens.
24. The ophthalmic device of claim 21 wherein the ophthalmic device is formed from a polymeric material and the photochromic material is at least one of blended with at least a portion of the polymeric material, bonded to at least a portion of the polymeric material, and imbibed into at least a portion of the polymeric material.
25. The ophthalmic device of claim 21 wherein at least a part of said ophthalmic device is coated with a coating comprising the photochromic material.
26. The ophthalmic device of claim 25 wherein the substrate is a polymeric material.
27. The ophthalmic device of claim 25 wherein said polymeric material is formed from components comprising hydrophilic monomers, hydrophilic polymers and silicone components.
28. The ophthalmic device of claim 25 wherein said ophthalmic device is a contact lens and said polymeric material comprises a hydrogel.
29. An ophthalmic device comprising at least one photochromic material comprising an indeno-fused naphthopyran, wherein the 13-position of the indeno-fused naphthopyran is unsubstituted, mono-substituted or di-substituted, provided that if the 13-position of the indeno-fused naphthopyran is di-substituted, the substituents do not together form norbornyl, and wherein the photochromic material has an integrated extinction coefficient greater than $1.0 \times 10^6 \text{ nm} \times \text{mol}^{-1} \times \text{cm}^{-1}$ as determined by integration of a plot of extinction coefficient for the photochromic material vs. wavelength over a range of wavelengths ranging from 320 nm to 420 nm, inclusive.

30. The ophthalmic device of claim 29 wherein the integrated extinction coefficient ranges from $1.1 \times 10^6 \text{ nm} \times \text{mol}^{-1} \times \text{cm}^{-1}$ to $4.0 \times 10^6 \text{ nm} \times \text{mol}^{-1} \times \text{cm}^{-1}$.

31. The ophthalmic device of claim 29 wherein the photochromic material comprises a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof, wherein said group is: a substituted or unsubstituted aryl; a substituted or unsubstituted heteroaryl; or a group represented by $-X=Y$ or $-X' \equiv Y'$, wherein:

(i) X is $-\text{CR}^1$, $-\text{N}$, $-\text{NO}$, $-\text{SR}^1$, $-\text{S}(=\text{O})\text{R}^1$ or $-\text{P}(=\text{O})\text{R}^1$, wherein R^1 is amino, dialkyl amino, diaryl amino, acyloxy, acylamino, a substituted or unsubstituted $\text{C}_1\text{-C}_{20}$ alkyl, a substituted or unsubstituted $\text{C}_2\text{-C}_{20}$ alkenyl, a substituted or unsubstituted $\text{C}_2\text{-C}_{20}$ alkynyl, halogen, hydrogen, hydroxy, oxygen, a polyol residue, a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, alkylamino, mercapto, alkylthio, a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heterocyclic group, a reactive substituent, a compatibilizing substituent or a photochromic material, provided that:

(a) if X is $-\text{CR}^1$ or $-\text{N}$, Y is $\text{C}(\text{R}^2)_2$, NR^2 , O or S, wherein each R^2 is independently chosen for each occurrence from amino, dialkyl amino, diaryl amino, acyloxy, acylamino, a substituted or unsubstituted $\text{C}_1\text{-C}_{20}$ alkyl, a substituted or unsubstituted $\text{C}_2\text{-C}_{20}$ alkenyl, a substituted or unsubstituted $\text{C}_2\text{-C}_{20}$ alkynyl, halogen, hydrogen, hydroxy, oxygen, a polyol residue, a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, alkylamino, mercapto, alkylthio, a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heterocyclic group, a reactive substituent, a compatibilizing substituent and a photochromic material; and

(b) if X is $-\text{NO}$, $-\text{SR}^1$, $-\text{S}(=\text{O})\text{R}^1$ or $-\text{P}(=\text{O})\text{R}^1$, Y is O; and

- (b) X' is -C or -N⁺, and Y' is CR³ or N; wherein R³ is amino, dialkyl amino, diaryl amino, acyloxy, acylamino, a substituted or unsubstituted C₁-C₂₀ alkyl, a substituted or unsubstituted C₂-C₂₀ alkenyl, a substituted or unsubstituted C₂-C₂₀ alkynyl, halogen, hydrogen, hydroxy, oxygen, a polyol residue, a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, alkylamino, mercapto, alkylthio, a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heterocyclic group, a reactive substituent, a compatibilizing substituent or a photochromic material; or

the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position of the indeno-fused naphthopyran together with a group bonded at the 12-position of the indeno-fused naphthopyran or together with a group bonded at the 10-position of the indeno-fused naphthopyran form a fused group, said fused group being indeno, dihydronaphthalene, indole, benzofuran, benzopyran or thianaphthene.

32. An ophthalmic device photochromic material comprising:

- (i) an indeno-fused naphthopyran chosen from an indeno[2',3':3,4]naphtho[1,2-b]pyran, an indeno[1',2':4,3]naphtho[2,1-b]pyran and mixtures thereof, wherein the 13-position of the indeno-fused naphthopyran is unsubstituted, mono-substituted or di-substituted, provided that if the 13-position of the indeno-fused naphthopyran is di-substituted, the substituent groups do not together form norbornyl; and
- (ii) a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof, wherein said group is: a substituted or unsubstituted aryl; a substituted or unsubstituted heteroaryl; or a group represented by -X=Y or -X'≡Y', wherein:

- (a) X is -CR¹, -N, -NO, -SR¹, -S(=O)R¹ or -P(=O)R¹, wherein R¹ is amino, dialkyl amino, diaryl amino, acyloxy, acylamino, a substituted or unsubstituted C₂-C₂₀ alkyl, a substituted or unsubstituted C₂-C₂₀

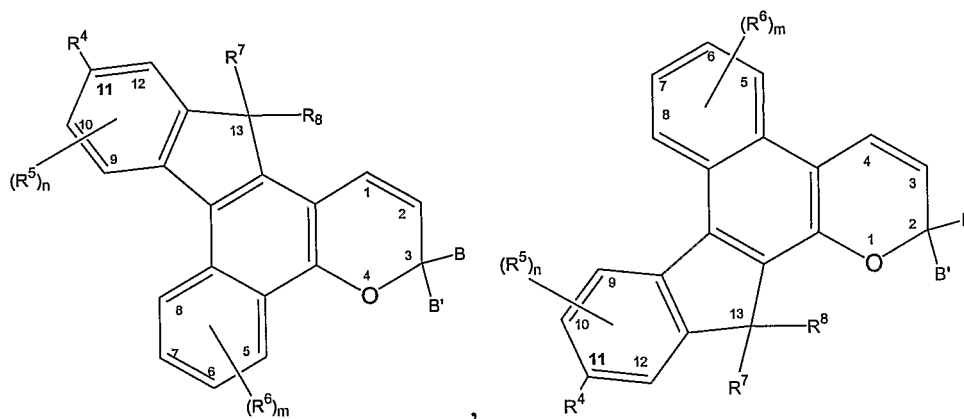
alkenyl, a substituted or unsubstituted C₂-C₂₀ alkynyl, halogen, hydrogen, hydroxy, oxygen, a polyol residue, a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, alkylamino, mercapto, alkylthio, a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heterocyclic group, a reactive substituent, a compatibilizing substituent or a photochromic material, provided that:

- (1) if X is -CR¹ or -N, Y is C(R²)₂, NR², O or S, wherein each R² is independently chosen for each occurrence from amino, dialkyl amino, diaryl amino, acyloxy, acylamino, a substituted or unsubstituted C₂-C₂₀ alkyl, a substituted or unsubstituted C₁-C₂₀ alkenyl, a substituted or unsubstituted C₂-C₂₀ alkynyl, halogen, hydrogen, hydroxy, oxygen, a polyol residue, a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, alkylamino, mercapto, alkylthio, a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heterocyclic group, a reactive substituent, a compatibilizing substituent and a photochromic material; and
 - (2) if X is -NO, -SR¹, -S(=O)R¹ or -P(=O)R¹, Y is O; and
- (b) X' is -C or -N⁺, and Y' is CR³ or N; wherein R³ is amino, dialkyl amino, diaryl amino, acyloxy, acylamino, a substituted or unsubstituted C₂-C₂₀ alkyl, a substituted or unsubstituted C₂-C₂₀ alkenyl, a substituted or unsubstituted C₂-C₂₀ alkynyl, halogen, hydrogen, hydroxy, oxygen, a polyol residue, a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, alkylamino, mercapto, alkylthio, a substituted or unsubstituted aryl, a substituted or

unsubstituted heteroaryl, a substituted or unsubstituted heterocyclic group, a reactive substituent, a compatibilizing substituent or a photochromic material; or

the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position of the indeno-fused naphthopyran together with a group bonded at the 12-position of the indeno-fused naphthopyran or together with a group bonded at the 10-position of the indeno-fused naphthopyran form a fused group, said fused group being indeno, dihydronaphthalene, indole, benzofuran, benzopyran or thianaphthene.

33. A photochromic material represented by:



or a mixture thereof, wherein:

(i) R^4 is a substituted or unsubstituted aryl; a substituted or unsubstituted

heteroaryl; or a group represented by $-X=Y$ or $-X'\equiv Y'$, wherein:

(a) X is $-CR^1$, $-N$, $-NO$, $-SR^1$, $-S(=O)R^1$ or $-P(=O)R^1$, wherein R^1 is amino, dialkyl amino, diaryl amino, acyloxy, acylamino, a substituted or unsubstituted C_1 - C_{20} alkyl, a substituted or unsubstituted C_2 - C_{20} alkenyl, a substituted or unsubstituted C_2 - C_{20} alkynyl, halogen, hydrogen, hydroxy, oxygen, a polyol residue, a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, alkylamino, mercapto, alkylthio, a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heterocyclic group, a reactive

substituent, a compatibilizing substituent or a photochromic material, provided that:

(1) if X is $-\text{CR}^1$ or $-\text{N}$, Y is $\text{C}(\text{R}^2)_2$, NR^2 , O, or S, wherein each R^2 is independently chosen for each occurrence from amino, dialkyl amino, diaryl amino, acyloxy, acylamino, a substituted or unsubstituted $\text{C}_2\text{-C}_{20}$ alkyl, a substituted or unsubstituted $\text{C}_2\text{-C}_{20}$ alkenyl, a substituted or unsubstituted $\text{C}_2\text{-C}_{20}$ alkynyl, halogen, hydrogen, hydroxy, oxygen, a polyol residue, a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, alkylamino, mercapto, alkylthio, a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heterocyclic group, a reactive substituent, a compatibilizing substituent and a photochromic material; and

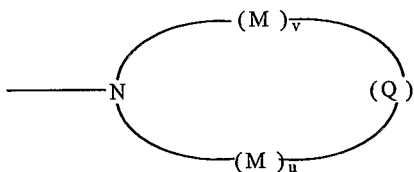
(2) if X is $-\text{NO}$, $-\text{SR}^1$, $-\text{S}(=\text{O})\text{R}^1$ or $-\text{P}(=\text{O})\text{R}^1$, Y is O; and

(b) X' is $-\text{C}$ or $-\text{N}^+$, and Y' is CR^3 or N; wherein R^3 is amino, dialkyl amino, diaryl amino, acyloxy, acylamino, a substituted or unsubstituted $\text{C}_1\text{-C}_{20}$ alkyl, a substituted or unsubstituted $\text{C}_2\text{-C}_{20}$ alkenyl, a substituted or unsubstituted $\text{C}_2\text{-C}_{20}$ alkynyl, halogen, hydrogen, hydroxy, oxygen, a polyol residue, a substituted or unsubstituted phenoxy, a substituted or unsubstituted benzyloxy, a substituted or unsubstituted alkoxy, a substituted or unsubstituted oxyalkoxy, alkylamino, mercapto, alkylthio, a substituted or unsubstituted aryl, a substituted or unsubstituted heteroaryl, a substituted or unsubstituted heterocyclic group, a reactive substituent, a compatibilizing substituent or a photochromic material; or

R^4 together with an R^5 group bonded at the 12-position of the indeno-fused naphthopyran or together with an R^5 group bonded at the 10-position of the indeno-fused naphthopyran form a fused group, said fused group being indeno, dihydronaphthalene, indole, benzofuran, benzopyran or thianaphthene;

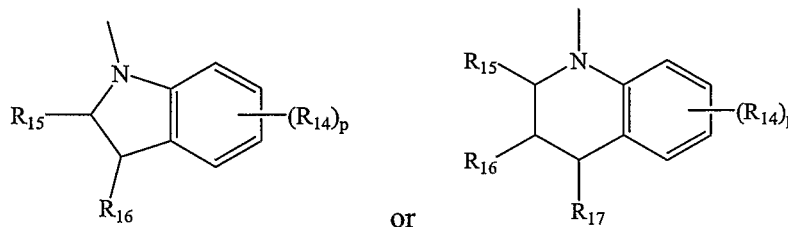
(ii) n ranges from 0 to 3;

- (iii) m ranges from 0 to 4;
- (iv) each R^5 and R^6 is independently chosen for each occurrence from:
 a reactive substituent; a compatibilizing substituent; hydrogen; C_1 - C_6 alkyl; chloro; fluoro; C_3 - C_7 cycloalkyl; a substituted or unsubstituted phenyl; said phenyl substituents being C_1 - C_6 alkyl or C_1 - C_6 alkoxy; $-OR^{10}$ or $-OC(=O)R^{10}$, wherein R^{10} is S, hydrogen, amine, 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, (C_1 - C_6)alkoxy(C_2 - C_4)alkyl, C_3 - C_7 cycloalkyl or mono(C_1 - C_4)alkyl substituted C_3 - C_7 cycloalkyl, a mono-substituted phenyl, said phenyl having a substituent located at the para position, the substituent being a dicarboxylic acid residue or derivative thereof, a diamine residue or derivative thereof, an amino alcohol residue or derivative thereof, a polyol residue or derivative thereof, $-(CH_2)-$, $-(CH_2)_t-$ or $-[O-(CH_2)_t]_k-$, wherein t ranges from 2 to 6, and k ranges from 1 to 50, and wherein the substituent is connected to an aryl group on another photochromic material; $-N(R^{11})R^{12}$, wherein R^{11} and R^{12} are each independently hydrogen, C_1 - C_8 alkyl, phenyl, naphthyl, furanyl, benzofuran-2-yl, benzofuran-3-yl, thienyl, benzothien-2-yl, benzothien-3-yl, dibenzofuranyl, dibenzothienyl, benzopyridyl and 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, or R^{11} and R^{12} come together with the nitrogen atom to form a C_3 - C_{20} hetero-bicycloalkyl ring or a C_4 - C_{20} hetero-tricycloalkyl ring; a nitrogen containing ring represented by:



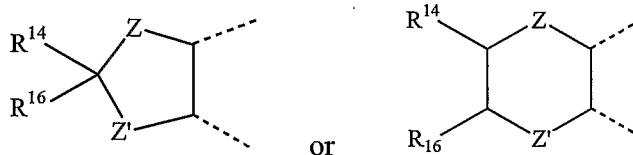
wherein each -M- is independently chosen for each occurrence from $-CH_2-$, $-CH(R_{13})-$, $-C(R_{13})_2-$, $-CH(aryl)-$, $-C(aryl)_2-$ and $-C(R_{13})(aryl)-$, and -Q- is -M-, -O-, -S-, $-S(O)-$, $-SO_2-$, $-NH-$, $-N(R^{13})-$ or $-N(aryl)-$, wherein each R^{13} is independently C_1 - C_6 alkyl, each (aryl) is independently phenyl or naphthyl, u

ranges from 1 to 3, and v ranges from 0 to 3, provided that if v is 0, -Q- is -M-; a group represented by:



wherein each R^{15} , R^{16} and R^{17} is independently hydrogen, C_1 - C_6 alkyl, phenyl or naphthyl, or R^{15} and R^{16} together form a ring of 5 to 8 carbon atoms, each R^{14} is independently C_1 - C_6 alkyl, C_1 - C_6 alkoxy, fluoro or chloro, and p ranges from 0 to 3; and a substituted or unsubstituted C_4 - C_{18} spirobicyclic amine or a substituted or unsubstituted C_4 - C_{18} spirotricyclic amine, wherein said substituents are independently aryl, C_1 - C_6 alkyl, C_1 - C_6 alkoxy or phenyl(C_1 - C_6)alkyl; or

an R^6 group in the 6-position and an R^6 group in the 7-position together form a group represented by:



wherein each Z and Z' is independently oxygen or the group $-NR^{11}-$; wherein R^{11} , R^{14} and R^{16} are as set forth above;

(v) R^7 and R^8 are each independently:

a reactive substituent; a compatibilizing substituent; hydrogen; hydroxy; C_1 - C_6 alkyl; C_3 - C_7 cycloalkyl; allyl; a substituted or unsubstituted phenyl or benzyl, wherein each of said phenyl and benzyl substituents is independently C_1 - C_6 alkyl or C_1 - C_6 alkoxy; chloro; fluoro; a substituted or unsubstituted amino; $-C(O)R^9$, wherein R^9 is hydrogen, hydroxy, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, an unsubstituted, mono- or di-substituted phenyl or naphthyl wherein each of said substituents are independently C_1 - C_6 alkyl or C_1 - C_6 alkoxy, phenoxy, mono- or di- $(C_1$ - C_6)alkoxy substituted phenoxy, mono- or di- $(C_1$ -

C₆)alkoxy substituted phenoxy, amino, mono- or di-(C₁-C₆)alkylamino, phenylamino, mono- or di-(C₁-C₆)alkyl substituted phenylamino or mono- or di-(C₁-C₆)alkoxy substituted phenylamino; -OR¹⁸, wherein R¹⁸ is 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, 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(R¹⁹)T, wherein R¹⁹ is hydrogen or C₁-C₃ alkyl, T is CN, CF₃ or COOR²⁰, wherein R²⁰ is hydrogen or C₁-C₃ alkyl, or wherein R¹⁸ is -C(=O)U, wherein U is hydrogen, C₁-C₆ alkyl, C₁-C₆ alkoxy, an unsubstituted, mono- or di-substituted phenyl or naphthyl, wherein each of said substituents are independently C₁-C₆ alkyl or C₁-C₆ alkoxy, phenoxy, mono- or di-(C₁-C₆)alkyl substituted phenoxy, mono- or di-(C₁-C₆)alkoxy substituted phenoxy, amino, mono- or di-(C₁-C₆)alkylamino, phenylamino, mono- or di-(C₁-C₆)alkyl substituted phenylamino or mono- or di-(C₁-C₆)alkoxy substituted phenylamino; and a mono-substituted phenyl, said phenyl having a substituent located at the para position, the substituent being a dicarboxylic acid residue or derivative thereof, a diamine residue or derivative thereof, an amino alcohol residue or derivative thereof, a polyol residue or derivative thereof, -(CH₂)_t-, -(CH₂)_t- or -[O-(CH₂)_t]_k-, wherein t ranges from 2 to 6 and k ranges from 1 to 50, and wherein the substituent is connected to an aryl group on another photochromic material; or

R⁷ and R⁸ together form an oxo group; a spiro-carbocyclic group containing 3 to 6 carbon atoms, provided that the spiro-carbocyclic group is not norbornyl; or a spiro-heterocyclic group containing 1 to 2 oxygen atoms and 3 to 6 carbon atoms including the spirocarbon atom, said spiro-carboxylic and spiro-heterocyclic groups being annellated with 0, 1, or 2 benzene rings, and (vi) B and B' are each independently:

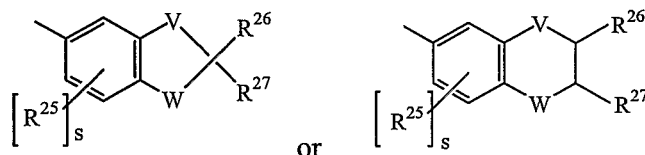
an aryl group that is mono-substituted with a reactive substituent or a compatibilizing substituent; an unsubstituted, mono-, di- or tri-substituted aryl

group, 9-julolidinyl, an unsubstituted, mono- or di-substituted heteroaromatic group chosen from pyridyl furanyl, benzofuran-2-yl, benzofuran-3-yl, thienyl, benzothien-2-yl, benzothien-3-yl, dibenzofuranyl, dibenzothienyl, carbazoyl, benzopyridyl, indolinyl and fluorenyl, wherein the aryl and heteroaromatic substituents are each independently:

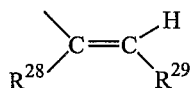
hydroxy, aryl, mono- or di-(C₁-C₁₂)alkoxyaryl, mono- or di-(C₁-C₁₂)alkylaryl, haloaryl, C₃-C₇ cycloalkylaryl, C₃-C₇ cycloalkyl, C₃-C₇ cycloalkyloxy, C₃-C₇ cycloalkyloxy(C₁-C₁₂)alkyl, C₃-C₇ cycloalkyloxy(C₁-C₁₂)alkoxy, aryl(C₁-C₁₂)alkyl, aryl(C₁-C₁₂)alkoxy, aryloxy, aryloxy(C₁-C₁₂)alkyl, aryloxy(C₁-C₁₂)alkoxy, mono- or di-(C₁-C₁₂)alkylaryl(C₁-C₁₂)alkyl, mono- or di-(C₁-C₁₂)alkoxyaryl(C₁-C₁₂)alkyl, mono- or di-(C₁-C₁₂)alkylaryl(C₁-C₁₂)alkoxy, mono- or di-(C₁-C₁₂)alkoxyaryl(C₁-C₁₂)alkoxy, amino, mono- or di-(C₁-C₁₂)alkylamino, diarylamino, piperazino, N-(C₁-C₁₂)alkylpiperazino, N-aryl piperazino, aziridino, indolino, piperidino, morpholino, thiomorpholino, tetrahydroquinolino, tetrahydroisoquinolino, pyrrolidyl, C₁-C₁₂ alkyl, C₁-C₁₂ haloalkyl, C₁-C₁₂ alkoxy, mono(C₁-C₁₂)alkoxy(C₁-C₁₂)alkyl, acryloxy, methacryloxy, halogen, or -C(=O)R²¹, wherein R²¹ is -OR²², -N(R²³)R²⁴, piperidino or morpholino, wherein R²² is allyl, C₁-C₆ alkyl, phenyl, mono(C₁-C₆)alkyl substituted phenyl, mono(C₁-C₆)alkoxy substituted phenyl, phenyl(C₁-C₃)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 or C₁-C₆ haloalkyl, and R²³ and R²⁴ are each independently C₁-C₆ alkyl, C₅-C₇ cycloalkyl or a substituted or unsubstituted phenyl, said phenyl substituents independently being C₁-C₆ alkyl or C₁-C₆ alkoxy;

an unsubstituted or mono-substituted group chosen from pyrazolyl, imidazolyl, pyrazolinyl, imidazolinyl, pyrrolinyl, phenothiazinyl, phenoxazinyl, phenazinyl and acridinyl, said substituents being C₁-C₁₂ alkyl, C₁-C₁₂ alkoxy, phenyl or halogen; a mono-substituted phenyl, said phenyl having a substituent located at the para position, the substituent being a dicarboxylic acid residue or

derivative thereof, a diamine residue or derivative thereof, an amino alcohol residue or derivative thereof, a polyol residue or derivative thereof, $-(CH_2)_t-$, $-(CH_2)_t-$ or $-[O-(CH_2)_t]_k-$, wherein t ranges from 2 to 6 and k ranges from 1 to 50, and wherein the substituent is connected to an aryl group on another photochromic material; a group represented by:



wherein V is $-CH_2-$ or O, and W is O or substituted nitrogen, provided that when W is substituted nitrogen, V is $-CH_2-$, the substituted nitrogen substituents being hydrogen, C_1-C_{12} alkyl or C_1-C_{12} acyl, each R^{25} independently being C_1-C_{12} alkyl, C_1-C_{12} alkoxy, hydroxy or halogen, R^{26} and R^{27} are each independently hydrogen or C_1-C_{12} alkyl, and s ranges from 0 to 2; or a group represented by:



wherein R^{28} is hydrogen or C_1-C_{12} alkyl, and R^{29} is an unsubstituted, mono- or di-substituted group chosen from naphthyl, phenyl, furanyl or thienyl, said substituents being C_1-C_{12} alkyl, C_1-C_{12} alkoxy or halogen; or

B and B' taken together form a fluoren-9-ylidene, or mono- or di- substituted fluoren-9-ylidene, each of said fluoren-9-ylidene substituents independently being C_1-C_{12} alkyl, C_1-C_{12} alkoxy or halogen.

34. The ophthalmic device of claim 33, wherein the photochromic material comprises at least one reactive substituents and a compatiblizing substituents, each of said reactive substituent and compatibilizing substituent being independently represented by one of:

$-A'-D-E-G-J;$	$-G-E-G-J;$	$-D-E-G-J;$
$-A'-D-J;$	$-D-G-J;$	$-D-J;$
$-A'-G-J;$	$-G-J;$ and	$-A'-J$

wherein:

- (i) each -A'- is independently -O-, -C(=O)-, -CH₂-, -OC(=O)- or -NHC(=O)-, provided that if -A'- is -O-, -A'- forms at least one bond with -J;
- (ii) each -D- is independently:
 - (a) a diamine residue or a derivative thereof, said diamine residue being an aliphatic diamine residue, a cyclo aliphatic diamine residue, a diazacycloalkane residue, an azacyclo aliphatic amine residue, a diazacrown ether residue or an aromatic diamine residue, wherein a first amino nitrogen of said diamine residue forms a bond with -A'-, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof, or a substituent or an available position on the indeno-fused naphthopyran, and a second amino nitrogen of said diamine residue forms a bond with -E-, -G- or -J; or
 - (b) an amino alcohol residue or a derivative thereof, said amino alcohol residue being an aliphatic amino alcohol residue, a cyclo aliphatic amino alcohol residue, an azacyclo aliphatic alcohol residue, a diazacyclo aliphatic alcohol residue or an aromatic amino alcohol residue, wherein an amino nitrogen of said amino alcohol residue forms a bond with -A'-, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof, or a substituent or an available position on the indeno-fused naphthopyran, and an alcohol oxygen of said amino alcohol residue forms a bond with -E-, -G- or -J, or said amino nitrogen of said amino alcohol residue forms a bond with -E-, -G- or -J, and said alcohol oxygen of said amino alcohol residue forms a bond with -A'-, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof, or a substituent or an available position on the indeno-fused naphthopyran;
- (iii) each -E- is independently a dicarboxylic acid residue or a derivative thereof, said dicarboxylic acid residue being an aliphatic dicarboxylic acid residue, a cycloaliphatic dicarboxylic acid residue or an aromatic dicarboxylic acid residue, wherein a first carbonyl group of said dicarboxylic acid residue forms

a bond with -G- or -D-, and a second carbonyl group of said dicarboxylic acid residue forms a bond with -G-;

(iv) each -G- is independently:

- (a) $-(OC_2H_4)_x(OC_3H_6)_y(OC_4H_8)_z-O-$, wherein x, y and z are each independently chosen and range from 0 to 50, and a sum of x, y, and z ranges from 1 to 50;
- (b) a polyol residue or a derivative thereof, said polyol residue being an aliphatic polyol residue, a cyclo aliphatic polyol residue or an aromatic polyol residue, wherein a first polyol oxygen of said polyol residue forms a bond with -A'-, -D-, -E-, the group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof, or a substituent or an available position on the indeno-fused naphthopyran, and a second polyol oxygen of said polyol forms a bond with -E- or -J; or
- (c) a combination thereof, wherein the first polyol oxygen of the polyol residue forms a bond with a group $-(OC_2H_4)_x(OC_3H_6)_y(OC_4H_8)_z-$ and the second polyol oxygen forms a bond with -E- or -J; and

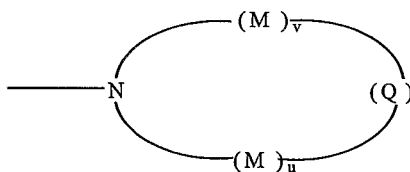
(v) each -J is independently:

- (a) a group -K, wherein -K is $-CH_2COOH$, $-CH(CH_3)COOH$, $-C(O)(CH_2)_wCOOH$, $-C_6H_4SO_3H$, $-C_5H_{10}SO_3H$, $-C_4H_8SO_3H$, $-C_3H_6SO_3H$, $-C_2H_4SO_3H$ or $-SO_3H$, wherein w ranges from 1 to 18;
- (b) hydrogen, provided that if -J is hydrogen, -J is bonded to an oxygen of -D- or -G-, or a nitrogen of -D-; or
- (c) a group -L or residue thereof, wherein -L is acryl, methacryl, crotyl, 2-(methacryloxy)ethylcarbamyl, 2-(methacryloxy)ethoxycarbonyl, 4-vinylphenyl, vinyl, 1-chlorovinyl or epoxy.

35. The ophthalmic device of claim 34 wherein at least one of an R^6 group at the 6-position, an R^6 group at the 7-position, B, B', R^7 , R^8 and R^4 comprises a reactive substituent.

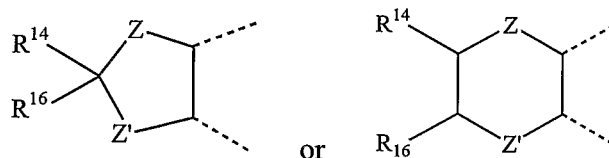
36. The ophthalmic device of claim 33 wherein the indeno-fused naphthopyran is an indeno[2',3':3,4]naphtho[1,2-b]pyran and wherein:

- (i) each of an R^6 group at the 7-position and an R^6 group at the 6-position of the indeno[2',3':3,4]naphtho[1,2-b]pyran is independently $-OR^{10}$, wherein R^{10} is C_1 - C_6 alkyl, a substituted or unsubstituted phenyl, said phenyl substituents being C_1 - C_6 alkyl or C_1 - C_6 alkoxy, 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 or mono(C_1 - C_4)alkyl substituted C_3 - C_7 cycloalkyl, $-N(R^{11})R^{12}$, wherein R^{11} and R^{12} are each independently hydrogen, 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, wherein said aryl group is phenyl or naphthyl; a nitrogen containing ring represented by:



wherein each $-M-$ is independently chosen for each occurrence from $-CH_2-$, $-CH(R^{13})-$, $-C(R^{13})_2-$, $-CH(aryl)-$, $-C(aryl)_2-$ and $-C(R^{13})(aryl)-$, and $-Q-$ is $-M-$, $-O-$, $-S-$, $-NH-$, $-N(R^{13})-$ or $-N(aryl)-$, wherein each R^{13} is independently C_1 - C_6 alkyl, each aryl is independently phenyl or naphthyl, u ranges from 1 to 3, and v ranges from 0 to 3, provided that if v is 0, $-Q-$ is $-M-$; and a reactive substituent or a compatibilizing substituent, provided that the reactive or compatibilizing substituent comprises a linking group comprising an aliphatic amino alcohol residue, a cyclo aliphatic amino alcohol residue, an azacyclo aliphatic alcohol residue, a diazacyclo aliphatic alcohol residue, a diamine residue, an aliphatic diamine residue, a cyclo aliphatic diamine residue, a diazacycloalkane residue, an azacyclo aliphatic amine residue, an oxyalkoxy group, an aliphatic polyol residue or a cyclo aliphatic polyol residue that forms a bond with the indeno[2',3':3,4]naphtho[1,2-b]pyran at the 6-position or the 7-position; or

- (ii) an R^6 group in the 6-position and an R^6 group in the 7-position of the indeno[2',3':3,4]naphtho[1,2-b]pyran together form a group represented by:



wherein Z and Z' are each independently oxygen or $-NR^{11}$ -, wherein R^{11} is as set forth above in (i).

37. The photochromic material of claim 33 wherein the photochromic material is chosen from: (i) a 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-cyano-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (ii) a 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-carboxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (iii) a 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-methoxycarbonyl-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (iv) a 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(2-(2-hydroxyethoxy)ethoxycarbonyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (v) a 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(4-fluorophenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (vi) a 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(4-(phenyl)phenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (vii) a 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(4-(hydroxymethyl)phenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (viii) a 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(3-hydroxy-3-methylbutyn)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (ix) a 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(2-phenylethynyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (x) a 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-phenyl-13-ethyl-13-methoxy-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xi) a 3-phenyl-3-(4-methoxyphenyl)-6,7-dimethoxy-11-(4-(2-methacryloxyethoxy)carbonylphenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]

naphtho[1,2-b]pyran; (xii) a 3,3-di(4-methoxyphenyl)-6-methoxy-7-((3-(2-methacryloxyethyl)carbamyloxymethylenepiperidino)-1-yl)-11-(4-(phenyl)phenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xiii) a 3-phenyl-3-(4-(2-(2-methacryloxyethyl)carbamyloxyethoxy)phenyl)-6-methoxy-11-phenyl-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xiv) a 3-phenyl-3-(4-methoxyphenyl)-6,7-dimethoxy-13,13-dimethyl-11-(2-(4-(3-phenyl-6,11-dimethoxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran-3-yl)phenoxy)ethoxycarbonyl)-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xv) a 3-phenyl-3-(4-(2-methacryloxyethyl)carbamyloxyphenyl)-6,7-dimethoxy-13,13-dimethyl-11-((1-(4-(4-(3-phenyl-6,11-dimethoxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran-3-yl)-phenyl)piperazino-4-yl)carbonyl)-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xvi) a 3,3-di(4-methoxyphenyl)-11-methoxycarboxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xvii) a 3-(4-morpholinophenyl)-3-phenyl-6,7-dimethoxy-11-carboxy-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xviii) a 3-(4-morpholinophenyl)-3-phenyl-6,7-dimethoxy-11-methoxycarbonyl-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xix) a 3-(4-morpholinophenyl)-3-(4-methoxyphenyl)-6,7-dimethoxy-11-(4-fluorophenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xx) a 3-(4-fluorophenyl)-3-(4-methoxyphenyl)-6,7-dimethoxy-11-cyano-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xxi) a 3-(4-morpholinophenyl)-3-(4-methoxyphenyl)-11-(2-phenylethynyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xxii) a 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(4-dimethylaminephenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xxiii) a 3,3-di(4-methoxyphenyl)-6,7-dimethoxy-11-(4-methoxyphenyl)-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xxiv) a 3,3-di(4-methoxyphenyl)-6-methoxy-7-morpholino-11-phenyl-13-butyl-13-(2-(2-hydroxyethoxy)ethoxy)-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xxv) a 3-(4-fluorophenyl)-3-(4-methoxyphenyl)-6-methoxy-7-morpholino-11-phenyl-13-butyl-13-(2-(2-

hydroxyethoxy)ethoxy)-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xxvi) a 3,3-di(4-fluorophenyl)-11-cyano-13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xxvii) a 3-(4-morpholinophenyl)-3-phenyl-6-methoxy-7-(3-(2-methacryloxyethyl)carbamyloxymethylenepiperidino-1-yl)-11-phenyl-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; (xxviii) a 3-(4-(2-(2-methacryloxyethyl)carbamylethoxy)phenyl)-3-phenyl-6,7-dimethoxy-11-phenyl-13,13-dimethyl-3H,13H-indeno[2',3':3,4]naphtho[1,2-b]pyran; and mixtures thereof.

38. An ophthalmic device adapted for use behind a substrate that blocks a substantial portion of electromagnetic radiation in the range of 320 nm to 390 nm, the ophthalmic device comprising a photochromic material comprising an indeno-fused naphthopyran and a group that extends the pi-conjugated system of the indeno-fused naphthopyran bonded at the 11-position thereof connected to at least a portion of the optical element, wherein the at least a portion of the optical element absorbs a sufficient amount of electromagnetic radiation having a wavelength greater than 390 nm passing through the substrate that blocks a substantial portion of electromagnetic radiation in the range of 320 nm to 390 nm such that the at least a portion of the optical element transforms from a first state to a second state.

39. The ophthalmic device of claim 38 wherein the substrate that blocks a substantial portion of electromagnetic radiation in the range of 320 nm to 390 nm is a windshield and wherein the first state of the optical element is a bleached state and the second state is a colored state.