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<p>(54) Title: POLYCYCLIC AROMATIC COMPOUNDS HAVING NONLINEAR OPTICAL PROPERTIES</p>		
<p>(57) Abstract</p> <p>Devices and materials containing certain stable, polycyclic aromatic compounds exhibit sensible, second order nonlinear optical effects. In general, useful polycyclic aromatic compounds possess electron-donating and electron-withdrawing chemical functionality but no center of inversion symmetry on either the molecular or crystalline unit cell level.</p>		

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**POLYCYCLIC AROMATIC COMPOUNDS HAVING
NONLINEAR OPTICAL PROPERTIES**

GOVERNMENT SUPPORT

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0105.

FIELD OF THE INVENTION

This invention relates to materials that are useful
in the fabrication of electro-optical, second harmonic
generating, electro-acoustic, waveguide, fiber, semiconductor,
5 and other useful photonic devices. In particular, this
invention is concerned with compounds that exhibit second order
nonlinear optical properties and possess suitable thermal,
mechanical, chemical and photo stabilities to withstand
processing conditions associated with such devices.

10 **BACKGROUND OF THE INVENTION**

There has been a growing interest over the last decade
in the nonlinear optical properties of conjugated organic and
polymeric materials having delocalized π -electron
distributions. Nonlinear optical properties are the basis of
15 newly emerging photonics technologies in which light works
with, or even replaces, electrons in applications traditionally
carried out by microelectronics. Organic materials are
advantageous in photonics because organic molecular design and

- 2 -

synthesis is flexible, and crystalline and thin-film phases are relatively easy to prepare.

Nonlinear optical responses can, in general, be classified as resonant or non-resonant, depending upon how close the optical frequencies employed are to the natural absorption frequencies of the material. Non-resonant, second-order processes, in which the response is proportional to the square of applied electric fields, arise only in materials that are noncentrosymmetric and possess both a suitably delocalized π -electronic system and a large dipole moment. Second-order processes include second-harmonic generation, in which a material generates light at twice the frequency of the incident light, and the electrooptic effect, wherein an applied electric field changes the refractive index of the material and, therefore, alters the propagation properties of the incident light.

Compounds having nonlinear optical properties typically find use as single crystals or films layered upon a substrate, as main chains or side chains appended to a polymer core, or as "guests" dispersed in "host" polymers such as polyimides. The fabrication of semiconductors and other devices incorporating these structures can subject the nonlinear optical compound to temperatures on the order of -40°C to about 320°C. These thermal requirements cannot be met by most known nonlinear optical compounds. The molecular units of crystals and films formed from such compounds typically are bound by relatively weak Van der Waals forces. Consequently, these crystals and films lack thermal and mechanical strength, and are highly susceptible to chemical attack and dissociation. For example, crystals of 2-methyl-4-nitroaniline, which are known to exhibit considerable nonlinearity, are so weakly bound that they actually sublime at room temperature.

Accordingly, there exists a need in the art for compounds that exhibit nonlinear optical properties yet can withstand semiconductor processing conditions. In particular, there is a need for compounds that are stable to high temperatures without detriment to their nonlinear optical

- 3 -

coefficients.

OBJECTS OF THE INVENTION

It is one object of the present invention to provide novel materials that exhibit nonlinear optical properties.

5 It is another object of the invention to provide materials that exhibit second order nonlinear optical properties.

10 It is yet another object to provide nonlinear optical compounds that can be used as single crystals, crystalline films, polymer side chains, or as guests in polymer hosts or sol-gel glasses in semiconductor and other useful electronic or photonic devices.

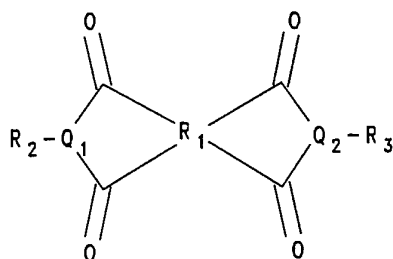
15 It is a further object of the invention to provide nonlinear optical compounds that can withstand high temperatures, high light intensity, and other processing conditions associated with such devices.

20 It is still another object to provide nonlinear optical compounds that can be elaborated into oligomers and/or polymers which exhibit second order nonlinear optical and electrooptical properties.

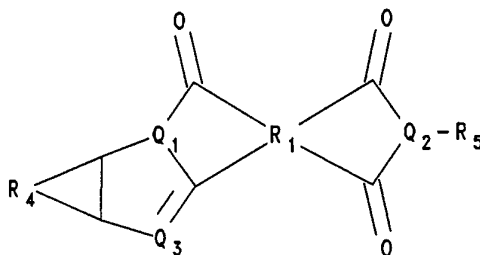
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SUMMARY OF THE INVENTION

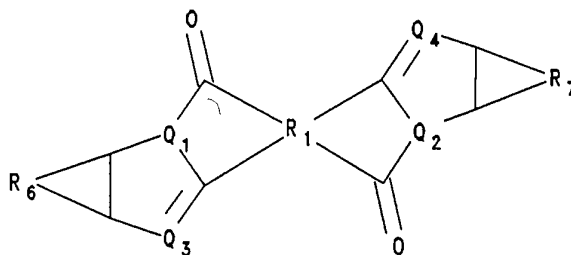
These and other objects are satisfied by the present invention, which provides polycyclic aromatic compounds that exhibit both nonlinear optical properties and excellent chemical, thermal, and photo stability. In certain embodiments, the polycyclic aromatic compounds have formulas (1), (2), (3), or (4):



(1)

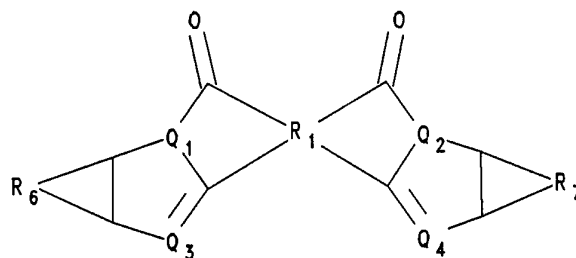


(2)



(3)

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(4)

wherein:

R_1 is a tetravalent aromatic radical;

Q_1 , Q_2 , Q_3 , and Q_4 are, independently, heteroatoms that participate in delocalized π -electron systems;

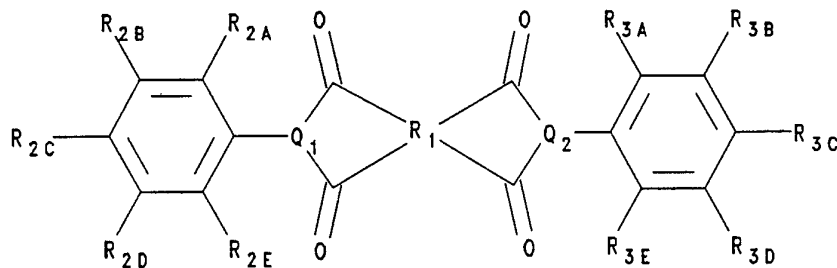
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and R_2 - R_7 are, independently, alkyl groups or aromatic groups.

In preferred embodiments, R_2 and R_6 are, independently, alkyl groups or aromatic groups that are electron-donating relative to hydrogen, and R_3 and R_7 are, independently, alkyl groups or aromatic groups that are electron-withdrawing relative to hydrogen. Preferably, one of R_4 and R_5 is an alkyl group or an aromatic group that is electron-donating relative to hydrogen, and the other is an alkyl group or an aromatic group that is electron-withdrawing relative to hydrogen.

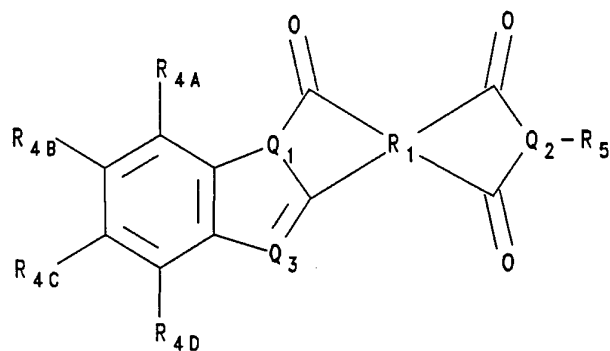
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In further preferred embodiments, the polycyclic aromatic compounds have formulas (5), (6), (7), or (8):

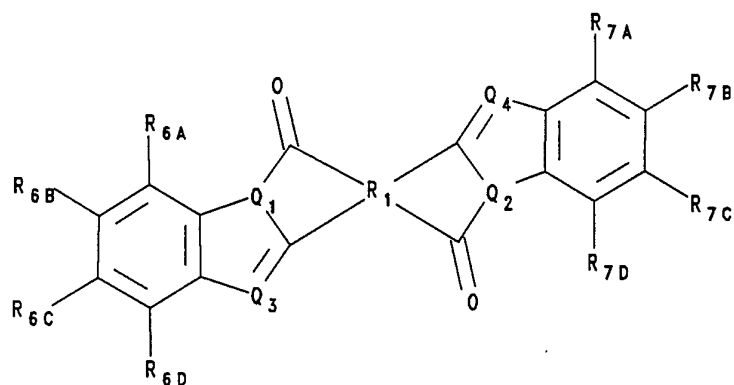


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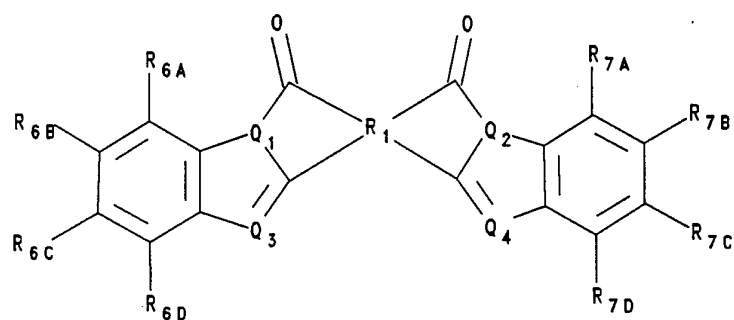
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(6)



(7)



(8)

wherein:

5

R_1 is a tetravalent aromatic radical;
 Q_1 , Q_2 , Q_3 , and Q_4 are, independently, heteroatoms that participate in delocalized π -electron systems;
 at least one of R_{2A} - R_{2E} is an aromatic or non-aromatic group that is electron-donating relative to

-7-

hydrogen;

at least one of R_{3A} - R_{3E} is an aromatic or non-aromatic group that is electron-withdrawing relative to hydrogen;

5 at least one of R_{4A} - R_{4D} is an aromatic or non-aromatic group that is electron-donating relative to hydrogen and R_5 is an alkyl or aromatic group that is electron-withdrawing relative to hydrogen, or at least one of R_{4A} - R_{4D} is an aromatic or non-aromatic group that is electron-withdrawing relative to hydrogen and R_5 is an alkyl or aromatic group that is electron-donating relative to hydrogen;

10 at least one of R_{6A} - R_{6D} is an aromatic or non-aromatic group that is electron-donating relative to hydrogen; and

15 at least one of R_{7A} - R_{7D} is an aromatic or non-aromatic group that is electron-withdrawing relative to hydrogen.

20 In preferred embodiments, R_1 is an aromatic hydrocarbon such as benzene, naphthalene or perylene and Q_1 - Q_5 are N. Compounds of this type have been found to exhibit second order nonlinear optical properties and decomposition temperatures greater than about 360°C.

25 The present invention further provides nonlinear optical materials and devices that exhibit sensible nonlinear optical, piezoelectric or pyroelectric effects. In general, the devices comprise a layer that contains at least one polycyclic aromatic compound of the invention disposed upon a substrate. The layer can contain the compound in pure or

30 substantially pure form (e.g., as crystals, oligomers, or polymers) or in combination with other chemical compounds such as known synthetic organic polymers or glasses made by a sol-gel method. See, e.g., L.C. Klein, "Sol-gel Technology for thin films, fibers, preforms, electronics, and specialty

35 shapes", Noyes publications 1988. In certain embodiments, for example, the layer comprises synthetic organic polymer in

admixture with a compound of the invention. In other embodiments, the synthetic polymer and compounds of the invention are covalently bound.

BRIEF DESCRIPTION OF THE DRAWINGS

5 The numerous objects and advantages of the present invention may be better understood by those skilled in the art by reference to the accompanying Figure 1, which shows a device according to the invention comprising a substrate and a layer that contains a polycyclic aromatic compound of the invention.

10 DETAILED DESCRIPTION OF THE INVENTION

 It has been found in accordance with the present invention that devices and materials containing certain thermally-stable, polycyclic aromatic compounds exhibit sensible nonlinear optical effects, particularly second order
15 nonlinear optical and electrooptic effects. In general, useful polycyclic aromatic compounds possess both electron-donating and electron-withdrawing chemical functionality but no center of inversion symmetry on either the molecular or crystalline unit cell level. Indeed, it is believed that judicious
20 placement of electron-donating and electron-withdrawing functionality within a compound of the invention actually contributes to an electronic asymmetry within the compound and, hence, to enhanced nonlinear optical effects.

 In preferred embodiments, the polycyclic aromatic
25 compounds that find use in practice of the present invention have formula (1), (2), (3), or (4). Typically, R_1 is a tetravalent aromatic radical. Preferably, R_1 is derived from an aromatic hydrocarbon such as, for example, benzene, perylene, phenanthrene, anthracene, naphthalene, pyrene,
30 chrysene, or naphthacene; aromatic groups derived from benzene, perylene, and naphthalene are particularly preferred. In accordance with the invention, Q_1 - Q_4 are independently selected heteroatoms that can participate in a delocalized π -electron system spanning essentially the entire length of the compounds
35 represented by formulas (1)-(4). Numerous suitable heteroatoms

are known to those skilled in the art, including N, O, S, Se, and Te. Preferably, each of Q₁-Q₄ is N.

In embodiments represented by formulas (1)-(4), R₂, R₆, and one of R₄ and R₅ are alkyl groups or aromatic groups that possess net electron-donating effects, including straight chain and branched chain aliphatic hydrocarbons, straight chain and branched chain aliphatic hydrocarbons substituted with at least one substituent that is electron-donating relative to hydrogen, aromatic hydrocarbons, aromatic heterocycles, aromatic hydrocarbons substituted with at least one substituent that is electron-donating relative to hydrogen, or aromatic heterocycles substituted with at least one substituent that is electron-donating relative to hydrogen. Conversely, R₃, R₇, and one of R₄ and R₅ are alkyl groups or aromatic groups that possess net electron-withdrawing effects, including straight chain and branched chain aliphatic hydrocarbons substituted with at least one substituent that is electron-withdrawing relative to hydrogen, aromatic heterocycles, aromatic hydrocarbons substituted with at least one substituent that is electron-withdrawing relative to hydrogen, or aromatic heterocycles substituted with at least one substituent that is electron-withdrawing relative to hydrogen.

In embodiments represented by formulas (5)-(8), R_{2A}-R_{2E}, and R_{6A}-R_{6D} can be substituents that possess net electron-donating effects. Conversely, R_{3A}-R_{3E} and R_{7A}-R_{7D} are substituents that possess net electron-withdrawing effects.

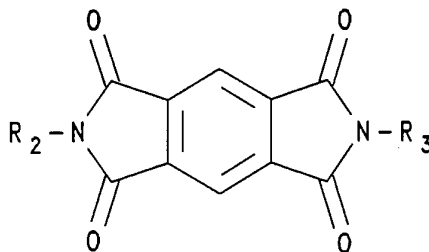
Numerous examples of electron-donating and electron-withdrawing aromatic functionality are well-known to those skilled in the art. Further, electron-donating and electron-withdrawing groups can be identified through routine experimentation (e.g., substitution for hydrogen in a molecule and testing of any resultant inductive effects). In preferred embodiments, electron-donating groups are aromatic hydrocarbons substituted with alkyl groups, alkylamino groups, NH₂, alkoxy groups, OH, alkylthio groups, SH, and/or -OC(O)-(alkyl), wherein alkyl groups have from about 1-10 carbon atoms.

Electron-withdrawing groups preferably are aromatic

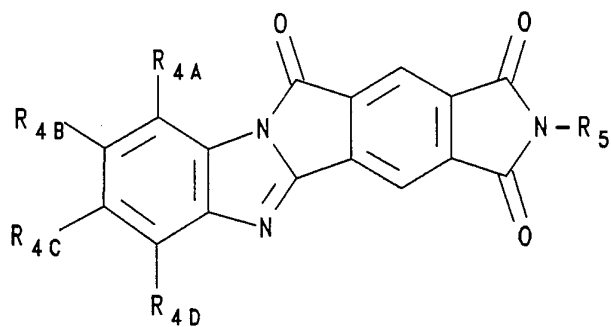
hydrocarbons substituted with one or more groups selected from N-(alkyl)₃⁺, S-(alkyl)₂⁺, NH₃⁺, NO₂, SO₂-(alkyl), CN, SO₂-(aromatic), C(O)OH, F, Cl, Br, I, C(O)O-(alkyl), C(O)-(alkyl), and/or CHO, wherein alkyl groups have from about 1-10 carbon atoms and aromatic groups have about 6-24 carbon atoms.

It has been found in accordance with the invention that polycyclic aromatic compounds exhibiting sensible, second order nonlinear optical effects can be identified (screened) on the basis of their UV/visible spectra. In general, useful compounds exhibit at least one UV/visible transition, or, equivalently, excitation, having an extinction coefficient greater than about $1 \times 10^5 \text{ l mole}^{-1} \text{ cm}^{-1}$ as determined by standard techniques. Such an electronic excitation should principally be responsible for a second order nonlinear optical effect, especially under non-resonant conditions.

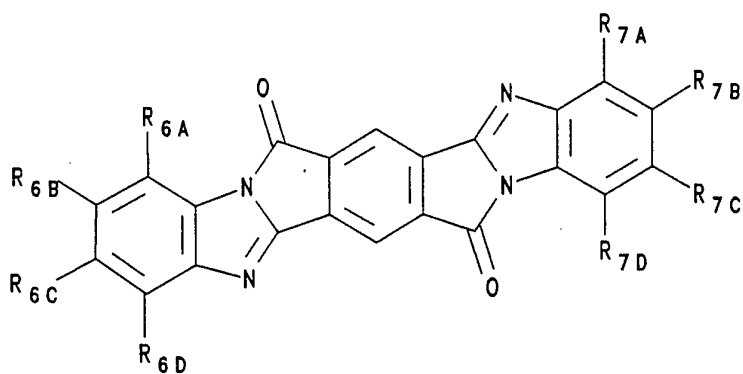
Preferred polycyclic aromatic compounds according to the present invention have formulas (9)-(20).



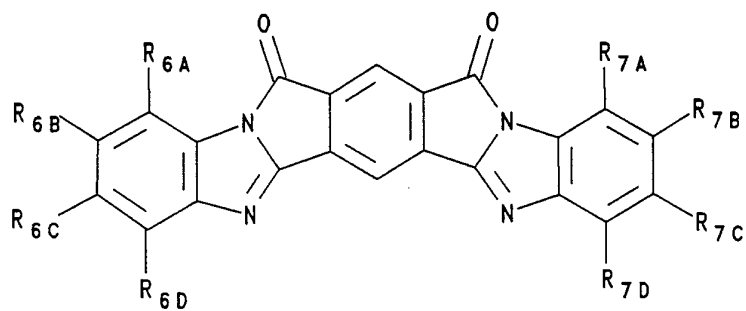
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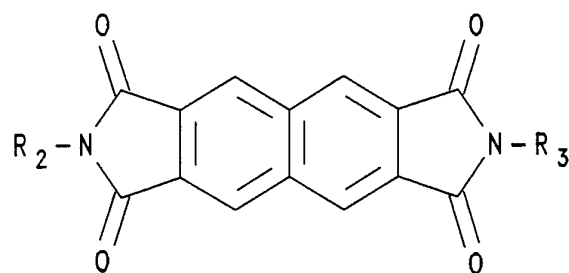
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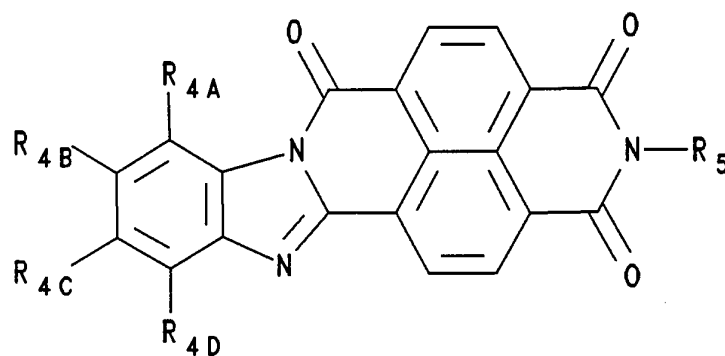
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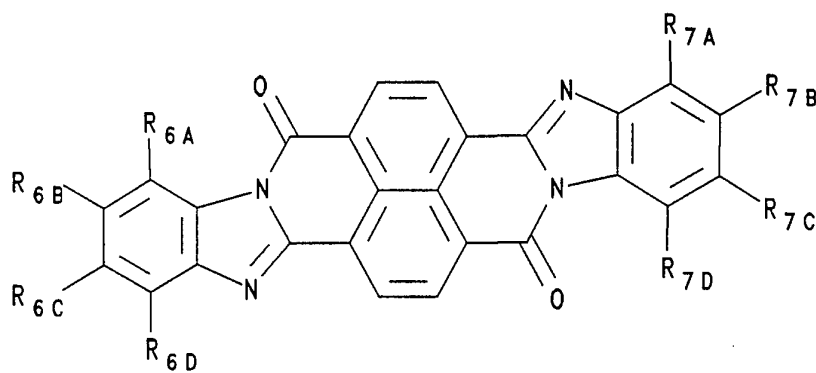
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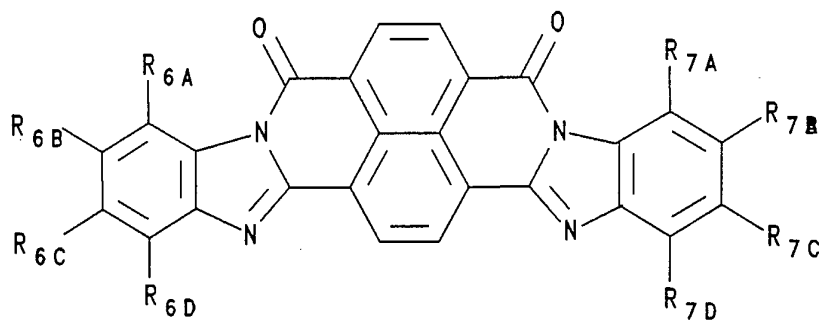
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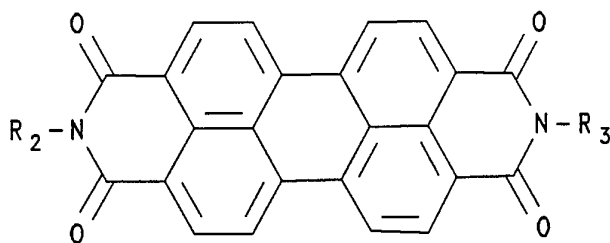
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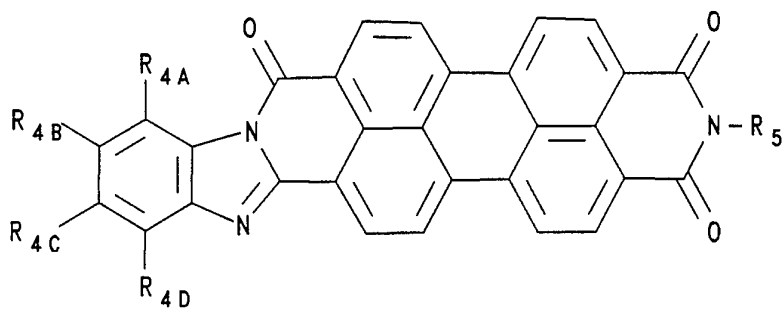
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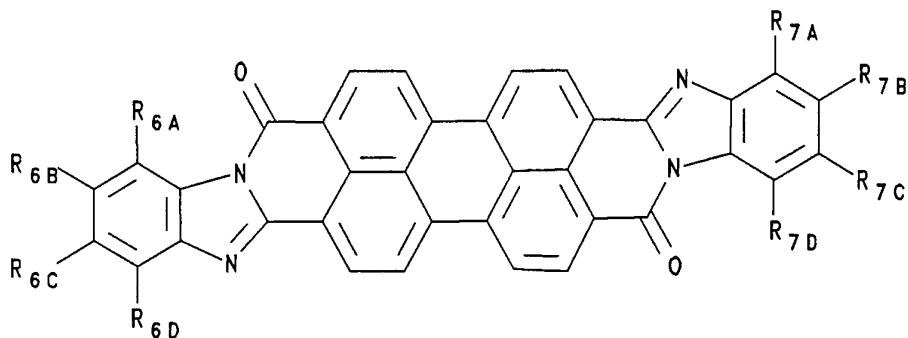


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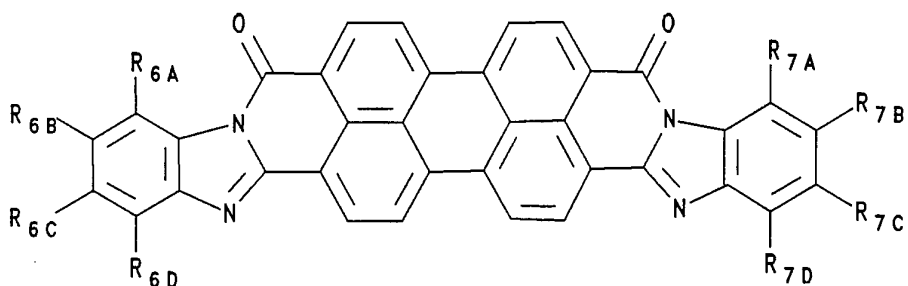


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- 14 -



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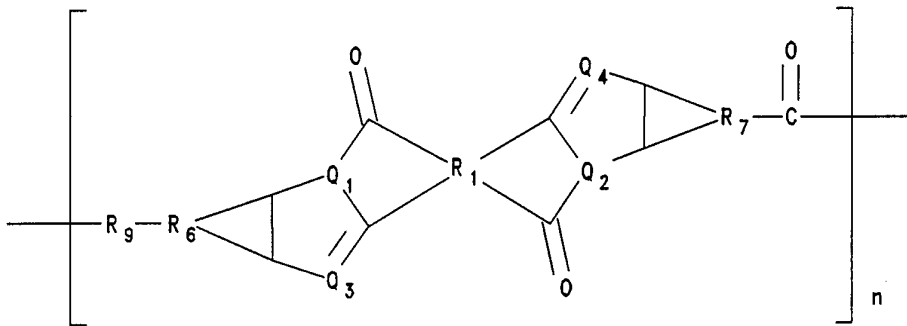


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The polycyclic aromatic compounds of the invention find use in a wide variety of devices, including electro-optical, second harmonic generating, electro-acoustic, waveguide, semiconductor, and other photonic or electronic devices.

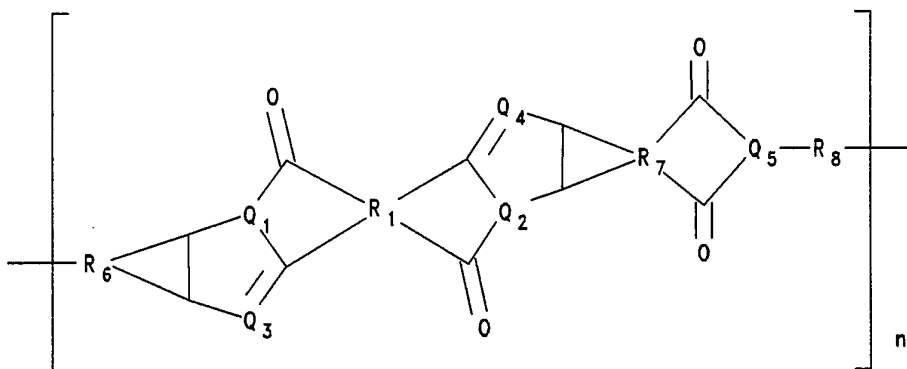
As shown in Figure 1, devices according to the invention generally comprise a dielectric or some other substrate 10 and a layer 12, disposed on the substrate, comprising at least one polycyclic aromatic compound of the invention. Useful substrates include semiconductors such as silicon gallium and arsenide or insulators such as glass or plastic. Layer 12 can contain a polycyclic aromatic compound of the invention in pure or substantially pure form as, for example, crystals, crystalline films, oligomers or polymers. Those skilled in the art will appreciate that a wide variety of polymeric and oligomeric structures can be constructed in accordance with the present invention using compounds having formulas (1), (2), (3), and/or (4) as monomeric building blocks. For example,

formulas (21) and (22) show representative structures wherein R_8 is alkyl or aromatic, R_9 is O or NH, Q_5 is a heteroatom that can participate in a delocalized π -electron system, and n is from 2 to about 2000.



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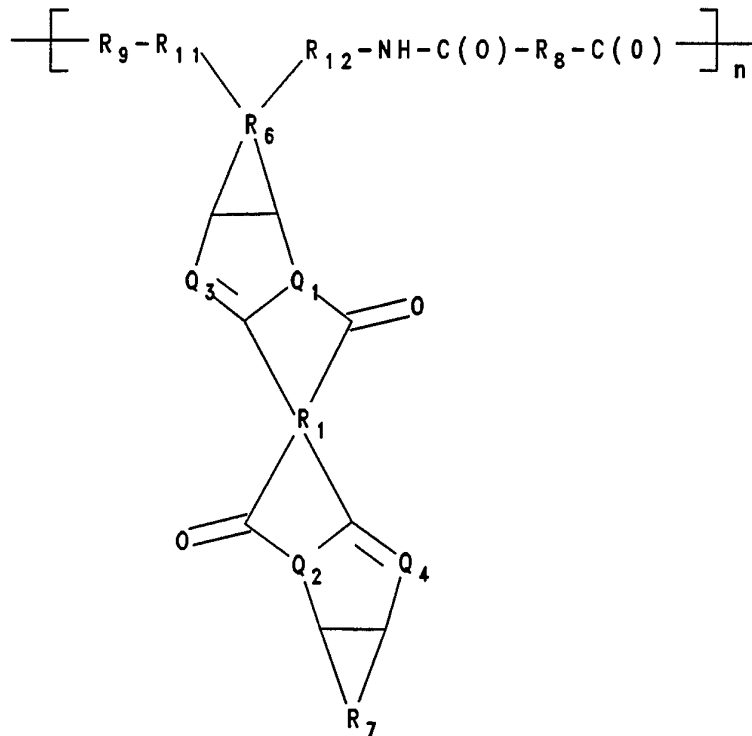


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Alternatively, layer 12 can contain a polycyclic aromatic compound of the invention in combination with one or more synthetic organic polymers. In certain embodiments, for example, the layer can include synthetic organic polymer or precursors thereof (e.g., monomers, catalysts, and sensitizers) in admixture with a compound having formula (1), (2), (3), and/or (4). As discussed below in greater detail, such embodiments offer the possibility of effecting cross-linking and/or *in situ* polymerization following mixture of the polymer or polymer precursor system with a compound of the invention. Where the polymer constitutes a major proportion of the layer and the polycyclic compound constitutes a minor proportion of the layer, the compound can be said to be a "guest" in the "host" polymer.

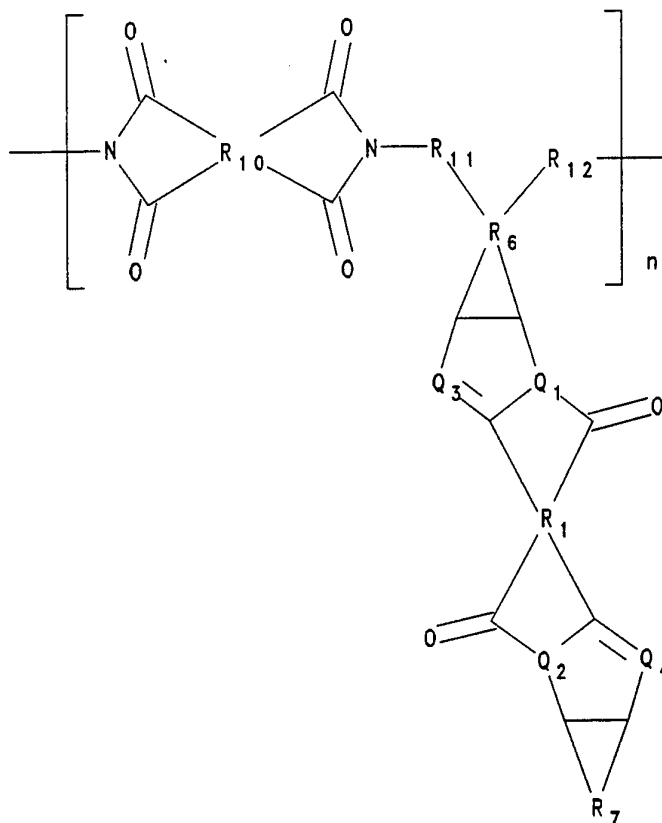
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In other embodiments, layer 12 includes one or more compounds of the invention covalently bound as side chains on a polymeric backbone or core. Exemplary backbone/side chain structures are provided by formulas (23) and (24), wherein: R_8 is alkyl or aromatic; R_9 is O or NH; R_{10} is a tetravalent aromatic radical; R_{11} and R_{12} are, independently, alkyl or aromatic; Q_5 is a heteroatom that can participate in a delocalized π -electron system; and n is from 2 to about 2000. Those skilled in the art will recognize that a wide variety of other structures are possible.



(23)

- 17 -



(24)

It is believed that the polycyclic aromatic compounds of the invention can be mixed with virtually any synthetic organic polymer or polymer precursor system known in the art.

5 It is also believed that the compounds of the invention can be covalently bound with an equally wide variety of polymers, possibly through use of linking moieties such as alkyl, alkoxy, and or alkylamino groups. Representative synthetic organic polymers include polyimides, polyacrylates, 10 polymethacrylates, polyesters, polycarbonates, polystyrenes, polyolefins, and polyvinyl ethers. Polyimides, particularly those disclosed in Harris, et al., *Polym. Prepr.*, 1990, 31, 342 are preferred polymers.

The coating of a substrate with a material comprising 15 a polycyclic aromatic compound of the invention can be accomplished by any means known in the art, preferably by spin-coating, role-coating, or physical vapor deposition. L.I. Maissel and R. Glang, *Handbook of Thin Film Technology*, McGraw-Hill (1970); Satas, *Coating Technology Handbook*, Marcel Dekker

- 18 -

(1991). The materials used to form layer 12 can further include other moieties such as, for example, pigments, dyes, filters and dopants.

Polymerization and/or crosslinking of a layer following its deposition on a substrate can be accomplished in any of the ways known to those skilled in the art. For example, certain polymerizations can be effected by simple heating in the presence of a suitable initiator or by the incidence of light or some other form of electromagnetic energy in the presence or absence of a sensitizer. The latter procedure is preferred due to the ability of those in the art to effect selective, patterned polymerization through the use of, for example, removable masking agents. As will be recognized, devices incorporating appropriately arrayed patterns of polymer can be employed in microcircuitry and other applications.

In embodiments such as shown in Figure 1, certain devices of the invention comprise a conductor superstrate 14 disposed on layer 12, control means 16, and contacts 18 attached to substrate 10 and superstrate 14. This arrangement allows an input light signal 20 from source 22 to be operated upon by virtue of a changing electric field within layer 12 generated by control means 16 in concert with contacts 18. Altered or "operated" light signal 24 is directed away from the layer to a suitable detector 26. A wide variety of devices fitting this general description are well-known to those skilled in the art. Representative examples are disclosed by Garito, et al., *Mat. Res. Soc. Symp. Proc.*, 1990, 173.

Those skilled in the art will recognize that devices according to the present invention offer the advantage of flexibility in their design and use. For example, the waveguiding properties of the compounds of the invention can be combined with the nonlinear optical properties so that a guided light wave can be operated upon electro-optically. Indeed, large arrays of nonlinear optical, semiconductor and other photonic or electronic devices can be formed within a waveguiding system so as to result in assemblies of devices of

- 19 -

diverse character and use.

Additional objects, advantages, and novel features of this invention will become apparent to those skilled in the art upon examination of the following examples thereof, which are
5 not intended to be limiting.

EXAMPLE 1**3,4-Peryloylene-benzimidazole-9,10-dicarbox-N-(2,5-di-tert-butyl)phenyl imide**

N-(2,5-Di-tert-butylphenyl)-3,4,9,10-perylene
10 tetracarboxylic acid-3,4-anhydride-9,10-imide (0.6 mmol) and
1,2-phenylene diamine (27 mmol) were heated to 180°C without
solvent for 4 hours. After cooling, the resulting solution was
poured into 70% ethanol, filtered, and washed with 90%
methanol. The residue was boiled with 1% potassium hydroxide
15 solution, filtered, washed with methanol, and dried. Yield =
88%.

The molecular second-order optical susceptibility (β)
was measured in 1,4-dioxane solution by DC-induced second
harmonic generation (DCSHG) using fundamental wavelength of
20 1.907 μm , obtained by stimulated Raman scattering from Q-
switched Nd:YAG laser. The product of β and ground state-
dipole moment (μ) was evaluated. $1 \beta\mu\text{l} < 100 \times 10^{-48}$ esu; UV-
Vis Absorption (CHCl_3) = 571, 527, 492 nm; Solubility (Dioxane)
= 0.5×10^{-3} M; TG-DTA (-3%) = 410°C.

- 20 -

EXAMPLE 2**3,4-Peryloylene-benzimidazole-9,10-dicarbox-N-(m-pentyl)phenyl imide**

N-(n-pentyl)-3,4,9,10-perylene tetracarboxylic acid-
5 3,4-anhydride-9,10-imide (2.6 mmol) and 1,2-phenylene diamine
(33.8 mmol) were heated to 190°C in 5 ml of quinoline for 4
hours. After cooling, the resulting solution was poured into
95% methanol, filtered, and washed with methanol. The residue
was boiled with 1% potassium hydroxide solution, filtered,
10 washed with methanol, and dried. Yield = 80%. $1 \beta \mu\text{l} < 100 \times 10^{-48}$ esu; UV-Vis Absorption (CHCl_3) = 570, 530 nm; Solubility
(Dioxane) $< 0.1 \times 10^{-3}\text{M}$; TG-DTA (-3%) = 420°C.

EXAMPLE 3**3,4-Peryloylene-(3'-nitro)benzimidazole-9,10-dicarbox-N-(2,5-
15 di-tert-butyl)phenyl imide**

N-(2,5-Di-tert-butylphenyl)-3,4,9,10-perylene
tetracarboxylic acid-3,4-anhydride-9,10-imide (0.6 mmol) and 4-
nitro-1,2-phenylene diamine (15.3 mmol) were heated to 220°C
without solvent for 2.5 hours. After cooling, the resulting
20 solution was poured into 95% methanol and filtered. The
residue was boiled with 1% potassium hydroxide solution,
filtered, washed with methanol, and dried. Yield = 45%. $1 \beta \mu\text{l} < 100 \times 10^{-48}$ esu; UV-Vis Absorption (CHCl_3) = 566, 528 nm;
Solubility (Dioxane) = TG-DTA (-3%) = 370°C.

25 EXAMPLE 4**3,4-Peryloylene-(3',4'-dimethyl)benzimidazole-9,10-dicarbox-N-
(2,5-di-tert-butyl)phenyl imide**

N-(2,5-di-tert-butylphenyl)-3,4,9,10-perylene
tetracarboxylic diimide (1.21 mmol) and 4,5-dimethyl-1,2-
30 phenylene diamine (14.7 mmol) were heated to 235°C in 2 ml
quinoline and 280 ml of zinc acetate for 4 hours. After
cooling, the resulting solution was poured into 80% methanol
and filtered. The residue was boiled with 10% potassium
carbonate solution, filtered, washed with methanol, and dried.
35 Yield = 70%. UV-Vis Absorption (CHCl_3) = 581, 551, 523, 488 nm;

- 21 -

TG-DTA (3%) = 420°C.

EXAMPLE 5**1,8-Naphthoylene-benzimidazole-4,5-dicarbox-N-(2,5-di-tert-butyl)phenylimide**

5 1,8-Naphthoylene-benzimidazole-4,5-carboxylic
anhydride (4.4 mmol) and 2,5-di-tert-butylaniline (13.2 mmol)
were heated to 230°C in 7.5 ml of quinoline and 530 mg of zinc
acetate for 2.5 hours. After cooling, the resulting solution
was poured into 80% methanol, filtered, and further purified by
10 column chromatography on silica gel with methylene chloride-
ethyl acetate. Yield = 83%. UV-Vis Absorption (CHCl₃) =
440,368,313 nm; TG-DTA (melt) = 335°C.

EXAMPLE 6**1,8-Naphthoylene-(4'-methoxy)benzimidazole-4,5-dicarbox-N-(2,5-
15 di-tert-butyl) phenyl imide**

 1,8-Naphthoylene-(4'-methoxy) benzimidazole-4,5-
dicarboxylic anhydride (1.62 mmol) and 2,5-di-tert-butyl
aniline (4.86 mmol) were heated to 225°C in 3 ml of quinoline
and 210 mg of zinc acetate for 4 hours. After cooling, the
20 resulting solution was poured into 70% methanol, filtered,
washed with 90% methanol, and further purified by column
chromatography on silica gel with methylene chloride. Yield =
76%. $\beta\mu = 40 \times 10^{48}$ esu. UV-Vis Absorption (CHCl₃) =
485,435,370,321 nm; TG-DTA (melt) = 299°C.

25 EXAMPLE 7**1,8-Naphthoylene-(3'-nitro)benzimidazole-4,5-dicarbox-N-(2,5-
di-tert-butyl)phenyl imide**

 1,8-Naphthoylene-(3'-nitro) benzimidazole-4,5-
dicarboxylic anhydride (2.60 mmol) and 2,5-di-tert-butylaniline
30 (7.79 mmol) were heated to 200°C in 5 ml of quinoline and 350
mg of zinc acetate for 2.5 hours. After cooling, the resulting
solution was poured into 70% methanol, filtered, washed with
80% methanol, and further purified by column chromatography on
silica gel with methylene chloride. Yield = 60%. UV-Vis

- 22 -

Absorption (CHCl₃) = 425 nm, 360 nm.

EXAMPLE 8

1,8-Naphthoylene-(3'-amino)benzimidazole-4,5-dicarbox-N-(2,5-di-tert-butyl)phenyl imide.

5 Sodium hydrosulfite (0.274 g) was added as a 20% aqueous solution into 0.524 mmol of 1,8-Naphthoylene-(3'-nitro-benzimidazole-4,5-dicarbox-N-(2,5-di-tert-butyl) phenyl imide in 10 ml of N,N-dimethyl acetamide at 80°C. It was purified by column chromatography on silica gel with chloroform. Yield =
10 25% $\beta\mu = 410 \times 10^{-48}$ esu; UV-Vis Absorption (CHCl₃) = 550.343 nm; TG-DTA (melt) = 360°C.

EXAMPLE 9

1,8-Naphthoylene-naphthopyrimidine-4,5-dicarbox-N-(2,5-di-tert-butyl)phenyl imide.

15 1,8-Naphthoylene-naphthopyrimidine-4,5-dicarboxylic anhydride (5.12 mmol) and 2,5-di-tert-butylaniline (15.4 mmol) were heated to 225°C in 10 ml of quinoline and 700 mg of zinc acetate for 3 hours. After cooling, the resulting solution was poured into 70% methanol, filtered, and further purified by
20 column chromatography on silica gel with methylene chloride. Yield = 53%. UV-Vis Absorption (CHCl₃) = 592, 560, 378 nm; TG-DTA (melt) = 363°C.

EXAMPLE 10

Thin film of 3,4-Peryloylene-(3'-nitro) benzimidazole-9,10-dicarbox-N-(2,5-di-tert-butyl)phenyl imide.

25 Using a syringe equipped with a 0.2 μ m filter, a nearly saturated solution of the perylene derivative in N-methyl-pyrrolidinone (NMP) was dispensed into LQ2200 polyimide resin (Hitachi Chemical) and made a 4% solution (dye/polymer.
30 weight ratio). The resulting solution was agitated slightly and then spin coated onto a glass-slide substrate, which was baked at 110°C in a vacuum oven for one hour, cured at 200°C for half an hour, and finally cured at 250°C and above. The perylene-based guest molecules were aligned by application of

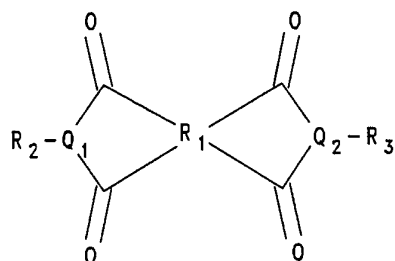
- 23 -

a DC field on a coplanar electrode in the host polyimide. The resulting clear, red-purple film was about 2-4 μm thick. The thickness of the film can be controlled by adjusting the spin speed.

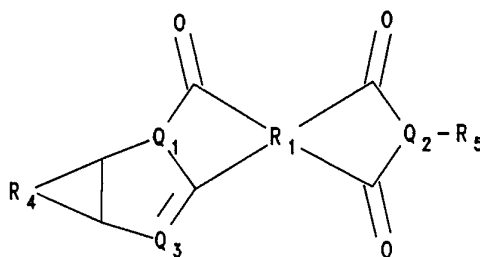
5 Those skilled in the art will appreciate that numerous changes and modifications may be made to the preferred
embodiments of the invention and that such changes and
modifications may be made without departing from the spirit of
the invention. It is therefore intended that the appended
10 claims cover all such equivalent variations as fall within the
true spirit and scope of the invention.

WHAT IS CLAIMED IS:

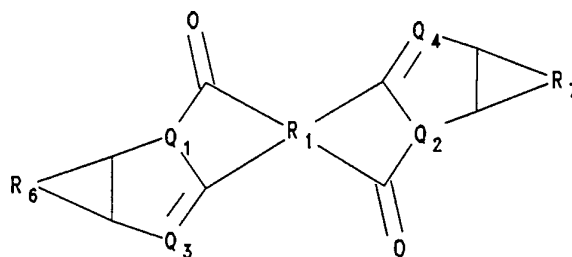
1. A device that exhibits at least one sensible, second order nonlinear optical effect, comprising:
 a substrate; and
 5 at least one layer on said substrate, said layer including a compound having formula (1), (2), (3), or (4):



(1)

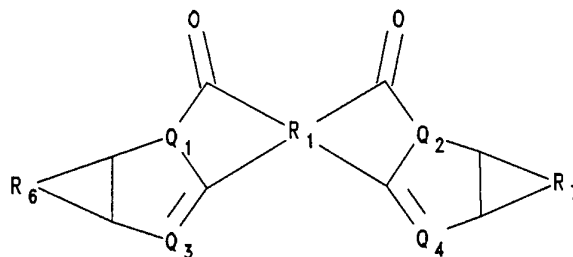


(2)



(3)

- 25 -



(4)

wherein:

R₁ is a tetravalent aromatic radical;

5 Q₁, Q₂, Q₃, and Q₄ are, independently, heteroatoms that participate in delocalized π -electron systems; and

R₂-R₇ are, independently, alkyl groups or aromatic groups.

2. The device of claim 1 wherein R₁ is an aromatic
10 hydrocarbon.

3. The device of claim 1 wherein R₁ is derived from benzene, perylene, phenanthrene, anthracene, naphthalene, pyrene, chrysene, or naphthacene.

4. The device of claim 1 wherein R₁ is derived from
15 benzene, naphthalene, or perylene.

5. The device of claim 1 wherein Q₁, Q₂, Q₃, and Q₄ are, independently, N, O, S, Se, or Te.

6. The device of claim 1 wherein Q₁, Q₂, Q₃, and Q₄ are N.

20 7. The device of claim 1 wherein:

R₂ and R₆ are, independently, alkyl groups or aromatic groups that are electron-donating relative to hydrogen;

R₃ and R₇ are, independently, alkyl groups or aromatic groups that are electron-withdrawing relative to hydrogen;

25 one of R₄ and R₅ is an alkyl group or an aromatic

- 26 -

group that is electron-donating relative to hydrogen, and the other of R_4 and R_5 is an alkyl group or an aromatic group that is electron-withdrawing relative to hydrogen.

8. The device of claim 1 wherein R_2 is an aromatic heterocycle, an aromatic hydrocarbon substituted with at least one substituent that is electron-donating relative to hydrogen, or aromatic heterocycle substituted with at least one substituent that is electron-donating relative to hydrogen.

9. The device of claim 8 wherein said electron-donating substituent is an alkyl group, an alkylamino group, NH_2 , an alkoxy group, OH, an alkylthio group, SH, or $-OC(O)-(alkyl)$.

10. The device of claim 8 wherein R_2 is an alkylamino group, NH_2 , an alkoxy group, or an alkylthio group.

11. The device of claim 1 wherein R_3 is an aromatic heterocycle, an aromatic hydrocarbon substituted with at least one substituent that is electron-withdrawing relative to hydrogen, or aromatic heterocycle substituted with at least one substituent that is electron-withdrawing relative to hydrogen.

12. The device of claim 11 wherein said electron-withdrawing substituent is $N-(alkyl)_3^+$, $S-(alkyl)_2^+$, NH_3^+ , NO_2 , $SO_2-(alkyl)$, CN, $SO_2-(aromatic)$, $C(O)OH$, F, Cl, Br, I, $C(O)O-(alkyl)$, $C(O)-(alkyl)$ or CHO.

13. The device of claim 11 wherein R_3 is NO_2 , CN, $C(O)OH$, or $C(O)O-(alkyl)$.

14. The device of claim 1 wherein at least one of $R_{4A}-R_{4D}$ or R_5 is an alkyl group, an alkylamino group, NH_2 , an alkoxy group, OH, an alkylthio group, SH, or $-OC(O)-(alkyl)$.

15. The device of claim 1 wherein at least one of

- 27 -

R_{4A} - R_{4D} or R_5 is an alkylamino group, NH_2 , an alkoxy group, or an alkylthio group.

16. The device of claim 1 wherein at least one of R_{4A} - R_{4D} or R_5 is N -(alkyl) $_3^+$, S -(alkyl) $_2^+$, NH_3^+ , NO_2 , SO_2 -(alkyl),
5 CN , SO_2 -(aromatic), $C(O)OH$, F , Cl , Br , I , $C(O)O$ -(alkyl), $C(O)$ -(alkyl) or CHO .

17. The device of claim 1 wherein at least one of R_{4A} - R_{4D} or R_5 is NO_2 , CN , $C(O)OH$, or $C(O)O$ -(alkyl).

18. The device of claim 1 wherein at least one of
10 R_{6A} - R_{6D} is an alkyl group, an alkylamino group, NH_2 , an alkoxy group, OH , an alkylthio group, SH , or $-OC(O)$ -(alkyl).

19. The device of claim 1 wherein at least one of R_{7A} - R_{7D} is N -(alkyl) $_3^+$, S -(alkyl) $_2^+$, NH_3^+ , NO_2 , SO_2 -(alkyl), CN ,
15 SO_2 -(aromatic), $C(O)OH$, F , Cl , Br , I , $C(O)O$ -(alkyl), O -(alkyl), $C(O)$ -(alkyl) or CHO .

20. The device of claim 1 wherein at least one of R_{7A} - R_{7D} is NO_2 , CN , $C(O)OH$, or $C(O)O$ -(alkyl).

21. The device of claim 1 wherein said compound produces a UV/visible spectra exhibiting at least one
20 transition that has an extinction coefficient greater than about $1 \times 10^5 \text{ l mole}^{-1} \text{ cm}^{-1}$.

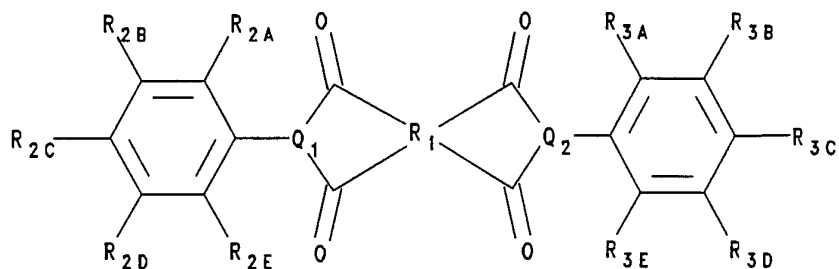
22. The device of claim 1 wherein said compound has formula (1).

23. The device of claim 1 wherein said compound has
25 formula (2).

24. The device of claim 1 wherein said compound has formula (3).

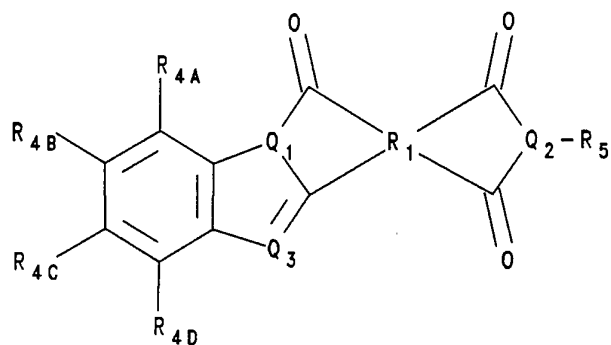
25. The device of claim 1 wherein said compound has formula (4).

26. The device of claim 1 wherein said compound has formula (5), (6), (7), or (8):

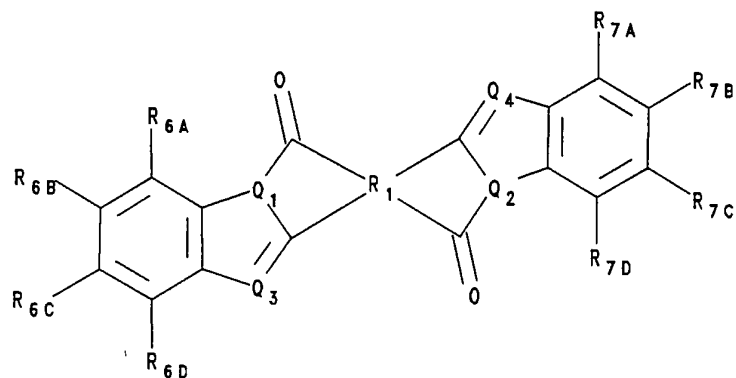


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(5)

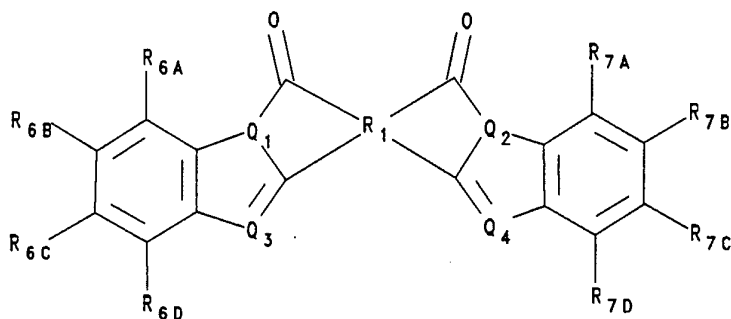


(6)



(7)

- 29 -



(8)

wherein:

5 at least one of R_{2A} - R_{2E} is an aromatic or non-aromatic group that is electron-donating relative to hydrogen;

at least one of R_{3A} - R_{3E} is an aromatic or non-aromatic group that is electron-withdrawing relative to hydrogen;

10 at least one of R_{4A} - R_{4D} is an aromatic or non-aromatic group that is electron-donating relative to hydrogen; or an aromatic or non-aromatic group that is electron-withdrawing relative to hydrogen;

15 at least one of R_{6A} - R_{6D} is an aromatic or non-aromatic group that is electron-donating relative to hydrogen; and

at least one of R_{7A} - R_{7D} is an aromatic or non-aromatic group that is electron-withdrawing relative to hydrogen.

20 27. The device of claim 1 wherein said compound has formula (9), (10), (11) or (12).

28. The device of claim 1 wherein said compound has formula (13), (14), (15), or (16).

29. The device of claim 1 wherein said compound has

- 30 -

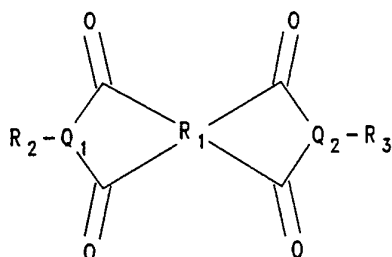
formula (17), (18), (19), or (20).

30. The device of claim 1 further comprising a superstrate on said layer.

31. The device of claim 1 further comprising means
5 for establishing an electric field across said layer.

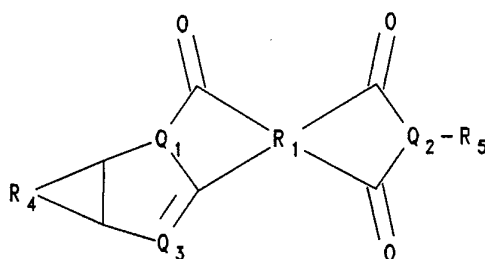
32. The device of claim 1 further comprising sensing means for detecting light transmitted by said layer.

33. A composition that exhibits at least one sensible, second order nonlinear optical effect, comprising
10 synthetic organic polymer and at least one compound having formula (1), (2), (3), or (4):

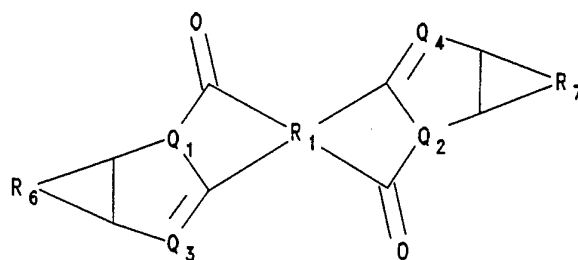


(1)

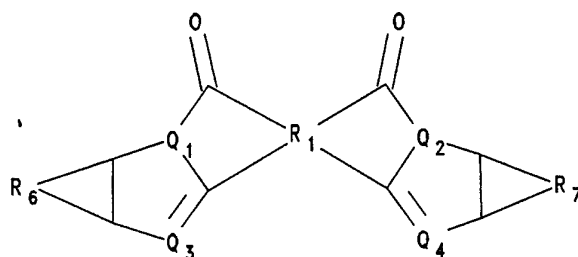
- 31 -



(2)



(3)



(4)

wherein:

5

R_1 is a tetravalent aromatic radical;

Q_1 , Q_2 , Q_3 , and Q_4 are, independently, heteroatoms that participate in delocalized π -electron systems; and

10

R_2 - R_7 are, independently, alkyl groups or aromatic groups.

34. The composition of claim 33 wherein said polymer is in admixture with said compound.

35. The composition of claim 33 wherein said polymer is covalently bound with said compound.

- 32 -

36. The composition of claim 33 wherein said polymer constitutes a major proportion of said composition and said compound constitutes a minor proportion of said composition.

37. The composition of claim 33 wherein said polymer
5 is a polyimide, a polyacrylate, a polymethacrylate, a polyester, a polycarbonate, a polystyrene, a polyolefin, a polyvinyl ether, or a mixture thereof.

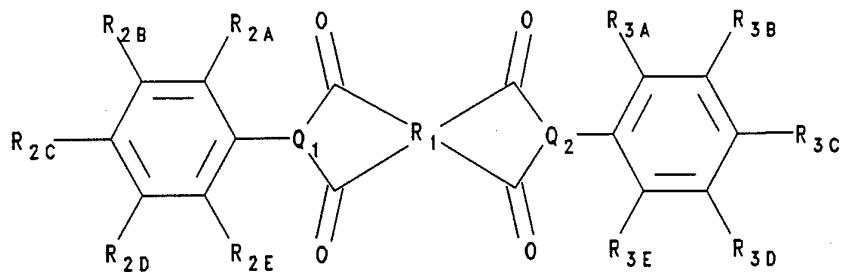
38. The composition of claim 33 wherein:

R_2 and R_6 are, independently, alkyl groups or aromatic
10 groups that are electron-donating relative to hydrogen;

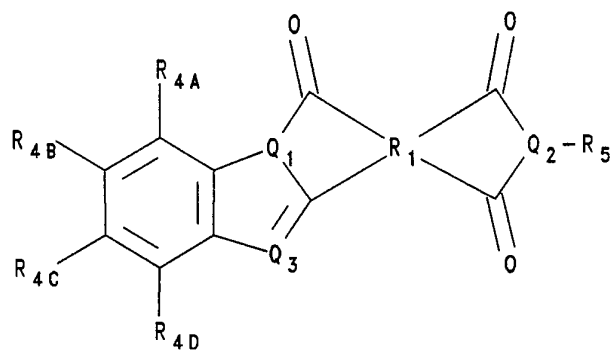
R_3 and R_7 are, independently, alkyl groups or aromatic groups that are electron-withdrawing relative to hydrogen;

one of R_4 and R_5 is an alkyl group or an aromatic group that is electron-donating relative to hydrogen, and the
15 other of R_4 and R_5 is an alkyl group or an aromatic group that is electron-withdrawing relative to hydrogen.

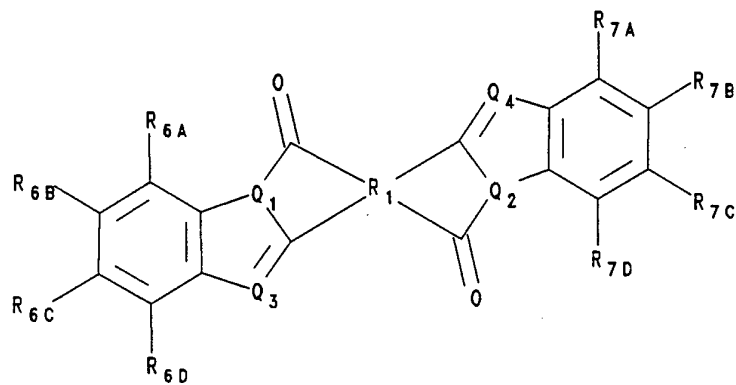
39. The composition of claim 33 wherein said compounds has formula (5), (6), (7), (8):



(5)

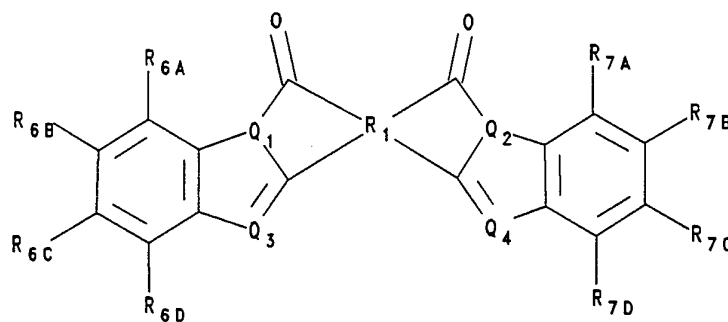


(6)



(7)

- 34 -



(8)

wherein:

at least one of R_{2A} - R_{2E} is an aromatic or non-aromatic group that is electron-donating relative to hydrogen;

5

at least one of R_{3A} - R_{3E} is an aromatic or non-aromatic group that is electron-withdrawing relative to hydrogen;

at least one of R_{4A} - R_{4D} is an aromatic or non-aromatic group that is electron-donating relative to hydrogen; or an aromatic or non-aromatic group that is electron-withdrawing relative to hydrogen;

10

at least one of R_{6A} - R_{6D} is hydrogen or an aromatic or non-aromatic group that is electron-donating relative to hydrogen; and

15

at least one of R_{7A} - R_{7D} is an aromatic or non-aromatic group that is electron-withdrawing relative to hydrogen.

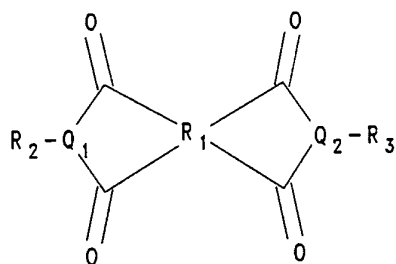
40. A process for preparing a device that exhibits at least one sensible, second order nonlinear optical effect, comprising the steps of:

20

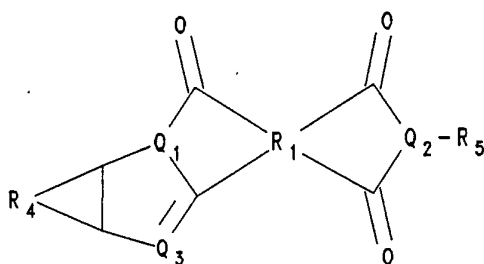
providing a substrate; and

placing upon said substrate at least one layer that includes a compound having formula (1), (2), (3), or (4):

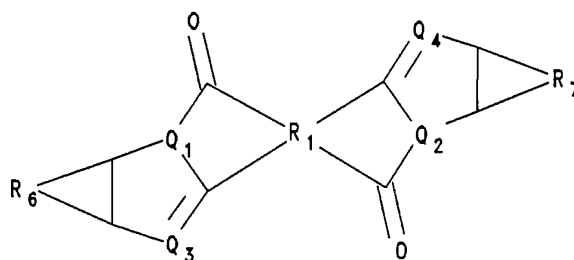
- 35 -



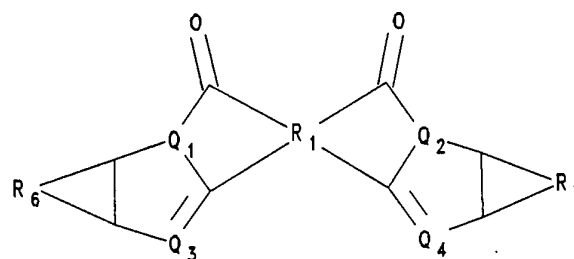
(1)



(2)



(3)



(4)

5 wherein:

R_1 is a tetravalent aromatic radical;

Q_1 , Q_2 , Q_3 , and Q_4 are, independently, heteroatoms that participate in delocalized π -electron systems;

and

- 36 -

R_2 - R_7 are, independently, alkyl groups or aromatic groups.

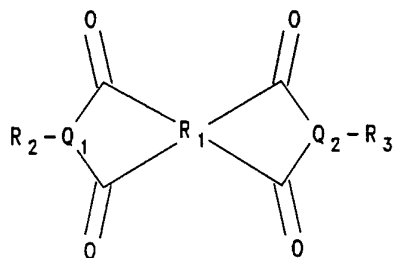
41. The process of claim 40 wherein:

R_2 and R_6 are, independently, alkyl groups or aromatic groups that are electron-donating relative to hydrogen;

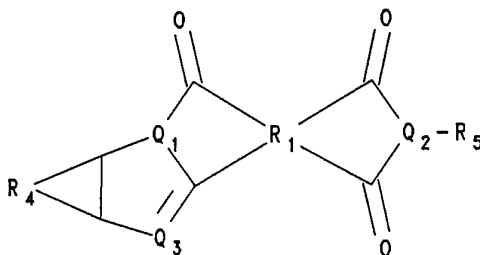
R_3 and R_7 are, independently, alkyl groups or aromatic groups that are electron-withdrawing relative to hydrogen;

one of R_4 and R_5 is an alkyl group or an aromatic group that is electron-donating relative to hydrogen, and the other of R_4 and R_5 is an alkyl group or an aromatic group that is electron-withdrawing relative to hydrogen.

42. A process for preparing a composition that exhibits at least one sensible, second order nonlinear optical effect, comprising the steps of mixing synthetic organic polymer with at least one compound having formula (1), (2), (3), or (4):

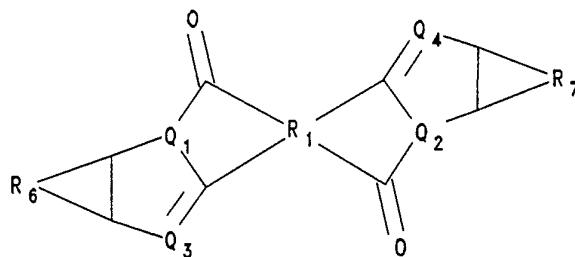


(1)

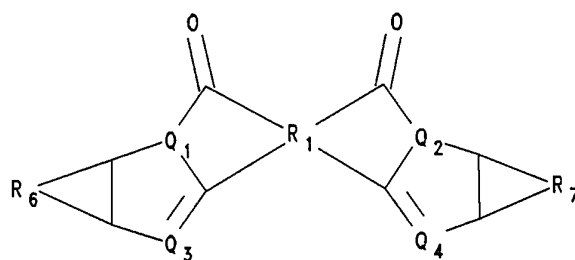


(2)

- 37 -



(3)



(4)

wherein:

R_1 is a tetravalent aromatic radical;

5 Q_1 , Q_2 , Q_3 , and Q_4 are, independently, heteroatoms that participate in delocalized π -electron systems; and

R_2 - R_7 are, independently, alkyl groups or aromatic groups.

10 43. The process of claim 42 wherein:

R_2 and R_6 are, independently, alkyl groups or aromatic groups that are electron-donating relative to hydrogen;

R_3 and R_7 are, independently, alkyl groups or aromatic groups that are electron-withdrawing relative to hydrogen;

15 one of R_4 and R_5 is an alkyl group or an aromatic group that is electron-donating relative to hydrogen, and the other of R_4 and R_5 is an alkyl group or an aromatic group that is electron-withdrawing relative to hydrogen.

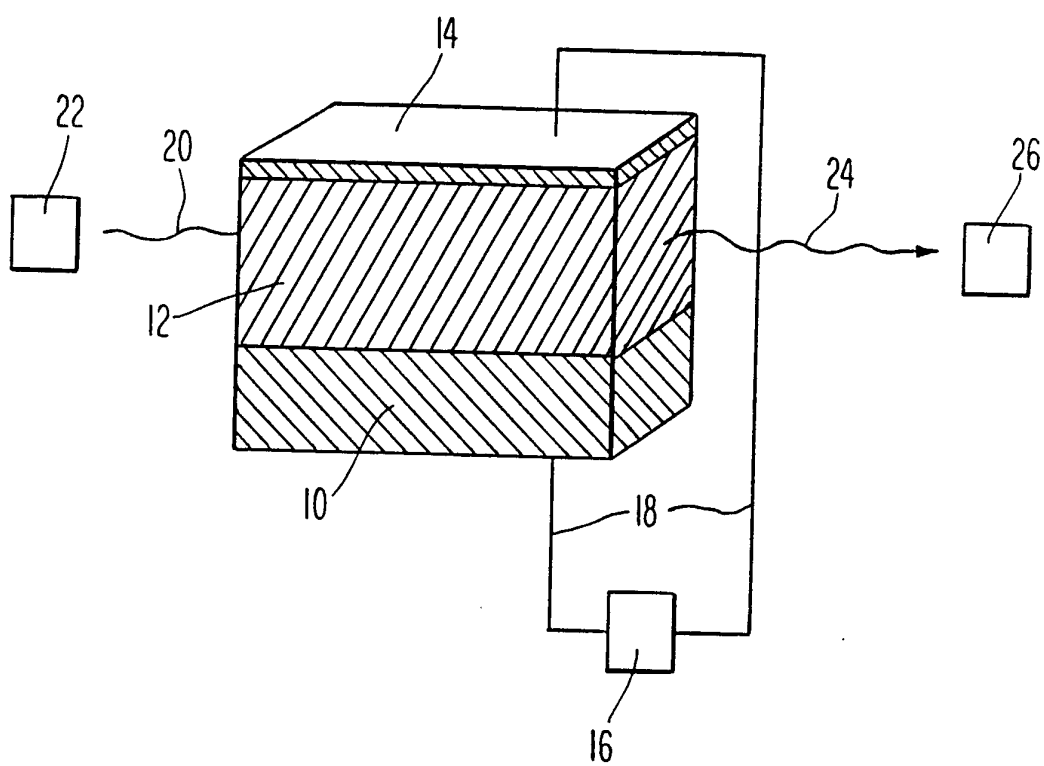


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/00385

A. CLASSIFICATION OF SUBJECT MATTER IPC(5) : C08G-75/18; B32B 9/04 US CL : 428/473.5 According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 428/473.5 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) STN: non-linear, optical, thermally stable				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	Journal of Applied Physics, Volume 69, No. 10, 15 May 1991, (WU et al), "Highly Thermally Stable Electrooptic Response in Poled Guest-Host Polyimide Systems Cured at 360 Degrees Centigrade", pages 7366-7368.	1-43		
X	Polymer Preprints, Volume 32, No. 3, published 15 December 1991, (ERMER et al), "Thermally Stable Electrooptic Polymers", pages 92-93	1-43		
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> * Special categories of cited documents: "A" document defining the general state of the art which is not considered to be part of particular relevance "E" earlier document published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; border: none;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family </td> </tr> </table>			* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be part of particular relevance "E" earlier document published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be part of particular relevance "E" earlier document published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family			
Date of the actual completion of the international search 10 MARCH 1994		Date of mailing of the international search report APR 25 1994		
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer <i>Renell Leavelle for</i> PATRICK R. DELANEY Telephone No. (703) 308-2351		