

COMPOUNDS, COMPOSITIONS CONTAINING COMPOUNDS, AND METHODS OF MANUFACTURING RESIST MEMBRANES

FIELD

[0001] The disclosed and claimed subject matter relates to compounds, compositions containing compounds, and methods for manufacturing resist membranes.

BACKGROUND

[0002] In recent years, the need for high integration of large-scale integrations (LSIs) has been increasing, and miniaturization of patterns is required of the system. This high integration enables miniaturization and high speed, which greatly contributes to improving the performance of electronic devices such as computers, smartphones, and network devices. Miniaturization technologies typically include KrF excimer laser, ArF excimer laser, extreme ultraviolet, X-ray, electron beam lithography processes, etc..

[0003] A curable composition containing a boron nitride atom and a bisaryl fluorene derivative with an epoxy group as a hardener has been proposed. *See* JP Patent Publication No. 2020-158623, A negative-type resist containing a core, a functional group that binds to the core, and a molecular glass containing a photosensitive part has been proposed. *See* U.S. Patent Publication No. 2011/097668.

DETAILED DESCRIPTION OF DRAWINGS

[0004] FIG. 1: Image showing EUV lithographic performance for formations Ex. 4, Ex. 5 and the comparative formulation containing compound Comp A-5.

[0005] FIG. 2: Image showing EUV lithographic performance for formation Ex. 6

[0006] FIG. 3: Image showing EUV lithographic performance for formation comp Ex. 4.

[0007] FIG. 4: Image showing summary of EUV lithographic performance for formations F00, F01, F02 and F03.

[0008] FIG. 5: Image showing EUV lithographic performance for formulations C06 and EX08.

SUMMARY OF DISCLOSED AND CLAIMED SUBJECT MATTER

[0009] To cope with such miniaturization of resist patterns, photosensitive resin compositions used as resists in microfabrication should have sufficiently high resolution, sufficiently low line width roughness (“LWR”), and sufficiently small optimal exposure dose (“Dose to Size”) and this required improvement of the crosslinking compounds that can be used in resist compositions, and this involves more than one issue that needs to be improved in such compounds. These include,

for example:

- Obtain a resist pattern with sufficient resolution; obtain a resist pattern with a sufficiently low LWR;
- Reduce the optimal exposure sufficiently;
- Obtain fine resist patterns useful as etching masks;
- Obtain resist patterns with sufficient etching resistance;
- Obtain sufficient resolution even when using a lithography tool with increased aperture ;
- Obtain fine patterns with reduced pattern width variation;
- Obtain resist patterns with high aspect ratios;
- Increase process windows; and
- Improve manufacturing yields

[0010] The disclosed and claimed subject crosslinking aromatic compounds described herein have two types of crosslinking moieties where the first type of crosslinking moieties are pendant substituents which contain, either an oxirane, an oxetane, or a mixture of pendant substituents containing either an oxirane or an oxetane, and the second type of crosslinking moiety is a $\text{-CH}_2\text{OH}$ substituent and may also additionally contain at least one halogen atom selected from Cl, Br and I situated ortho on the aryl moiety of the aromatic compound's core to the attachment point to pendant substituents containing either an oxirane or an oxetane. Without being bound by theory, it is believed that in photoresist compositions comprising the disclosed and claimed crosslinking compounds with an aromatic core having either two different types of crosslinking moieties attached to said aromatic core, one of which is an oxetane and/or an oxirane moiety and the other is a $\text{-CH}_2\text{OH}$ moiety and/or the presence of at least one halogen atom selected from F, Cl, Br and I, preferably Cl, Br and I, ortho to the attachment point of an oxetane and/or and oxirane crosslinking moiety to the aromatic core, which is formulated in these compositions with a photoacid generator, which generates an acid upon exposure to radiation, the reaction of the two types of crosslinking moieties with the acid generated by irradiation of the photoacid generator produces a higher density of crosslinking, which may also be increased further by the presence of the ortho halogen substituent which may increase the production of acid generated by the PAG by irradiation, which in turn improves the resolution of the photoresist. Another aspect of the disclosed and claimed subject matter are compositions including these compounds, for instance

ones also comprising a photoacid generator. Another aspect of the disclosed and claimed subject matter is the method of using such compound or composition to coat a substrate and by exposing it to radiation producing an image which may be used as a mask in the manufacture of microelectronics.

[0011] The disclosed and claimed subject matter described herein also pertains to crosslinking compounds with an aromatic core having at least three pendant substituent attached through an oxy (-O-) moiety which are selected from an oxirane moiety and or an oxetane moiety, and have at least one halogen atom selected from F, Cl, Br and I, preferably Cl, Br and I situated ortho on the aromatic core of the crosslinking compound to the attachment point of the pendant substituents containing either an oxirane or an oxetane. Without being bound by theory, it is believed that such an approach with a high density of these crosslinking moieties adjacent to a halogen, when this compound is used in a photoresist composition also comprising a photoacid generator, results upon exposure to radiation, (*e.g.*, UV, EUV, e-beam), in a higher density of crosslinking, which in turn improves the resolution of these photoresist composition. Another aspect of the disclosed and claimed subject matter are said compositions comprising these aromatic crosslinking compounds, and a photoacid generator. Another aspect of the disclosed and claimed subject matter is the method of using such composition to coat a substrate and by exposing it to radiation producing an image which may be used as a mask in the manufacture of microelectronics.

[0012] The disclosed subject matter also pertains to a selective iodination method for multi-phenolic compounds at the ortho position to the phenol, where the resultant multi-phenolic compounds selectively iodinated at the position ortho to the phenol are precursors of said crosslinking compounds, where this method employs 1-iodopyrrolidine in the presence of an arylsulfonic acid.

DETAILED DESCRIPTION

[0013] It is to be understood that both the foregoing general description and the following detailed description are illustrative and explanatory, and are not restrictive of the subject matter, as claimed. In this application, the use of the singular includes the plural, the word "a" or "an" means "at least one", and the use of "or" means "and/or," unless specifically stated otherwise. Furthermore, the use of the term "including," as well as other forms such as "includes" and "included," is not limiting. Also, terms such as "element" or "component" encompass both elements and components comprising one unit and elements or components that comprise more than one unit, unless

specifically stated otherwise. As used herein, the conjunction "and" is intended to be inclusive and the conjunction "or" is not intended to be exclusive unless otherwise indicated. For example, the phrase "or, alternatively" is intended to be exclusive. As used herein, the term "and/or" refers to any combination of the foregoing elements including using a single element.

[0014] The term "PAG," unless otherwise described, refers to a photoacid generator that can generate acid (a.k.a. photoacid) under e-beam, deep UV or UV irradiation such as 200-300 nm, i-line, h-line, g-line and/or broadband irradiation and EUV radiation (13.5 nm).

[0015] The term C₁₋₅ alkyl embodies methyl and C₂ to C₅ linear alkyls and C₃ to C₅ branched alkyl moieties, for example as follows: methyl (-CH₃), ethyl (-CH₂-CH₃), n-propyl (-CH₂-CH₂-CH₃), isopropyl (-CH(CH₃)₂), n-butyl (-CH₂-CH₂-CH₂-CH₃), tert-butyl (-C(CH₃)₃), isobutyl (CH₂-CH(CH₃)₂), 2-butyl (-CH(CH₃)CH₂-CH₃). Similarly, the term C₁₋₆ alkyl embodies methyl, C₂ to C₆ linear, C₃ to C₆ branched alkyls, C₄ to C₆ cycloalkyls (e.g., cyclopentyl, cyclohexyl, etc.) or C₅ to C₆ alkylencycloalkyls (e.g., -CH₂-cyclohexyl, CH₂-CH₂-cyclopentyl etc.). Similarly, the term C₁₋₈ alkyl embodies methyl, C₂ to C₈ linear, C₃ to C₈ branched alkyls, C₄ to C₈ cycloalkyls (e.g., cyclopentyl, cyclohexyl etc) or C₅ to C₈ alkylencycloalkyls (e.g., -CH₂-cyclohexyl, CH₂-CH₂-cyclopentyl etc.). Similarly, the terms C₁₋₁₅ alkyl encompass within their scope branched alkyls, linear alkyls, cyclic alkyls including multicyclic alkyls having higher numbers of carbons such as adamantyl, norbornyl and the like.

[0016] The term C₁₋₈ alkylene embodies C₁ to C₈ linear alkylene moieties (e.g., methylene ethylene, propylene etc.) and C₂ to C₈ branched alkylene moieties (e.g., -CH(CH₃)-, -CH(CH₃)-CH₂-, etc.).

[0017] The term C₁₋₂ straight chain alkylene encompasses methylene (-CH₂-) and ethylene (-CH₂-CH₂-)

[0018] The term C₁₋₆ fluorosubstituted alkyl encompasses both perfluoralkyls and partially fluorinated alkyls and embodies C₁ to C₆ linear fluorosubstituted moieties and C₃ to C₈ branched fluorosubstituted moieties.

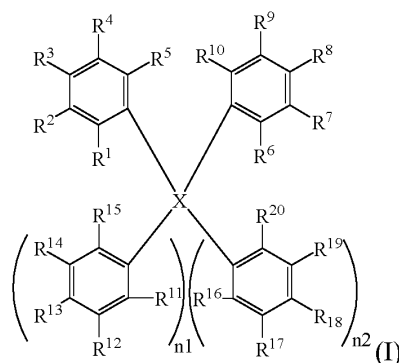
[0019] The term C₆₋₁₂ fluorosubstituted aryl, encompasses both perfluoroaryls and partially fluorinated aryls.

[0020] The term C₂₋₁₂ fluorine substituted acyl, encompasses acyl moieties whose C₁₋₁₁ alkyl portion or C₆₋₁₁ aryl portion are either perfluorinated or partially fluorinated.

[0021] The term C₆₋₁₂ fluorine substituted alkoxyaryl encompasses alkoxyaryl moieties whose

alkyl portion or aryl portion is either perfluorinated or partially fluorinated.

[0022] One aspect of the disclosed and claimed subject matter is a crosslinking compound of structure (I):



wherein in structure (I), n_1 and n_2 are each independently 1 or 0, X is $C_pH_{2p-n_1-n_2}$ or $C_{6+4(q-1)}H_{4+2(q-1)-n_1-n_2}$, p is 1 to 6, q is 1 to 3, wherein one or more H of X may be each independently substituted with C_{1-5} straight-chain alkyl or C_{3-5} branched alkyl.

[0023] In one embodiment, in structure (I), R^1 to R^{20} are each independently H, a halogen selected from F, Cl, Br, and I, C_{1-15} straight-chain alkyl, C_{3-15} branched alkyl, C_{3-15} alkyl containing a cyclic structure, C_{1-15} straight-chain alkoxy, C_{3-15} branched alkoxy, C_{3-15} alkoxy containing a cyclic structure, CH_2OH , $-CH_2OR^{22}$, $-COOH$, $-OH$, or Y represented by formula (II), for example formula (IIa), where R^{22} is C_{1-15} straight-chain alkyl, C_{3-15} branched alkyl, or C_{3-15} alkyl containing a cyclic structure.

[0024] In a further embodiment, in structure (I), R^{11} and R^{16} may together form a single bond. In an aspect of this embodiment, where R^{11} and R^{16} together form a single bond, at least one of R^1 to R^{20} is CH_2OH .

[0025] In a further embodiment, in structure (I), when R^1 to R^{20} are each independently alkyl, where one or more non-adjacent methylene ($-CH_2-$) of the alkyl may be each independently substituted with $-O-$, $-S-$, $-CO-$, $-CO-O-$, $-O-CO-$, $-O-CO-O-$, $-CH=CH-$, or $-C\equiv C-$.

[0026] In a further embodiment, in structure (I), when R^1 to R^{20} are each independently alkyl, where one or more H of the alkyl may be each independently substituted with F, Cl, Br, I, $COOH$, OH , or OR^{22} .

[0027] Further in structure (I), at least one of R^1 to R^5 and/or R^{11} to R^{15} is Y and at least one of R^1 to R^5 and/or R^{11} to R^{15} is selected from the group consisting of CH_2OH , F, Cl, Br, and I and/or

wherein at least one of R^6 to R^{10} and/or R^{16} to R^{20} is Y and/or at least one of R^6 to R^{10} or R^{16} to R^{20} is selected from the group consisting of CH_2OH , F, Cl, Br, and I.

[0028] In another aspect of this embodiment in structure (I), at least one of R^1 to R^5 and R^{11} to R^{15} is Y and at least one of R^1 to R^5 and R^{11} to R^{15} is selected from the group consisting of CH_2OH , F, Cl, Br, and I and wherein at least one of R^6 to R^{10} and R^{16} to R^{20} is Y and at least one of R^6 to R^{10} or R^{16} to R^{20} is selected from the group consisting of CH_2OH , F, Cl, Br, and I.

[0029] In another aspect of this embodiment in structure (I), at least one of R^1 to R^5 or R^{11} to R^{15} is Y and at least one of R^1 to R^5 or R^{11} to R^{15} is selected from the group consisting of CH_2OH , F, Cl, Br, and I and wherein at least one of R^6 to R^{10} or R^{16} to R^{20} is Y and at least one of R^6 to R^{10} or R^{16} to R^{20} is selected from the group consisting of CH_2OH , F, Cl, Br, and I.

[0030] In another aspect of this embodiment in structure (I), at least one of R^1 to R^5 and R^{11} to R^{15} is Y and at least one of R^1 to R^5 or R^{11} to R^{15} is selected from the group consisting of CH_2OH , F, Cl, Br, and I and wherein at least one of R^6 to R^{10} or R^{16} to R^{20} is Y and at least one of R^6 to R^{10} or R^{16} to R^{20} is selected from the group consisting of CH_2OH , F, Cl, Br, and I.

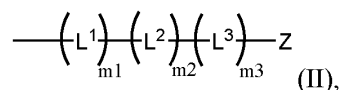
[0031] In another aspect of this embodiment in structure (I), at least one of R^1 to R^5 or R^{11} to R^{15} is Y and at least one of R^1 to R^5 and R^{11} to R^{15} is selected from the group consisting of CH_2OH , F, Cl, Br, and I or wherein at least one of R^6 to R^{10} and R^{16} to R^{20} is Y or at least one of R^6 to R^{10} or R^{16} to R^{20} is selected from the group consisting of CH_2OH , F, Cl, Br, and I.

[0032] In another aspect of this embodiment in structure (I), at least one of R^1 to R^5 and R^{11} to R^{15} is Y and at least one of R^1 to R^5 and R^{11} to R^{15} is selected from the group consisting of CH_2OH , F, Cl, Br, and I or wherein at least one of R^6 to R^{10} or R^{16} to R^{20} is Y or at least one of R^6 to R^{10} or R^{16} to R^{20} is selected from the group consisting of CH_2OH , F, Cl, Br, and I.

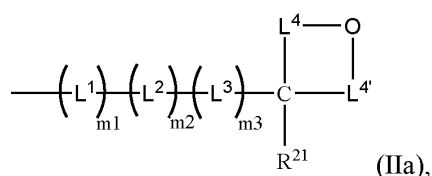
[0033] In another aspect of this embodiment in structure (I), at least one of R^1 to R^5 or R^{11} to R^{15} is Y and at least one of R^1 to R^5 or R^{11} to R^{15} is selected from the group consisting of CH_2OH , F, Cl, Br, and I or wherein at least one of R^6 to R^{10} and R^{16} to R^{20} is Y and at least one of R^6 to R^{10} or R^{16} to R^{20} is selected from the group consisting of CH_2OH , F, Cl, Br, and I.

[0034] In structure (II), L^1 is each independently C_{1-5} straight-chain alkylene or C_{3-5} branched alkylene, L^2 is each independently -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O-, -CH=CH-, or -C≡C-, L^3 is each independently C_{1-15} straight-chain alkylene or C_{3-15} branched alkylene, where Z is an oxirane or an oxetane moiety, and said oxirane moiety or oxetane moiety may further comprise as a substituent a C_{1-8} linear alkyl, C_{3-8} branched alkyl, or - CH_2OH , and further where m_1 , m_2 , and m_3

are each independently 0 or 1, and when m2 is 0, m1 is 0.



[0035] In another embodiment structure (II) more specifically has structure (IIa), L¹ is each independently C₁₋₅ straight-chain alkylene or C₃₋₅ branched alkylene, L² is each independently -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O-, -CH=CH-, or -C≡C-, L³ is each independently C₁₋₁₅ straight-chain alkylene or C₃₋₁₅ branched alkylene, L⁴ is C₁₋₂ straight-chain alkylene, and L^{4'} is either a direct valence bond or a C₁ straight chain alkylene, and R²¹ is H, C₁₋₈ linear alkyl, C₃₋₈ branched alkyl, or -CH₂OH, and further where m1, m2, and m3 are each independently 0 or 1, and when m2 is 0, m1 is 0.



[0036] In a another embodiment, in structure (I) n1 and n2 are each independently 1 or 0; X is C_pH_{2p-n1-n2} or C_{6+4(q-1)}H_{4+2(q-1)-n1-n2}; p is 1 to 6; q is 1 to 3 and also includes the following characteristics:

[0037] In structure (I), R¹ and R⁶ are the same and are selected from, H or a C₁₋₈ alkyl, I, Cl, and Br.

[0038] In structure (I), R² and R⁷ are the same moiety having structure (III).

[0039] In structure (I), R³ and R⁸ are the same and have structure (II-1), where L⁴ is C₁₋₂ straight-chain alkylene, and L^{4'} is either a direct valence bond or a C₁ straight chain alkylene and L⁵ is a C₁₋₅ linear chain alkylene or a C₃₋₅ branched alkylene, and R²¹ is, H, a C₁₋₈ linear alkyl, a C₃₋₈ branched alkyl, or a -CH₂OH.

[0040] In structure (I), R⁴ and R⁹ are individually selected from, H, a C₁₋₈ alkyl, I, Cl, and Br.

[0041] In a further aspect of this embodiment, in structure (I), R⁵ and R¹⁰ are individually selected from, H or a C₁₋₈ alkyl, I, Cl, and Br.

[0042] In a further aspect of this embodiment, in structure (I), R⁶ and R¹ are individually selected from, H or a C₁₋₈ alkyl, I, Cl, and Br.

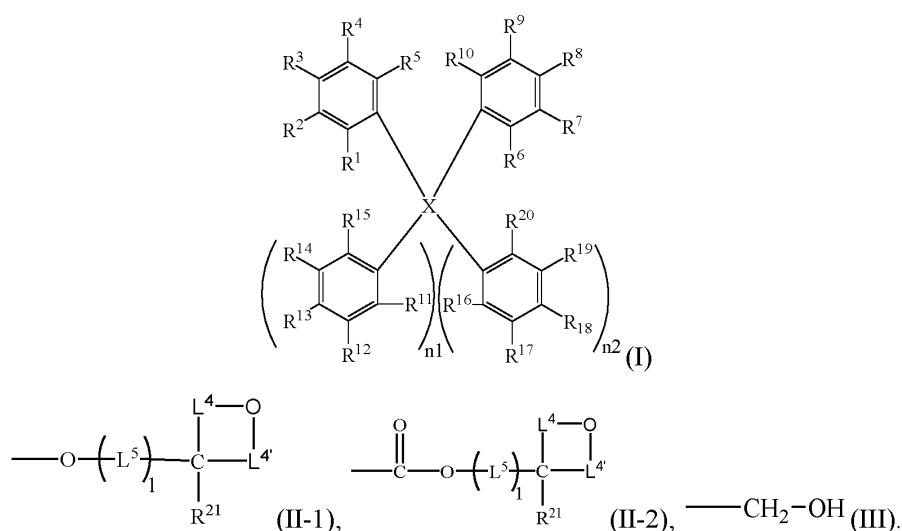
[0043] In a further aspect of this embodiment, in structure (I), R¹⁴ and R¹⁹ are individually selected from H, I, Cl, Br.

[0044] In a further aspect of this embodiment, in structure (I), R^{13} and R^{18} are individually selected from H, I, Cl, Br.

[0045] In a further aspect of this embodiment, in structure (I), R^{12} and R^{17} are individually selected from H, I, Cl, Br.

[0046] In a further aspect of this embodiment, in structure (I), R^{11} and R^{16} are individually selected from H, I, Cl, Br, or where R^{11} and R^{16} form a single valence bond together.

[0047] In a further aspect of this embodiment, in structure (I), R^{12} and R^{17} are individually selected from H, structure (II-1), or structure (II-2), where L^4 is a C_{1-2} linear -chain alkylene, $L^{4'}$ is either a direct valence bond or a C_1 straight chain alkylene, and L^5 is a C_{1-5} linear chain alkylene or a C_{3-5} branched alkylene.



[0048] In another aspect of the above-described embodiments, in structure (I), at least one of R^1 to R^5 and/or R^{11} to R^{15} is Y and at least one of R^1 to R^5 and/or R^{11} to R^{15} is selected from the group consisting of CH_2OH and/or wherein at least one of R^6 to R^{10} and/or R^{16} to R^{20} is Y and/or at least one of R^6 to R^{10} or R^{16} to R^{20} is CH_2OH . In another aspect of this embodiment, in structure (I), at least one of R^1 to R^5 and R^{11} to R^{15} is Y and at least one of R^1 to R^5 and R^{11} to R^{15} is selected from the group consisting of CH_2OH and wherein at least one of R^6 to R^{10} and R^{16} to R^{20} is Y and at least one of R^6 to R^{10} or R^{16} to R^{20} is CH_2OH . In another aspect of this embodiment, at least one of R^1 to R^5 or R^{11} to R^{15} is Y and at least one of R^1 to R^5 or R^{11} to R^{15} is selected from the group consisting of CH_2OH or wherein at least one of R^6 to R^{10} or R^{16} to R^{20} is Y or at least one of R^6 to R^{10} or R^{16} to R^{20} is CH_2OH . In another aspect of this embodiment, in structure (I), at least one of

R^1 to R^5 and R^{11} to R^{15} is Y and at least one of R^1 to R^5 or R^{11} to R^{15} is selected from the group consisting of CH_2OH and wherein at least one of R^6 to R^{10} or R^{16} to R^{20} is Y and at least one of R^6 to R^{10} or R^{16} to R^{20} is CH_2OH . In another aspect of this embodiment, in structure (I), at least one of R^1 to R^5 or R^{11} to R^{15} is Y and at least one of R^1 to R^5 and R^{11} to R^{15} is selected from the group consisting of CH_2OH or wherein at least one of R^6 to R^{10} and R^{16} to R^{20} is Y or at least one of R^6 to R^{10} or R^{16} to R^{20} is CH_2OH . In another aspect of this embodiment, in structure (I), at least one of R^1 to R^5 or R^{11} to R^{15} is Y and at least one of R^1 to R^5 and R^{11} to R^{15} is selected from the group consisting of CH_2OH or wherein at least one of R^6 to R^{10} and R^{16} to R^{20} is Y or at least one of R^6 to R^{10} or R^{16} to R^{20} is CH_2OH . In another aspect of this embodiment, in structure (I), at least one of R^1 to R^5 and R^{11} to R^{15} is Y and at least one of R^1 to R^5 and R^{11} to R^{15} is selected from the group consisting of CH_2OH and wherein at least one of R^6 to R^{10} and/or R^{16} to R^{20} is Y or at least one of R^6 to R^{10} or R^{16} to R^{20} is CH_2OH . In another aspect of this embodiment, in structure (I), at least one of R^1 to R^5 or R^{11} to R^{15} is Y and at least one of R^1 to R^5 or R^{11} to R^{15} is selected from the group consisting of CH_2OH or wherein at least one of R^6 to R^{10} and/or R^{16} to R^{20} is Y and at least one of R^6 to R^{10} or R^{16} to R^{20} is CH_2OH .

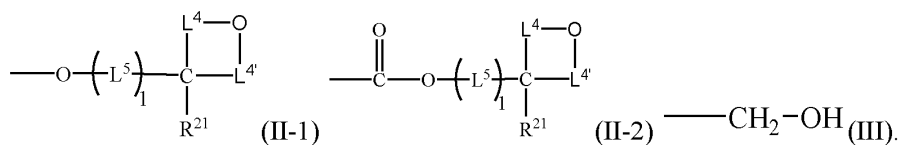
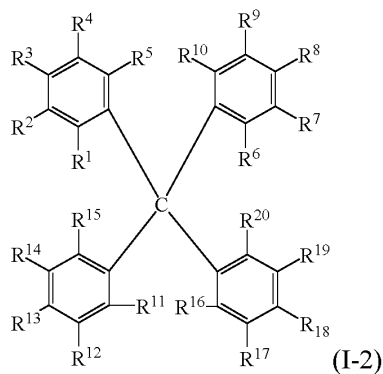
[0049] In a further aspect of this embodiment, the compound of structure (I) has structure (I-2), wherein, R^1 and R^6 are the same and are selected from, H or a C_{1-8} alkyl, I, Cl, and Br, R^2 and R^7 are the same moiety having structure (III).

[0050] In a further aspect of this embodiment, in the compound of structure (I-2), R^3 and R^8 are the same and have structure (II-1), where L^4 is a C_{1-2} linear -chain alkylene, $L^{4'}$ is either a direct valence bond or a C_1 straight chain alkylene, and L^5 is a C_{1-5} linear chain alkylene or a C_{3-5} branched alkylene, and R^{21} is, H, a C_{1-8} linear alkyl, a C_{3-8} branched alkyl, or a $-CH_2OH$.

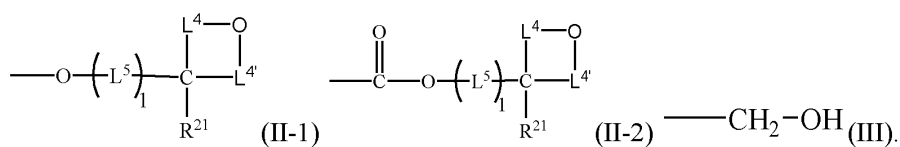
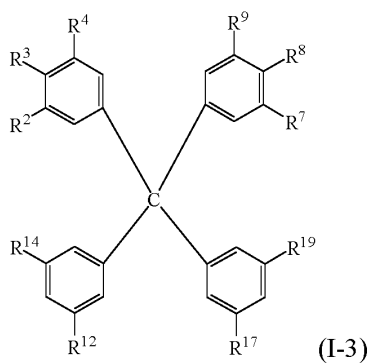
[0051] In a further aspect of this embodiment, in the compound of structure (I-2), R^4 and R^9 are individually selected from, H, a C_{1-8} alkyl, I, Cl, and Br, R^5 and R^{10} are individually selected from, H or a C_{1-8} alkyl, I, Cl, and Br, R^6 and R^1 are individually selected from, H or a C_{1-8} alkyl, I, Cl, and Br, R^{14} and R^{19} are individually selected from H, I, Cl, Br, R^{13} and R^{18} are individually selected from H, I, Cl, Br, R^{11} and R^{16} are individually selected from H, I, Cl, Br, or together form a single valence bond.

[0052] In a further aspect of this embodiment, R^{12} and R^{17} are individually selected from H, I, Cl, Br, structure (II-1), or structure (II-2), where L^4 is a C_{1-2} linear chain alkylene, $L^{4'}$ is either a direct valence bond or a C_1 straight chain alkylene, and L^5 is a C_{1-5} linear chain alkylene or a C_{3-5}

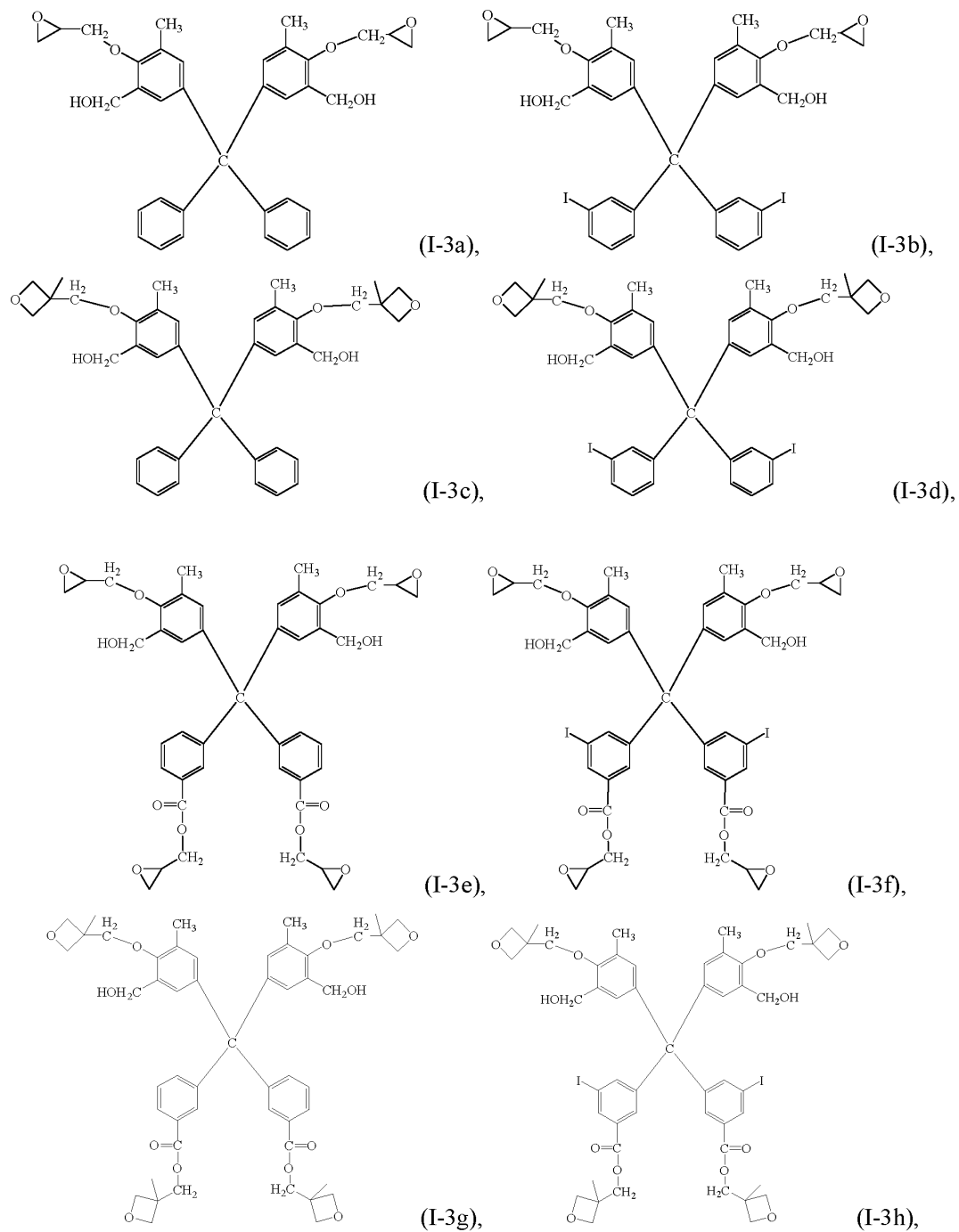
branched alkylene.

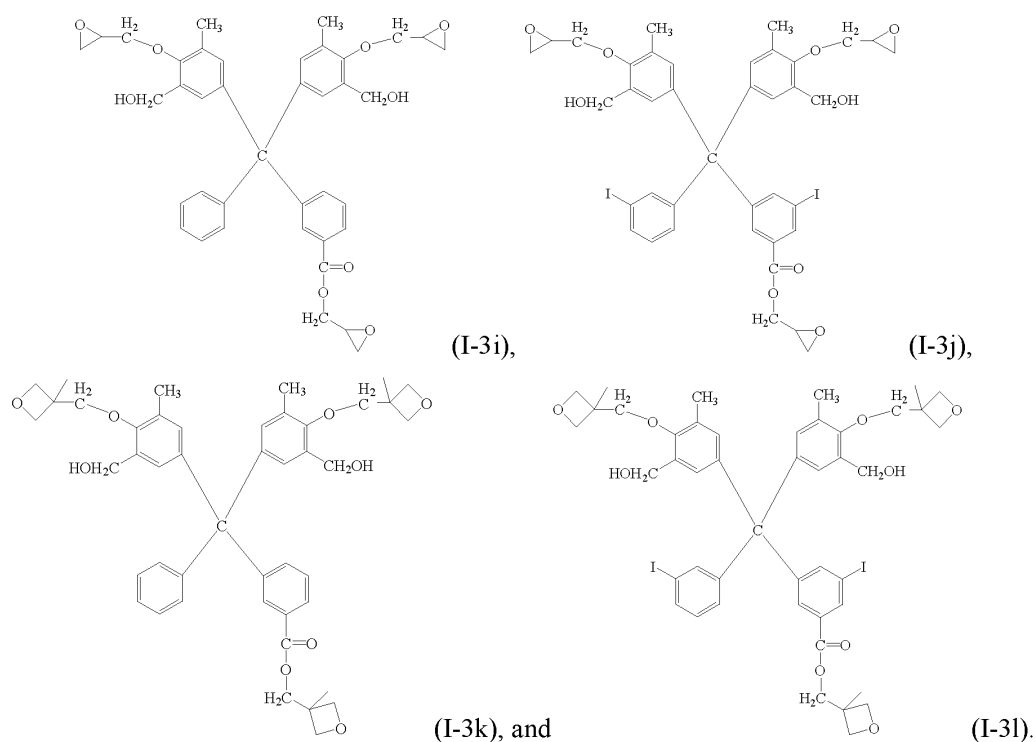


[0053] In a further embodiment, the compound of structure (I) has structure (I-3), where R^2 and R^7 are the same moiety having structure (III), R^3 and R^8 are the same and have structure (II-1), where L^4 is a C_{1-2} linear -chain alkylene, $L^{4'}$ is either a direct valence bond or a C_1 straight chain alkylene, and L^5 is a C_{1-5} linear -chain alkylene or a C_{3-5} branched alkylene, and R^{21} is, H, a C_{1-8} linear alkyl, a C_{3-8} branched alkyl, or a $-CH_2OH$, R^4 and R^9 are the same and are selected from, H or a C_{1-8} alkyl, I, Cl, and Br, R^{12} and R^{17} are individually selected from H, structure (II-1), or structure (II-2), R^{14} and R^{19} are the same and are selected from H, I, Cl, Br.

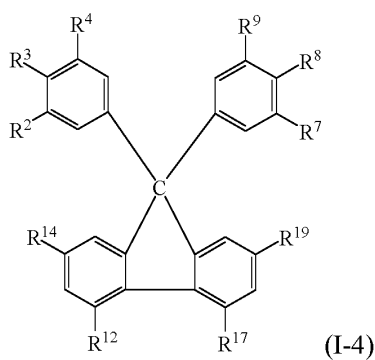


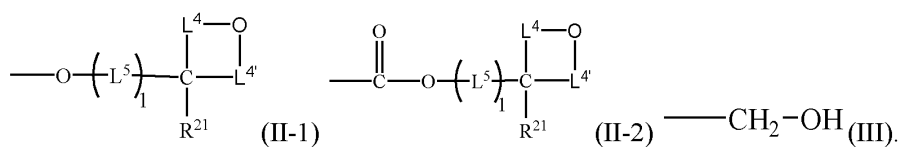
[0054] The crosslinking compound of (I-3) may be selected for example from the following more specific structure:



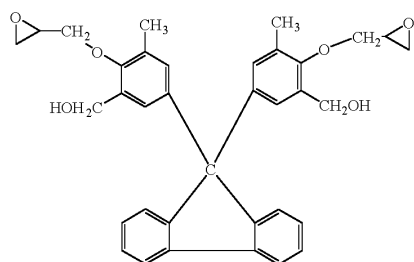


[0055] In a further embodiment, the compound of structure (I) has structure (I-4), where R^2 and R^7 is a moiety having structure (III), R^3 and R^8 are the same and have structure (II-1), where L^4 is a C_{1-2} linear -chain alkylene, L^4 is either a direct valence bond or a C_1 straight chain alkylene, and L^5 is a C_{1-5} linear -chain alkylene or a C_{3-5} branched alkylene, and R^{21} is, H, a C_{1-8} linear alkyl, a C_{3-8} branched alkyl, or a $-CH_2OH$, R^4 and R^9 are individually selected from, H, a C_{1-8} alkyl, I, Cl, and Br, R^{14} and R^{19} are individually selected from H, I, Cl, and Br, R^{21} is, H, a C_{1-8} linear alkyl, a C_{3-8} branched alkyl, or a $-CH_2OH$, R^{12} and R^{17} are individually selected from H, structure (II-1), and structure (II-2).

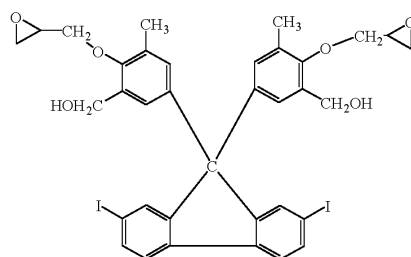




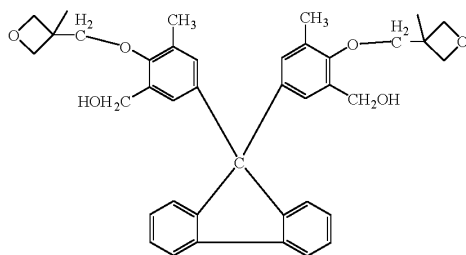
[0056] The crosslinking compound of (I-4) may be selected for example from the following more specific structure:



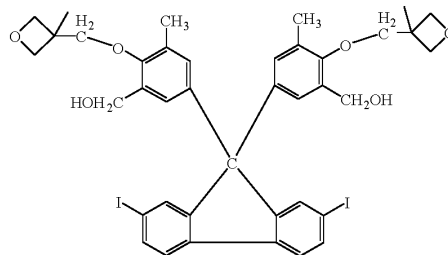
(I-4a),



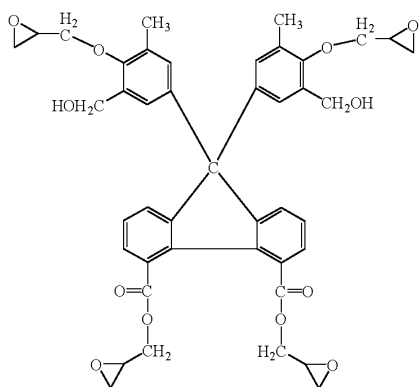
(I-4b),



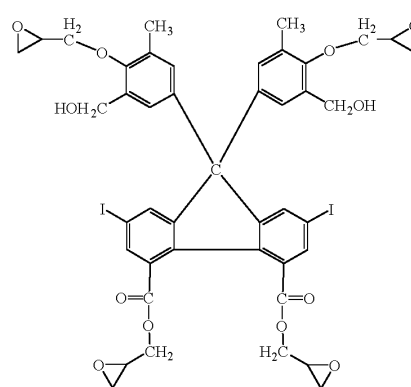
(I-4c),



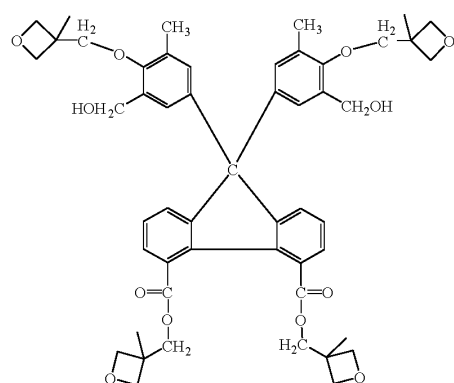
(I-4d),



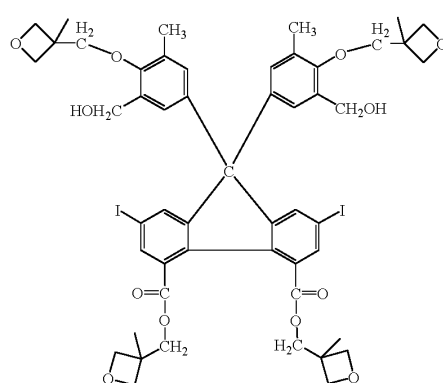
(I-4e),



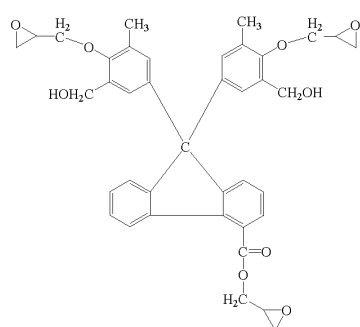
(I-4f),



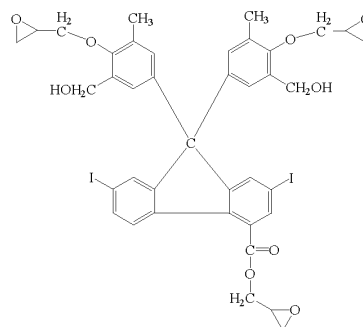
(I-4g),



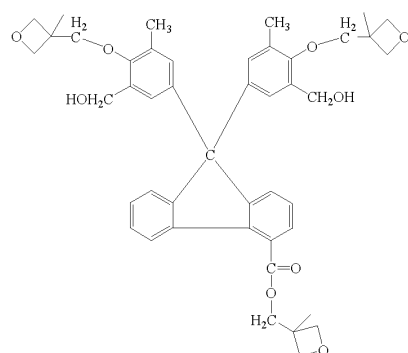
(I-4h),



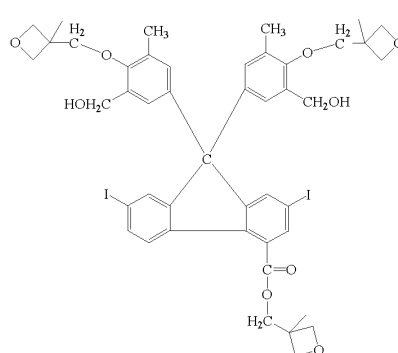
(I-4i),



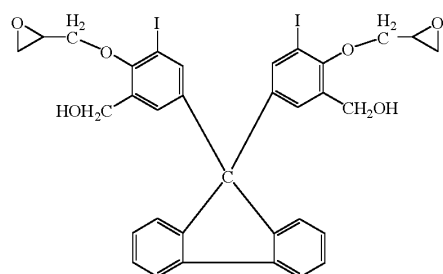
(I-4j),



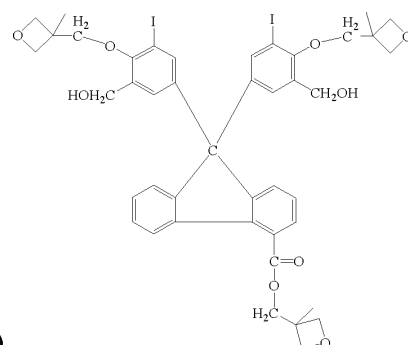
(I-4k),



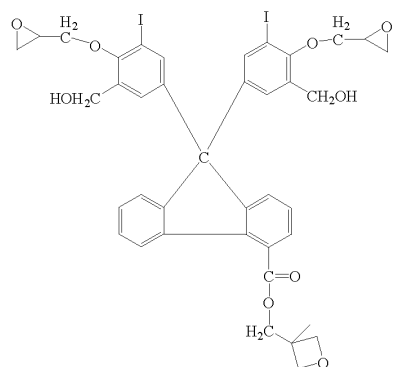
(I-4l),



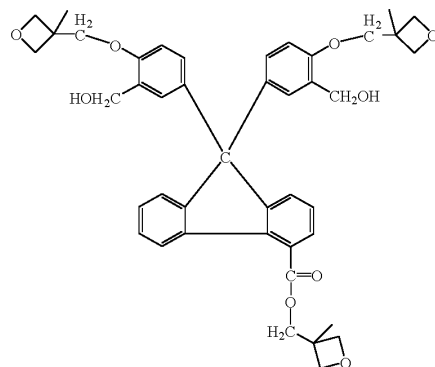
(I-4m),



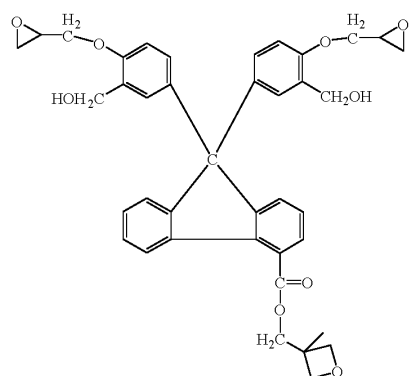
(I-4n),



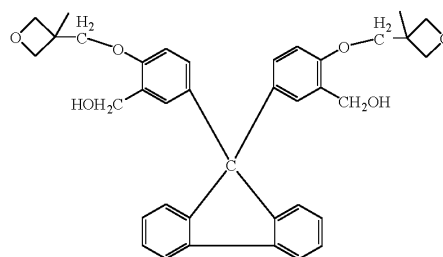
(I-4o),



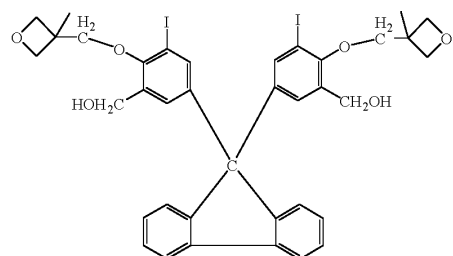
(I-4p),



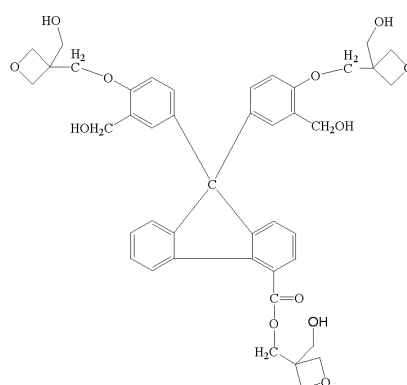
(I-4q),



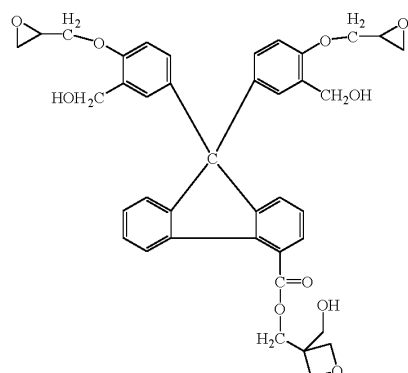
(I-4r),



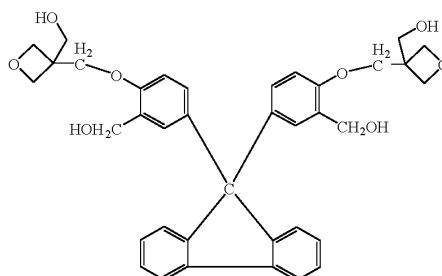
(I-4s),



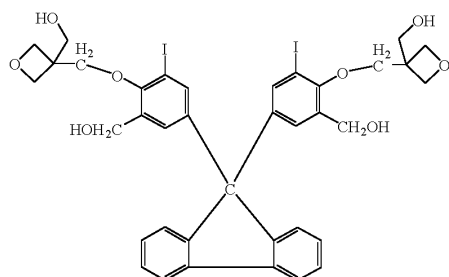
(I-4t),



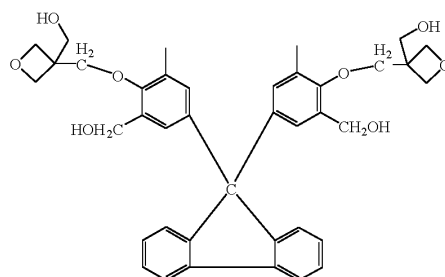
(I-4u),



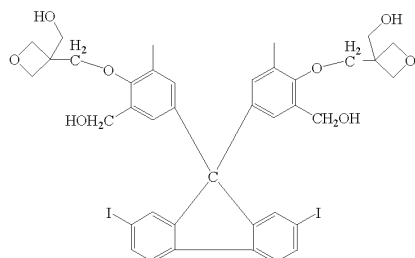
(I-4v),



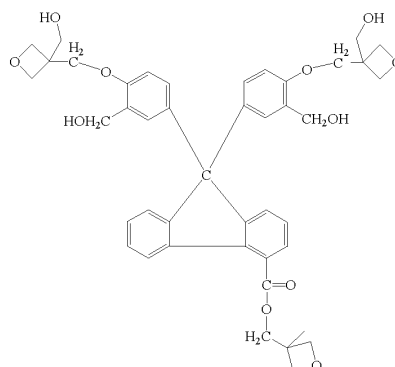
(I-4w),



(I-4x),

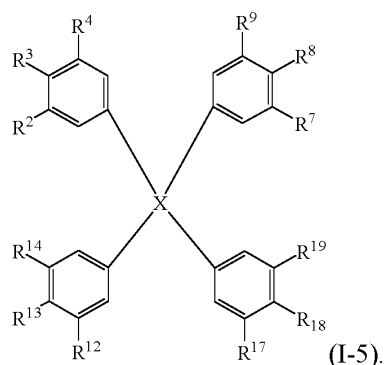


(I-4y),

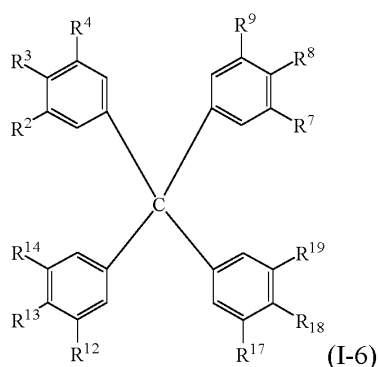


(I-4z).

[0057] In another embodiment of said crosslinking compound of structure (I) it more specifically has structure (I-5), wherein n_1 and n_2 are each independently 1 or 0, X is $C_pH_{2p-n_1-n_2}$ or $C_{6+4(q-1)}H_{4+2(q-1)-n_1-n_2}$, p is 1 to 6, and q is 1 to 3, wherein one or more H of X may be each independently substituted with C_{1-5} straight-chain alkyl or C_{3-5} branched alkyl, and further wherein R^3 , R^8 , R^{13} , and R^{18} are individually selected from Y, where R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{19} , R^{17} are selected from the group consisting of H, Cl, Br, and I, and at least one of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{19} , R^{17} is a halogen selected from the group consisting of, Cl, Br, and I,



[0058] In another embodiment of the crosslinking compound of structure (I-5), it more specifically has structure (I-6), wherein R^3 , R^8 , R^{13} , and R^{18} are individually selected from Y, R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{19} , R^{17} are selected from the group consisting of H, Cl, Br, and I, and at least one of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{19} , R^{17} is a halogen selected from the group consisting of Cl, Br, and I.



[0059] In another embodiment of the crosslinking compound of structure (I-5) or (I-6), it is one wherein only one of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} is selected from the group consisting of Cl, Br, I.

[0060] In another embodiment of the crosslinking compound of structure (I-5) or (I-6), it is one wherein only two of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} are selected from the group consisting of Cl, Br, I.

[0061] In another embodiment of the crosslinking compound of structure (I-5) or (I-6), it is one wherein only three of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} are selected from the group consisting of Cl, Br, I.

[0062] In another embodiment of the crosslinking compound of structure (I-5) or (I-6), it is one wherein only four of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} are selected from the group consisting of Cl, Br, I.

Br, I.

[0063] In another embodiment of the crosslinking compound of structure (1-5) or (I-6), it is one wherein only five of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} are selected from the group consisting of Cl, Br, and I.

[0064] In another embodiment of the crosslinking compound of structure (1-5) or (I-6), it is one wherein only five of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} are selected from the group consisting of Br, and I.

[0065] In another embodiment of the crosslinking compound of structure (1-5) or (I-6), it is one wherein only six of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} are selected from the group consisting of Cl, Br, I.

[0066] In another embodiment of the crosslinking compound of structure (1-5) or (I-6), it is one wherein only seven of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} are selected from the group consisting of Cl, Br, I.

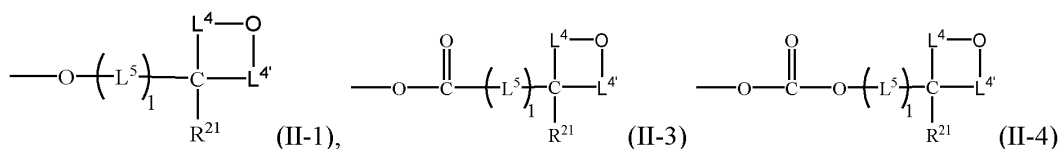
[0067] In another embodiment of the crosslinking compound of structure (1-5) or (I-6), it is one wherein R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} are all selected from the group consisting of Cl, Br, I.

[0068] In another embodiment of the crosslinking compound of structure (1-5) or (I-6), it is one wherein said halogen is Cl.

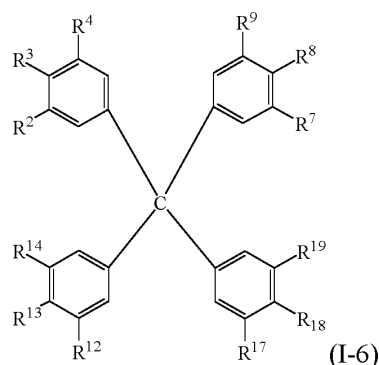
[0069] In another embodiment of the crosslinking compound of structure (1-5) or (I-6), it is one wherein said halogen is Br.

[0070] In another embodiment of the crosslinking compound of structure (1-5) or (I-6), it is one wherein said halogen is I.

[0071] In another embodiment of the crosslinking compound of structure (1-5) or (I-6), it is one wherein R^3 , R^8 , R^{13} , and R^{18} are individually selected from structure (II-1), structure (II-3) or structure (II-4), where L^4 is a C_{1-2} linear -chain alkylene, $L^{4'}$ is either a direct valence bond or a C_1 straight chain alkylene, and L^5 is a C_{1-5} linear chain alkylene or a C_{3-5} branched alkylene, and R^{21} is H, C_{1-8} linear alkyl, C_{3-8} branched alkyl, or $-CH_2OH$.



[0072] In another embodiment of the crosslinking compound of structure (I-5), it is one which more specifically has structure (I-6).



[0073] In another embodiment of the crosslinking compound of structure (I-6), it is one wherein only one of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} is selected from the group consisting of Cl, Br, I.

[0074] In another embodiment of the crosslinking compound of structure (I-6), it is one wherein only two of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} are selected from the group consisting of Cl, Br, and I.

[0075] In another embodiment of the crosslinking compound of structure (I-6), it is one wherein only three of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} are selected from the group consisting of Cl, Br, and I.

[0076] In another embodiment of the crosslinking compound of structure (I-6), it is one wherein only four of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} are selected from the group consisting of Cl, Br, and I.

[0077] In another embodiment of the crosslinking compound of structure (I-6), it is one wherein only five of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} are selected from the group consisting of Cl, Br, and I.

[0078] In another embodiment of the crosslinking compound of structure (I-6), it is one wherein only six of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} are selected from the group consisting of Cl, Br, and I.

[0079] In another embodiment of the crosslinking compound of structure (I-6), it is one wherein only seven of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} are selected from the group consisting of Cl, Br, and I.

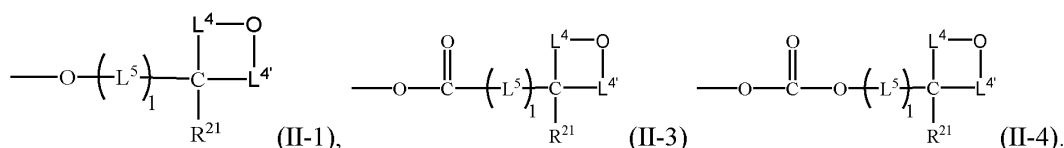
[0080] In another embodiment of the crosslinking compound of structure (I-6), it is one wherein all eight of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} are selected from the group consisting of Cl, Br, and I.

[0081] In another embodiment of the crosslinking compound of structure (I-6), said halogen is Cl.

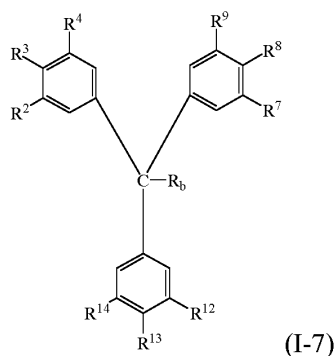
[0082] In another embodiment of the crosslinking compound of structure (I-6), said halogen is Br.

[0083] In another embodiment of the crosslinking compound of structure (I-6), said halogen is I.

In another embodiment of the crosslinking compound of structure (I-6), R^3 , R^8 , R^{13} , and R^{18} are individually selected from structure (II-1), structure (II-3) or structure (II-4), where L^4 is a C_{1-2} linear -chain alkylene, $L^{4'}$ is either a direct valence bond or a C_1 straight chain alkylene, and L^5 is a C_{1-5} linear chain alkylene or a C_{3-5} branched alkylene.



[0084] In another embodiment, said compound has structure (I-7), wherein R_b is selected from the group consisting of a C_{1-6} straight-chain alkyl or C_{3-15} branched alkyl, and further wherein R^3 , R^8 and R^{13} are individually selected from Y where R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , are selected from the group consisting of, H, Cl, Br, and I, and at least one of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} is a halogen selected from the group consisting of, Cl, Br, and I,



[0085] In a further embodiment, said crosslinking compound of structure (I-7), is one wherein only one of R^2 , R^4 , R^7 , R^9 , R^{12} , and R^{14} is selected from the group consisting of Cl, Br, and I.

[0086] In a further embodiment, said compound of structure (I-7), is one wherein only two of R^2 , R^4 , R^7 , R^9 , R^{12} , and R^{14} are selected from the group consisting of Cl, Br, and I.

[0087] In a further embodiment, said crosslinking compound of structure (I-7), is one wherein only three of R^2 , R^4 , R^7 , R^9 , R^{12} , and R^{14} are selected from the group consisting of Cl, Br, and I.

[0088] In a further embodiment, said crosslinking compound of structure (I-7), is one wherein only four of R^2 , R^4 , R^7 , R^9 , R^{12} , and R^{14} are selected from the group consisting of Cl, Br, and I.

[0089] In a further embodiment, said crosslinking compound of structure (I-7), is one wherein only five of R^2 , R^4 , R^7 , R^9 , R^{12} , and R^{14} are selected from the group consisting of Cl, Br, and I.

[0090] In a further embodiment, said crosslinking compound of structure (I-7), is one wherein only five of R^2 , R^4 , R^7 , R^9 , R^{12} , and R^{14} are selected from the group consisting of Br and I.

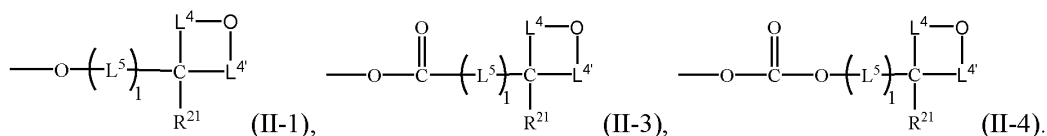
[0091] In a further embodiment, said crosslinking compound of structure (I-7), is one wherein R^2 , R^4 , R^7 , R^9 , R^{12} , and R^{14} are all selected from the group consisting of Cl, Br, and I.

[0092] In a further embodiment, crosslinking compound of structure (I-7), is one wherein said halogen is Cl.

[0093] In a further embodiment, said crosslinking compound of structure (I-7), is one wherein said halogen is Br.

[0094] In a further embodiment, said crosslinking compound of structure (I-7), is one wherein said halogen is I.

[0095] In a further embodiment, said crosslinking compound of structure (I-7), is one wherein R^3 , R^8 and R^{13} are individually selected from structure (II-1), structure (II-3) or structure (II-4), where L^4 is a C_{1-2} linear chain alkylene, $L^{4'}$ is either a direct valence bond or a C_1 straight chain alkylene, and L^5 is a C_{1-5} linear chain alkylene or a C_{3-5} branched alkylene.



[0096] In a further embodiment, said crosslinking compound of structure (I-7), it is one wherein R^3 , R^8 and R^{13} all have structure (II-1).

[0097] In a further embodiment, said crosslinking compound of structure (I-7), it is one wherein R^3 , R^8 and R^{13} all have structure (II-3).

[0098] In a further embodiment, said crosslinking compound of structure (I-7), it is one wherein R^3 , R^8 and R^{13} all have structure (II-3).

[0099] In a further embodiment, said crosslinking compound of structure (I-7), it is one wherein R^3 , R^8 and R^{13} all have structure (II-4).

[0100] In a further embodiment, said crosslinking compound of structure (I-7), it is one wherein R^3 , has structure (II-1) and R^8 and R^{13} all have structure (II-3).

[0101] In a further embodiment, said crosslinking compound of structure (I-7), it is one wherein R^3 , has structure (II-1) and R^8 and R^{13} all have structure (II-4).

[0102] In a further embodiment, said crosslinking compound of structure (I-7), it is one wherein R^3 , has structure (II-3) and R^8 and R^{13} all have structure (II-4).

[0103] In a further embodiment, said crosslinking compound of structure (I-7), it is one wherein R^3 , has structure (II-4) and R^8 and R^{13} all have structure (II-3).

[0104] In a further embodiment, said crosslinking compound of structure (I-7), it is one wherein R^3 , has structure (II-3) and R^8 and R^{13} all have structure (II-1).

[0105] In a further embodiment, said crosslinking compound of structure (I-7), it is one wherein R^3 , has structure (II-4) and R^8 and R^{13} all have structure (II-1).

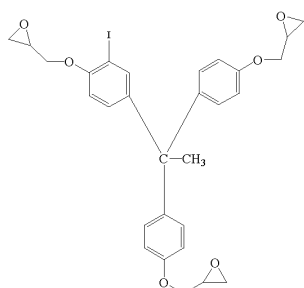
[0106] In a further embodiment said crosslinking compound of structure (I-7), it is one wherein R^3 has structure (II-1), R^8 has structure (II-3) and R^{13} has structure (II-4)

[0107] In a further embodiment, said crosslinking compound of structure (I-7), it is one wherein L^4 is $-\text{CH}_2-$, L^4 is a direct valence bond and R_{21} is H.

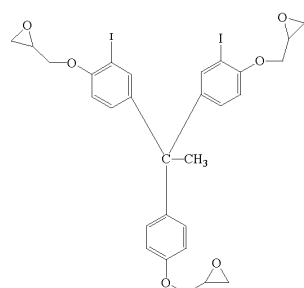
[0108] In a further embodiment, said crosslinking compound of structure (I-7), it is one wherein L^4 is $-\text{CH}_2-$, L^4 is $-\text{CH}_2-$ and R_{21} is a C_1 to C_4 linear alkyl.

[0109] In a further embodiment, said crosslinking compound of structure (I-7), it is one, wherein L^4 is $-\text{CH}_2-$, L^4 is $-\text{CH}_2-$ and R_{21} is a $-\text{CH}_2-\text{OH}$.

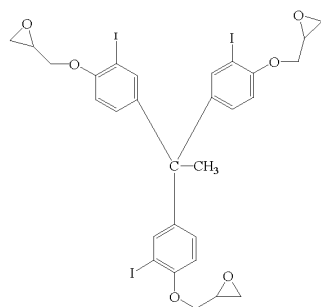
[0110] In a further embodiment, said crosslinking compound of structure (I-7), it is selected from the group consisting of the following structures:



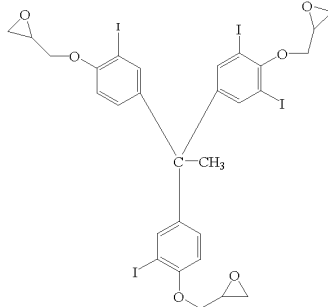
(I-7a),



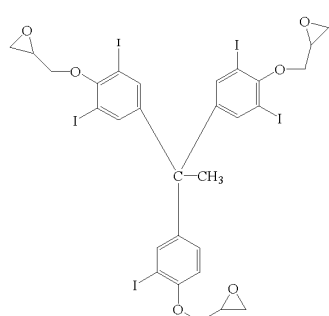
(I-7b),



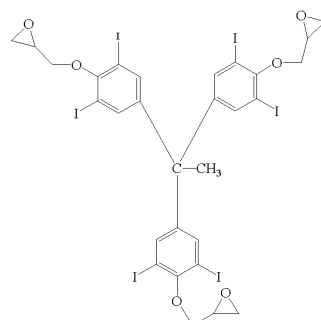
(I-7c),



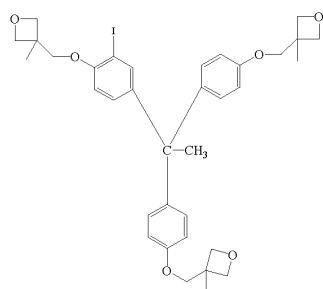
(I-7d),



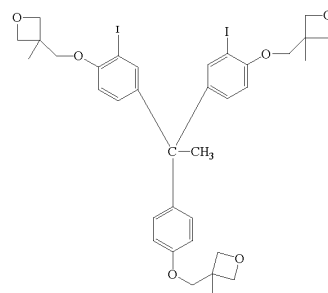
(I-7e),



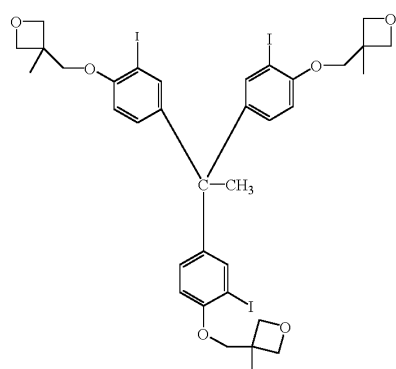
(I-7f),



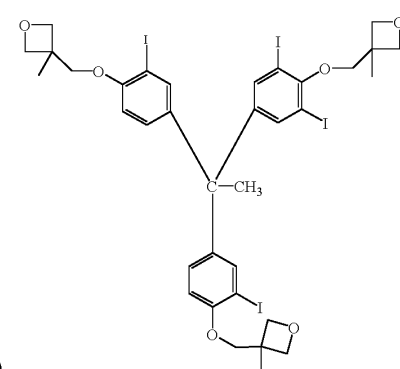
(I-7g),



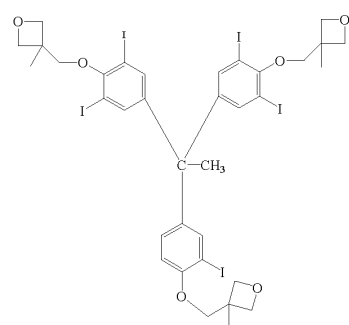
(I-7h),



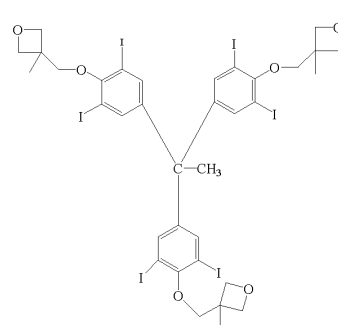
(I-7i),



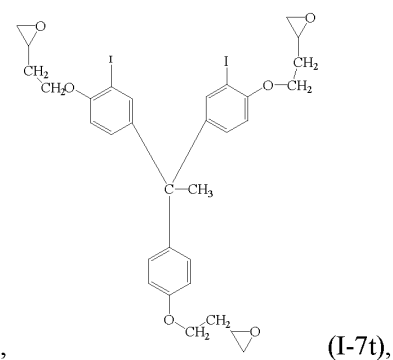
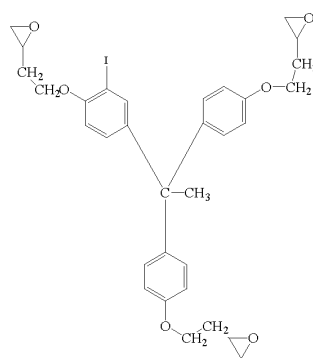
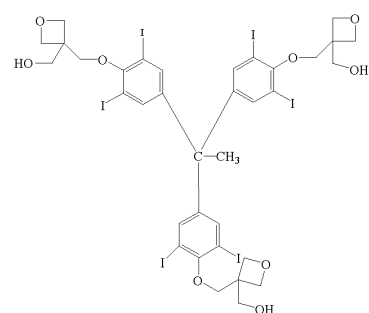
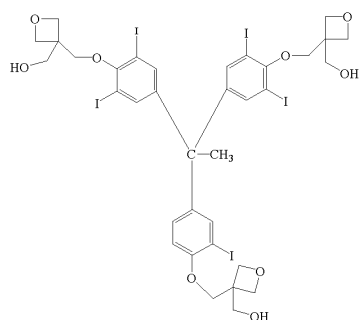
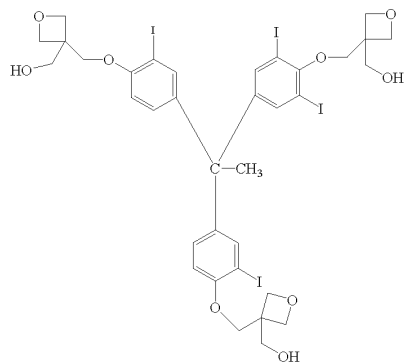
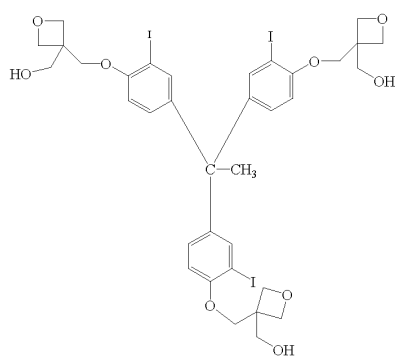
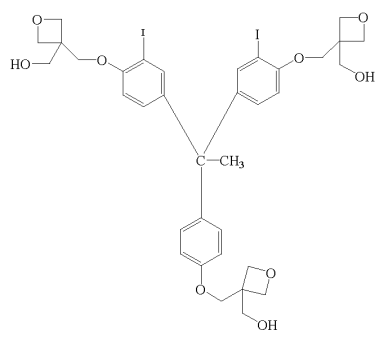
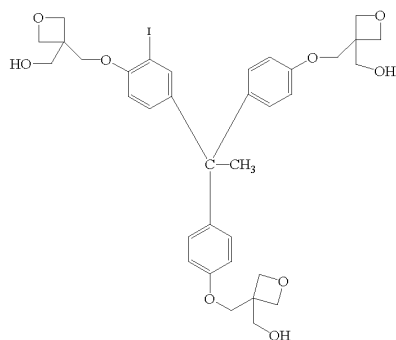
(I-7j),

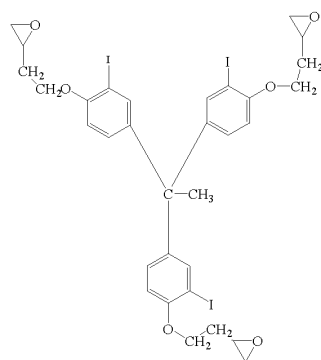


(I-7k),

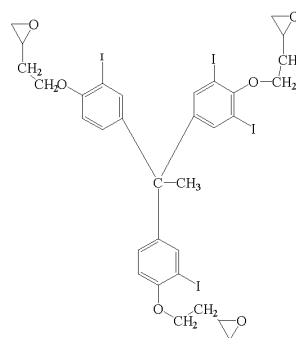


(I-7l),

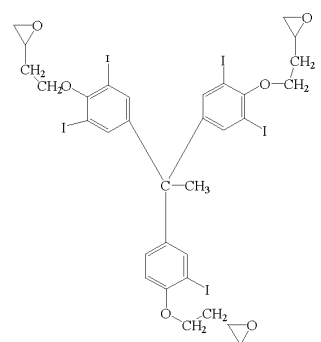




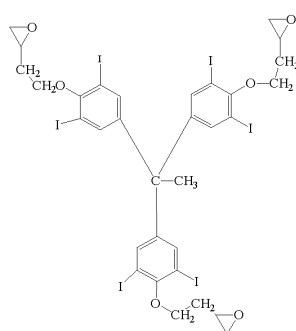
(I-7u),



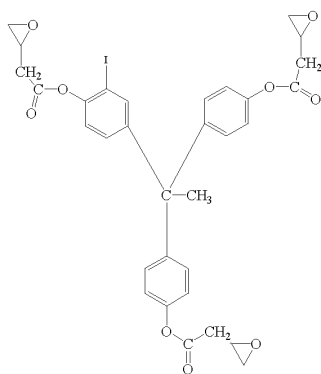
(I-7v),



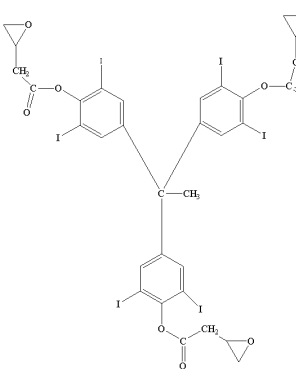
(I-7w),



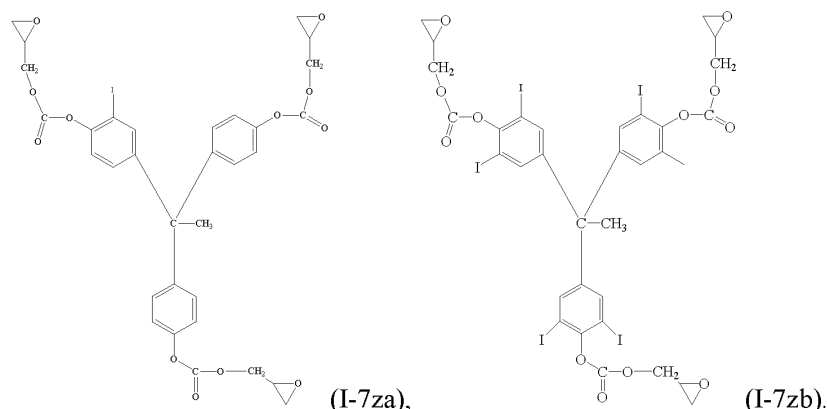
(I-7x),



(I-7y),



(I-7z),



[0111] Crosslinking Compositions

[0112] In a further aspect disclosed and claimed compounds can be a component in crosslinking formulations. Such formulations comprise as a minimum:

- Component (A) at least one crosslinking component which is a compound of structure (I), or any one of its substructures as described herein which may be present as a single type of these compound or as a mixture of at least two different of these compounds; and
- Component (B) at least one an acid-generating agent component, which may include, for example, photoacid generators (PAG) that produce acids by light and thermal acid generators (TAG) that produce acids by heat. Examples of thermal acid generators are for instance ionic thermal acid generators such as ammonium salts of perfluorinated alkylsulfonic acids or covalent thermal acid generators such as alkyl esters of sulfonic acids. Preferably embodiment are those containing photoacid generators (PAGs). Examples of PAGs will be discussed in more detail as follows in relation to further descriptions of Component (B).

[0113] The composition according to the disclosed and claimed subject matter is preferably a resist composition, containing said crosslinking compound of structure (I), and where Component (B) is a PAG, as described in more details as follows. More preferably this composition is a negative type of resist composition imageable by radiation (e.g., i-line, UV, deep UV, EUV, e-beam), and even more preferably a negative type EUV or e-beam type photoresist composition, and most preferentially imageable by EUV.

[0114] Although not constrained by the theory, it is believed that for these crosslinking compositions, said compounds of structure (I) in Component (A), (or any one of its structures as

described herein), contribute to the improvement of the resolution because these compounds have substituents with a certain volume, which can interact with acid generated by the photoacid generator upon irradiation. These substituents of a certain volume can be, for example, a substituent with an epoxy, an iodine atom, etc.. Because of the high concentration of these substituents, they can absorb the acid generated by the acid generator, upon irradiation. This prevents excessive acid diffusion, and because of this the resolution is expected to improve.

[0115] Although not constrained by theory, in these crosslinking compositions, for component (A) each of the crosslinking compound of structure (I) (or any one of its substructures as described herein), has a substituent group (e.g., an oxygen atom) with an unpaired electron pair (e.g., a halogen such as an iodine atom, epoxy, hydroxy, ether, etc.) and such atoms with unpaired electrons will also contribute to improved resolution.

[0116] Although not constrained by theory, in order to suppress the diffusion of acid, the resolution is thought to be improved in these crosslinking compositions in embodiments of Component (A), where the crosslinking compound of structure (I) contain several substituents in the same ring structure with a certain volume or atoms with unpaired electron pairs, as described above: it is expected to contribute to the improvement of resolution.

[0117] Further, although not constrained by theory, it is believed that in some embodiments of these compositions the presence of two types of crosslinking pendant moieties on the aromatic rings of the crosslinking compounds of structure (I) or any one of its substructures, where one type is an oxirane or oxetane pendant crosslinking moiety and in some embodiments the additional presence of a -CH₂OH moiety improves crosslinking density induced by reaction with photoacid generated by Component (B) during irradiation of photoresist films and that this is also expected to contribute to improvement in resolution. More specific examples of such compounds with additional -CH₂OH moiety in these compositions are as noted above structures (I-2), structure (I-3), structures (I-3a to I-3l), structure (I-4), and structures (I-4a to I-4z).

[0118] Further, although not constrained by theory, it is believed that in some embodiments of these compositions in the crosslinking compounds of structures (I) which have a halogen substituent, most preferentially ortho to the phenolic moiety with a crosslinking pendant moieties on the aromatic also contribute to improved resolution. One embodiment of this aspect are when component (A) is selected from a compound of structures (I-5), (I-6), or (I-7). In one embodiment it is selected from any one of structures (I-7a) to (I-7zb). In another aspect of this embodiment, it

is any of the compounds described herein which contain both a $\text{-CH}_2\text{OH}$, and an iodine substituent ortho to the phenolic moiety containing with a crosslinking pendant moieties on the aromatic rings. Specific non-limiting examples of such structures are structures (I-4m), (I-4n), (I-4o), (I-4s), and (I-4y).

[0119] In the disclosed and claimed subject matter, in one embodiment of the disclosed and claimed composition, the compound of structure (I) or any one of its substructures, is present in this composition in an amount preferably in the range from 50 to 95 mass %, more preferably 60 to 90 mass %, very preferably 70 to 85 mass % based on the total mass of the components except for organic spin casting solvent.

[0120] The molar ratio of component (A) containing a compound of structure (I) is preferably in the range from 0.53 to 0.90, more preferably 0.60 to 0.85, more preferably 0.61 to 0.80, more preferably 0.65 to 0.80 based on the total molar of the components except for any organic spin casting solvent which may be present. For instance, in a composition only containing Component (A) and Component (B), this would mean that the molar ratio of moles of component (A) containing a compound of structure (I) to the total moles of Component (A) and component (B) (containing a PAG), would preferably be in the range from 0.53 to 0.90, more preferably 0.60 to 0.85, more preferably 0.61 to 0.80, more preferably 0.65 to 0.80.

[0121] These photoresist formulations in addition to the compounds of structure (I), may optionally contain polymers. The polymer content is 0 to 20 mass %, preferably 0 to 10 mass %, preferably 0 to 5 mass % and even more preferably 0, relative to the total weight of the other components, excluding the solvent.

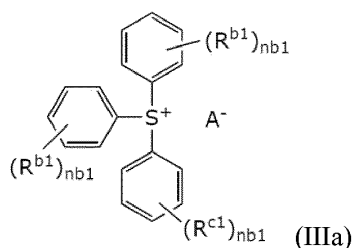
[0122] Although not constrained by theory, in the composition of the disclosed and claimed subject matter, the crosslinking compounds of structure (I) is the main component of the other components, excluding solvents, and constitutes the matrix of the resist film. Therefore, it is not necessary to include polymers in addition to the compounds of structure (I) as part of said photoresist formulation.

[0123] A more detailed description of possible compositional formulations using the compound of structure (I) in a negative chemically amplified photoresist useful for EUV or e-beam are as follows:

[0124] In the disclosed and claimed compositions, where said acid generating agent (B) is a PAG, where acids produced by irradiation, these acid generators (B) are preferably iodonium salts,

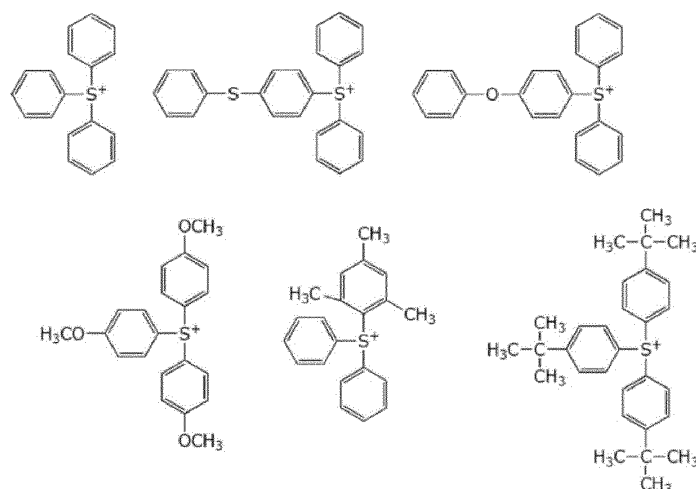
tetrahydrothiophenium salts, sulfonium salts, it is selected from groups consisting of diazonium salts, and pyridinium salts, for example diphenyliodonium trifluoromethanesulfonate, diphenyliodonium nonafluoro-n-butanesulfonate, diphenyliodonium perfluoro-n-octanesulfonate, diphenyliodonium 2-bicyclonal [2.2.1] hepta-2-il-1,2,2-ethofluoronate bis(4-t-butyl phenyl) iodonium trifluoromethanesulfonate, bis(4-t-butyl phenyl) iodonium nonafluoro-n-butanesulfonate, bis(4-t-butyl phenyl) iodonium perfluoro-n-octanesulfonate, bis(4-t-butyl phenyl) Cyclohexyl 2-oxocyclohexyl methylsulfonium trifluoromethanesulfonate, Dicyclohexyl 2-oxocyclohexylsulfonium trifluoromethanesulfonate, 2-oxocyclohexyl dimethylsulfonium trifluoromethanesulfonate, and so on.

[0125] The PAG Acid generators Component (B) are preferably sulfonium salts, preferably triphenylsulfonium salts, and preferably expressed by the following structure (IIIa).



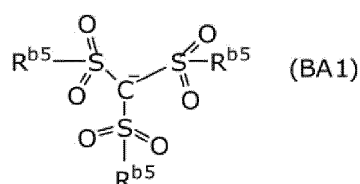
[0126] Where in structure (IIIa), R^{b1} contains C_{1-6} alkyl, C_{1-6} alkoxy, C_{6-12} aryl, C_{6-12} arylthio, or C_{6-12} aryloxy, preferably methyl, ethyl, t-butyl, methoxy, ethoxy, phenylthio, or phenyloxy, more preferably, t-butyl, methoxy, ethoxy, phenylthio, or phenyloxy, $nb1$ is 0, 1, 2 or 3, respectively.

[0127] It is a preferred form that all $nb1$ s are 1. It is also preferable that all $nb1$ s are identical. The fact that all $nb1$ s are 0 is also a good form. One $nb1$ is 3 and the other two $nb1$ is 0 is also a good form. Specific examples of cations having structure (IIIa) are as follows:



[0128] A- is a monovalent anion, examples of anions in equation (IIIa) include for example, halide ion, hexafluoroantimonate ion, hexafluorophosphate ion, the following ions are represented by equations (BA1) through (BA4), preferably hexafluoroantimonic acid ions, ions represented by structure (BA1), or ions represented by equations (BA2).

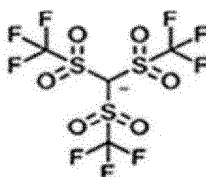
[0129] The structure of (BA1) is as follows:



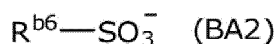
[0130] In structure (BA1), R^{b5} is independently selected from C_{1-6} fluorine substituted alkyl, C_{1-6} fluorine substituted alkyl, or C_{1-6} alkyl. For example, $-CF_3$ means that all hydrogen in methyl (C_1) has been substituted with fluorine. In the disclosed and claimed subject matter, fluorine substitution means that some or all the hydrogen present in the alkyl portion of an alkyl or alkyl portion of an alkoxy is substituted by fluorine, preferably all of which is substituted by fluorine.

[0131] R^{b5} is preferably fluorinated or unsubstituted, methyl, ethyl, t-butyl, methoxy, ethoxy, or t-butoxy, preferably fluorosubstituted or non-substituted methyl R^{b5} is preferably fluorine-substituted alkyl; more preferably $-CF_3$.

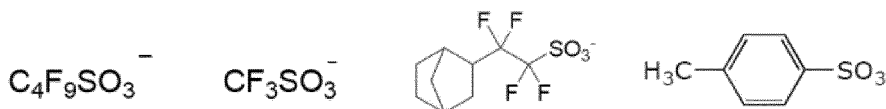
[0132] The following is a specific example of structure (BA1).



[0133] Another example of an anion is one of structure (BA2), as follows, where R^{b6} is C₁₋₁₀ fluorine substituted alkyl, C₁₋₆ fluorine substituted alkyl, and C₆₋₁₂ fluorine substituted aryl, C₂₋₁₂ fluorine substituted acyl, C₆₋₁₂ fluorine substituted alkoxyaryl, or C₆₋₁₂ alkyl substituted aryl; preferably C₁₋₁₀ fluorine substituted alkyl or C₆₋₁₂ alkyl substituted aryl. In R^{b6} the alkyl or alkyl portion is preferable to be linear or cyclic and is also preferably C₁₋₆ fluorine substituted alkyl; more preferably C₂₋₆ fluorine substituted alkyl. In PAG's for use in photo-imageable formulations containing the claimed and described compound of structure (I), PAG's with sulfonate anions whose corresponding photo-released acid have a pK_a value smaller than -2 are preferred. This is because anions (e.g., tosylate whose parent acid tosic acid has a calculated (ACD)* pK_a of -0.43) and would not affect as long a catalytic chain for ring opening of oxirane and/or oxetane moieties in the claimed compounds of structure compared to super-acids such as for example, triflic acid (Calculated pK_a -6.85), and even more acidic HSbF₆ or HAsF₆. As such, onium salts PAG's of stronger acids, such as super acids, are preferred. Indeed, onium salts PAGs of weaker sulfonic acids, because of their comparatively poor acidity, are used in the described compositions as a component which will act as photo-decomposable quencher/base in formulations containing onium salt PAGs of super acids and compounds of structure (I). This was found to be experimentally useful in EUV/e-beam formulations containing the compounds of structure (I) intended for use in negative chemically amplified photoresist compositions, as will be discussed shortly. *(ACD/pK_a software version 4.0 for Microsoft windows, Advanced Chemistry development Inc 8 King Street East, Suite 107, Toronto, Ontario Canada).

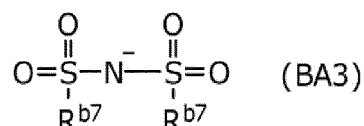


[0134] The following are specific example of equation (BA2):

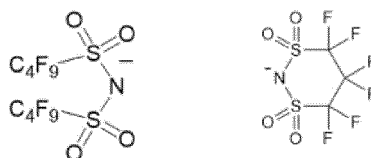


[0135] Another example of an anion is one of structure (BA3), as follows, where R^{b7} is independently selected from C₁₋₆ fluorosubstituted alkyl, C₁₋₆ fluorosubstituted alkyl, C₆₋₁₂

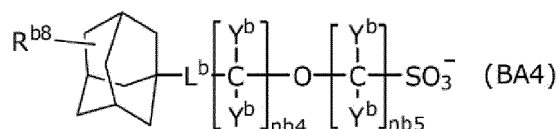
fluorosubstituted aryl, C₂₋₁₂ fluorine substituted acyl, or C₆₋₁₂ fluorine substituted alkoxyaryl; preferably C₂₋₆ fluorine substituted alkyl. Two R^{b7}s may be connected to each other to form a fluorine-substituted heteroring structure. The heteroring structure is preferably a saturated ring. The heteroring structure, including N and S, is preferably a monocyclic structure of 5 to 8; more preferably a five-membered or six-membered ring; more preferably a six-membered ring.



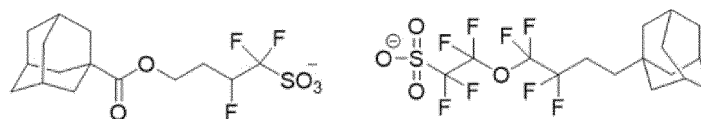
[0136] The following is a specific example of structure (BA3):



[0137] Another example of a suitable anion is one of structure (BA4), as follows, where R^{b8} is hydrogen, C₁₋₆ alkyl, C₁₋₆ alkoxy, or hydroxy; preferably hydrogen, methyl, ethyl, methoxy, or hydroxy; preferably hydrogen or hydroxy. L^b can be methylene, ethylene, carbonyl, oxy or carbonyloxy, preferably ethylene or carbonyl. Y^b can be either hydrogen or fluorine independently of each other; preferably 1 or more fluorine. Further, in structure (BA4), nb4 is an integer from 0 to 10; preferably 0, 1 or 2. nb5 is an integer from 0 to 21; preferably 4, 5, or 6.



[0138] The following is a specific example of structure (BA4):



[0139] Component (B) may one or more type of photoacid generator, preferably two or more, preferably two. In the preferred form, the (B) component consists of two types of photoacid generators. In component (B), when there are two components, a first photoacid generator and a second acid generator (where the pK_a (H₂O) of the acid from the first photoacid generator < (smaller than) the pK_a (H₂O) of the acid from the second photoacid generator), the ratio of the

molar number of the first photoacid generator/the molar number of the second photoacid generator is preferably 0.0-9.0.

[0140] In one embodiment, the content of component (B) is preferably in the range of 2 to 45 mass %, more preferably 5 to 40 mass %, and very preferably 10 to 35 mass % relative to the total weight of the other components excluding the solvent.

[0141] In another embodiment, the molar ratio of the component (B) to the component (A) (the number of moles of the (B) component / the number of moles of the component (A)) is 0.66 or less, preferably less than 0.55, preferably between 0.10 and 0.50, and preferably between 0.25 and 0.45. Viewed in an alternative way, this means that the mole fraction of component (B) to the sum of moles of component (A) and (B) is 0.39 or less, preferably 0.35 or less, more preferably 0.09 to 0.33, further preferably 0.20 to 0.31.

Negative Chemically Amplified Photoresist Compositions

[0142] More specifically the above-described composition useful as a negative chemically amplified EUV or e-beam photoresist composition is comprising the following component and possible optional components:

(A) a crosslinker which comprises at least one compound of structure (I), or any one of its substructures described herein,

(B) at least one photoacid generator (PAG) component,

(C) an optional additional crosslinking component, not having structure (I),

(D) an optional acid quencher component,

(E) an organic spin coating solvent component,

[0143] In one aspect of said negative chemically amplified photoresist composition Component (D) is not an optional component but is present.

Component (A):

[0144] In one aspect of this embodiment said component (A) is at least one compound of structure (I) where at least one of R^1 to R^5 and/or R^{11} to R^{15} is Y and at least one of R^1 to R^5 and/or R^{11} to R^{15} is CH_2OH or any of its substructures as described herein. A more specific example of such substructures is structure (I-2), or more specifically structure (I-3), or more specifically any one of structures (I-3a) to (I-3l), structure (I-4), and structures (I-4a) to (I-4z).

[0145] In another aspect of this embodiment component (A) is at least one compound having structure (I-5), or more specifically structure (I-6), or more specifically structure (I-7), or even

more specifically any one of structures (I-7a) to (I-7zb).

[0146] In another aspect this embodiment component (A) is a mixture comprising two compounds where the first compound is compound of structure is at least one compound of structure (I) where at least one of R^1 to R^5 and/or R^{11} to R^{15} is Y and at least one of R^1 to R^5 and/or R^{11} to R^{15} is CH_2OH or more specifically, structure (I-2), or more specifically structure (I-3), or more specifically (I-3a) to (I-3l), or more specifically structure (I-4), or even more specifically any one of structures (I-4a) to (I-4z) and the second compound is one having structure (I-5), or more specifically structure (I-6), or more specifically structure (I-7), or even more specifically any one of structures (I-7a) to (I-7zb). In this embodiment, which comprises a mixture of a first compound and a second compound, the mole % of the first compound versus the total mole % of the first and second compound ranges from about 5 mole % to about 95 mole %. In another embodiment the mole % of the first compound versus the total mole % of the first and second compound ranges from about 10 mole % to about 90 mole %. In another embodiment the mole % of the first compound versus the total mole % of the first and second compound ranges from about 15 mole % to about 85 mole %. In another embodiment the mole % of the first compound versus the total mole % of the first and second compound ranges from about 20 mole % to about 80 mole %. In another embodiment the mole % of the first compound versus the total mole % of the first and second compound ranges from about 25 mole % to about 75 mole %. In another embodiment the mole % of the first compound versus the total mole % of the first and second compound ranges from about 30 mole % to about 70 mole %. In another embodiment the mole % of the first compound versus the total mole % of the first and second compound ranges from about 35 mole % to about 65 mole %. In another embodiment the mole % of the first compound versus the total mole % of the first and second compound ranges from about 40 mole % to about 60 mole %. In another embodiment the mole % of the first compound versus the total mole % of the first and second compound ranges from about 45 mole % to about 55 mole %. In another embodiment the mole % of the first compound versus the total mole % of the first and second compound is about 50 mole %.

[0147] For Component (A) containing a single compound of structure (I), or a mixture of two different compound, as described above, it is preferable that the molar ratio of the total moles of Component (A) is in the range from 0.55 to 0.90, more preferably 0.60 to 0.85, very preferably 0.61 to 0.80 based on the total molar of the components except for Component (E), the organic

spin casting solvent.

[0148] For the disclosed and claimed negative chemically amplified EUV or e-beam photoresist composition described above in addition to the disclosed and claimed compound the other components or optional component are described as follows:

Component (B): PAG

[0149] The molar ratio of Component (B), in said negative chemically amplified EUV or e-beam photoresist composition, to the total moles of Components (A) and (B) ranges from about 0.10 to about 0.45. In another embodiment it ranges from about 0.10 to about 0.40. In another embodiment it ranges from about 0.15 to about 0.40. In another embodiment it ranges from about 0.15 to about to about 0.40. In another embodiment it ranges from about 0.17 to about to about 0.40. In another embodiment it ranges from about 0.20 to about 0.40. In another embodiment it ranges from about 0.21 to about 0.40. In another embodiment it ranges from about 0.22 to about 0.40. In another embodiment it ranges from about 0.24 to about 0.40.

[0150] Component (B) these may include, for example, photoacid generators that produce acids by light (e.g., UV, Deep UV, EUV) or radiation (e-beam) preferably ones that which produce or irradiation a super acid with a very low pK_a such as triflic acid, perfluoroalkylsulfonic acid, $HSbF_6$, and $HAsF_6$, as previously described in more detail above.

[0151] The component (B) may be one type or two or more types; preferably two, or more two types; more preferably two types. In a preferable embodiment, the component (B) consists of two types of photoacid generators. When the component (B) consists of two types, with respect to the compounding ratio of the first photoacid generator and the second acid generator (it is taken as $pK_a(H_2O)$ of the acid generated from the first photoacid generator which has a smaller $pK_a(H_2O)$ than the acid generated from the second photoacid generator), the number of moles of the first photoacid generator/the number of moles of the second acid generator is preferably 0.1 to 0.9; more preferably 0.15 to 0.85. If the first photoacid generator generating a stronger acid (a.k.a. smaller pK_a), is an onium salt type PAG which photo releases an acid whose $pK_a(H_2O)$ smaller than -5 (as calculated by ACD*) and the second photoacid generator photoreleases a much weaker acid which has a $pK_a(H_2O)$ greater than -2 (as calculated by ACD*), then because of the resultant basicity of the conjugate base of this weaker acid present as an anion is this onium salt PAG, then the second onium salt photoacid generator is considered a photodecomposable quencher and part of component (D), the Acid Quencher Component.

Component (C): Optional Additional Crosslinker

[0152] The EUV and e-beam compositions describe herein intended for negative tone development with an organic solvent may additionally contain as an optional additional crosslinker component, which is not a crosslinking compound of structure (I).

[0153] These additional crosslinker component are multifunctional compounds containing a moiety which under the influence of photogenerated acid form crosslinks in the photoresist film.

[0154] Examples of such components are multifunctional alkyl and aryl epoxides, which form crosslinking through ring opening of epoxides or N-methoxymethylated melamine crosslinker derivatives, benzyl alcohol derivatives or vinyl cyclic acetal derivatives which form crosslinks through the formation of reactive carbocations (Polymers for Microelectronics ACS Symposium Series ACS, (1993), Chapter 1 Chemically Amplification Mechanisms for Microlithography, E. Reichmanis *et al.*, pages 3) and (Chemical Amplification Resists for Microlithography Adv Polymer Sci, Hiroshi Ito (2005) 172, page 37).

[0155] Other examples of optional additional crosslinking components are recently described monomolecular epoxide [C. Popescu; G. O'Callaghan; A. McClelland; J. Roth; T. Lada; T. Kudo; R. Dammel; M. Moinpour; Y. Cao; A. P. G. Robinson, Proc. SPIE 11612, Advances in Patterning Materials and Processes XXXVIII, 116120K (5 April 2021); doi: 10.1117/12.2583888], [Richard A. Lawson, Clifford L. Henderson, Journal of Micro/Nanolithography, MEMS, and MOEMS, Vol. 9, Issue 1, 013016 (January 2010). DOI: 10.1117/1.3358383], [R. A. Lawson, C. T. Lee, C. L. Henderson, R. Whetsell, L. Tolbert, and Y. Wang, J. Vac. Sci. Technol. B, 25 (6), 2140 –2144 (2007).DOI 10.1116/1.2801885].

Component (D): Optional Acid Quencher

[0156] The composition comprising the crosslinker compounds of structure (I) of the disclosed and claimed subject matter may additionally contain an acid quencher component which may be either a non-photodecomposable acid quencher, a photodecomposable acid quencher or a mixture of the two type of acid quencher. When the acid quencher component Component (D) is present it may range from about 0.04 to about 0.40 mole fraction compared to the molar amount of Component (A), the crosslinking compound of structure (I). In another embodiment it ranges from about 0.05 to about 0.40 mole fraction of Component (A), the crosslinking compounds of structure (I). In another embodiment it ranges from about 0.1 to about 0.35 mole fraction compared to the molar amount of Component (A). In another embodiment it ranges from about 0.15 to about 0.35

of component (A). In another embodiment it ranges from about 0.15 to about 0.30 mole fraction compared to the molar amount of component (A).

[0157] Without being bound by theory, non-photodecomposable quenchers have the effect of suppressing the diffusion of acid generated in the exposed area and are thought to contribute to the improvement of resolution.

[0158] Without being bound by theory, photo-decomposable quenchers are also material when formulated into chemically amplified photoresist of suppressing the diffusion of acid in the radiation exposed area, but because they are photodecomposable the concentration of the quencher in the exposed area is lower than in the unexposed area, creating a greater contrast between the concentration of quencher in unexposed and exposed areas which is thought to contribute further in the improvement of resolution.

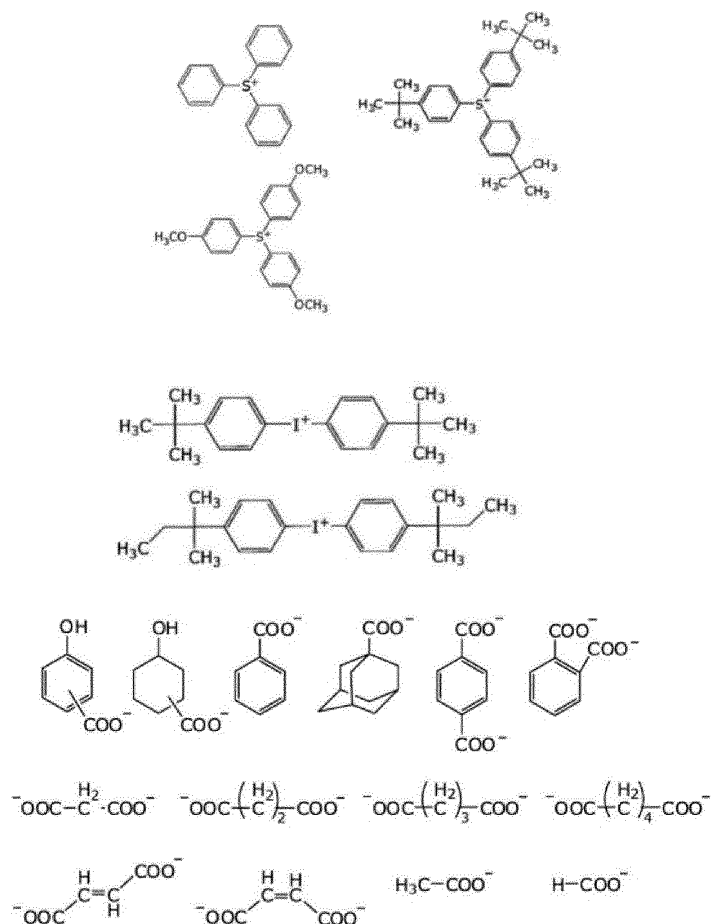
[0159] Photo-decomposable quenchers are different from the photo acid generator component (PAG) component (B). As a preferred form of the disclosed and claimed subject matter, Component (B) PAG's, as discussed above, are for instance onium salts of the conjugate base of very strong acid (a.k.a. anion). In a photoresist formulation photodecomposition of these onium salts releases in the areas exposed to radiation a very strong super acid released from the PAG (e.g., perfluoralkylsulfonic acid such as triflic acid which have a pka of ~ -6.85 as measured by ACD/LABS*, also see above detailed description of PAG component). As a preferred form, of the disclosed and claimed subject matter photodecomposition quencher are also onium salts of stronger conjugate bases (a.k.a. anions of weaker acids), which on irradiation releases a proton which protonates the conjugate base anion and thus removing this conjugate base as an acid quencher in the photoresist areas exposed to radiation.

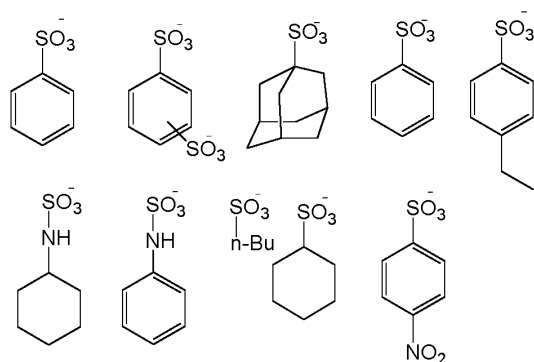
[0160] An example of photo-decomposable quenchers are photosensitive onium salt (e.g., diaryliodonium, triarylsulfonium) of a weak acid such as an photosensitive onium carboxylate or a photosensitive onium sulfonate of a weaker sulfonic acid, where the photodecomposition of the onium cation during lithographic exposure releases respectively converts a carboxylate anion to a free carboxylic acid, or converts this sulfonate anion a weak sulfonic acid having a pKa of higher than -2 (as measured by ACD/Labs*). Example such weak sulfonic are alkyl sulfonic acid (e.g., mesic acid, n-butylsulfonic acid), arylsulfonic acids (e.g., tosic acid, 4-ethylbenzenesulfonic acid) aminosulfonic acid (e.g., cyclamic acid) and the like. *(ACD/pK_a software version 4.0 for Microsoft windows, Advanced Chemistry development Inc 8 King Street East, Suite 107, Toronto,

Ontario Canada).

[0161] . These weak acids preferably have an acid dissociation constant pK_a as measured by ACD/Labs* of -1.9 to 8 (preferably -1 to 5).

[0162] The photoreaction quencher consists of cations and anions, and illustrative examples of specific cations and anions of weak acids are as follows:





[0163] Component (D), the acid quencher, may also be a non-photodecomposable quencher component in the disclosed and claimed composition containing the disclosed and claimed compound having structure (I) or any of its substructures described herein, if present, may be any suitable acid quenchers including amine compound or a mixture of amine compounds and a pK_a of at least 1 and up to 9, and having a boiling point above 100 °C at atmospheric pressure or non-photolabile onium salts of an acid having a pK_a of at least -1.9 such as ammonium salts of carboxylic acids with a pK_a of at least 0.5 or weak sulfonic acids as described above with a pK_a of at least -1.9. When Component (D) comprises a non-photodecomposable acid quencher either present alone or in combination with a photodecomposable acid quencher it is preferred if the content of this non-photodecomposable quencher is 0 to 1 mass %, relative to the total weight of the composition (preferably 0.01 to 0.5 mass %; preferably 0.02 to 0.1 mass %). The absence of a non-photodecomposable acid quencher is also an embodiment of this composition.

[0164] The content of this non-photodecomposable is preferably 0.1 to 20 mass % (preferably 0.1 to 5 mass %; preferably 0.1 to 1.0 mass %), relative to the total weight of component (A), more preferably 0.1 to 0.5 mass %).

[0165] Non-limiting exemplified embodiments of the non-photodecomposable acid quencher additive are amine basic compound which are preferably selected from the group consisting of C_{1-16} primary aliphatic amine compound, C_{2-32} secondary aliphatic amine compound, C_{3-48} tertiary aliphatic amine compound, C_{6-30} aromatic amine compound and C_{5-30} heterocyclic amine compounds.

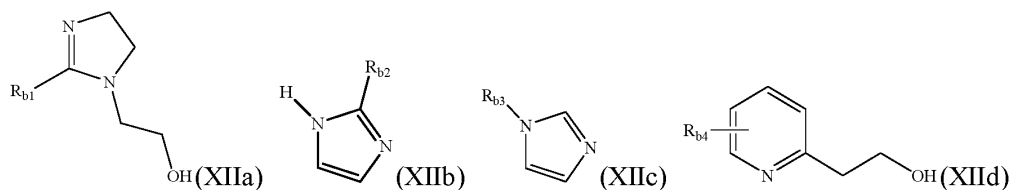
[0166] Further examples of basic compounds include ethylamine, n-octylamine, n-heptylamine, ethylenediamine, Triethylamine, tri-n-octylamine, diethylamine, triethanolamine, tris[2-(2-methoxyethoxy)ethyl]amine, 1,8-Diazabicyclo[5.4.0]-7-undecene, 1,5-Diazabicyclo[4.3.0]-5-

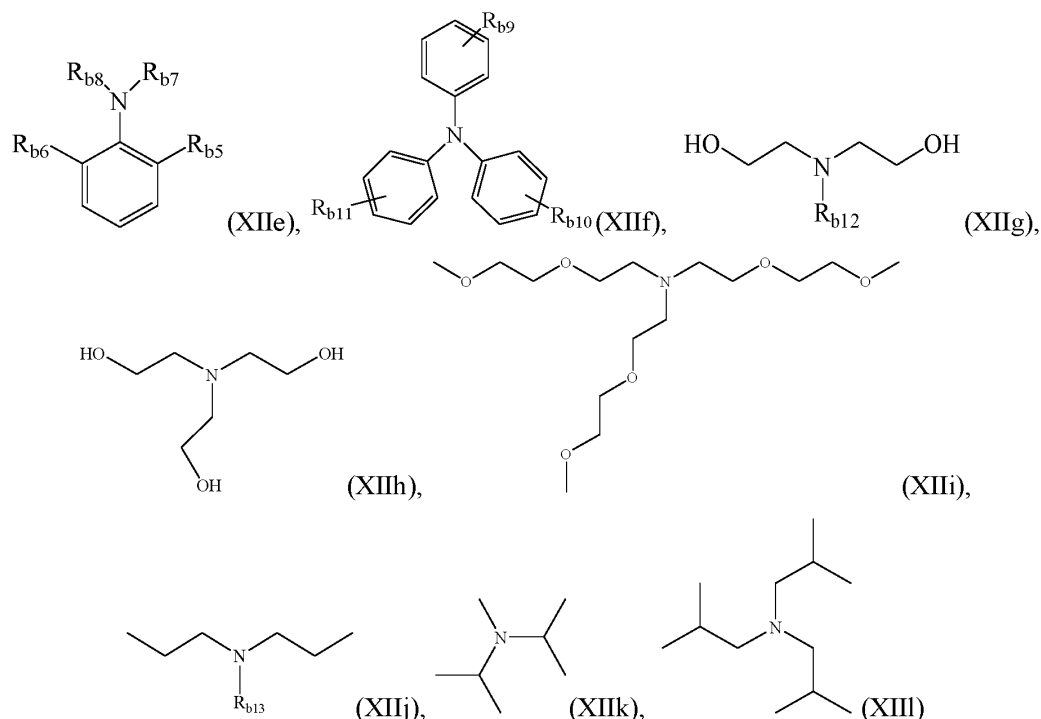
nonene, 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, 1,5,7-Triazabicyclo[4.4.0]dec-5-ene.

[0167] In one embodiment of the non-photodecomposable quencher when it is an amine is one which has a base dissociation constant pK_b (H_2O) of basic compounds is preferably -12 to 5 (preferably 1 to 4) and a molecular weight preferably between 20 and 500 (preferably between 60 and 40)

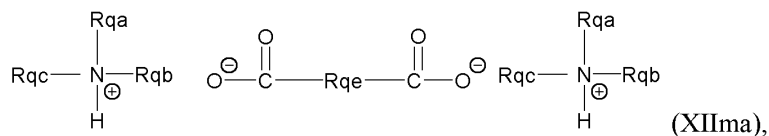
[0168] In another embodiment, when said acid quenchers are present as amine acid quenchers, these include, but are not limited to, C₁₋₁₆ primary aliphatic amine compound, C₂₋₃₂ aromatic secondary aliphatic amine compound, C₃ to C₄₈ tertiary aliphatic amine compound, C₆₋₃₀. Another examples of amine compounds are C₅ to C₃₀ heterocyclic amine compounds, preferably selected from the group consisting of C₁ to C₁₆ primary aliphatic amine compound, C₂ to C₃₂ secondary aliphatic amine compound, C₃ to C₄₈ tertiary aliphatic amine compound, C₆ to C₃₀ aromatic amine compound and C₅ to C₃₀ heterocyclic amine compounds and amine compounds having structures (XIIa), (XIIb), (XIIc), (XIId), (XIIe), (XIIf), (XIIf), (XIIg), (XIIh), (XIIi) (XIIj), (XIIk) and (XIII) or a mixture of compounds from this group; wherein R_{b1} is C₁ to C₂₀ saturated alkyl chain or a C₂ to C₂₀ unsaturated alkyl chain; R_{b2}, R_{b3}, R_{b4}, R_{b5}, R_{b6}, R_{b7}, R_{b8}, R_{b9}, R_{b10}, R_{b11}, R_{b12} and R_{b13} are independently selected from the group of H, and a C₁ to C₂₀ alkyl as shown below:

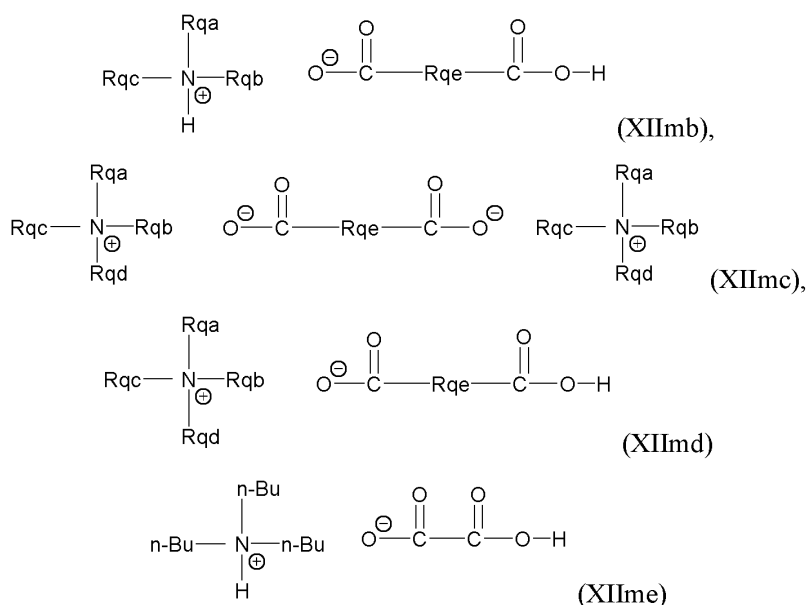
[0169] In another embodiment-amine compound, where component (D), said acid quencher, is present, it may be an amine or a mixture of amine compounds having a boiling point above 100 °C, at atmospheric pressure, and which have a pK_a of at least 1. Such acid quenchers include, but are not limited to, amine compounds having structures (XIIa), (XIIb), (XIIc), (XIId), (XIIe), (XIIf), (XIIg), (XIIh), (XIIi) (XIIj), (XIIk) and (XIII) or a mixture of compounds from this group; wherein R_{b1} is C₁ to C₂₀ saturated alkyl chain or a C₂ to C₂₀ unsaturated alkyl chain; R_{b2}, R_{b3}, R_{b4}, R_{b5}, R_{b6}, R_{b7}, R_{b8}, R_{b9}, R_{b10}, R_{b11}, R_{b12} and R_{b13} are independently selected from the group of H, and a C₁ to C₂₀ alkyl as shown below:





[0170] In one particular embodiment of Component (D), it is a non-photo-decomposable onium salt such as tetraalkylammonium or trialkylammonium salts of carboxylic acids. Specific non limiting examples are mono(tetraalkyl ammonium) of dicarboxylic acid, di(tetraalkyl ammonium) salts of dicarboxylic acid, mono(trialkyl ammonium) of dicarboxylic acid, or di(trialkyl ammonium) salts of dicarboxylic acid. Non-limiting examples of suitable dicarboxylic acid for these salts are oxalic acid, maleic acid, malonic acid, fumaric acid, phthalic acid and the like. Structure (XIIma) to (XIImd) gives a general structure for such materials wherein R_{qa} to R_{qd} are independently a C₄ to C₈ alkyl group, R_{qe} is a valence bond, an arylene moiety, a C₁ to C₄ alkylene moiety, an alkenyl moiety(-C(R_{qf})=C(R_{qg})-, wherein R_{qf} and R_{qg} are independently H or a C₁ to C₄ alkyl). Structure (XIIme) gives a specific example of such a material.





Component (E): Optional Spin coating solvent

[0171] The composition of the disclosed and claimed subject matter preferably contains an additional component (E), which is a solvent.

[0172] Examples of solvents are water, hydrocarbon solvents, ether solvents, ester solvents, alcohol solvents, ketone solvents or a combination of any of these.

[0173] Examples of solvent component (E) include water, and organic solvent. Examples of organic solvents are n-pentane, I-pentane, n-hexane, I-hexane, n-heptane, I-heptane, 2, 4-trimethylpentane, n-octane, I-octane, cyclohexane, methylcyclohexane, benzene, toluene, xylene, ethylbenzene, trimethylbenzene, methyl ethylbenzene, n-propylbenzene, I-propylbenzene, diethylbenzene, I-butylbenzene, triethylbenzene, di-I-propylbenzene, n-amylnaphthalene, trimethylbenzene, methanol, ethanol, n-propanol, I-propanol, n-butanol, i-butanol, sec-butanol, t-butanol, n-pentanol, I-pentanol, 2-methylbutanol, sec-pentanol, t-pentanol, 3-methoxybutanol, n-hexanol, 2-methylpentanol, sec-hexanol, 2-ethylbutanol, sec-heptanol, heptanol-3, n-octanol, 2-ethylhexanol, sec-octanol, n-nonyl alcohol, 2,6-dimethylheptanol-4, n-decanol, sec-undecyl alcohol, trimethylnonyl alcohol, sec-tetradecyl alcohol, sec-heptadecyl alcohol, phenol, cyclohexanol, methylcyclohexanol, 3,3,5-trimethylcyclohexanol, benzyl alcohol, phenylmethylcarbinol, diacetone alcohol, cresol, ethylene glycol, propylene glycol, 1,3-butylene glycol, pentanediol-2,4, 2-methylpentanediol-2,4, hexanediol-2,5, heptanediol-2,4, 2-

ethylhexanediol-1,3, diethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, tripropylene glycol glycerin, acetone, methyl ethyl ketone, methyl-n-propyl ketone, methyl-n-butyl ketone, diethyl ketone, methyl-I-butyl ketone, methyl-n-pentyl ketone, ethyl-n-butyl ketone, methyl-n-hexylketone, butylketone, trimethylnonanone, cyclohexanone, cyclopentanone, methylcyclohexanone, 2,4-pentandione, acetonylacetone, diacetone alcohol, acetophenone, ethyl ether, i-propyl ether, n-butyl ether, n-hexyl ether, 2-ethylhexyl ether, ethylene oxide, 2-propylene oxide, dioxolane, 4-methyldioxolane, dioxane, dimethyldioxane, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol diethyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-n-hexyl ether, ethylene glycol monophenyl ether, ethylene glycol mono-2-ethyl butyl ether, ethylene glycol dibutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol diethyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol di-n-butyl ether, diethylene glycol mono-n-hexyl ether, ethoxytriglycol, tetraethylene glycol di-n-butyl ether, propylene glycol monomethyl ether (PGME), propylene glycol monoethyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol monopropyl ether, dipropylene glycol monobutyl ether, tripropylene glycol monomethyl ether, tetrahydrofuran, 2-methyltetrahydrofuran, diethylcarbonate, methyl acetate, ethyl acetate, γ -butyrolactone, γ -valerolactone, n-propyl acetate, I-propyl acetate, n-butyl acetate, I-butyl acetate, sec-butyl acetate, n-pentyl acetate, sec-pentyl acetate, 3-methoxybutyl acetate, methylpentyl acetate, 2-ethylbutyl acetate, 2-ethylhexyl acetate, benzyl acetate, cyclohexyl acetate, methylcyclohexyl acetate, n-nonyl acetate, methyl acetate, ethyl acetate, ethylene glycol acetate monomethyl ether, ethylene glycol acetate monoethyl acetate ether, diethylene glycol acetate monomethyl ether, diethylene glycol acetate monoethyl ether, diethylene glycol acetate mono-n-butyl ether, propylene glycol acetate monomethyl ether, propylene glycol acetate monoethyl ether, propylene glycol acetate monopropyl ether, propylene glycol acetate monobutyl ether, dipropylene glycol acetate monomethyl ether, dipropylene glycol acetate monoethyl ether, glycol diacetate, methoxytriglycol acetate, ethyl propionate, n-butyl propionate, I-amyl propionate, diethyl oxalate, di n-butyl oxalate, methyl lactate, ethyl lactate (EL), γ -butyrolactone, n-butyl lactate, n-Amyl lactate, diethyl malonate, dimethyl phthalate, diethyl phthalate, ester solvents such as propylene glycol 1-monomethyl ether 2-acetate (PGMEA), propylene glycol monoethyl ether acetate, and propylene glycol monopropyl ether acetate; N-methylformamide,

N,N-dimethylformamide, N,N-diethylformamide, acetamide, N-methylacetamide, N, N-dimethylacetamide, N-methylpropionamide, N-methylpyrrolidone, dimethyl sulfide, diethyl sulfide, these include thiophene, tetrahydrothiophene, dimethylsulfoxide, sulforane, and 1,3-propane sultones. These solvents can be used alone or mixed with two or more species.

[0174] A preferred embodiment is where the spin coating solvent is an organic spin coating solvent, which is any of the above described organic solvents or mixtures of two or more species which specifically excludes water.

[0175] When Component (E) is an organic spin coating solvent in one preferred embodiment it is one consisting of practically only PGMEA, PGME, EL or a mixture of any of these; and preferably it consists practically only of PGMEA, PGME, or EL; more preferably, it consists practically only of EL.

[0176] In relation to other layers and membranes, solvent component (E) is also water-free. For example, solvents the total amount of water is preferably less than 0.1 mass % (preferably less than 0.1 mass %). 0.01 mass % or less; preferably 0.001 mass % or less). The fact that the solvent does not contain any water (0.000 mass %) is also a preferred form of the disclosed and claimed subject matter.

[0177] The content of the solvent (E) is preferably in the range from 95.0 to 99.9 mass%, more preferably 96.0 to 99.9 mass%, and very preferably 97.0 to 99.9 mass % based on the total mass of the composition.

[0178] Also, these organic spin coating solvents may also be used as “organic solvent developer” for developing the negative photoresist compositions comprising Component (A), said compound of structure (I) after it is coated on a substrate and exposed through a mask to e-beam or EUV radiation as described below, the unexposed regions of the coated film as delineated by the mask pattern are removable by using development using these “organic solvent developers,” while the exposed regions of this coated film are crosslinked and not removable by this organic solvent development, forming a negative image. Although any organic spin casting solvent or mixture thereof as described herein may be used as an organic solvent developer, preferred organic solvent developers are ethyl lactate, PGME, PGMEA, n-butyl acetate (BuAC), ethyl lactate or mixtures thereof.

Component F: Other Optional Components

[0179] The composition of the disclosed and claimed subject matter may additionally other additives

other than non-solvent components (A) through (D). Where the additive (F) is dye, low alcohol, radicals, surfactants, surface smoothing agents, acids, basic compounds, substrate adhesion enhancing agent, antifoaming agent, preservative, or a combination of any of these. If this additives contains an acid or a base, it is also a preferred form of the disclosed and claimed subject matter to contain only one or the other.

[0180] The content of additive component (F) is preferably 0 to 10 mass % relative to the component (A), preferably 0 to 5 mass %, and preferably 0 to 1 mass %. The absence of additives (0.0 mass %) is also a preferred form of the present composition.

[0181] Acid can be used to adjust the pH value of the composition or to improve the solubility of additive components. The acids used are not limited, but include formic acid, acetic acid, propionic acid, benzoic acid, phthalic acid, salicylic acid, lactic acid, malic acid, citric acid, oxalic acid, malonic acid, succinic acid, fumaric acid, maleic acid, aconitic acid, glutaric acid, adipic acid, p-toluenesulfonic acid, this includes camphorsulfonic acid, any of these hydrates, and combinations of these. The acid content is preferably between 0.005 and 2, mass % based on the total weight of the composition. In one embodiment it is below 1 mass % (preferably 0.01 to 0.1 by mass %).

[0182] The surfactant can improve the applicability. Surfactants that may be used for the disclosed and claimed subject matter include (I) anionic surfactants, (II) cationic surfactants, or nonionic surfactants, more specifically (I) alkyl sulfonate, alkylbenzenesulfonic acid, and alkylbenzenesulfonate, (II) laurylpyridinium chloride, and laurylmethylammonium chloride, as well polyoxyethylene octyl ether, polyoxyethylene lauryl ether, polyoxyethylene acetylenic glycol ether, fluorine-containing surfactants (e.g., Florard (3M), Megaface (DIC), Surflon (AGC Seimi Chemical) and organic siloxane surfactants such as KF-53 and KP341 (Shin-Etsu Chemical) are examples.

[0183] These surfactants can be used alone or in a mixture of two or more types. The content of the surfactant is preferably 0 to 3 mass % relative to the total weight of the composition (more preferably 0.005 to 0.5 mass %; and most preferably 0.01 to 0.2 mass %).

[0184] The content of the surfactant is preferably in the range from 0.01 to 5 mass %, more preferably 0.01 to 1 mass %, very preferably 0.05 to 0.5 mass % based on the mass of the Component (A).

Preferred Composition Embodiments

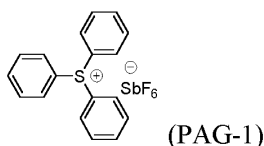
[0185] In one aspect of the disclosed and claimed subject matter, it is a formulations which

contains 1.0 to 1.5% w/w (preferentially 1.0 to 1.25% w/w) solution of solid compounds in an organic spin coating solvent and contains the following non-solvent components, Component (A) said crosslinking compound of structure (I), Component (B) said PAG, and component (D) said acid quencher.

[0186] The following are preferred solid components and their preferred ranges:

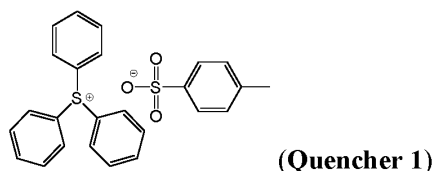
[0187] For component (A), at least one disclosed and claimed compound of structure (I) or any of its substructures described herein, in one embodiment, the amount thereof in the disclosed and claimed composition is in a range from about 95 mol% to about 10 mol% compared to the total moles of all solid components including component (A).

[0188] Component (B) is at least one photoacid generator (PAG) as described herein. In one embodiment this is triarylsulfonium salt of a diaryliodonium salt PAG which releases upon exposure a superacid having a pK_a (H_2O) smaller than -5 (as calculated by ACD*), such as triflic acid, nonafluorobutanesulfonic acid, $HAsF_6$ or $HSbF_6$, (as described in more detail in the section on Component (B), where the amount of this component is from about 0.15 to about 0.64 mole fraction compared to the number of moles of Component (A) the crosslinking compound of structure (I) (moles of Component (B)/moles of component (A)). In another embodiment its amount is from about 0.15 to about 0.50 mole fraction compared to the number of moles of Component (A). In another embodiment its amount is from about 0.20 to about 0.50 mole fraction compared to the number of moles of Component (A). In another embodiment its amount is from about 0.20 to about 0.40 mole fraction compared to the number of moles of Component (A). In another embodiment its amount is from about 0.20 to about 0.35. In one embodiment Component (B) is a triarylsulfonium salt of a super acid, which has structure (IIIa), where the anion A^- is the conjugate base of a super acid. In one preferred embodiment Component (B) is a triphenylsulfonium salt of a super acid. In another it is triphenylsulfonium hexafluoroantimonate (PAG-1).



[0189] In this preferred embodiment Component (C), the acid quencher component, as described herein, is present in an amount from about 0.13 to about 0.80 mole fraction compared to the molar amount of the PAG component (moles of Component (C)/moles of Component (B)). In another

embodiment its amount is from about 0.2 to about 0.7 mole fraction. In another embodiment its amount is from about 0.20 to about 0.6 mole fraction. In another embodiment its amount is from about 0.20 to about 0.5 mole fraction. In another embodiment its amount is from about 0.20 to about 0.4 mole fraction. In one embodiment its amount is about 0.35 mole fraction. In one preferred embodiment the acid quencher component is at least one photodecomposable acid quencher, as described herein, which is a triarylsulfonium or diaryliodonium salt of a weak acid with a pK_a (H_2O) (as calculated by ACD*) higher than -2. In one embodiment it is a triphenylsulfonium salt of a weak sulfonic acid, as described herein. In one embodiment it is triphenylsulfonium tosylate (Quencher-1). In one aspect of this embodiment, it is preferred if Component (E) said organic spin coating solvent is selected from ethyl lactate, PGMEA, PGME and mixtures thereof.



Manufacturing Methods: Resist Films and Resist Patterns

[0190] The manufacturing method of the resist film by the disclosed and claimed subject matter involves applying the above composition above the substrate and heating it form a film.

[0191] Another aspect of the disclosed and claimed subject matter is the process of forming negative image with a negative photoresist by EUV or e beam exposure, comprising step ia) to va)

i) coating the negative chemically amplified EUV photoresist or beam composition described herein on a substrate, to form a coated film,

ii) baking said coated film to form a baked coated film,

iii) exposing regions of the baked coated film through a mask with EUV or e-beam radiation, forming exposed and unexposed regions,

iv) an optional post exposure baking step,

v) developing away the unexposed regions with an organic solvent developer forming a negative image pattern in said coated photoresist on the substrate,

vi) etching the substrate with a plasma or a chemical etchant using said negative image pattern as a mask, forming a negative image in the substrate.

[0192] The manufacturing method of the resist film according to the present disclosed and claimed

subject matter comprises applying the above-described composition above the substrate; and optionally heating the applied composition.

[0193] The resist film according to the disclosed and claimed subject matter is manufactured by the above-described method.

[0194] The manufacturing method of the resist pattern according to the disclosed and claimed subject matter comprises; producing a resist film by the above-described method; exposing the resist film; optionally heating the exposed resist film; and developing the exposed resist film.

[0195] The following describes one form of the manufacturing process of the disclosed and claimed subject matter.

[0196] First, the composition according to the disclosed and claimed subject matter is applied above the substrate, and heated, and a resist film is formed.

[0197] Examples of substrates are silicon/silicon dioxide coated substrates, silicon nitride substrates, silicon wafer substrates, glass substrates and ITO substrates. The composition is applied by an appropriate method.

[0198] For the purposes of the disclosed and claimed subject matter this includes the case where it is formed directly above these substrates and the case where it is formed on other layers coating these substrates. For example, a flattening film and/or a lower layer film may be formed directly above the substrate, and the composition of the disclosed and claimed subject matter may be applied directly above it. The method of application is not specifically limited, but can be, for example, by application with a spinner or coater. After application, a resist film is formed by optionally heating (pre-exposure bake or post-application bake (PAB)). This heating is also called pre-bake and is carried out, for example, by a hot plate. The heating temperature is preferably between 60 and 120 °C (more preferably 80 to 100 °C). The temperature here is the heating atmosphere, for example, the heating surface temperature of the hotplate. The heating time is preferably 30-300 seconds (more preferably 30-180 seconds; more preferably 50-90 seconds). Heating is carried out preferably in atmospheric or nitrogen gas atmosphere.

[0199] Resist film thickness is preferably 5 to 70 nm (preferably 7 to 55 nm).

[0200] The resist film is exposed through a predetermined mask. The wavelength of light used for exposure is not particularly limited.

[0201] Specifically, although it is not limited, exposure at wavelengths between 13.5 and 248 nm is preferable.

[0202] Specific examples of radiation are KrF excimer laser (wavelength 248 nm), ArF excimer laser (wavelength 193 nm), and extreme ultraviolet (EUV) (wavelength 13.5 nm) can be used, preferably EUV. These wavelengths allow a range of $\pm 1\%$.

[0203] Post-exposure baking (PEB) can also be performed if necessary. The temperature of the PEB is preferably 50 to 200 °C (preferably 60 to 110 °C) and the heating time is preferably 30 to 240 seconds (preferably 45 to 100 seconds).

[0204] On the exposed resist film, a resist pattern is formed by developing with a developer. Development includes alkaline development and organic solvent development, but preferably organic solvent development. The developer contains organic solvents and more preferably consists of organic solvents. For organic solvent development, the developer is hydrocarbon, ether, ester, ketone solvents and alcoholic solvents are listed, preferably ester solvents or ketone solvents. Examples of developing solutions include 2-heptanone, butyl acetate, and PGMEA.

[0205] The manufacturing method of the fabricated substrate by the disclosed and claimed subject matter is as follows:

[0206] To fabricate a substrate, you first need to use the process described above to form a resist pattern and use this resist pattern as a mask.

[0207] Preferably, this resist pattern is used as a mask, processing the resist underlayer and/or substrate as required. By etching the resist lower layer film and substrate at once.

[0208] The substrate may be processed, and after etching the resist lower layer film, this lower etched resist film may be used as a mask.

[0209] It is also possible to process it in stages, such as etching the substrate.

[0210] The method of manufacturing the device by the disclosed and claimed subject matter would include the above method, preferably further including the process of forming wiring on the processed substrate. These processing can be applied using well-known methods. After that, if necessary, the substrate is cut into chips and connected to the lead frame.

[0211] It is then packaged in resin. For the purpose of the disclosed and claimed subject matter, this packaged product is called a device. Devices include semiconductor devices, liquid crystal display devices, organic EL display devices, plasma display devices, and solar cell elements are listed, preferably semiconductor devices.

[0212] The disclosed and claimed subject matter relates to the use of a composition containing a compound represented by structure (I) or any one of its substructures described above for the

formation of a resist film. The preferred form of the composition is described above.

[0213] More generally, the subject matter relates to a composition comprising at least one crosslinking compound described herein, and an acid generating agent.

[0214] Another aspect of said composition is one which comprises at least two different crosslinking compound described herein, and an acid generating agent.

[0215] Another aspect of said composition is one wherein said acid generator contains a photoacid generator.

[0216] Another aspect of said composition is one wherein said photoacid generator are selected from the group consisting of iodonium salts, tetrahydrothiophenium salts, sulfonium salts, diazonium salts pyridinium salts.

[0217] Another aspect of said composition is one wherein the molar ratio of the photoacid generator to the compound represented by structure (I) (the molar number of the photoacid generator/ the molar number of the compound represented by structure (I)) is 0.66 or less. In another embodiment 0.55 or less.

[0218] Another aspect of said composition is one wherein at least two acid generators are present.

[0219] Another aspect of said composition is one which including additional solvents.

[0220] Another aspect of said composition is one wherein it is a photoresist composition.

[0221] Another aspect of said composition is one wherein it is negative photoresist composition.

[0222] Another aspect of the subject matter is a method for producing a resist film comprising:

applying any of these compositions according as a resist film on a substrate.

[0223] Another aspect of the subject matter is a method for producing a resist pattern comprising:

producing a resist film by the method according as described above;

exposing the resist film;

optionally, heating the exposed resist film; and

developing the exposed resist film.

[0224] Another aspect of the subject matter is a method for producing a processed substrate comprising:

producing a resist pattern by the method described above; and processing a substrate

by using the resist pattern as a mask.

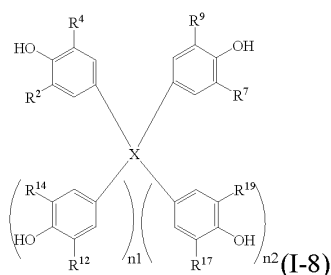
[0225] The method for producing a processed substrate, further comprises the step of forming wiring on the processed substrate.

Method for selective iodination of phenolic compound

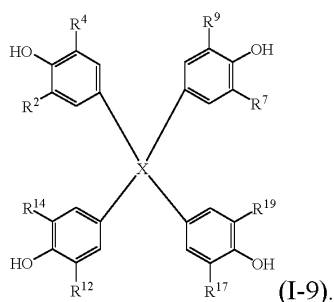
[0226] The disclosed subject matter also pertains to a selective iodination method for multi-phenolic compounds at the ortho position to the phenol, where the resultant multi-phenolic compounds selectively iodinated at the position ortho to the phenol precursors of said crosslinking compounds where this methods employs a reagent comprising 1-iodopyrrolidine in the presence of a reagent comprising an arylsulfonic acid.

[0227] More specifically this is a method for the selective iodination of a multi-phenolic compound of structure (I-8) which employs both a reagent comprising a 1-iodopyrrolidine-2,5-dione moiety and a reagent comprising an aryl sulfonic acid moiety, to selectively effect iodination at position R^2 , R^4 , R^9 , R^7 , R^{12} , R^{14} , R^{17} , or R^{19} , originally substituted by H, where single iodination or multiple iodation may be selected by increasing the molar amount of these reagents relative to the number of these positions to be iodinated, where in structure (I-8), n_1 and n_2 are each independently 1 or 0, X is $C_pH_{2p-n_1-n_2}$ or $C_{6+4(q-1)}H_{4+2(q-1)-n_1-n_2}$, p is 1 to 6, q is 1 to 3.

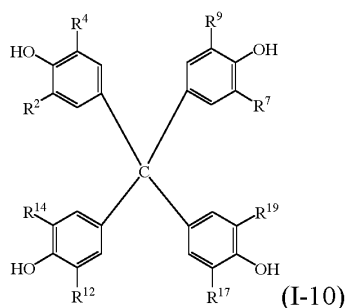
- a. dissolving said multi-phenolic compound of structure (I-8) where the group R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} or R^{19} to be iodinated is H and the reagent comprising an aryl sulfonic acid in an alkylcyano solvent with stirring at temperature of about -5°C to about 5°C ,
- b. keeping the temperature of the stirred reaction solution at about -5°C to about 5°C , adding to it said reagent comprising a 1-iodopyrrolidine-2,5-dione moiety dissolved in an alkylcyano solvent,
- c. stirring the resultant reaction mixture at a temperature of about -5°C to about 5°C , until the reaction is complete,
- d. isolating the resultant iodinated multi-phenolic compound.



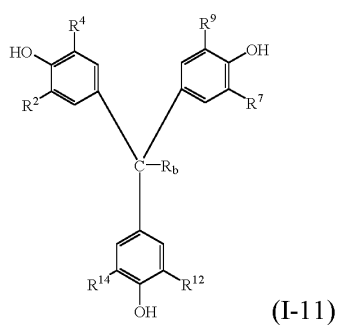
[0228] In one aspect of this method said multi-phenolic compound more specifically has structure (I-9). where R^2 , R^4 , R^9 , R^7 , R^{12} , R^{14} , R^{17} , or R^{19} , are positions to selectively effect iodination, originally substituted by H,



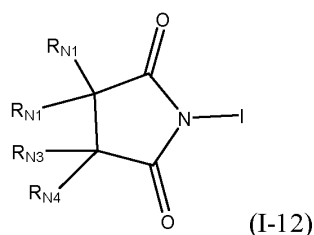
[0229] In one aspect of this method said multi-phenolic compound said phenolic compound more specifically has structure (I-10), where R^2 , R^4 , R^9 , R^7 , R^{12} , R^{14} , R^{17} , or R^{19} , are positions to selectively effect iodination, originally substituted by H,



[0230] In one aspect of this method said multi-phenolic compound said phenolic compound more specifically has structure (I-11) where R^2 , R^4 , R^9 , R^7 , R^{12} , R^{14} , are positions to selectively effect iodination, originally substituted by H, and R_b is selected from the group consisting of a C_{1-6} straight-chain alkyl or C_{3-15} branched alkyl.

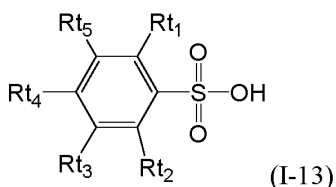


[0231] In one aspect of this method said reagent comprising a 1-iodopyrrolidine-2,5-dione moiety has structure (I-12), where R_{N1} , R_{N2} , R_{N3} , and R_{N4} are individually selected from H, a C_{1-5} straight-chain alkyl or C_{3-5} branched alkyl.



[0232] In one aspect of this method said reagent comprising a 1-iodopyrrolidine-2,5-dione moiety is 1-iodopyrrolidine-2,5-dione.

[0233] In one aspect of this method said reagent comprising an aryl sulfonic acid has structure (I-13), wherein substituents Rt₁ to Rt₅ are individually selected from H, a C₁₋₅ straight-chain alkyl or C₃₋₅ branched alkyl, C₁₋₅ straight-chain alkoxy or C₃₋₅ branched alkoxy, a halide, a C₁₋₅ straight-chain fluorinated alkyl or C₃₋₅ branched fluorinated alkyl, and nitro.



[0234] In one aspect of this method said reagent comprising an aryl sulfonic acid moiety is toluene sulfonic acid.

[0235] In one aspect of this method said alkylcyano solvent is one where the alkyl moiety is a C₁₋₅ straight-chain alkyl or C₃₋₅ branched alkyl.

[0236] In one aspect of this method said alkylcyano solvent is acetonitrile.

EXAMPLES

[0237] Reference will now be made to more specific embodiments of the present disclosure and experimental results that provide support for such embodiments. The examples are given below to more fully illustrate the disclosed subject matter and should not be construed as limiting the disclosed subject matter in any way.

[0238] It will be apparent to those skilled in the art that various modifications and variations can be made in the disclosed subject matter and specific examples provided herein without departing from the spirit or scope of the disclosed subject matter. Thus, it is intended that the disclosed subject matter, including the descriptions provided by the following examples, covers the modifications and variations of the disclosed subject matter that come within the scope of any claims and their equivalents.

[0239] Chemicals and Characterization

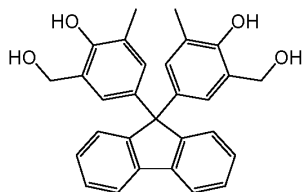
[0240] All chemicals unless otherwise indicated were purchased from Sigma Aldrich (3050 Spruce St., St. Louis, MO 63103) or Fisher Scientific International, Inc. (Hampton, New Hampshire) and used as received without further purification unless otherwise specified. Anhydrous or high-performance liquid chromatography (HPLC) grade solvents were used unless otherwise stated.

[0241] Characterization Methods

[0242] ^1H NMR spectra were recorded on a Bruker Avance HD 400 (400 MHz) spectrometer at room temperature using deuterated solvents from Sigma-Aldrich (Merck). Chemical shifts were reported as δ values in part per million (ppm) and were calibrated according to a residual protic solvent (chloroform at δ 7.26 ppm, acetone at δ 2.05 ppm, DMSO at 2.50 ppm or methanol at δ 3.31 ppm) as an internal reference. ^{13}C NMR spectra were recorded on a Bruker Avance HD 400 (101 MHz) spectrometer using the central resonance of the triplet of CDCl_3 at δ 77.16 ppm, the central resonance of the septuplet of MeOD at 49.09 ppm, the central resonance of the septuplet of DMSO- d_6 at 39.51, or the central resonance of the septuplet of acetone- d_6 at 29.84 ppm as an internal reference. The glass transition temperature, T_g , of the crosslinker compounds was measured on a TA Instruments Q1000 modulated differential scanning calorimeter (DSC) at a heat/cool rate of $10^\circ\text{C}/\text{min}$ under N_2 flow for three heat/cool cycles. T_g was determined from the second heating/cooling cycle.

Synthesis Example 1: Synthesis of ((9H-fluorene-9,9-diyl)bis(5-methyl-6-(oxiran-2-ylmethoxy)-3,1-phenylene))dimethanol

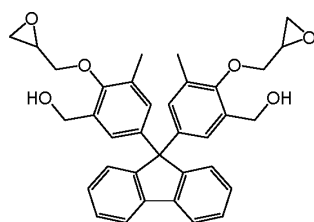
1.1 Synthesis of 4,4'-(9H-fluorene-9,9-diyl)bis(2-(hydroxymethyl)-6-methylphenol)



[0243] 48.39 g of 9,9-bis(4'-hydroxy-3'-methylphenyl)fluorene (CAS: 88938-12-9) was stirred in 96.8 g of methanol in a 2L flask. 121.5 g of 10 wt % sodium hydroxide in water was slowly added to obtain a solution. Under a gentle nitrogen stream, 194 ml of 37 wt% aqueous formaldehyde (CAS: 50-00-0) was dropwise added. After addition, the mixture was stirred for 4 days at room temperature. 800 ml of water was added. With ice cooling, 10 wt % HCl aqueous solution was slowly added until PH 4, resulting in a thick solid suspension. Suitable amount of saturated sodium

chloride solution was added. The solid formed was collected by filtering and water rinse. The solid was dried in 56 °C vacuum oven to obtain 71.4 g off-white solid. ¹H NMR (400 MHz, DMSO-d₆): 2.05 ppm (6H), 4.45 ppm (4H), 5.2 ppm (2H), 6.7 ppm (2H), 6.8 ppm(2H), 7.3-7.5 ppm (6H), 7.9 ppm (2H) and 8.4 ppm (2H).

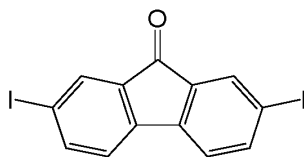
1.2 Synthesis of ((9H-fluorene-9,9-diyl)bis(5-methyl-6-(oxiran-2-ylmethoxy)-3,1-phenylene))dimethanol



[0244] 30 g of 4,4'-(9H-fluorene-9, 9-diyl)bis(2-(hydroxymethyl)-6-methylphenol) prepared above was dissolved in 250 g of DMF to obtain a solution to which 72 g of cesium carbonate was added and stirred for 1 hr under a gentle nitrogen stream. After 29.32 g of epibromohydrin was added dropwise over 30 min, the mixture was stirred at room temperature for 44 hrs. The mixture was filtered to remove the solids. The filtrate was slowly poured into 2L 1 wt % aqueous ammonium chloride solution with stirring. The solid formed was collected by filtering and washed thoroughly with water. The solid was dried in 50 °C vacuum oven to obtain 28.2 g off-white solid. ¹H NMR (400MHz, DMSO-d₆): 2.1 ppm (6H), 2.6-2.8 ppm (4H), 3.1 ppm (2H), 3.6 ppm (2H), 4.1 ppm (2H), 4.5 ppm (4H), 5.0 ppm (2H), 6.8 ppm (2H), 7.0 ppm(2H), 7.3-7.5 ppm (6H), and 7.9 ppm (2H).

Synthesis Example 2: Synthesis of ((2,7-diiodo-9H-fluorene-9,9-diyl)bis(5-methyl-6-(oxiran-2-ylmethoxy)-3,1-phenylene))dimethanol

2.1 Synthesis of 2,7-diiodo-9H-fluorene-9-one

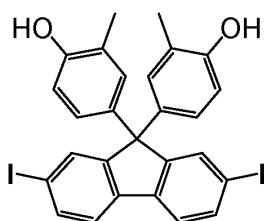


[0245] 28.3 g of 9-fluorenone (CAS: 486-25-9) was dissolved in 500 ml glacial acetic acid in a flask with cold water condenser and a magnetic stir bar. To the clear solution was added 45.3 g of iodine (CAS: 7553-56-2). Under stirring, 45.3 g of 95-98% sulfuric acid was added dropwise, followed by 50 ml carbon tetrachloride. Under a gentle nitrogen stream, the flask was immersed in 8 °C oil bath. 130 ml of 30 wt % aqueous hydrogen peroxide solution was added dropwise over

3 hr. After addition stirring was continued at 80°C for another hour to obtain a suspension. After the mixture was allowed to cool to room temperature, the crude target compound was collected by filtering and acetic acid washing. The crude compound was stirred in water and residue acid was neutralized by adding aqueous sodium bicarbonate solution. The solid was collected by filtering, water rinse and dried in a 50 °C vacuum oven to obtain about 50 g of crude compound.

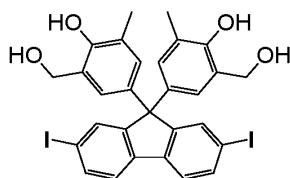
[0246] Another batch was prepared in a similar manner. Crude compound combined from the 2 batches was dissolved in about 650 g of toluene at 110 °C to obtain a clear colored solution. The solution was allowed to cool to room temperature, producing needle crystal. The crystal was collected by filtering and toluene washing. This process was repeated one more time. The purified crystal was dried in 80 °C vacuum oven to obtain about 84 g of 2,7-diiodo-9H-fluorene-9-one. ¹H NMR (400 MHz, methanol-d₄): 7.25 ppm (2H), 7.8 ppm (2H) and 7.9 ppm (2H).

2.2 Synthesis of 4,4'-(2,7-diiodo-9H-fluorene-9,9-diyl)bis(2-methylphenol)



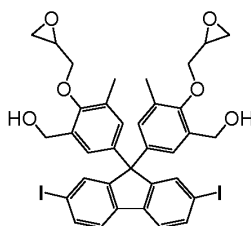
[0247] 83.8 g of 2,7-diiodo-9H-fluorene-9-one prepared above was stirred in 470 g of toluene into which 131.6 g of o-cresol (CAS: 95-48-7), 3.6 g of 3-mercaptopropionic acid (CAS: 107-96-0) and 40.1 g of methanesulfonic acid (CAS: 75-75-2) were added. Under a gentle nitrogen stream the mixture was agitated at room temperature for about 3 days, resulting in a thick suspension. The crude target compound was collected by filtering and toluene washing. The solid was stirred in water and the mixture was neutralized by aqueous sodium bicarbonate solution, followed by filtering and water washing. The solid was dried in a 60 °C vacuum oven. The dried solid was dissolved in acetone and slowly poured into 2L heptane with stirring. The solid obtained was recovered by filtering, heptane washing and oven drying to give about 112 g of 4,4'-(2,7-diiodo-9H-fluorene-9,9-diyl)bis(2-methylphenol). ¹H NMR (400MHz, DMSO-d₆): 2.0 ppm (6H), 6.7 ppm (6H), 7.6-7.8 ppm (6H) and 9.3 ppm (2H).

2.3 Synthesis of 4,4'-(2,7-diiodo-9H-fluorene-9,9-diyl)bis(2-(hydroxymethyl)-6-methylphenol)



[0248] 101 g of 4,4'-(2,7-diiodo-9H-fluorene-9,9-diyl)bis(2-methylphenol) prepared above was stirred with a mixture of 200 g of methanol and 200 g of 8 wt% NaOH aqueous solution under ice cooling to obtain a solution. Under nitrogen purge, 360 ml 37 % aqueous formaldehyde solution (CAS: 50-50-0) was added dropwise, followed by stirring at room temperature for about 3 days. The reaction mixture was slowly poured into 1.5 L water with stirring. The mixture was acidified by aqueous oxalic acid. The solid formed was recovered by filtering and water rinse. The solid was purified by dissolving in acetone and precipitation in water again. The solid was dried in a vacuum oven to obtain about 100 g of desired 4,4'-(2,7-diiodo-9H-fluorene-9,9-diyl)bis(2-(hydroxymethyl)-6-methylphenol). ¹H NMR (400 MHz, DMSO-d₆): 2.05 ppm (6H), 4.5 ppm (4H), 5.2 ppm (2H), 6.6 ppm (2H), 6.8 ppm (2H), 7.6-7.8 ppm (6H) and 8.4 ppm (2H).

2.4 Synthesis of ((2,7-diiodo-9H-fluorene-9,9-diyl)bis(5-methyl-6-(oxiran-2-ylmethoxy)-3,1-phenylene))dimethanol

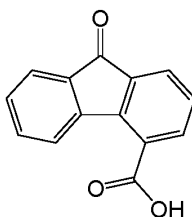


[0249] 95.6 g 4,4'-(2,7-diiodo-9H-fluorene-9,9-diyl)bis(2-(hydroxymethyl)-6-methylphenol) prepared above was dissolved in 400 g of DMF and 133 g of cesium carbonate was added, followed by stirring for 1 hr in nitrogen. After 47.3 g of epibromohydrin (CAS: 3132-64-7) was added dropwise, the reaction mixture was agitated for about 3 days. The inorganic salts were filtered out. The filtrate was slowly poured into 3 L water with stirring. The suspension was acidified to PH 3.5 by aqueous oxalic acid solution. The solid formed was recovered by filtering and water rinse, followed by drying in a vacuum oven. The dried solid was dissolved in acetone and the solution was stirred overnight with added activated carbon. After filtering out the activated carbon, the filtrate was poured into water, filtered and dried to obtain about 98 g of desired ((2,7-diiodo-9H-fluorene-9,9-diyl)bis(5-methyl-6-(oxiran-2-ylmethoxy)-3,1-phenylene))dimethanol. ¹H NMR

(400 MHz, DMSO-d₆): 2.2 ppm (6H), 2.6-2.8 ppm (4H), 3.3 ppm (2H), 3.5 ppm-4.1 ppm (4H), 4.5 ppm (4H), 5.0 ppm (2H), 6.8-7.1 ppm (4H), and 7.7-7.8 ppm (6H).

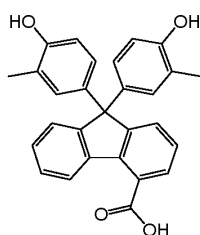
Comparative Synthesis Example 3: Oxiran-2-ylmethyl 9,9-bis(3-(methoxymethyl)-5-methyl-4-(oxiran-2-ylmethoxy)phenyl)-9H-fluorene-4-carboxylate (Comp A-5)

3.1 Synthesis of 9-oxo-9H-fluorene-4-carboxylic acid



[0250] 100.8 g of diphenic acid was dissolved in 200 ml 95-98 wt% sulfuric acid in a 500 ml flask with a magnetic bar and a cold-water condenser. Under a gentle nitrogen stream, the flask was immersed into a 120 °C oil bath. The reaction solution was agitated at this temperature for 50 min and allowed to cool to room temperature. The mixture was slowly poured into 3L water with stirring. The solid formed was collected by filtering, water rinse and dried in a vacuum oven. The solid was dissolved in aqueous sodium bicarbonate solution and the solution was stirred overnight with added activated carbon. After filtering out the carbon, the filtrate was diluted to about 2 L by water and acidified to PH 3 with 10 wt % HCl aqueous solution. The solid was recovered by filtering, water rinse and dried in an 80°C vacuum oven to give 79 g of 9-oxo-9H-fluorene-4-carboxylic acid. ¹H NMR (400 MHz, DMSO-d₆): 7.5 ppm (2H), 7.6 ppm (2H), 7.7 ppm (1H), 7.9 ppm (1H) and 8.3 ppm (1H).

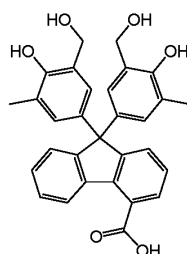
3.2 Synthesis of 9,9-bis(4-hydroxy-3-methylphenyl)-9H-fluorene-4-carboxylic acid



[0251] 30.82 g of 9-oxo-9H-fluorene-4-carboxylic acid prepared above, 151 g of o-cresol and about 700 ml of toluene were charged in a 1L plastic bottle. With stirring, 2 g of 3-mercaptopropionic acid (CAS: 107-96-0) and 22.3 g of methanesulfonic acid (CAS: 75-75-2) were added. The bottle was rolled on a mechanical roller for 3 days, resulting in a thick suspension. The crude target compound

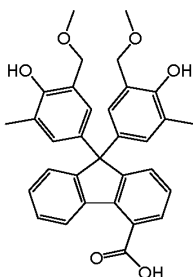
was collected by filtering and toluene washing. The solid was dissolved in 800 ml acetone and to the solution was added 37.37 g of triethyl amine under stirring. The solid formed was collected by filtering and acetone rinse. The solid was dispersed in water with stirring and the mixture was acidified to pH 0.65 with 10 wt % aqueous HCl solution. Filtering, water rinse and oven drying produced 57.3 g of off-white solid which was identified by ^1H NMR as 9,9-bis(4-hydroxy-3-methylphenyl)-9H-fluorene-4-carboxylic acid. ^1H NMR (400 MHz, DMSO- d_6): 2.0 ppm (6H), 6.6-6.8 ppm (6H), 7.45 ppm (4H), 7.6-7.7 ppm (2H), 8.3 ppm (1H) and 9.3 ppm (2H).

3.3 Synthesis of 9,9-bis(4-hydroxy-3-(hydroxymethyl)-5-methylphenyl)-9H-fluorene-4-carboxylic acid



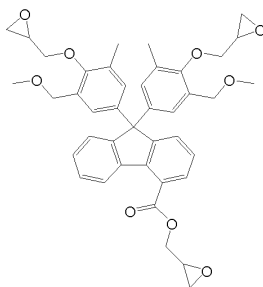
[0252] 30 g of 9,9-bis(4-hydroxy-3-methylphenyl)-9H-fluorene-4-carboxylic acid prepared above was stirred with 138.5 g of 8 wt% NaOH aqueous solution under ice cooling to obtain a solution. Under nitrogen purge, 122 ml 37 % aqueous formaldehyde solution (CAS: 50-50-0) was added dropwise, followed by stirring at room temperature for about 2 days. Under stirring, the reaction mixture was diluted to 3L with water and acidified to pH 2 with 10 wt % HCl. The solid formed was recovered by filtering and water rinse. The solid was dried in a rt vacuum oven to obtain about 31 g of desired 9,9-bis(4-hydroxy-3-(hydroxymethyl)-5-methylphenyl)-9H-fluorene-4-carboxylic acid. ^1H NMR (400 MHz, DMSO- d_6): 2.05 ppm (6H), 4.5 ppm (4H), 5.2 ppm (2H), 6.6 - 6.8 ppm (4H), 7.4-7.7 ppm (6H) and 8.4 ppm (1H).

3.4 Synthesis of 9,9-bis(4-hydroxy-3-(methoxymethyl)-5-methylphenyl)-9H-fluorene-4-carboxylic acid



[0253] 31 g of 9,9-bis(4-hydroxy-3-(hydroxymethyl)-5-methylphenyl)-9H-fluorene-4-carboxylic acid prepared above was dissolved in 710 g of methanol and 7 g of p-toluenesulfonic acid monohydrate dissolved in 70 g of methanol was added. Under nitrogen protection, the reaction solution was refluxed for 26 hrs and allowed to cool to room temperature. The solution was concentrated on a rotary evaporator and the residue was dissolved in diluted aqueous sodium hydroxide solution to obtain a solution. The solution was agitated with activated carbon overnight and filtered. The filtrate was acidified to pH 2.6 by 10 wt % HCl aqueous solution. The solid formed was filtered and washed with water. Drying in a rt vacuum oven produced 27.5 g of desired 9,9-bis(4-hydroxy-3-(methoxymethyl)-5-methylphenyl)-9H-fluorene-4-carboxylic acid. ¹H NMR (400MHz, DMSO-d₆): 2.05 ppm (6H), 3.2 ppm (6H), 4.3 ppm (4H), 6.6 - 6.8 pp (4H), 7.4-7.7 ppm (6H) and 8.2 ppm (1H).

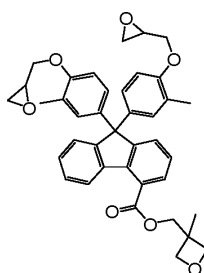
3.5 Synthesis of oxiran-2-ylmethyl 9,9-bis(3-(methoxymethyl)-5-methyl-4-(oxiran-2-ylmethoxy)phenyl)-9H-fluorene-4-carboxylate (Comp A-5)



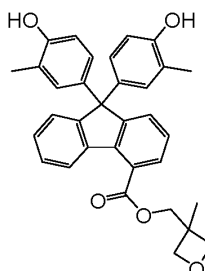
[0254] 2 g 9,9-bis(4-hydroxy-3-(methoxymethyl)-5-methylphenyl)-9H-fluorene-4-carboxylic acid prepared above was dissolved in 30 g of DMF and 4.6 g of cesium carbonate and 2.5 g of sodium sulfate were added, followed by stirring for 30 min in nitrogen. After 2 g of epibromohydrin (CAS: 3132-64-7) was added, the reaction mixture was agitated for about 3 days. The inorganic salts were filtered out. The filtrate was slowly poured into water with stirring. The resultant solid was filtered and washed by water. The solid was purified by dissolving in acetone,

precipitation in water and oven drying to obtain about 2.3 g of desired oxiran-2-ylmethyl 9,9-bis(3-(methoxymethyl)-5-methyl-4-(oxiran-2-ylmethoxy)phenyl)-9H-fluorene-4-carboxylate. ¹H NMR (400 MHz, CDCl₃): 2.2 ppm (6H), 2.7-2.9 ppm (6H), 3.3-3.5 ppm (3H), 3.4 ppm (6H), 3.7 ppm-4.8 ppm (6H), 4.4 ppm (4H), 6.8-7.1 ppm (4H), 7.3-7.8 ppm (6H) and 8.4 (1H).

Comparative Synthesis Example 4: Synthesis of (3-methyloxetan-3-yl)methyl 9,9-bis(3-methyl-4-(oxiran-2-ylmethoxy)phenyl)-9H-fluorene-4-carboxylate (comp A-6)



4.1 Synthesis of (3-methyloxetan-3-yl)methyl 9,9-bis(4-hydroxy-3-methylphenyl)-9H-fluorene-4-carboxylate



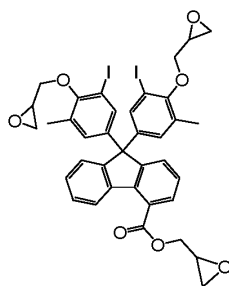
[0255] 8 g of triethyl amine salt of 9,9-bis(4-hydroxy-3-methylphenyl)-9H-fluorene-4-carboxylic acid prepared in a manner similar to example 3.2 was suspended in 90 g of DMF with stirring under a gentle nitrogen stream in a 70 °C oil bath. After 2.2 g of 3-(bromomethyl)-3-methyloxetane (CAS: 78385-26-9) was added, the reaction mixture was stirred for 19 hrs. The reaction mixture was poured into 1 L water containing 0.5 wt % triethyl amine. The resultant solid was filtered, washed with water and oven dried to give 5.3 g of (3-methyloxetan-3-yl)methyl 9,9-bis(4-hydroxy-3-methylphenyl)-9H-fluorene-4-carboxylate. ¹H NMR (400 MHz, DMSO-d₆): 1.4 ppm (3H), 2.0 ppm (6H), 4.3-4.6 ppm (6H), 6.6-6.8 ppm (6H), 7.4 ppm (4H), 7.6-7.8 ppm (2H) and 8.2 ppm (1H).

4.2 Synthesis of (3-methyloxetan-3-yl)methyl 9,9-bis(3-methyl-4-(oxiran-2-ylmethoxy)phenyl)-9H-fluorene-4-carboxylate

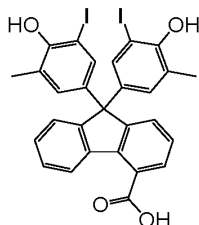
[0256] 5.3 g of (3-methyloxetan-3-yl)methyl 9,9-bis(4-hydroxy-3-methylphenyl)-9H-fluorene-4-

carboxylate prepared in Example 4.1 was dissolved in 31 g of DMF and stirred with 11.5 g of cesium carbonate for 40 min under nitrogen protection. After 4.13 g of epibromohydrin was added, the reaction mixture was stirred at room temperature for 3 days. The inorganic salt was filtered out. The filtrate was poured into water to obtain a solid. The mixture was acidified to pH 4 with aqueous oxalic acid solution. 5.6 g of desired product was recovered by filtering, water rinse and 50 °C vacuum oven drying. ¹H NMR (400 MHz, DMSO-d₆): 1.5 ppm (3H), 2.1 ppm (6H), 2.7-2.9 ppm (4H), 3.4 ppm (2H), 3.9-4.2 (4H), 4.5-4.7 ppm (6H), 6.6-6.8 ppm (6H), 7.4 ppm (4H), 7.6-7.8 ppm (2H) and 8.2 ppm (1H).

Synthesis Example 5: synthesis of oxiran-2-ylmethyl 9,9-bis(3-iodo-5-methyl-4-(oxiran-2-ylmethoxy)phenyl)-9H-fluorene-4-carboxylate (A-4)



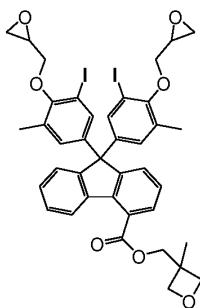
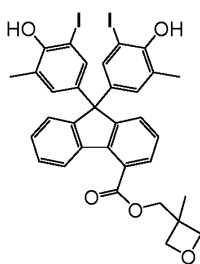
5.1. Synthesis of 9,9-bis(4-hydroxy-3-iodo-5-methylphenyl)-9H-fluorene-4-carboxylic acid



[0257] 43 g of 9,9-bis(4-hydroxy-3-methylphenyl)-9H-fluorene-4-carboxylic acid prepared in a manner similar to example 3.2 was dissolved in 860 g of glacial acetic acid and 46.7 g of potassium iodide was added. Under ice cooling, 36.16 g of 30 wt % aqueous hydrogen peroxide solution was dropwise added over 60 min. After addition, the mixture was stirred at room temperature overnight. The resultant solid suspension was filtered, and the cake was washed with acetic acid. The solid was stirred in water containing sodium thiosulfate to remove colored impurities, followed by filtering, water rinse and 55 °C vacuum oven drying to give 41 g of desired 9,9-bis(4-hydroxy-3-iodo-5-methylphenyl)-9H-fluorene-4-carboxylic acid. ¹H NMR (400 MHz, DMSO-d₆): 2.1 ppm (6H), 6.9-7.1 ppm (4H), 7.4 ppm (4H), 7.6-7.8 ppm (2H) and 8.2 ppm (1H).

5.2 Synthesis of oxiran-2-ylmethyl 9,9-bis(3-iodo-5-methyl-4-(oxiran-2-ylmethoxy)phenyl)-9H-fluorene-4-carboxylate

[0258] 13.63 g of 9,9-bis(4-hydroxy-3-iodo-5-methylphenyl)-9H-fluorene-4-carboxylic acid prepared above was dissolved in 240 g of DMF and stirred with 23 g of cesium carbonate for 60 min. After 8.87 g of epibromohydrin was added, the reaction mixture was stirred at room temperature for 2 days. The inorganic salt was filtered out. The filtrate was poured into water and the mixture was acidified to pH 3.4 with aqueous oxalic acid to give a solid. 12 g of desired product was recovered by filtering, water rinse and 50°C vacuum oven drying. ¹H NMR (400 MHz, DMSO-d₆): 2.2 ppm (6H), 2.7-2.9 ppm (6H), 3.4 ppm (3H), 3.8 (2H), 4.2 ppm (2H), 4.4 ppm (1H), 4.8 ppm (1H), 6.9 ppm (2H), 7.4 ppm (4H), 7.3-7.5 ppm (6H), 7.6 ppm (1H), 7.9 ppm (1H) and 8.4 ppm (1H).

Synthesis Example 6: synthesis of (3-methyloxetan-3-yl)methyl 9,9-bis(3-iodo-5-methyl-4-(oxiran-2-ylmethoxy)phenyl)-9H-fluorene-4-carboxylate (A-7)**6.1. Synthesis of (3-methyloxetan-3-yl)methyl 9,9-bis(4-hydroxy-3-iodo-5-methylphenyl)-9H-fluorene-4-carboxylate**

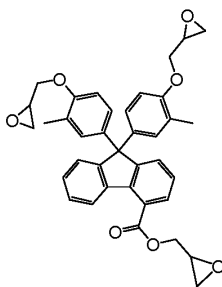
[0259] 10.05 g of triethyl amine salt of 9,9-bis(4-hydroxy-3-iodo-5-methylphenyl)-9H-fluorene-4-carboxylic acid prepared in a manner similar to example 5.1 and 3.23 g of potassium iodide were suspended in 90 g of DMF by stirring under a gentle nitrogen stream. After 6.38 g of 3-(bromomethyl)-3-methyloxetane (CAS: 78385-26-9) was added, the reaction mixture was stirred

for 4 days. The reaction mixture was poured into 700 ml a mixture of 1:1 water/acetic acid. The solid was recovered by filtering, water rinse and oven drying to give 9 g of (3-methyloxetan-3-yl)methyl 9,9-bis(4-hydroxy-3-iodo-5-methylphenyl)-9H-fluorene-4-carboxylate. ¹H NMR (400 HMz, DMSO-d₆): 1.4 ppm (3H), 2.1 ppm (6H), 4.3-4.6 ppm (6H), 6.8-7.2 ppm (4H), 7.5 ppm (4H), 7.6-7.8 ppm (2H) and 8.2 ppm (1H).

6.2 Synthesis of (3-methyloxetan-3-yl)methyl 9,9-bis(3-iodo-5-methyl-4-(oxiran-2-ylmethoxy)phenyl)-9H-fluorene-4-carboxylate

[0260] Under nitrogen protection, 9 g of (3-methyloxetan-3-yl)methyl 9,9-bis(4-hydroxy-3-iodo-5-methylphenyl)-9H-fluorene-4-carboxylate prepared above was stirred with 12 g of cesium carbonate in 60 g of DMF for 30 min, followed by addition of 4.06 g of epibromohydrin. The mixture was agitated at room temperature for 4 days. The reaction mixture was poured into water and acidified to pH 4.6 with aqueous oxalic acid. The resultant solid was isolated and dried in a 50°C vacuum oven. The dried solid was dissolved in acetone and agitated with activated charcoal overnight followed by filtering. The filtrate was poured into water containing oxalic acid. The solid was recovered by filtering, water rinse and vacuum oven drying to give 7.5 g of desired (3-methyloxetan-3-yl)methyl 9,9-bis(3-iodo-5-methyl-4-(oxiran-2-ylmethoxy)phenyl)-9H-fluorene-4-carboxylate. ¹H NMR (400 MHz, DMSO-d₆): 1.4 ppm (3H), 2.1 ppm (6H), 2.7-2.9 ppm (4H), 3.4 ppm (2H), 3.6 ppm (2H), 4.1 (2H), 4.4 ppm (2H), 4.6 ppm (4H), 7.1-7.3 (4H), 7.5 ppm (4H), 7.8 ppm (2H) and 8.2 ppm (1H).

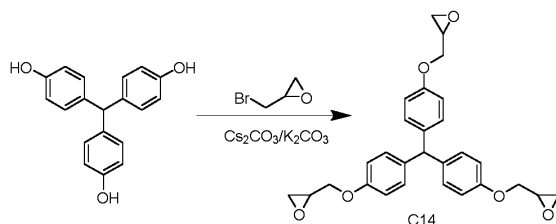
Comparative Synthesis Example 7: Synthesis of oxiran-2-ylmethyl 9,9-bis(3-methyl-4-(oxiran-2-ylmethoxy)phenyl)-9H-fluorene-4-carboxylate (Comp A-8)



[0261] Under nitrogen protection 5 g of 9,9-bis(4-hydroxy-3-methylphenyl)-9H-fluorene-4-carboxylic acid prepared in a similar manner to example 3.2 was dissolved in 80 g of DMF and stirred with 15 g of cesium carbonate for 60 min. After 6 g of epibromohydrin was added, the reaction mixture was stirred at room temperature for 3 days. The inorganic salt was filtered out. The

filtrate was poured into water and the mixture was acidified to pH 4.3 with aqueous oxalic acid to give a solid. 4.6 g of desired product was recovered by filtering, water rinse and 50°C vacuum oven drying. ¹H NMR (400 MHz, DMSO-d₆): 2.1 ppm (6H), 2.7-2.9 ppm (6H), 3.4 ppm (3H), 3.7 (2H), 4.3 ppm (3H), 4.8 ppm (1H), 6.9 ppm (6H), 7.4 ppm (4H), 7.7 ppm (2H), and 8.2 ppm (1H).

Comparative Synthesis Example 8 (Comp A-3)



[0262] To a solution of 1,4,4'-methanetriyltriphenol (3.60 g, 12.3 mmol) in anhydrous DMF (50 mL) in an EasyMax 401 Reactor (Mettler Toledo), was added cesium carbonate (24.1 g, 73.9 mmol) and potassium carbonate (10.21 g, 73.9 mmol) in three portions under stirring, followed addition of epibromohydrin (20.44 g, 12.77 mL, 147.7 mmol) dropwise at 10 °C. The reaction mixture was then stirred overnight at 10 °C and then poured into DI water (100 mL) under continuous stirring. The aqueous layer was extracted with diethyl ether (2 x 150 mL), the organic layer was washed with water (100 mL), dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using ethyl acetate/heptane solvent gradient (70:30 to 100% EA) to afford 5.02 g of the product as viscous semi-solid, assigned as C14, yield = 89%. T_g = 9°C (DSC). ¹H NMR (400 MHz, CDCl₃) δ 7.00, 6.98, 6.84, 6.82, 5.39, 4.20, 4.17, 3.94, 3.92, 3.33, 2.89, 2.75, 1.57. ¹³C NMR (101 MHz, CDCl₃) δ 157.01, 137.31, 130.39, 114.49, 68.89, 54.45, 50.30, 44.91.

Formulations with Novel Crosslinking Compounds and Exposures

EUV Testing of Composition of working Examples 1-3 and Comparative Examples 1-3

[0263] Dissolve the components listed in Table 1 (the unit are relative molar content normalized to 100) in ethyl lactate (E-L), which is a solvent, and prepare so that the concentration of the solid component is 1.25 mass%. Components other than solvents are solid components. The resulting solution is filtered with a 0.2 μm pore size filter. This yields the composition of examples 1-3 and comparative examples 1-3.

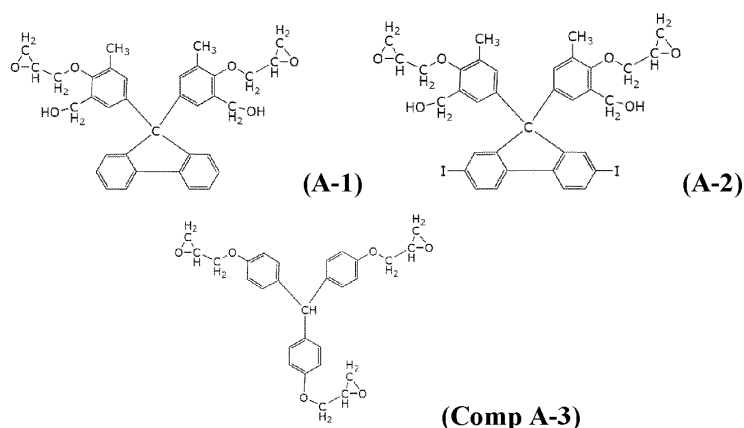
[0264]

Examples	Comparative Examples
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		1	2	3	1	2	3
A Crosslinker Component	A-1	100	100	-	-	-	-
	A-2	-	-	100	-	-	-
	Comp. A-3	-	-		100	100	100
B PAG Component	B-1	30.7	30.7	20.7	46.1	-	-
	B-2	-	-	-	-	46.1	-
	B-3	-	-	-	-	-	46.1
Photodecomposable Quencher	B-4	6	8.5	16.4	9	9	9
D Quencher Component	D-1	-	-	-	6.5	-	-
Minimum CD Size (nm)		10	10	11	15	NA	NA
LWR (nm)		6	5.3	4.3	4.7	NA	NA
DtOS (mJ/cm²)		20	22	88	67	>100	>100

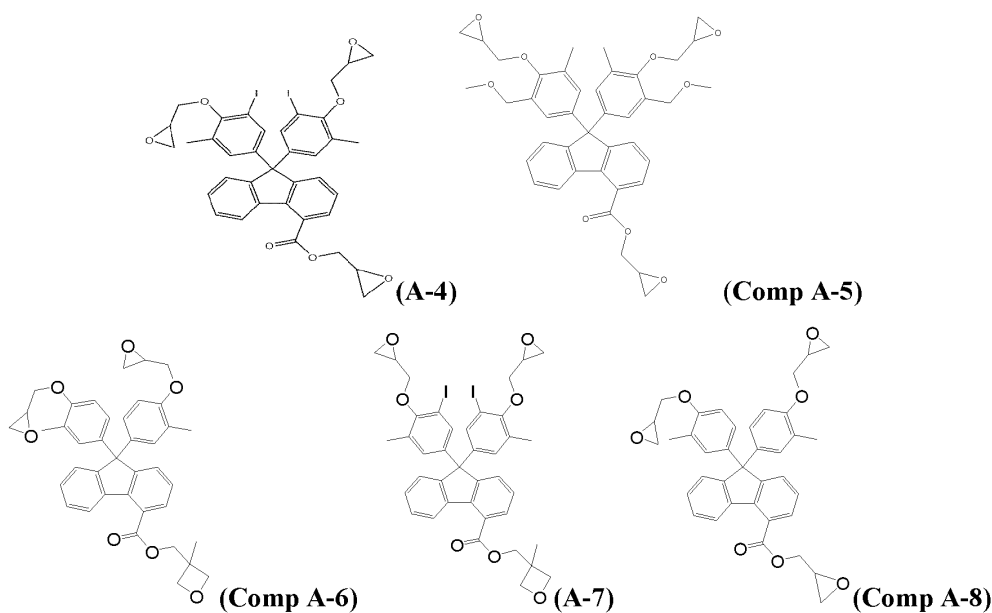
Table 1

[0265] In Table 1 the following compounds are used (A-1) and (A-2) and Comp (A-3):

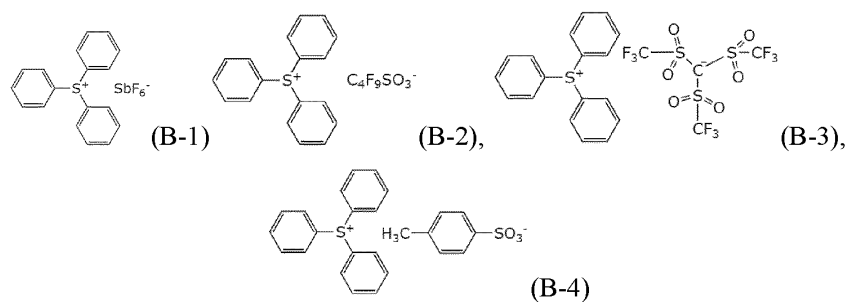


[0266] Also tested were other comparative examples based on other crosslinkers which shared the same fluorene aromatic cores which either did not have a pendant $-\text{CH}_2\text{OH}$ moiety or where the hydroxyl group was masked by a methyl group (i.e. $-\text{CH}_2\text{OCH}_3$), these were formulated in the same manner as comparative examples 1, 2 and 3, using the same molar loading of the crosslinker component as shown in Table 1 and the same additives, but either gave much poorer resolution than the equivalent formulation with A-1 and A-2 as shown in Table 1 or did not image at all. The compounds used in these additional comparative example are A-4 (Synthesis example 5), Comp A-5 (Comparative Synthesis Example 3), Comp A-6 (Comparative Synthesis example 4), A-7

(Synthesis Example 6), and Comp A-8 (Comparative Synthesis Example 7). Comparative Lithographic results obtained with A-4 and Comp A-5 are specifically shown in more detail, as follows, in Table 2 (Comp Ex 5), and in Table 4 (Comp Ex 4), and in the discussion associated with these Tables.



[0267] In table 1 PAG components (B-1), (B-2), (B-3) and (B-3) have the following structures and is the following compound:



[0268] The base component (D-1) is tris[2-(2-methoxyethoxy)ethyl]amine.

Formation of Resist Patterns

[0269] Photoresist AL412 (BrewerScience) was spin-coated on a 12-inch silicon wafer and heated at 205 °C for 60 seconds to obtain a 20-nm lower layer. On it, the composition prepared above were spin coated on this photoresist coating.

[0270] The resist film thickness of 26 nm is obtained by heating in a hot plate (pre-bake) at 0 °C

for 60 seconds.

[0271] A EUV Exposure tool ASML NXE3400B (0.33NA) was used to expose the resist film. Then the resist coating was heated (post-exposure bake) on a hot plate for 60 seconds at 70 °C and developing with butyl acetate for 30 seconds to form a resist pattern with a line width of 16 nm.

[0272] The shape of the obtained resist pattern is observed using the CD-SEM "CG7300" (Hitachi High-Tech).

[0273] .

[0274] Evaluation of optimal exposure dose (D_{toS}) The line width is 16 nm and the pitch is 3

[0275] Optimal Exposure (D_{toS}) MJ for a 2 nm line-and-space pattern /Cm². The results obtained are shown in Table 1.

Resolution

[0276] The resist pattern obtained by reducing the exposure dose from D_{toS} is observed by CD-SEM, and the minimum line width is the resolution limit. The results obtained are shown in Table 1. Comparative example 1 gave much worse resolution, while Comparative examples 2 and 3 did not form a resist pattern after development. Also,

LWR and LWR evaluation

[0277] The line width of the line-and-space pattern obtained with D_{toS} exposure is measured and the LWR is 3 times the standard deviation (σ) (3σ). The results obtained are shown in Table 1. The lower the value, the better the pattern.

EUV Testing of Composition of working Examples and comparative Examples

[0278] The surface of a silicon substrate (12 inches) is treated with a EUV-UL, AL412, solution at 205 ° C. for 60 seconds. A negative tone EUV resist composition is spin-coated using CLEAN TRACK™ LITHIUS Pro™ (Tokyo Electron) thereto and soft-baked at 80 ° C. for 60 seconds to form a resist film having a film thickness of 26 nm on the same substrate. This is exposed with an EUV exposure apparatus NXE: 3400 (manufactured by ASML) through a mask having a size of 16 nm (line: space = 1: 1). A plurality of exposure amounts is set, and a substrate under each condition is obtained. As the amount of exposure increases, the pattern width of the resist pattern formed by later development increases. This substrate is PEBed at 80 ° C. for 60 seconds. Then, the resist film is paddle-developed with a nBA for 30 seconds, and the substrate is rotated at high speed to spin dry.

Evaluation of EUV performance

[0279] On the above evaluation substrate, a resist pattern having a space size of 16 nm formed on a mask of 16 nm is observed using CG5000(Hitachi High-Tech), and DtS, EL, and LWR are observed.

Components

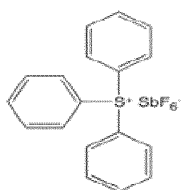
[0280] Table 2 shows the details of the tested compositions including, DtS, Exposure Latitude (EL), line edge roughness (LER), and Line width roughness (LWR), Ex. 4, Ex. 5 and Comp Ex. 5 which respectively containing crosslinker A-1, A-2 and Comp A-5 using the same PAG B-1 and quencher B-4. These results confirm that crosslinker Ex. 4 and Ex. 5 which include two different types of pendant crosslinkers moieties (a.k.a. oxirane and $-\text{CH}_2\text{OH}$), performs very well lithographically. Table 2 also shows Comp A-5 which did not image. As this comparative example contains a crosslinker where the OH group $-\text{CH}_2\text{OH}$ moiety is blocked by a methyl group (a.k.a. $-\text{CH}_2\text{OMe}$) this highlighted the unexpected benefit, in term of resolution, of having a free $-\text{CH}_2\text{OH}$ moiety as an additional crosslinking moiety. The appearance of the imaged substrates is shown in FIG. 1. Similarly, the comparative examples Comp A-3 (Comparative Synthesis Example 8), A-4 (Synthesis example 5), Comp A-5 (comparative Synthesis Example 3) Comp A-6 (Comparative Synthesis example 4), A-7 (Synthesis Example 6), and Comp A-8 (Comparative Synthesis Example 7), which do not contain a free CH_2OH moiety, when formulated in the same fashion as comp Ex A-5 as noted in Table 2, also gave similar poor results, highlighting the unexpected benefit of having a free CH_2OH .

Sam- ple		Cross- linker	PAG	Quen- cher	Sol- vent		PEB (°C)	DtS (mJ/cm ²)	EL (%)	LER (nm)	LWR (nm)
Ex. 4	Name	A-1	B-1	TPS- 1000 B-4	EL		70	31	15	-	5.9
	Weight Ratio	0.943	0.262	0.044	98.75						
Ex.5	Name	A-2	TPS- 103 B-1	TPS- 1000 B-4	EL		70	-	-	5.3	6.4

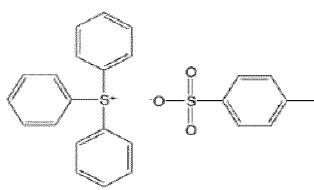
	Weight Ratio	1.022	0.195	0.033	98.75						
Comp. Ex. 5	Name	Comp A-5	TPS-103 B-1	TPS-1000 B-4	EL		80	-	-	-	-
	Weight Ratio	0.989	0.223	0.038	98.75						

Table 2

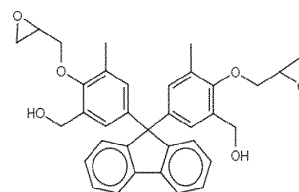
[0281] The structures of these components are shown below. The solvent employed in these tested composition was ethyl lactate (EL).

**B-1**

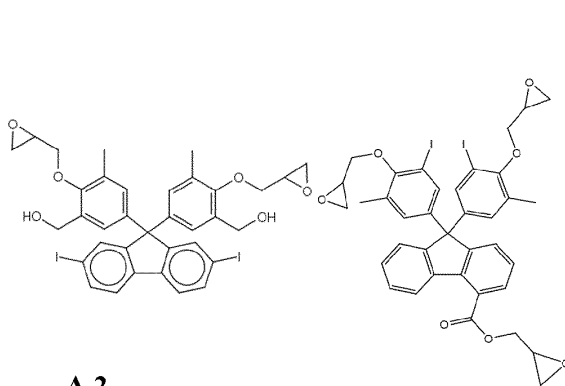
MW=499.13

**B-4**

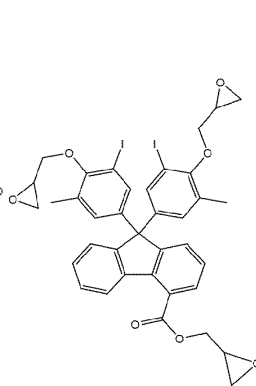
MW=434.57

**A-1**

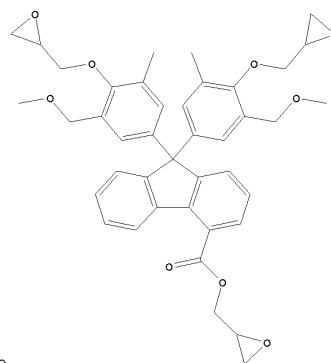
MW=550.65

**A-2**

MW=802.44

**A-4**

MW=842.46

**Comp A-5**

(MW 678.78)

Table 3 shows the details of the EUV tested composition Ex. 6 which contained crosslinkers A-1, the PAG B-1 and the quencher component was B-4. solvent employed in these tested composition

was ethyl lactate (EL). Ex. 6 contains the same components as Ex.4, but in a different ratio of the components which gave better performance The appearance of the imaged substrate of Ex. 6 is shown in FIG. 2. Table 4 shows the details of the tested composition Comp Ex. 4 which included the listed crosslinkers A-4, the PAG components B-1 and the quencher component B-4. The solvent employed in these tested composition was ethyl lactate (EL). In can bee see in FIG. 3 that A-4 gave very poor resolution compared to the working examples whose performance are shown in Table 1 to 3. This again highlighted the unexpected benefit of having pendant -CH₂OH moieties, which A-4 lacked.

Sample	Formulation			PEB (°C)	DtS (mJ/cm ²)	EL %	LER (nm)	LWR (nm)
	PAG	Quencher	crosslinker					
EX. 6	B-1	B-4	A-1	70	56	16.5	3.9	5.2
	30.7	12.0	100					

Table 3

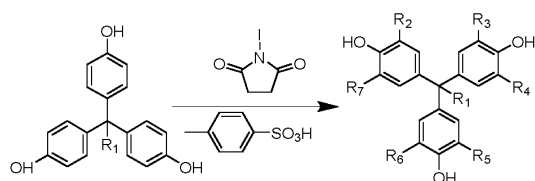
	B-1	B-4	A-4
Formulation Comp. Ex. 4	63	23.1	100

Table 4

[0282] In summary, Comp Ex. 1 to 5 which do not contain an oxirane and -CH₂OH show less resolution, and generally more LR, LWR than Ex. 1 to 6 containing both oxirane and -CH₂OH crosslinking group demonstrating the unexpected synergy of have both types of these different crosslinking groups in a crosslinker when formulated with a PAG and used as a EUV photoresist.

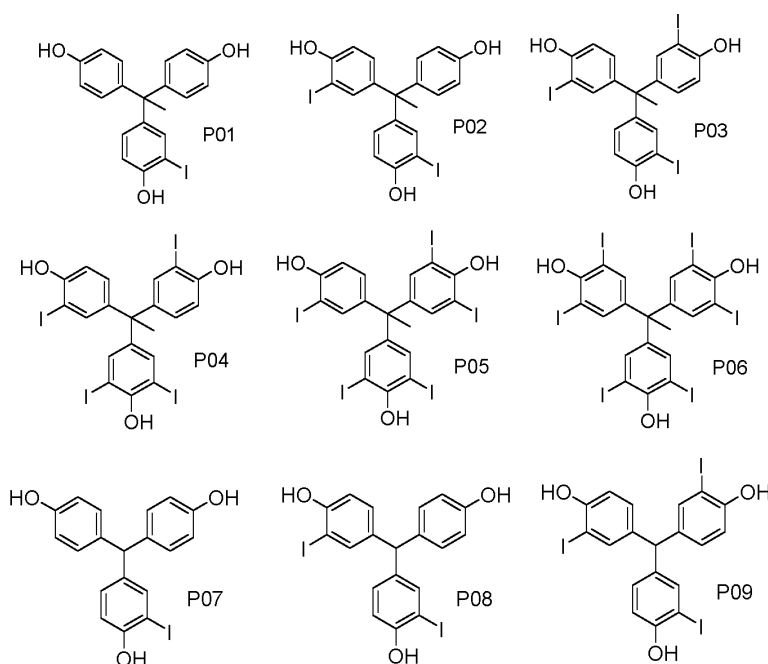
Iodination

[0283] Summary Reaction:

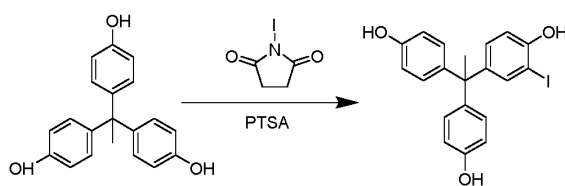


R1 = H, CH₃; R2, R3, R4, R5, R6, R7 = H, I

[0284] Selected Precursor List:



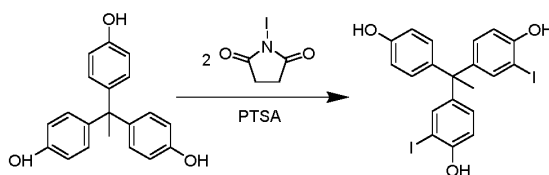
[0285] Preparation of 4,4'-(1-(4-hydroxy-3-iodophenyl) ethane-1,1-diyl) diphenol, P01



[0286] To acetonitrile (300 mL) in OptiMax 1001 Reactor (Mettler Toledo), was added, 4,4',4''-(ethane-1,1,1-triyl)triphenol (16.24 g, 51 mmol) and *p*-toluenesulfonic acid monohydrate, PTSA (10.48g, 54 mmol), and this solution was stirred for about 15 minutes at 0 °C, at which time, N-iodosuccinimide (12.79g, 54 mmol) in acetonitrile (100 mL) was added dropwise within 5 hours, and the reaction was stirred for an additional 13 hours at 0 °C. The reaction flask was placed in a -20 °C freezer for 48 hours, and the PTSA precipitate was filtered off. The filtrate was concentrated

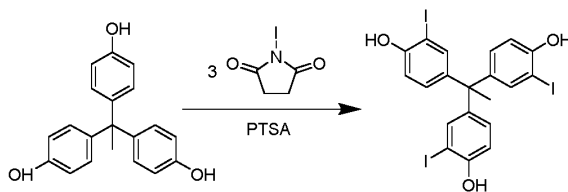
to dryness and dissolved in methylene chloride (200 mL). The organic phase was washed with 100 mL each of 10 wt% aqueous sodium thiosulfates, water, and then brine, and then dried with anhydrous MgSO_4 , filtered through a pad of silica gel, and then concentrated to afford 20.73 g of product as white powder, yield=92%, assigned as P01. ^1H NMR (400 MHz, MeOD) δ 7.31, 6.87, 6.85, 6.74, 6.72, 6.69, 6.67, 6.64, 4.90, 4.63, 2.00. ^1H NMR (400 MHz, Acetone) δ 8.60, 7.39, 6.94, 6.90, 6.88, 6.86, 6.78, 6.76, 6.73, 6.71, 3.34, 2.03. ^{13}C NMR (101 MHz, Acetone) δ 156.23, 156.04, 155.35, 144.33, 143.62, 141.68, 141.00, 139.76, 130.71, 130.30, 115.32, 83.94, 50.83, 31.02.

[0287] Preparation of 4,4'-(1-(4-hydroxyphenyl) ethane-1,1-diyl) bis(2-iodophenol), P02



[0288] To acetonitrile (500 mL) in OptiMax 1001 Reactor (Mettler Toledo), was added, 4,4',4''-(ethane-1,1,1-triyl)triphenol (21.71 g, 69 mmol) and *p*-toluenesulfonic acid monohydrate, PTSA (28.02g, 144 mmol), and this solution was stirred for about 15 minutes at 0 °C, at which time, N-iodosuccinimide (33.37 g, 144 mmol) in acetonitrile (200 mL) was added dropwise within 8 hours, and the reaction was stirred for an additional 18 hours at 0 °C. Then NaOH (5.76 g, 144 mmol) in water (60 mL) was added into the mixture dropwise to neutralize PTSA at 0°C. Then, thiosulfate pentahydrate (4.65 g, 19 mmol) in water (40 mL) was added into the solution to consume trace amount of free iodine. After concentrated under vacuum, the mixture was dropwise added into DI water (2000 mL) and stirring overnight. The precipitate was filtered to get wet powder, and washed with DI water, until no by-products presence, checked by NMR. Finally, the product was dried under vacuum to afford 20.73 g of product as white powder, yield=92%, assigned as P02. ^1H NMR (400 MHz, MeOD) δ 7.32, 6.86, 6.85, 6.75, 6.73, 6.71, 6.70, 6.68, 6.66, 2.00. ^1H NMR (400 MHz, Acetone) δ 9.05, 8.31, 7.40, 6.94, 6.91, 6.88, 6.86, 6.85, 6.77, 6.75, 6.73, 2.04.

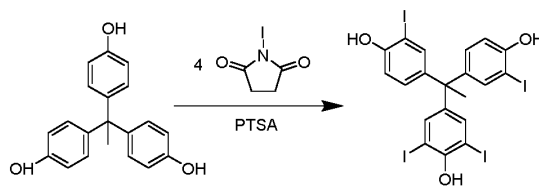
[0289] Preparation of 4,4',4''-(ethane-1,1,1-triyl) tris(2-iodophenol), P03



[0290] To acetonitrile (500 mL) in OptiMax 1001 Reactor (Mettler Toledo), was added, 4,4',4''-

(ethane-1,1,1-triyl)triphenol (21.55 g, 68 mmol) and *p*-toluenesulfonic acid monohydrate, PTSA (41.05g, 212 mmol), and this solution was stirred for about 15 minutes at 0 °C, at which time, N-iodosuccinimide (50.09 g, 212 mmol) in acetonitrile (400 mL) was added dropwise within 14 hours, and the reaction was stirred for an additional 18 hours at 0 °C. Then NaOH (8.48 g, 212 mmol) in water (80 mL) was added into the mixture dropwise to neutralize PTSA at 0°C. Then, thiosulfate pentahydrate (4.65 g, 19 mmol) in water (40 mL) was added into the solution to consume trace amount of free iodine. After concentrated under vacuum down to 200 mL volume, the mixture was dropwise added into DI water (4000 mL) and stirring overnight. The precipitate was filtered to get wet powder, and washed with DI water, until no by-product presence, checked by NMR. Finally, the precipitate was dried under vacuum to afford 45.50 g of product as off-white powder, yield=97%, assigned as P03. ¹H NMR (400 MHz, Acetone) δ 9.06, 7.38, 6.90, 6.88, 6.86, 6.83, 2.02. ¹H NMR (400 MHz, MeOD) δ 7.31, 6.86, 6.84, 6.75, 6.73, 1.97. ¹³C NMR (101 MHz, MeOD) δ 156.09, 143.15, 140.02, 130.73, 114.97, 84.31, 50.59, 31.11.

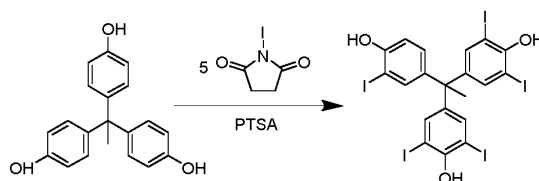
[0291] Preparation of 4,4'-(1-(4-hydroxy-3,5-diiodophenyl) ethane-1,1-diyl) bis(2-iodophenol), P04



[0292] To acetonitrile (300 mL) in OptiMax 1001 Reactor (Mettler Toledo), was added, 4,4',4''-(ethane-1,1,1-triyl)triphenol (10.20 g, 32 mmol) and *p*-toluenesulfonic acid monohydrate, PTSA (25.39 g, 131 mmol), and this solution was stirred for about 15 minutes at 0 °C, at which time, N-iodosuccinimide (30.98 g, 131 mmol) in acetonitrile (300 mL) was added dropwise within 18 hours, and the reaction was stirred for an additional 18 hours at 0 °C. Then NaOH (5.24 g, 131 mmol) in water (40 mL) was added into the mixture dropwise to neutralize PTSA at 0 °C. Then, thiosulfate pentahydrate (4.65 g, 19 mmol) in water (40 mL) was added into the solution to consume trace amount of free iodine. After concentrated under vacuum, the mixture was dropwise added into DI water (2000 mL) and stirring overnight, then the precipitate was filtered out as wet powder, and washed with DI water, until no by-products was present. Finally, the precipitate was dried under vacuum to afford 22.50 g of product as light-yellow powder, yield=86%, as assigned as P04. ¹H NMR (400 MHz, CDCl₃) δ 7.33, 7.31, 6.90, 6.89, 5.74, 5.40, 2.00. ¹H NMR (400

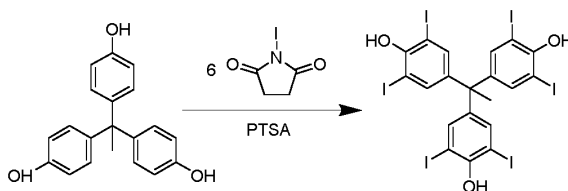
MHz, MeOD) δ 7.35, 7.31, 6.86, 6.84, 6.77, 6.75, 6.73, 1.97. ^{13}C NMR (101 MHz, MeOD) δ 156.11, 155.18, 145.96, 143.16, 142.42, 140.59, 139.94, 130.74, 115.10, 84.45, 78.84, 50.32, 31.03.

[0293] Preparation of 4,4'-(1-(4-hydroxy-3-iodophenyl) ethane-1,1-diyl) bis(2,6-diiodophenol), P05



[0294] To acetonitrile (300 mL) in OptiMax 1001 Reactor (Mettler Toledo), was added, 4,4',4''-(ethane-1,1,1-triyl)triphenol (5.86 g, 19 mmol) and *p*-toluenesulfonic acid monohydrate, PTSA (18.37 g, 95 mmol), and this solution was stirred for about 15 minutes at 0 °C, at which time, N-iodosuccinimide (22.19 g, 94 mmol) in acetonitrile (250 mL) was added dropwise within 8 hours, and the reaction was stirred for an additional 18 hours at 0 °C. Then NaOH (3.8 g, 95 mmol) in water (40 mL) was dropwise added into the mixture to neutralize PTSA at 0°C. Then, thiosulfate pentahydrate (4.65 g, 19 mmol) in water (40 mL) was added into the solution to consume trace amount of free iodine. After concentrated under vacuum, the mixture was dropwise added into DI water (2000 mL) and stirring overnight, then the precipitate was filtered out as wet powder, and washed with DI water, until no by-products was present. Finally, the product was dried under vacuum to get 17.42 g of product as light-yellow powder, yield=98%, assigned as P05. ^1H NMR (400 MHz, MeOD) δ 7.35, 7.32, 6.86, 6.85, 6.84, 6.77, 6.76, 6.74, 6.72, 1.95. ^{13}C NMR (101 MHz, MeOD) δ 156.42, 156.20, 155.98, 155.05, 154.80, 146.11, 145.32, 143.10, 142.34, 141.61, 140.46, 139.88, 130.69, 115.08, 85.07, 84.55, 50.29, 30.50.

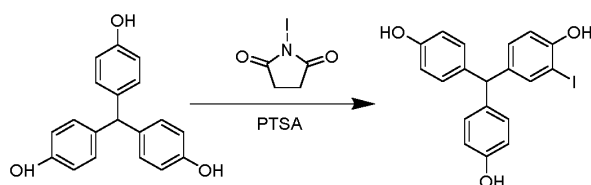
[0295] Preparation of 4,4',4''-(ethane-1,1,1-triyl) tris(2,6-diiodophenol), P06



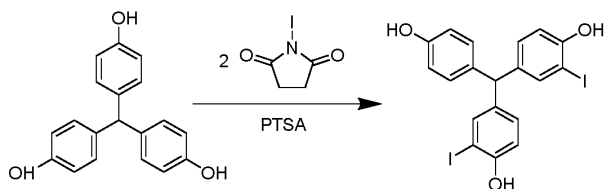
[0296] To acetonitrile (250 mL) in OptiMax 1001 Reactor (Mettler Toledo), was added, 4,4',4''-(ethane-1,1,1-triyl)triphenol (9.66 g, 31 mmol) and *p*-toluenesulfonic acid monohydrate, PTSA (36.21 g, 187 mmol), and this solution was stirred for about 30 minutes at 0 °C, at which time, N-

iodosuccinimide (43.82 g, 185 mmol) in acetonitrile (400 mL) was added dropwise within 14 hours, and the reaction was stirred for an additional 18 hours at 0 °C. NaOH (7.54 g, 187 mmol) in water (80 mL) was added into the mixture dropwise to neutralize PTSA at 0 °C. Then, thiosulfate pentahydrate (7.67 g, 31 mmol) in water (70 mL) was added into the solution to consume trace amount of free iodine. After concentrated under vacuum, the mixture was poured into DI water (2000 mL), stirring overnight, then filtered to get organic product as wet powder, and washed with DI water, until no by-product succinimide or PTSA salt was present. Finally, the precipitate was dried under vacuum to get 28.24 g (yield: 87%) of product as light-yellow powder, assigned as P06. ¹H NMR (400 MHz, CDCl₃) δ 7.31, 5.77(-OH), 1.97. ¹H NMR (400 MHz, MeOD) δ 7.35, 1.94. ¹³C NMR (101 MHz, MeOD) δ 155.11, 145.35, 140.50, 85.07, 50.02, 30.51.

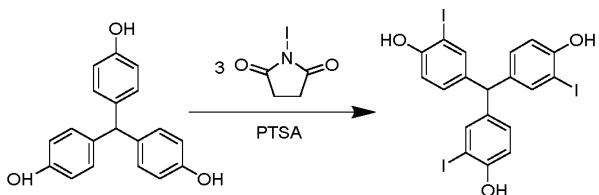
[0297] Preparation of 4,4'-((4-hydroxy-3-iodophenyl) methylene) diphenol, P07



[0298] To acetonitrile (400 mL) in OptiMax 1001 Reactor (Mettler Toledo), was added, 4,4',4''-methane-triyltriphenol (23.22 g, 77 mmol) and *p*-toluenesulfonic acid monohydrate, PTSA (15.72 g, 81 mmol), and this solution was stirred for about 15 minutes at 0 °C, at which time, N-iodosuccinimide (19.16 g, 81 mmol) in acetonitrile (200 mL) was added dropwise within 8 hours, and the reaction was stirred for an additional 18 hours at 0 °C. The reaction flask was placed in a -20 °C freezer for 48 hours, and the PTSA precipitate was filtered off. The filtrate was concentrated to dryness and dissolved in methylene chloride (250 mL). The organic phase was washed with 100 mL each of 10 wt% aqueous sodium thiosulfates, water, and then brine, and then dried with anhydrous MgSO₄, filtered through a pad of silica gel, and then concentrated, to afford 28.00 g (yield: 87%) of product as red powder, assigned as P07. ¹H NMR (400 MHz, MeOD) δ 7.33, 6.87, 6.85, 6.70, 6.68, 6.66, 5.23. ¹H NMR (400 MHz, CDCl₃) δ 7.34, 6.92, 6.90, 6.76, 6.74, 5.29. ¹H NMR (400 MHz, Acetone) δ 7.42, 6.93, 6.91, 6.77, 6.75, 6.73, 5.31.

[0299] Preparation of 4,4'-((4-hydroxyphenyl) methylene) bis(2-iodophenol), P08

[0300] To acetonitrile (400 mL) in OptiMax 1001 Reactor (Mettler Toledo), was added, 4,4',4''-methane-triyltriphenol (21.29 g, 71 mmol) and *p*-toluenesulfonic acid monohydrate, PTSA (29.48 g, 152 mmol), and this solution was stirred for about 15 minutes at 0 °C, at which time, N-iodosuccinimide (35.13 g, 148 mmol) in acetonitrile (350 mL) was added dropwise within 8 hours, and the reaction was stirred for an additional 18 hours at 0 °C. The reaction flask was placed in a -20 °C freezer for 48 hours, and the PTSA precipitate was filtered off. The filtrate was concentrated to dryness and dissolved in methylene chloride (350 mL). The organic phase was washed with 100 mL each of 10 wt% aqueous sodium thiosulfates, water, and then brine, and then dried with anhydrous MgSO₄, filtered through a pad of silica gel, and then concentrated, to afford 37.36 g (yield: 97%) of product as red powder, assigned as P08. ¹H NMR (400 MHz, Acetone) δ 7.33, 6.94, 6.89, 6.79, 6.77, 6.75, 5.35.

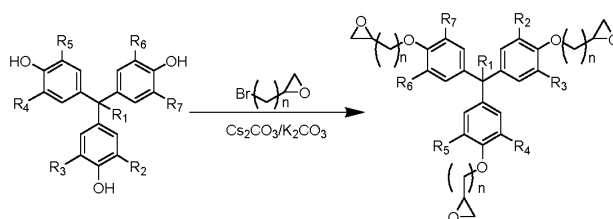
[0301] Preparation of 4,4',4''-methanetriyl tris(2-iodophenol), P09

[0302] To acetonitrile (300 mL) in OptiMax 1001 Reactor (Mettler Toledo), was added, 4,4',4''-methane-triyltriphenol (16.22 g, 54 mmol) and *p*-toluenesulfonic acid monohydrate, PTSA (32.91 g, 170 mmol), and this solution was stirred for about 15 minutes at 0 °C, at which time, N-iodosuccinimide (40.15 g, 170 mmol) in acetonitrile (400 mL) was added dropwise within 8 hours, and the reaction was stirred for additional 18 hours at 0 °C. The reaction flask was placed in a -20 °C freezer for 48 hours, and the PTSA precipitate was filtered off. The filtrate was concentrated to dryness and dissolved in methylene chloride (350 mL). The organic phase was washed with 100 mL each of 10 wt% aqueous sodium thiosulfates, water, and then brine, and then dried with anhydrous MgSO₄, filtered through a pad of silica gel, and then concentrated, to afford 35.36 g

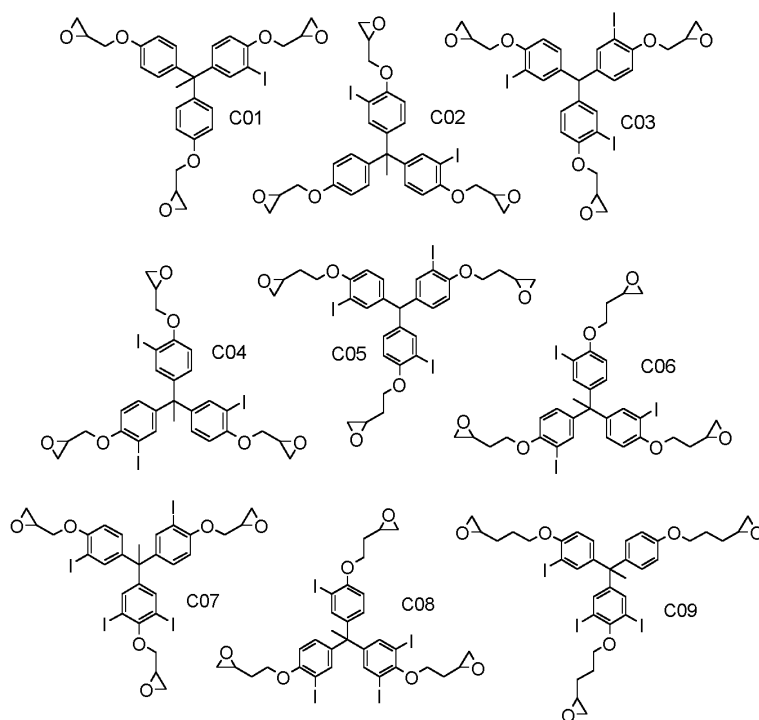
(yield: 95%) of product as red powder, assigned as P09. ^1H NMR (400 MHz, CDCl_3) δ 7.32, 6.87, 6.29, 5.20. ^1H NMR (400 MHz, MeOD) δ 7.33, 6.85, 6.83, 6.77, 6.75, 5.18. ^1H NMR (400 MHz, Acetone) δ 9.43, 7.45, 6.95, 6.93, 6.89, 6.87, 5.36. ^{13}C NMR (101 MHz, Acetone) δ 156.01, 140.27, 138.05, 131.05, 115.56, 84.46, 53.13.

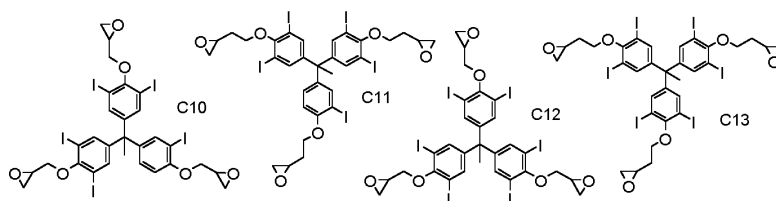
Epoxidation

[0303] Summary Reaction:

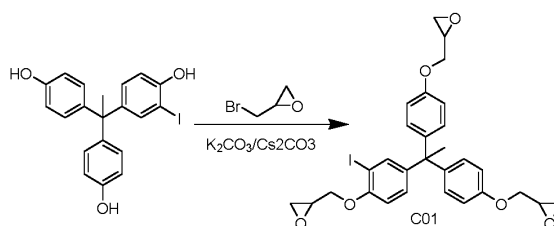


Selected Crosslinker Examples:





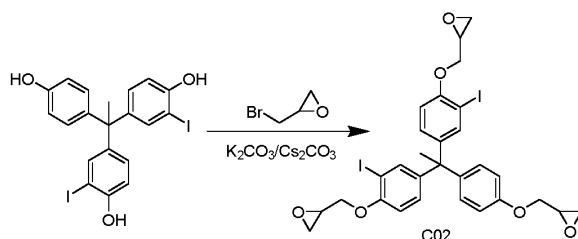
[0304] Preparation of 2,2'-((((1-(3-iodo-4-(oxiran-2-ylmethoxy) phenyl) ethane-1,1-diyl) bis(4,1-phenylene)) bis(oxy)) bis(methylene)) bis(oxirane), C01



[0305] To a solution of 4,4'-(1-(4-hydroxy-3-iodophenyl)ethane-1,1-diyl)diphenol, assigned as P01 (7.09 g, 16.4 mmol) in anhydrous DMF (100 mL) in an EasyMax 401 Reactor (Mettler Toledo), was added cesium carbonate (32.06 g, 98.4 mmol) and potassium carbonate (20.40 g, 147.6 mmol) in three portions under stirring, followed addition of epibromohydrin (34.04 g, 21.3 mL, 246.0 mmol) dropwise at 0 °C. The reaction mixture was then stirred for 48 hours at 10°C under Nitrogen atmosphere and then poured into DI water (200 mL) under continuous stirring. The aqueous layer was extracted with diethyl ether (2 x 150 mL), the organic layer was washed with water (100 mL), dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using ethyl acetate/heptane solvent gradient (70:30 to 100% EA) to afford 8.50 g of the product as amorphous powder, assigned as C01, yield = 82%. *T_g* = 36°C (DSC). ¹H NMR (400 MHz, CDCl₃) δ 7.51, 6.96, 6.82, 6.70, 4.25,

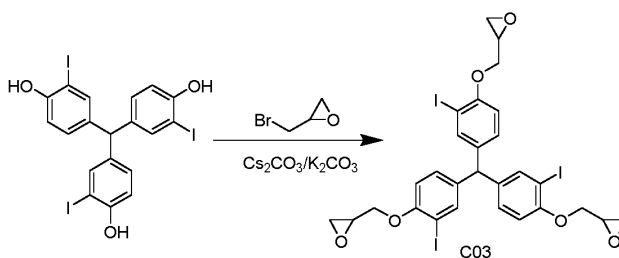
4.18, 4.02, 3.93, 3.34, 2.89, 2.74, 2.07. ^{13}C NMR (101 MHz, CDCl_3) δ 156.66, 155.18, 144.51, 142.22, 141.52, 139.38, 129.68, 113.95, 111.58, 86.39, 69.44, 68.75, 50.45, 50.21, 44.79, 30.76.

[0306] Preparation of 2,2'-((((1-(4-(oxiran-2-ylmethoxy) phenyl) ethane-1,1-diyl) bis(2-iodo-4,1-phenylene)) bis(oxy)) bis(methylene)) bis(oxirane), C02



[0307] To a solution of 4,4'-(1-(4-hydroxyphenyl)ethane-1,1-diyl)bis(2-iodophenol), assigned as P02 (5.76 g, 10.3 mmol) in anhydrous DMF (100 mL) in an EasyMax 401 Reactor (Mettler Toledo), was added cesium carbonate (20.17 g, 61.9 mmol) and potassium carbonate (12.84 g, 92.9 mmol) in three portions under stirring, followed addition of epibromohydrin (12.85 g, 8.0 mL, 92.9 mmol) dropwise at 0 °C. The reaction mixture was then stirred for 48 hours at 10 °C under Nitrogen atmosphere and then poured into DI water (200 mL) under continuous stirring. The aqueous layer was extracted with ethyl acetate/dichloromethane 50/50 mixture (2 x 150 mL), the organic layer was washed with water (100 mL), dried over MgSO_4 , and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using ethyl acetate/heptane solvent gradient (70:30 to 100% EA) to afford 5.34 g of the product as amorphous powder, assigned as C02, yield=71%. $T_g = 53^\circ\text{C}$ (DSC). ^1H NMR (400 MHz, CDCl_3) δ 7.48, 6.89, 6.83, 6.72, 4.26, 4.18, 4.05, 3.94, 3.39, 2.90, 2.75, 2.05. ^{13}C NMR (101 MHz, CDCl_3) δ 156.87, 155.55, 143.92, 143.25, 141.01, 139.20, 129.94, 129.61, 114.15, 111.75, 86.70, 69.51, 68.83, 50.20, 50.01, 44.90, 30.84.

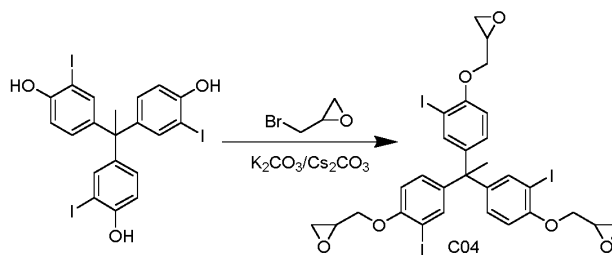
[0308] Preparation of tris(3-iodo-4-(oxiran-2-ylmethoxy) phenyl) methane, C03



[0309] To a solution of 4,4',4''-methanetriyltris(2-iodophenol), assigned as P09 (6.73 g, 10.0

mmol) in anhydrous DMF (50 mL) equipped in an EasyMax 401 Reactor (Mettler Toledo), was added cesium carbonate (19.64 g, 60.3 mmol) and potassium carbonate (8.33 g, 60.3 mmol) in three portions under stirring, followed addition of epibromohydrin (16.68 g, 10.4 mL, 120.5 mmol) dropwise at 0 °C. The reaction mixture was then stirred for 48 hours at 10 °C under Nitrogen and then poured into DI water (100 mL) under continuous stirring conditions. The aqueous layer was extracted with ethyl acetate/dichloromethane 50/50 mixture (2 x 150 mL), the organic layer was washed with water (100 mL), dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using ethyl acetate/heptane solvent gradient (70:30 to 100% EA) to afford 6.90 g of the product as amorphous powder, assigned as C03, yield=82%. *T_g* = 47°C (DSC). ¹H NMR (400 MHz, CDCl₃) δ 7.46, 6.94, 6.92, 6.76, 6.74, 5.25, 4.28, 4.25, 4.04, 4.02, 3.39, 2.92, 2.89. ¹³C NMR (101 MHz, CDCl₃) δ 155.89, 140.00, 138.08, 130.20, 112.38, 87.01, 69.57, 52.95, 50.17, 44.85.

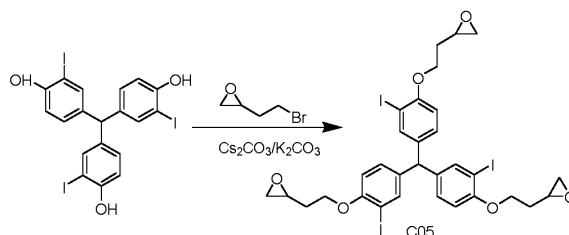
[0310] Preparation of 2,2',2''-(((ethane-1,1,1-triyltris(2-iodobenzene-4,1-diyl)) tris(oxy)) tris(methylene)) tris(oxirane), C04



[0311] To an OptiMax 1001 Reactor (Mettler Toledo), 4,4',4''-(ethane-1,1,1-triyl)tris(2-iodophenol), assigned as P03 (55.50 g, 81.1 mmol) was dissolved into anhydrous DMF (400 mL), then added cesium carbonate (158.6 g, 486.8 mmol) and potassium carbonate (67.28 g, 486.8 mmol) in three portions under stirring, followed addition of epibromohydrin (134.7 g, 84.14 mL, 973.6 mmol) dropwise at 0 °C. The reaction mixture was then stirred for 48 hours at 10 °C under Nitrogen atmosphere. The excessive catalysts and other insoluble by-product were removed by filtration. The DMF solution was concentrated to 100 mL under vacuum, and then dropwise added into DI water (4000 mL) under continuous stirring to precipitate the product. Water was removed by filtration with 0.2μm Omnipore™ PTFE Membrane Filters (Sigma Aldrich). The crude product was purified by dissolving into acetone (200 mL) and then precipitating into 20-fold excess of DI water. The dissolving/precipitating cycle was repeated twice to fully remove residual solvent and trace metals.

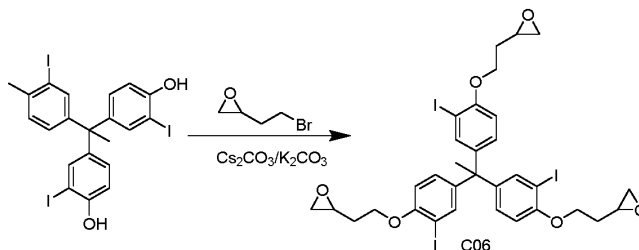
The white precipitate was dried under vacuum to afford 62.66 g of final product as amorphous powder, assigned as C04, yield=91%. $T_g = 62^\circ\text{C}$ (DSC). ^1H NMR (400 MHz, CDCl_3) δ 7.49, 7.48, 6.89, 6.87, 6.72, 6.70, 4.29, 4.26, 4.05, 4.02, 3.39, 2.92, 2.90, 2.03. ^{13}C NMR (101 MHz, CDCl_3) δ 155.48, 143.17, 139.12, 129.83, 111.73, 86.65, 69.48, 50.12, 49.94, 44.79, 30.78.

[0312] Preparation of tris(3-iodo-4-(2-(oxiran-2-yl) ethoxy) phenyl) methane, C05



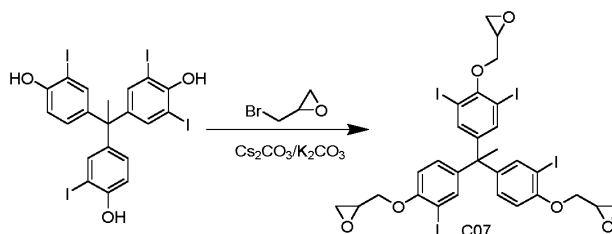
[0313] To a solution of 4,4',4''-methanetriyltris(2-iodophenol), assigned as P09 (6.73 g, 10.0 mmol) in anhydrous DMF (50 mL) equipped in an EasyMax 401 Reactor (Mettler Toledo), was added cesium carbonate (19.64 g, 60.3 mmol) and potassium carbonate (8.33 g, 60.3 mmol) in three portions under stirring, followed addition of 2-(2-bromoethyl)oxirane (18.38 g, 12.1 mL, 120.5 mmol) dropwise at 0°C . The reaction mixture was then stirred for 48 hours at 10°C under Nitrogen and then poured into DI water (100 mL) under continuous stirring conditions. The aqueous layer was extracted with ethyl acetate/dichloromethane 50/50 mixture (2 x 150 mL), the organic layer was washed with water (100 mL), dried over MgSO_4 , and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using ethyl acetate/heptane solvent gradient (70:30 to 100% EA) to afford 6.64 g of the product as amorphous powder, assigned as C05, yield=75%. $T_g = 39^\circ\text{C}$ (DSC). ^1H NMR (400 MHz, CDCl_3) δ 7.48, 7.47, 6.95, 6.93, 6.74, 6.72, 5.25, 4.13, 3.24, 2.86, 2.66, 2.10, 2.04. ^{13}C NMR (101 MHz, CDCl_3) δ 156.05, 139.91, 137.80, 130.20, 111.72, 86.89, 65.96, 53.01, 49.92, 47.65, 32.56.

[0314] Preparation of 2,2',2''-(((ethane-1,1,1-triyltris(2-iodobenzene-4,1-diyl)) tris(oxy)) tris(ethane-2,1-diyl) tris(oxirane), C06



[0315] To an OptiMax 1001 Reactor (Mettler Toledo), 4,4',4''-(ethane-1,1,1-triyl)tris(2-iodophenol), assigned as P03 (55.55 g, 81.3 mmol) was dissolved into anhydrous DMF (400 mL), then added cesium carbonate (158.8 g, 487.3 mmol) and potassium carbonate (67.34 g, 487.3 mmol) in three portions under stirring, followed addition of 2-(2-bromoethyl)oxirane (148.63 g, 97.7 mL, 974.5 mmol) dropwise at 0 °C. The reaction mixture was then stirred for 24 hours at 10°C under Nitrogen atmosphere. The excessive catalysts and other insoluble by-product were removed by filtration. The DMF solution was concentrated down to 100 mL under vacuum, and then dropwise added into DI water (4000 mL) under continuous stirring to precipitate the product. Water was removed by filtration with 0.2μ Omnipore™ PTFE Membrane Filters (Sigma Aldrich). The crude product was purified by dissolving into acetone (200 mL) and then precipitating into 20-fold excess of DI water. The dissolving/precipitating cycle was repeated twice to fully remove residual solvent and trace metals. The white precipitate was dried under vacuum to afford 67.15 g of final product as amorphous powder, assigned as C06, yield=92%. $T_g = 47\text{ °C}$ (DSC). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50, 6.91, 6.89, 6.70, 6.68, 4.14, 3.25, 2.87, 2.66, 2.17, 2.12, 2.04, 1.64. $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 155.62, 142.87, 139.02, 129.84, 111.05, 86.53, 65.85, 49.89, 47.63, 32.50, 30.84.

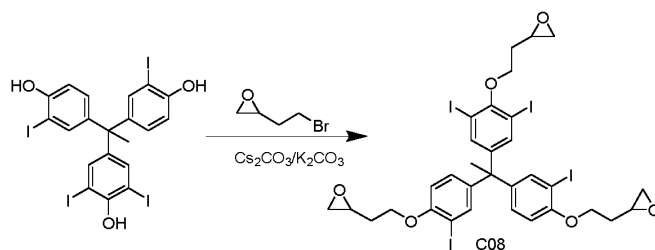
[0316] Preparation of 2,2'-((((1-(3,5-diiodo-4-(oxiran-2-ylmethoxy) phenyl) ethane-1,1-diyl) bis(2-iodo-4,1-phenylene)) bis(oxy)) bis(methylene)) bis(oxirane), C07



[0317] To an EasyMax 402 Reactor (Mettler Toledo), 4,4'-(1-(4-hydroxy-3,5-diiodophenyl)ethane-1,1-diyl)bis(2-iodophenol), assigned as P04 (6.50 g, 8.03 mmol) was dissolved into anhydrous DMF (50 mL), then added cesium carbonate (15.7 g, 48.2 mmol) and potassium carbonate (6.65 g, 48.2 mmol) in three portions under stirring, followed addition of epibromohydrin (13.3 g, 8.32 mL, 96.3 mmol) dropwise at 10 °C. The reaction mixture was then stirred for 48 hours at 10 °C under Nitrogen atmosphere. The excessive catalysts and other insoluble by-product were removed by filtration. The DMF solution was dropwise added into DI water (2000 mL) under continuous stirring to precipitate the product. Water was removed by filtration with 0.2μ Omnipore™ PTFE Membrane Filters (Sigma Aldrich). The crude product was

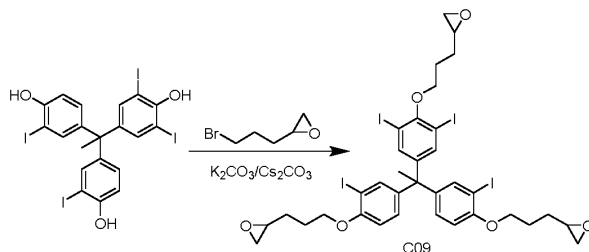
purified by dissolving into acetone (50 mL) and then precipitating into 20-fold excess of DI water. The dissolving/precipitating cycle was repeated twice to fully remove residual solvent and trace metals. The white precipitate was dried under vacuum to afford 6.34 g of final product as amorphous powder, assigned as C07, yield=81%. $T_g = 72\text{ }^\circ\text{C}$ (DSC). ^1H NMR (400 MHz, CDCl_3) δ 7.47, 7.40, 6.89, 6.87, 6.85, 6.74, 6.72, 6.69, 4.28, 4.14, 4.06, 3.52, 3.38, 2.91, 2.79, 2.01. ^{13}C NMR (101 MHz, CDCl_3) δ 155.67, 155.45, 148.57, 143.15, 142.15, 139.88, 139.10, 138.93, 129.82, 111.77, 90.59, 86.65, 73.96, 69.44, 50.19, 50.09, 49.84, 45.17, 44.79, 30.78.

[0318] Preparation of 2,2'-((((1-(3,5-diiodo-4-(2-(oxiran-2-yl) ethoxy) phenyl) ethane-1,1-diyl) bis(2-iodo-4,1-phenylene)) bis(oxy)) bis(ethane-2,1-diyl)) bis(oxirane), C08



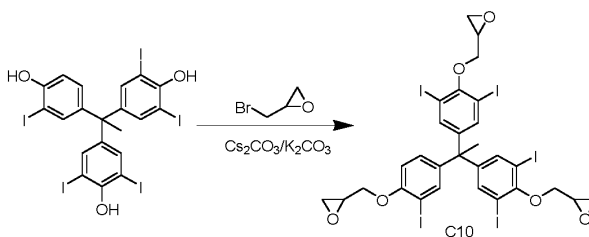
[0319] To an EasyMax 402 Reactor (Mettler Toledo), 4,4'-((1-(4-hydroxy-3,5-diiodophenyl)ethane-1,1-diyl)bis(2-iodophenyl))ethane, assigned as P04 (6.85 g, 8.46 mmol), was dissolved into anhydrous DMF (50 mL), then added cesium carbonate (16.53 g, 50.74 mmol) and potassium carbonate (7.01 g, 50.74 mmol) in three portions under stirring, followed addition of 2-(2-bromoethyl)oxirane (15.48 g, 10.18 mL, 101.5 mmol) dropwise at $10\text{ }^\circ\text{C}$. The reaction mixture was then stirred for 48 hours at $10\text{ }^\circ\text{C}$ under Nitrogen atmosphere. The excessive catalysts and other insoluble by-product were removed by filtration. The DMF solution was dropwise added into DI water (2000 mL) under continuous stirring to precipitate the product. Water was removed by filtration with 0.2 μ Omnipore™ PTFE Membrane Filters (Sigma Aldrich). The crude product was purified by dissolving into acetone (50 mL) and then precipitating into 20-fold excess of DI water. The dissolving/precipitating cycle was repeated twice to fully remove residual solvent and trace metals. The white precipitate was dried under vacuum to afford 7.50 g of final product as amorphous powder, assigned as C08, yield=87%. $T_g = 51\text{ }^\circ\text{C}$ (DSC). ^1H NMR (400 MHz, CDCl_3) δ 7.49, 7.42, 6.91, 6.89, 6.87, 6.72, 6.70, 6.68, 4.14, 3.33, 3.25, 2.87, 2.67, 2.11, 2.01. ^{13}C NMR (101 MHz, CDCl_3) δ 156.00, 155.83, 155.62, 148.49, 142.87, 141.87, 139.82, 139.02, 138.85, 129.84, 111.05, 90.71, 86.55, 69.97, 65.87, 49.86, 47.62, 47.50, 33.37, 32.50, 30.85.

[0320] Preparation of 2,2'-((((1-(3,5-diiodo-4-(3-(oxiran-2-yl) propoxy) phenyl) ethane-1,1-diyl) bis(2-iodo-4,1-phenylene)) bis(oxy)) bis(propane-3,1-diyl)) bis(oxirane), C09



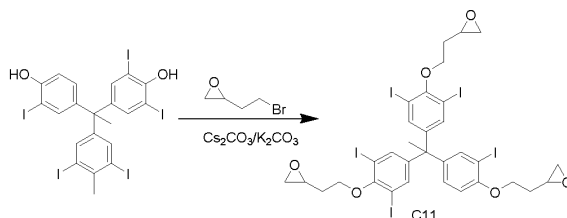
[0321] To an EasyMax 402 Reactor (Mettler Toledo), 4,4'-(1-(4-hydroxy-3,5-diiodophenyl)ethane-1,1-diyl)bis(2-iodophenol), assigned as P04 (3.40 g, 4.11 mmol), was dissolved into anhydrous DMF (50 mL), then added cesium carbonate (8.12 g, 24.7 mmol) and potassium carbonate (3.45 g, 24.7 mmol) under stirring, followed addition of 2-(3-bromopropyl)oxirane (8.40 g, 5.68 mL, 49.4 mmol) dropwise at 10 °C. The reaction mixture was then stirred for 48 hours at 10 °C under Nitrogen atmosphere. The excessive catalysts and other insoluble by-product were removed by filtration. The DMF solution was dropwise added into DI water (2000 mL) under continuous stirring conditions to precipitate the product. Water was removed by filtration with 0.2µm Omnipore™ PTFE Membrane Filters (Sigma Aldrich). The crude product was purified by dissolving into acetone (50 mL) and then precipitating into 20-fold excess of DI water. The dissolving/precipitating cycle was repeated twice to fully remove residual solvent and trace metals. The white precipitate was dried under vacuum to afford 3.50 g of final product as amorphous powder, assigned as C09, yield=80%. $T_g = 39^\circ\text{C}$ (DSC). ^1H NMR (400 MHz, CDCl_3) δ 7.55, 7.48, 7.40, 7.17, 7.07, 6.88, 6.68, 4.23, 4.04, 3.41, 3.02, 2.79, 2.52, 2.00, 1.90, 1.72. ^{13}C NMR (101 MHz, CDCl_3) δ 155.97, 148.42, 141.77, 139.85, 138.85, 129.84, 111.25, 90.97, 90.76, 86.80, 68.63, 52.05, 51.31, 47.24, 29.32, 26.61, 25.80.

[0322] Preparation of 2,2'-((((1-(3-iodo-4-(oxiran-2-ylmethoxy) phenyl) ethane-1,1-diyl) bis(2,6-diiodo-4,1-phenylene)) bis(oxy)) bis(methylene)) bis(oxirane), C10



[0323] To an EasyMax 402 Reactor (Mettler Toledo), 4,4'-(1-(4-hydroxy-3-iodophenyl)ethane-1,1-diyl)bis(2,6-diiodophenol), assigned as P05 (5.05 g, 5.40 mmol), was dissolved into anhydrous DMF (50 mL), then added cesium carbonate (10.55 g, 32.38 mmol) and potassium carbonate (4.47 g, 32.38 mmol) under stirring, followed addition of 2-(bromomethyl)oxirane (14.86 g, 9.28 mL, 107.38 mmol) dropwise at 10 °C. The reaction mixture was then stirred for 48 hours at 10 °C under Nitrogen atmosphere. The excessive catalysts and other insoluble by-product were removed by filtration. The DMF solution was dropwise added into DI water (2000 mL) under continuous stirring to precipitate the product. Water was removed by filtration with 0.2μ Omnipore™ PTFE Membrane Filters (Sigma Aldrich). The crude product was purified by dissolving into acetone (50 mL) and then precipitating into 20-fold excess of DI water. The dissolving/precipitating cycle was repeated twice to fully remove residual solvent and trace metals. The precipitate was dried under vacuum to afford 5.54 g of final product as amorphous powder, assigned as C10, yield=93%. $T_g = 79^\circ\text{C}$ (DSC). ^1H NMR (400 MHz, CDCl_3) δ 7.48, 7.39, 6.87, 6.85, 6.74, 6.72, 4.30, 4.14, 4.07, 3.53, 3.40, 2.92, 2.79, 2.01. ^{13}C NMR (101 MHz, CDCl_3) δ 156.01, 148.65, 147.66, 142.26, 140.36, 139.86, 129.90, 111.77, 91.06, 87.06, 74.04, 69.52, 50.27, 44.86, 30.86.

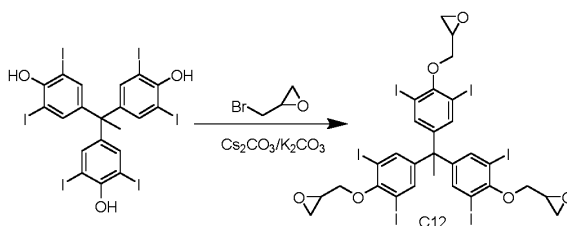
[0324] Preparation of 2,2'-((((1-(3-iodo-4-(2-(oxiran-2-yl) ethoxy) phenyl) ethane-1,1-diyl) bis(2,6-diiodo-4,1-phenylene)) bis(oxy)) bis(ethane-2,1-diyl)) bis(oxirane), C11



[0325] To an EasyMax 402 Reactor (Mettler Toledo), 4,4'-(1-(4-hydroxy-3-iodophenyl)ethane-1,1-diyl)bis(2,6-diiodophenol), assigned as P05 (5.03 g, 5.40 mmol), was dissolved into anhydrous DMF (50 mL), then added cesium carbonate (10.51 g, 32.25 mmol) and potassium carbonate (4.46 g, 32.25 mmol) under stirring, followed addition of 2-(2-bromoethyl)oxirane (14.76 g, 9.70 mL, 96.75 mmol) dropwise at 10 °C. The reaction mixture was then stirred for 48 hours at 10 °C under Nitrogen atmosphere. The excessive catalysts and other insoluble by-product were removed by filtration. The DMF solution was dropwise added into DI water (2000 mL) under continuous stirring to precipitate the product. Water was removed by filtration with 0.2μ Omnipore™ PTFE Membrane Filters (Sigma Aldrich). The crude product was purified by dissolving into acetone (50 mL) and then

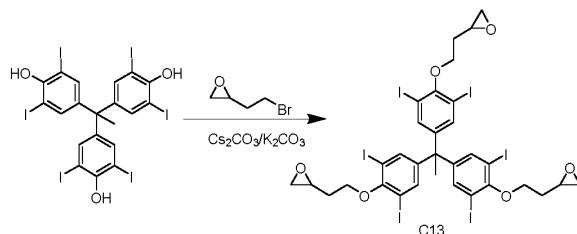
precipitating into 20-fold excess of DI water. The dissolving/precipitating cycle was repeated twice to fully remove residual solvent and trace metals. The precipitate was dried under vacuum to afford 5.50 g of final product as amorphous powder, assigned as C11, yield=89%. $T_g = 57^\circ\text{C}$ (DSC). ^1H NMR (400 MHz, CDCl_3) δ 7.49, 7.42, 7.40, 7.38, 6.88, 6.86, 6.71, 6.69, 4.15, 3.34, 3.25, 2.87, 2.66, 2.17, 2.10, 2.02. ^{13}C NMR (101 MHz, CDCl_3) δ 155.91, 147.57, 141.95, 139.79, 129.90, 111.20, 90.94, 86.75, 70.10, 65.94, 49.93, 47.69, 33.44, 32.57, 31.99, 30.91.

[0326] Preparation of 2,2',2''-(((ethane-1,1,1-triyltris(2,6-diiodobenzene-4,1-diyl)) tris(oxy)) tris(methylene)) tris(oxirane), C12



[0327] To an EasyMax 402 Reactor (Mettler Toledo), 4,4',4''-(ethane-1,1,1-triyl)tris(2,6-diiodophenol), assigned as P06 (10.46 g, 9.85 mmol), was dissolved into anhydrous DMF (50 mL), then added cesium carbonate (14.45 g, 44.33 mmol) and potassium carbonate (6.13 g, 44.33 mmol) under stirring, followed addition of 2-(bromomethyl)oxirane (12.27 g, 7.66 mL, 88.67 mmol) dropwise at 10°C . The reaction mixture was then stirred for 48 hours at 10°C under Nitrogen atmosphere. The excessive catalysts and other insoluble by-product were removed by filtration. The DMF solution was dropwise added into DI water (2000 mL) under continuous stirring to precipitate the product. Water was removed by filtration with 0.2 μ Omnipore™ PTFE Membrane Filters (Sigma Aldrich). The crude product was purified by dissolving into acetone (50 mL) and then precipitating into 20-fold excess of DI water. The dissolving/precipitating cycle was repeated twice to fully remove residual solvent and trace metals. The precipitate was dried under vacuum to afford 10.09 g of final product as amorphous powder, assigned as C12, yield=83%. $T_g = 89^\circ\text{C}$ (DSC). ^1H NMR (400 MHz, CDCl_3) δ 7.49, 7.39, 6.84, 6.74, 4.30, 4.16, 4.07, 3.54, 3.40, 2.94, 2.80, 2.00. ^1H NMR (400 MHz, Acetone) δ 7.61, 7.58, 7.04, 6.94, 4.41, 4.38, 4.19, 4.16, 4.00, 3.47, 3.34, 2.84, 2.72, 2.14. ^{13}C NMR (101 MHz, Acetone) δ 206.26, 157.29, 157.05, 148.87, 147.98, 143.10, 142.22, 140.80, 139.67, 130.87, 112.84, 91.44, 86.97, 79.00, 75.41, 70.70, 50.69, 50.49, 44.81, 44.51, 30.70.

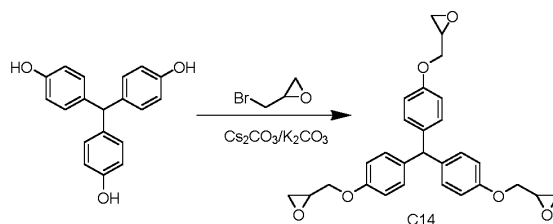
[0328] Preparation of 2,2',2''-(((ethane-1,1,1-triyl)tris(2,6-diiodobenzene-4,1-diyl)) tris(oxy)) tris(ethane-2,1-diyl) tris(oxirane), C13



[0329] To an EasyMax 402 Reactor (Mettler Toledo), 4,4',4''-(ethane-1,1,1-triyl)tris(2,6-diiodophenol), assigned as P06 (10.45 g, 9.84 mmol), was dissolved into anhydrous DMF (50 mL), then added cesium carbonate (14.43 g, 44.29 mmol) and potassium carbonate (6.12 g, 44.29 mmol) under stirring, followed addition of 2-(2-bromoethoxy)oxirane (13.51 g, 8.88 mL, 88.58 mmol) dropwise at 10 °C. The reaction mixture was then stirred for 48 hours at 10 °C under Nitrogen atmosphere. The excessive catalysts and other insoluble by-product were removed by filtration. The DMF solution was dropwise added into DI water (2000 mL) under continuous stirring to precipitate the product. Water was removed by filtration with 0.2μ Omnipore™ PTFE Membrane Filters (Sigma Aldrich). The crude product was purified by dissolving into acetone (50 mL) and then precipitating into 20-fold excess of DI water. The dissolving/precipitating cycle was repeated twice to fully remove residual solvent and trace metals. The precipitate was dried under vacuum to afford 10.36 g of final product as amorphous powder, assigned as C13, yield=83%. $T_g = 67\text{ }^{\circ}\text{C}$ (DSC). ^1H NMR (400 MHz, CDCl_3) δ 7.40, 4.14, 3.34, 2.88, 2.66, 2.20, 2.09, 2.00. ^{13}C NMR (101 MHz, CDCl_3) δ 156.59, 147.51, 146.50, 139.71, 129.88, 111.24, 91.15, 90.93, 86.89, 70.04, 65.87, 49.93, 47.65, 47.52, 33.38, 32.50.

[0330] Comparative Examples

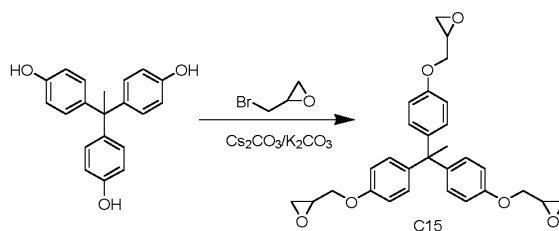
[0331] Preparation of tris(4-(oxiran-2-ylmethoxy) phenyl) methane, C14



[0332] To a solution of 1 4,4',4''-methanetriyltriphenol (3.60 g, 12.3 mmol) in anhydrous DMF (50 mL) in an EasyMax 401 Reactor (Mettler Toledo), was added cesium carbonate (24.1 g, 73.9

mmol) and potassium carbonate (10.21 g, 73.9 mmol) in three portions under stirring, followed addition of epibromohydrin (20.44 g, 12.77 mL, 147.7 mmol) dropwise at 10 °C. The reaction mixture was then stirred overnight at 10 °C and then poured into DI water (100 mL) under continuous stirring. The aqueous layer was extracted with diethyl ether (2 x 150 mL), the organic layer was washed with water (100 mL), dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using ethyl acetate/heptane solvent gradient (70:30 to 100% EA) to afford 5.02 g of the product as viscous semi-solid, assigned as C14, yield = 89%. *T_g* = 9 °C (DSC). ¹H NMR (400 MHz, CDCl₃) δ 7.00, 6.98, 6.84, 6.82, 5.39, 4.20, 4.17, 3.94, 3.92, 3.33, 2.89, 2.75, 1.57. ¹³C NMR (101 MHz, CDCl₃) δ 157.01, 137.31, 130.39, 114.49, 68.89, 54.45, 50.30, 44.91.

[0333] Preparation of 2,2',2''-(((ethane-1,1,1-triyltris(benzene-4,1-diyl))tris(oxy)) tris(methylene)) tris(oxirane), C00



[0334] To a solution of 1,1,1-Tris(4-hydroxyphenyl)ethane (3.50 g, 11.4 mmol) in anhydrous DMF (50 mL) in an EasyMax 401 Reactor (Mettler Toledo), was added cesium carbonate (21.0 g, 64.4 mmol) and potassium carbonate (9.47 g, 68.5 mmol) in three portions under stirring, followed addition of epibromohydrin (10.08 g, 73.6 mmol) dropwise at 10 °C. The reaction mixture was then stirred overnight at 10 °C and then poured into DI water (100 mL) under continuous stirring conditions. The aqueous layer was extracted with diethyl ether (2 x 150 mL), the organic layer was washed with water (100 mL), dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using ethyl acetate/heptane solvent gradient (70:30 to 100% EA) to afford 4.42 g of the product as viscous semi-solid, assigned as C00, yield = 82%. *T_g* = 15°C (DSC). ¹H NMR (400 MHz, CDCl₃) δ 6.99, 6.97, 6.81, 6.80, 4.20, 4.18, 3.96, 3.92, 3.35, 2.90, 2.76, 2.10. ¹³C NMR (101 MHz, CDCl₃) δ 156.58, 142.28, 129.72, 113.86, 68.79, 50.70, 50.25, 44.83, 30.80.

[0335] Table 5 gives a summary of the yields, numbers of iodine per molecules, and the observed *T_g* for the crosslinkers, whose synthesis is described above.

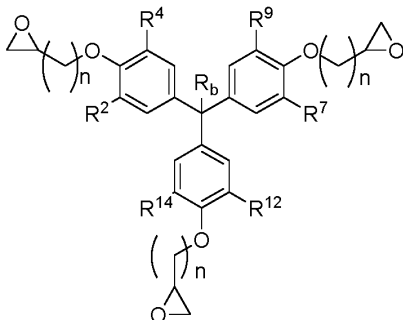
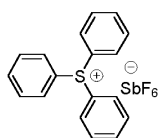
						
Compound	Structure	Iodine /molecule	Mw (g/mole)	Yield (%)	T _g (°C)	
C14	R _b =H; R ² , R ⁴ , R ⁷ , R ⁹ , R ¹² , R ¹⁴ =H; n=1	0	460.53	89	9	
C00	R _b =CH ₃ ; R ² , R ⁴ , R ⁷ , R ⁹ , R ¹² , R ¹⁴ =H; n=1	0	474.55	82	15	
C01	R _b =CH ₃ ; R ² , R ⁴ , R ⁷ , R ⁹ , R ¹² =H; R ¹⁴ =I; n=1	1	600.45	82	36	
C02	R _b =CH ₃ ; R ² , R ⁴ , R ⁷ , R ¹² =H; R ⁹ , R ¹⁴ =I; n=1	2	726.35	71	53	
C03	R _b =H; R ² , R ⁷ , R ¹² =H; R ⁴ , R ⁹ , R ¹⁴ =I; n=1	3	838.22	82	47	
C04	R _b =CH ₃ ; R ² , R ⁷ , R ¹² =H; R ⁴ , R ⁹ , R ¹⁴ =I; n=1	3	852.24	91	62	
C05	R _b =H; R ² , R ⁷ , R ¹² =H; R ⁴ , R ⁹ , R ¹⁴ =I; n=2	3	880.30	75	39	
C06	R _b =CH ₃ ; R ² , R ⁷ , R ¹² =H; R ⁴ , R ⁹ , R ¹⁴ =I; n=2	3	894.32	92	47	
C07	R _b =CH ₃ ; R ² , R ⁷ =H; R ⁴ , R ⁹ , R ¹² , R ¹⁴ =I; n=1	4	978.14	81	72	
C08	R _b =CH ₃ ; R ² , R ⁷ =H; R ⁴ , R ⁹ , R ¹² , R ¹⁴ =I; n=2	4	1020.22	87	51	
C09	R _b =CH ₃ ; R ² , R ⁷ =H; R ⁴ , R ⁹ , R ¹² , R ¹⁴ =I; n=3	4	1062.30	80	39	
C10	R _b =CH ₃ ; R ² =H; R ⁴ , R ⁷ , R ⁹ , R ¹² , R ¹⁴ =I; n=1	5	1104.04	93	79	
C11	R _b =CH ₃ ; R ² =H; R ⁴ , R ⁷ , R ⁹ , R ¹² , R ¹⁴ =I; n=2	5	1156.12	89	57	
C12	R _b =CH ₃ ; R ² , R ⁴ , R ⁷ , R ⁹ , R ¹² , R ¹⁴ =I; n=1	6	1229.93	83	89	
C13	R _b =CH ₃ ; R ² , R ⁴ , R ⁷ , R ⁹ , R ¹² , R ¹⁴ =I; n=2	6	1272.01	83	67	

Table 5 Summary of the yield and the observed T_g for crosslinker compounds C00-C14.

[0336] Formulations with Novel Crosslinking Compounds and Exposures**[0337] Formulations**

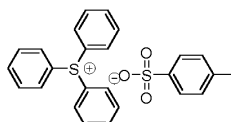
[0338] Dissolve the components listed in Tables 6 and 7 (the unit are relative molar content normalized to 100) in ethyl lactate (EL), which is a solvent, and prepare so that the concentration of the solid component is 1.25 mass%. Components other than solvents are solid components. The resulting solution is filtered with a 0.2 μ m pore size filter.

[0339] The structure of the components employed in the formulations listed in Table 6 and Table 7 where the Tables list shown in the structures as follows, where for the crosslinkers the number under parenthesis is the synthetic sample number given above.



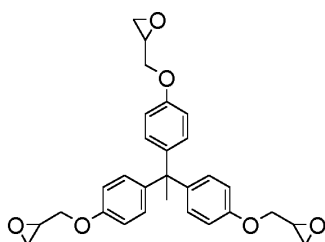
Chemical Formula: $C_{18}H_{15}F_6SSb$
Molecular Weight: 499.13

(TPS-103)



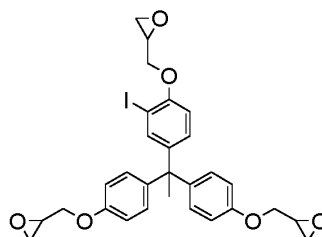
Chemical Formula: $C_{25}H_{22}O_3S_2$
Molecular Weight: 434.57

(TPS-1000)



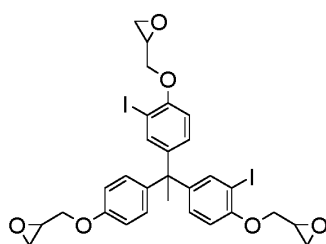
Chemical Formula: $C_{29}H_{30}O_6$
Molecular Weight: 474.55

(C00)



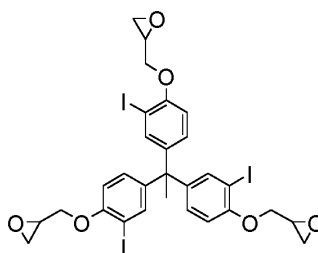
Chemical Formula: $C_{29}H_{29}IO_6$
Molecular Weight: 600.45

(C01)



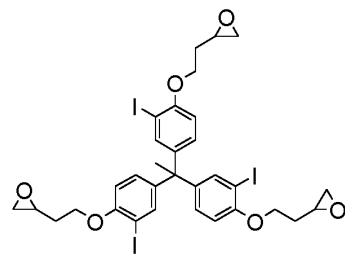
Chemical Formula: $C_{29}H_{28}I_2O_6$
Molecular Weight: 726.35

(C02)



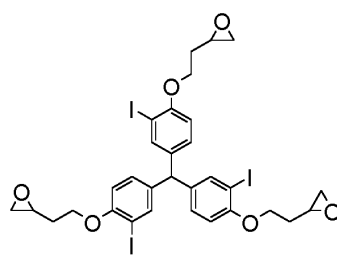
Chemical Formula: $C_{29}H_{27}I_3O_6$
Molecular Weight: 852.24

(C04)



Chemical Formula: C₃₂H₃₃I₃O₆
Molecular Weight: 894.32

(C06)



Chemical Formula: C₃₁H₃₁I₃O₆
Molecular Weight: 880.30

(C05)

Exposures

[0340] The surface of a silicon substrate (12 inches) is treated with a EUV-UL, AL412, solution at 205°C. for 60 seconds. A negative tone EUV resist composition is spin-coated using CLEAN TRACK™ LITHIUS Pro™ (Tokyo Electron) thereto and soft-baked at 80 °C for 60 seconds to form a resist film having a film thickness of 26 nm on the same substrate. This is exposed with an EUV exposure apparatus NXE: 3400 (manufactured by ASML) through a mask having a size of 16 nm (line: space = 1: 1). A plurality of exposure amounts is set, and a substrate under each condition is obtained. As the amount of exposure increases, the pattern width of the resist pattern formed by later development increases.

[0341] On the above evaluation substrate, a resist patten having a space size of 16 nm formed on a mask of 16 nm is observed using CG5000(Hitachi High-Tech), and DtS, Exposure Latitude (EL), and LWR are observed.

[0342] Table 6 shows a summary of the composition and EUV lithographic results obtained with formulations F00, F02, F02 and F03. These results demonstrate the dramatic improvement in lithographic performance with increasing ortho iodine substitution compared to the crosslinker of formulation F00 which does not contain any iodine. The appearance of the imaged substrates is shown in FIG. 4.

Formula		Crosslinker	PAG	Quencher	Solvent	PEB (°C)	DtS (MJ/CM ²)	EL %	LER (NM)	LWR (NM)
F00	Name	C00	TPS-103	TPS-1000	EL	70	-	-	-	-
	mole Ratio	100	30.7	6.0	--					
F01	Name	C01	TPS-103	TPS-1000	EL	70	-	-	-	-
	mole Ratio	100	30.7	6.0	--					

F02	Name	C02	TPS-103	TPS-1000	EL	70	38	27.7	4.1	5.1
	moleRatio	100	30.7	6.0	--					
F03	Name	C04	TPS-103	TPS-1000	EL	80	28	-	3.4	4.3

Table 6

[0343] Table 7 shows a summary of the composition and EUV lithographic results obtained with formulation F06 and EX08. The appearance of the imaged substrates is shown in FIG. 5. The crosslinkers in these two formulations have a longer spacer $-\text{CH}_2-\text{CH}_2-$ rather than $-\text{CH}_2-$ for the pendant oxirane moiety compared to those in Table 6. These two formulations also give better performance consistent with their higher iodine content which is consistent with was observed in Table 6. Compared to formulation EX08 with crosslinker C05, formulation F06 with crosslinker C06 resulted in an improved LER and LWR, under the similar processing conditions. The only difference between crosslinker C06 and C05 is C06 with a methyl group in the molecular core, but only with a hydrogen in the C05 core. LER and LWR evaluation.

Formula		Crosslinker	PAG	Quencher	Solvent	PEB (°C)	DtS (MJ/CM ²)	EL %	LER (NM)	LWR (NM)
F06	Name	C06	TPS-103	TPS-1000	EL	70	49.4	23.4	3.2	3.7
	mole Ratio	100	62.9	23.1	--					
EX08	Name	C05	TPS-103	TPS-1000	EL	70	49.5	28.1	3.8	4.5
	mole Ratio	100	62.9	23.1	--					

Table 7

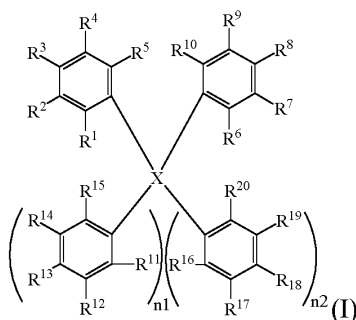
[0344] The line width of the line-and-space pattern obtained with DToS exposure is measured and the LWR is 3 times the standard deviation (σ) (3σ). The results obtained are shown in Tables 6 and 7. The lower the value, the better the pattern.

[0345] Although the disclosed and claimed subject matter has been described and illustrated with a certain degree of particularity, it is to be understood that the disclosure has been made only by way of example, and that numerous changes in the conditions and order of steps can be resorted to by those skilled in the art without departing from the spirit and scope of the disclosed and claimed subject matter.

CLAIMS

What is claimed is:

1. A compound of structure (I):



wherein n_1 and n_2 are each independently 1 or 0,

X is $C_pH_{2p-n_1-n_2}$ or $C_{6+4(q-1)}H_{4+2(q-1)-n_1-n_2}$,

p is 1 to 6,

q is 1 to 3,

wherein one or more H of X may be each independently substituted with C_{1-5} straight-chain alkyl or C_{3-5} branched alkyl,

R^1 to R^{20} are each independently H, a halogen selected from F, Cl, Br, and I, C_{1-15} straight-chain alkyl, C_{3-15} branched alkyl, C_{3-15} alkyl containing a cyclic structure, C_{1-15} straight-chain alkoxy, C_{3-15} branched alkoxy, C_{3-15} alkoxy containing a cyclic structure, $-CH_2OH$, $-CH_2OR^{22}$, $-COOH$, $-OH$, or Y represented by formula (II), where R^{22} is C_{1-15} straight-chain alkyl, C_{3-15} branched alkyl, or C_{3-15} alkyl containing a cyclic structure,

R^{11} and R^{16} may together form a single bond,

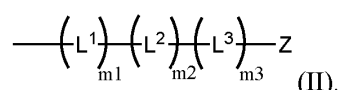
when R^1 to R^{20} are each independently alkyl, one or more non-adjacent methylene ($-CH_2-$) of the alkyl may be each independently substituted with $-O-$, $-S-$, $-CO-$, $-CO-O-$, $-O-CO-$, $-O-CO-O-$, $-CH=CH-$, or $-C\equiv C-$,

when R^1 to R^{20} are each independently alkyl, one or more H of the alkyl may be each independently substituted with F, Cl, Br, I, $COOH$, OH or OR^{22} ,

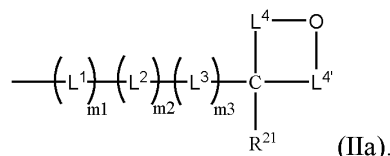
wherein at least one of R^1 to R^5 and/or R^{11} to R^{15} is Y and at least one of R^1 to R^5 and/or R^{11} to R^{15} is selected from the group consisting of CH_2OH , F, Cl, Br, and I,

and/or wherein at least one of R^6 to R^{10} and/or R^{16} to R^{20} is Y and/or at least one of R^6 to R^{10} or R^{16} to R^{20} is selected from the group consisting of CH_2OH , F, Cl, Br, and I,

where in structure (II), L^1 is each independently C_{1-5} straight-chain alkylene or C_{3-5} branched alkylene, L^2 is each independently -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O-, -CH=CH-, or -C≡C-, L^3 is each independently C_{1-15} straight-chain alkylene or C_{3-15} branched alkylene, where Z is an oxirane or an oxetane moiety, and said oxirane moiety or oxetane moiety may further comprise as a substituent a C_{1-8} linear alkyl, C_{3-8} branched alkyl, or -CH₂OH, and further where m_1 , m_2 , and m_3 are each independently 0 or 1, and when m_2 is 0, m_1 is 0,



2. The crosslinking compound of claim 1, where structure (II), more specifically has structure (IIa), wherein L^1 is each independently C_{1-5} straight-chain alkylene or C_{3-5} branched alkylene; L^2 is each independently -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O-, -CH=CH-, or -C≡C-, L^3 is each independently C_{1-15} straight-chain alkylene or C_{3-15} branched alkylene, L^4 is C_{1-2} straight-chain alkylene, and $L^{4'}$ is either a direct valence bond or a C_1 straight chain alkylene, and R^{21} is H, C_{1-8} linear alkyl, C_{3-8} branched alkyl, or -CH₂OH, m_1 , m_2 , and m_3 are each independently 0 or 1, and when m_2 is 0, m_1 is 0,



3. The crosslinking compound of claim 1 or 2, wherein in structure (I), at least one of R^1 to R^5 and/or R^{11} to R^{15} is Y and at least one of R^1 to R^5 and/or R^{11} to R^{15} is -CH₂OH, and/or wherein at least one of R^6 to R^{10} and/or R^{16} to R^{20} is Y and/or at least one of R^6 to R^{10} or R^{16} to R^{20} is CH₂OH.

4. The crosslinking compound of any one of claims 1 to 3, having structure (I), wherein n_1 and n_2 are each independently 1 or 0;

X is $C_p H_{2p-n_1-n_2}$ or $C_{6+4(q-1)} H_{4+2(q-1)-n_1-n_2}$;

p is 1 to 6;

q is 1 to 3;

R^1 and R^6 are the same and are selected from, H or a C_{1-8} alkyl, I, Cl, and Br,

R^2 and R^7 are the same moiety having structure (III),

R^3 and R^8 are the same and have structure (II-1), where L^4 is C_{1-2} straight-chain alkylene, and $L^{4'}$

is either a direct valence bond or a C₁ straight chain alkylene,

L⁵ is a C₁₋₅ linear chain alkylene or a C₃₋₅ branched alkylene, and R²¹ is, H, a C₁₋₈ linear alkyl, a C₃₋₈ branched alkyl, or a -CH₂OH,

R⁴ and R⁹ are individually selected from, H, a C₁₋₈ alkyl, I, Cl, and Br,

R⁵ and R¹⁰ are individually selected from, H or a C₁₋₈ alkyl, I, Cl, and Br,

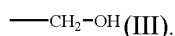
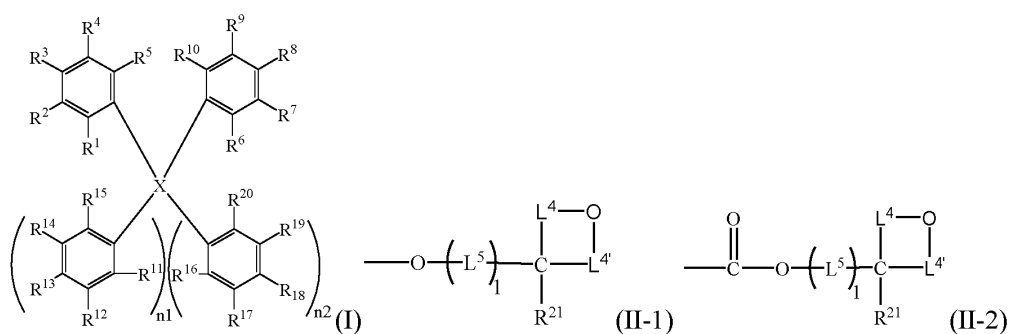
R⁶ and R¹ are individually selected from, H or a C₁₋₈ alkyl, I, Cl, and Br,

R¹⁴ and R¹⁹ are individually selected from H, I, Cl, Br,

R¹³ and R¹⁸ are individually selected from H, I, Cl, Br,

R¹¹ and R¹⁶ are individually selected from H, I, Cl, Br, or where R¹¹ and R¹⁶ form a single valence bond together,

R¹² and R¹⁷ are individually selected from, H, I, Cl, Br, structure (II-1), or structure (II-2), where L⁴ is a C₁₋₂ linear -chain alkylene, L^{4'} is either a direct valence bond or a C₁ straight chain alkylene, and L⁵ is a C₁₋₅ linear chain alkylene or a C₃₋₅ branched alkylene,



5. The crosslinking compound of any one of claims 1 to 4, which has structure (I-2), wherein,

R¹ and R⁶ are the same and are selected from, H or a C₁₋₈ alkyl, I, Cl, and Br,

R² and R⁷ are the same moiety having structure (III),

R³ and R⁸ are the same and have structure (II-1), where L⁴ is a C₁₋₂ linear -chain alkylene, L^{4'} is either a direct valence bond or a C₁ straight chain alkylene, and L⁵ is a C₁₋₅ linear chain alkylene or a C₃₋₅ branched alkylene, and R²¹ is, H, a C₁₋₈ linear alkyl, a C₃₋₈ branched alkyl, or a -CH₂OH,

R⁴ and R⁹ are individually selected from, H, a C₁₋₈ alkyl, I, Cl, and Br,

R⁵ and R¹⁰ are individually selected from, H or a C₁₋₈ alkyl, I, Cl, and Br,

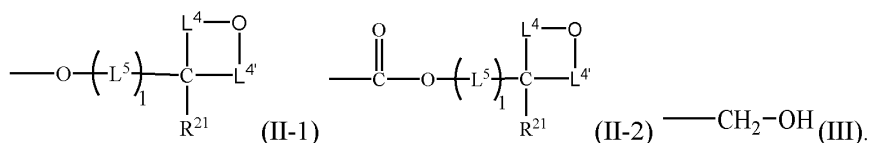
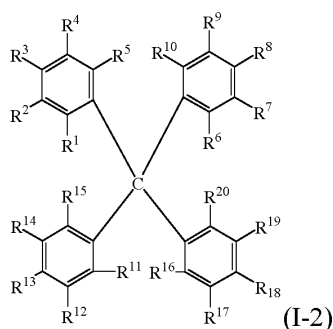
R^6 and R^1 are individually selected from, H or a C_{1-8} alkyl, I, Cl, and Br,

R^{14} and R^{19} are individually selected from H, I, Cl, Br,

R^{13} and R^{18} are individually selected from H, I, Cl, Br,

R^{11} and R^{16} are individually selected from H, I, Cl, and Br, or where R^{11} and R^{16} may form a single bond,

R^{12} and R^{17} are individually selected from H, I, Cl, Br, structure (II-1), or structure (II-2), where L^4 is a C_{1-2} linear -chain alkylene, $L^{4'}$ is either a direct valence bond or a C_1 straight chain alkylene, and L^5 is a C_{1-5} linear chain alkylene or a C_{3-5} branched alkylene,



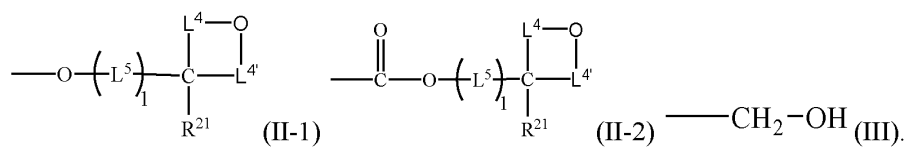
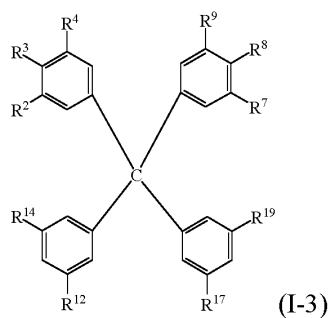
6. The crosslinking compound of any one of claims 1 to 5, which has structure (I-3), where R^2 and R^7 are the same moiety having structure (III),

R^3 and R^8 are the same and have structure (II-1), where L^4 is a C_{1-2} linear -chain alkylene, $L^{4'}$ is either a direct valence bond or a C_1 straight chain alkylene, and L^5 is a C_{1-5} linear -chain alkylene or a C_{3-5} branched alkylene, and R^{21} is, H, a C_{1-8} linear alkyl, a C_{3-8} branched alkyl, or a $-CH_2OH$,

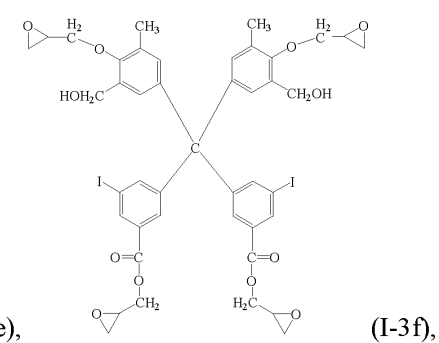
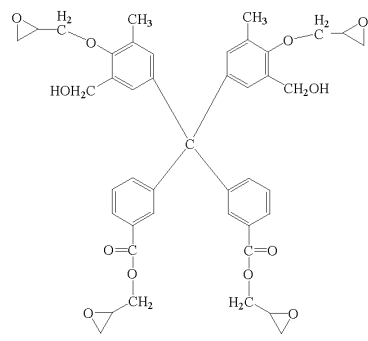
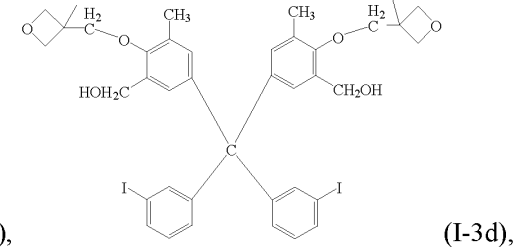
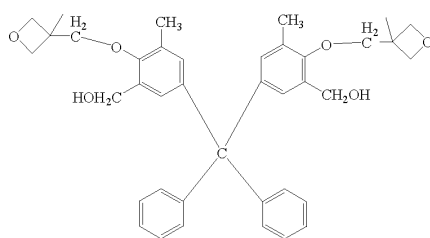
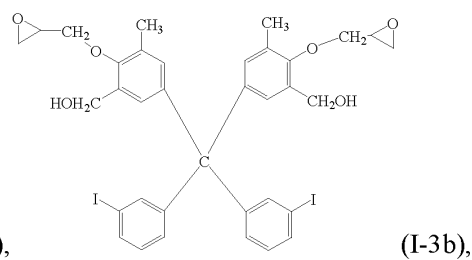
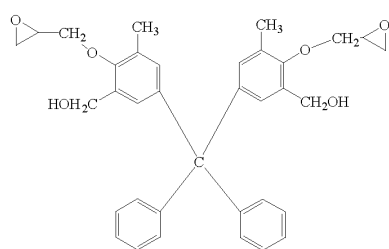
R^4 and R^9 are the same and are selected from, H or a C_{1-8} alkyl, I, Cl, and Br,

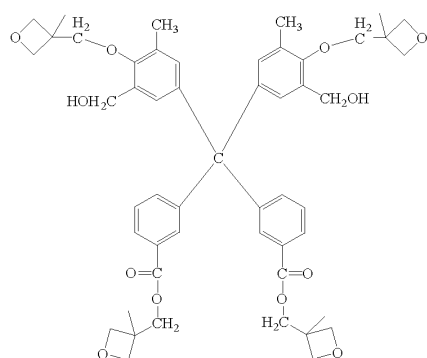
R^{12} and R^{17} are individually selected from H, structure (II-1), or structure (II-2),

R^{14} and R^{19} are the same and are selected from H, I, Cl, Br,

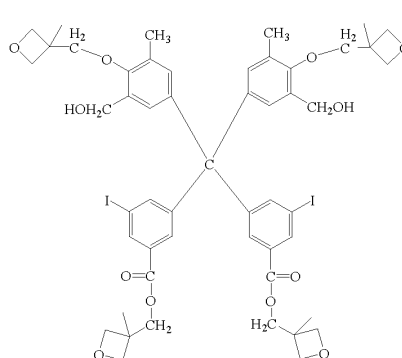


7. The crosslinking compound of any one of claims 1 to 6, which is selected from the group consisting of any one of the following compounds:

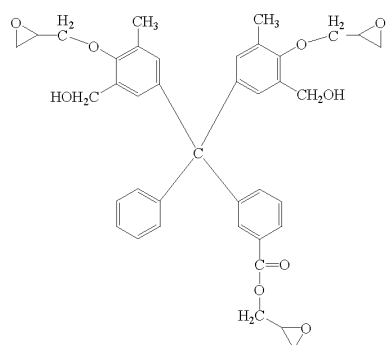




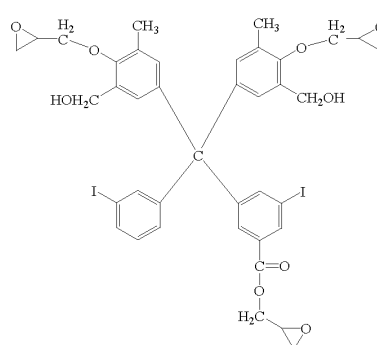
(I-3g),



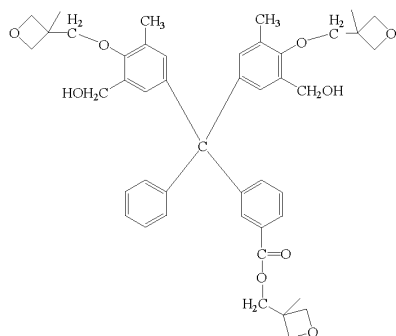
(I-3h),



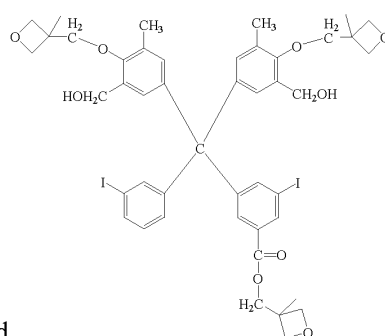
(I-3i),



(I-3j),



(I-3k), and



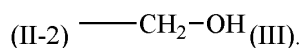
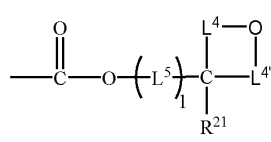
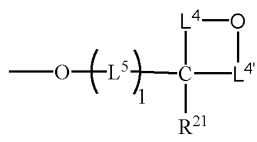
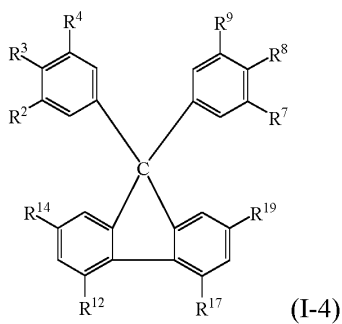
(I-3l).

8. The crosslinking compound of any one of claims 1 to 5, which has structure (I-4), where R^2 and R^7 is a moiety having structure (III),

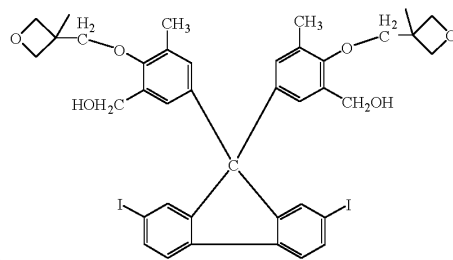
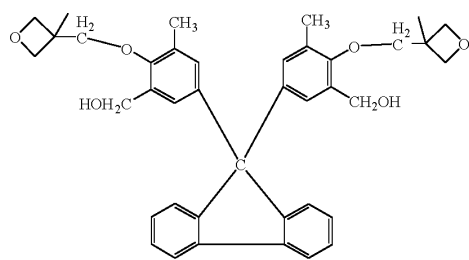
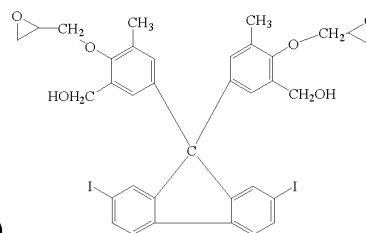
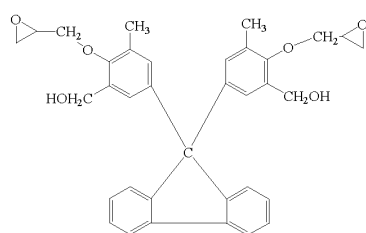
R^3 and R^8 are the same and have structure (II-1), where L^4 is a C_{1-2} linear -chain alkylene, $L^{4'}$ is either a direct valence bond or a C_1 straight chain alkylene, and L^5 is a C_{1-5} linear -chain alkylene or a C_{3-5} branched alkylene, and R^{21} is, H, a C_{1-8} linear alkyl, a C_{3-8} branched alkyl, or a $-CH_2OH$, R^4 and R^9 are individually selected from, H, a C_{1-8} alkyl, I, Cl, and Br,

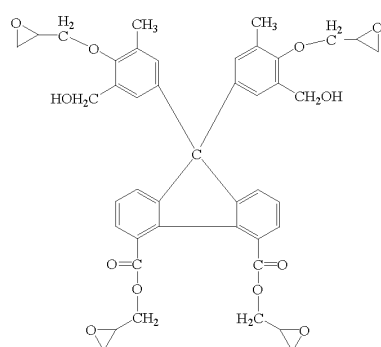
R^{14} and R^{19} are individually selected from H, I, Cl, and Br,

R^{12} and R^{17} are individually selected from H, structure (II-1), and structure (II-2),

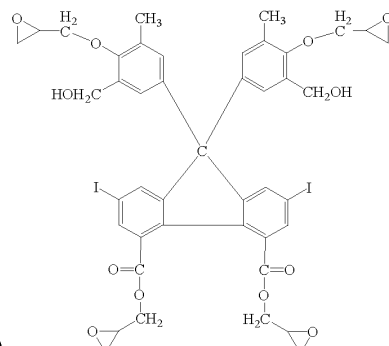


9. The crosslinking compound of any one of claim 1 to 5 and 8, which is selected from the group consisting of any one of the following compounds:

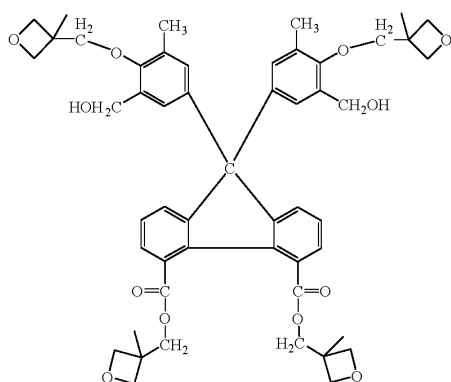




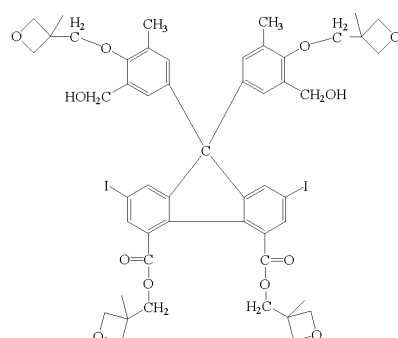
(I-4e),



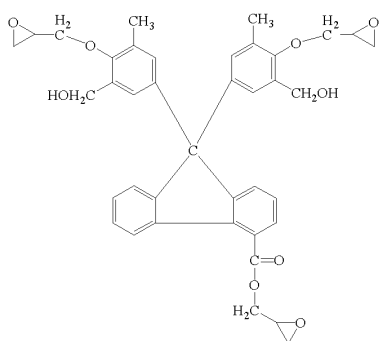
(I-4f),



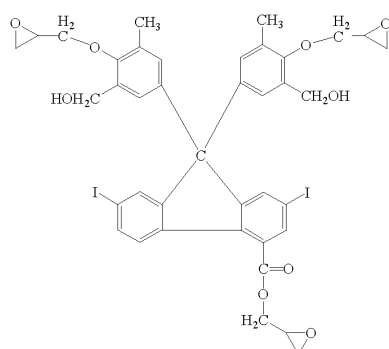
(I-4g),



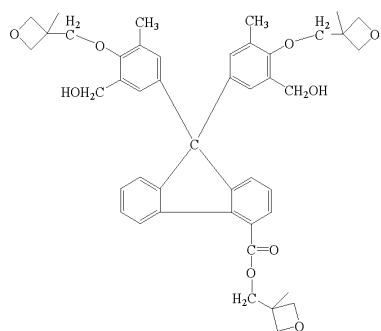
(I-4h),



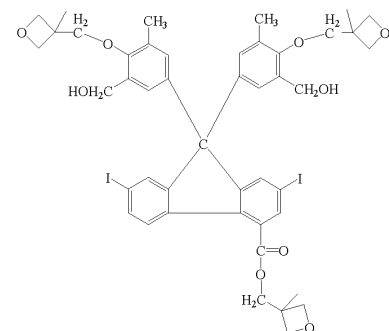
(I-4i),



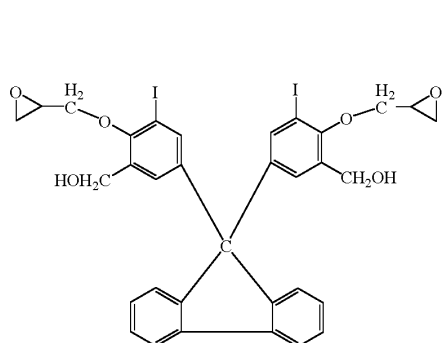
(I-4j),



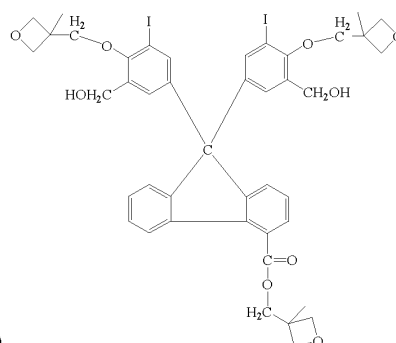
(I-4k),



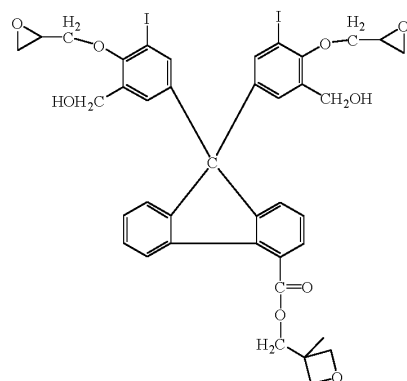
(I-4l),



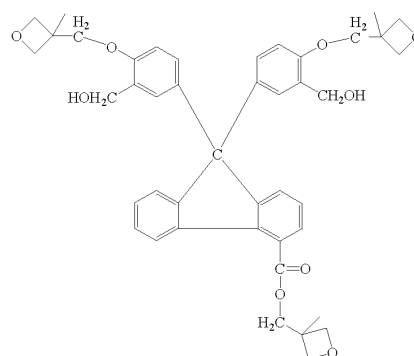
(I-4m),



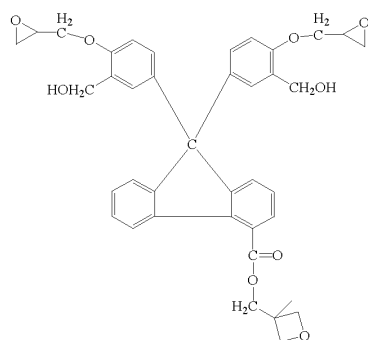
(I-4n),



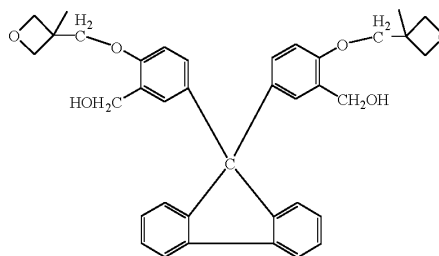
(I-4o),



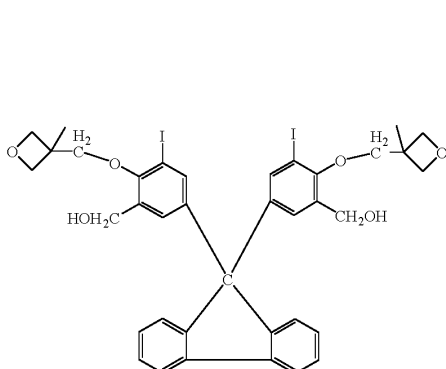
(I-4p),



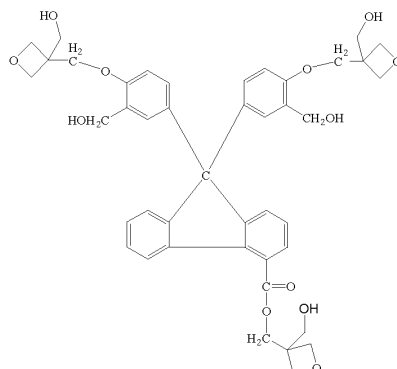
(I-4q),



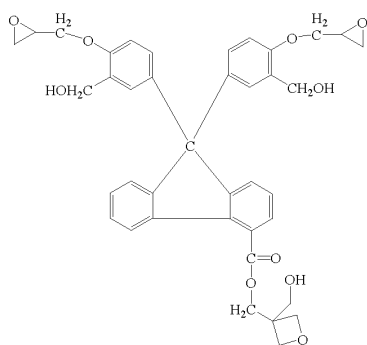
(I-4r),



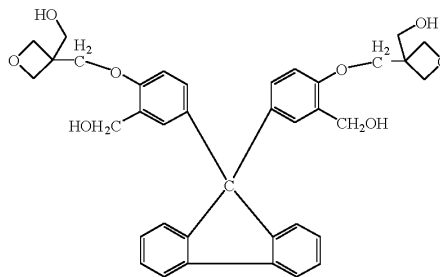
(I-4s),



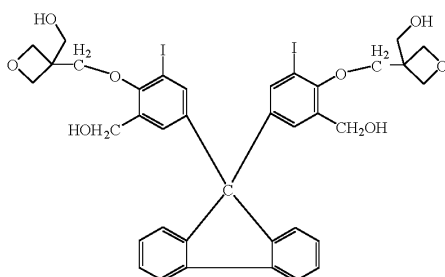
(I-4t),



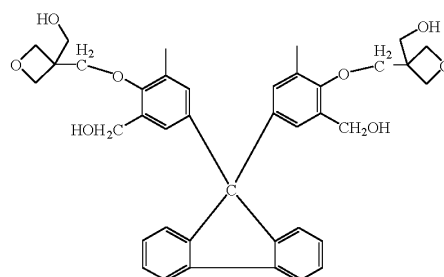
(I-4u),



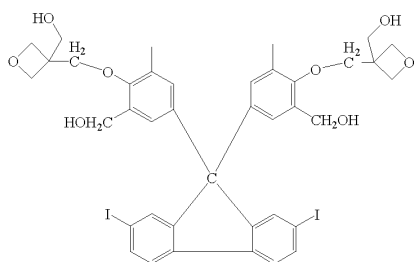
(I-4v),



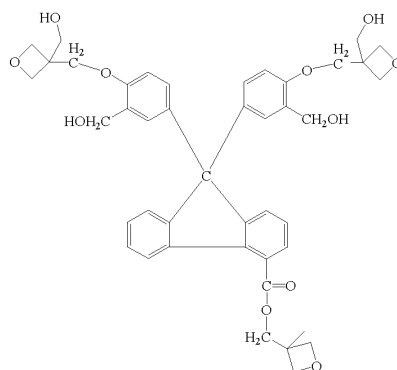
(I-4w),



(I-4x),



(I-4y), and



(I-4z).

10. The crosslinking compound of claim 1 or 2, wherein said compound has structure (I-5),

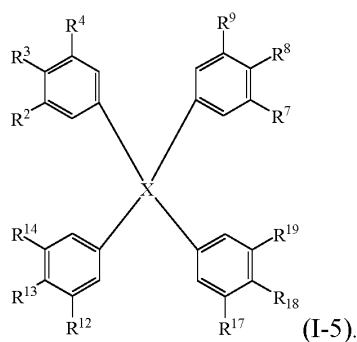
wherein n_1 and n_2 are each independently 1 or 0,

X is $C_pH_{2p-n_1-n_2}$ or $C_{6+4(q-1)}H_{4+2(q-1)-n_1-n_2}$,

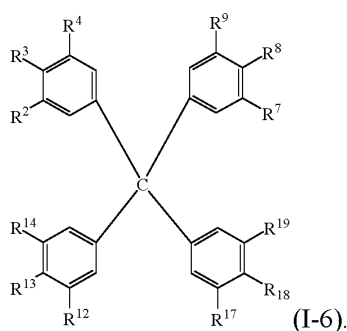
p is 1 to 6,

q is 1 to 3,

wherein one or more H of X may be each independently substituted with C_{1-5} straight-chain alkyl or C_{3-5} branched alkyl, and further wherein R^3 , R^8 , R^{13} , and R^{18} are individually selected from Y, R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{19} , R^{17} are selected from the group consisting of H, Cl, Br, and I, and at least one of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{19} , R^{17} is a halogen selected from the group consisting of, Cl, Br, and I,



11. The crosslinking compound of any one of claim 1, 2 and 10, which has structure (I-6), wherein R^3 , R^8 , R^{13} , and R^{18} are individually selected from Y, R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{19} , R^{17} are selected from the group consisting of, H, Cl, Br, and I, and at least one of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{19} , R^{17} is a halogen selected from the group consisting of, Cl, Br, and I,



12. The crosslinking compound of any one of claims 1, 2, 10 and 11, wherein only one of R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} , R^{19} is selected from the group consisting of Cl, Br, and I.

13. The crosslinking compound of any one of claims 1, 2, 10 and 11, wherein only two of R^2 ,

$R^4, R^7, R^9, R^{12}, R^{14}, R^{17}, R^{19}$ are selected from the group consisting of Cl, Br, and I.

14. The crosslinking compound of any one of claims 1, 2, 10 and 11, wherein only three of $R^2, R^4, R^7, R^9, R^{12}, R^{14}, R^{17}, R^{19}$ are selected from the group consisting of Cl, Br, and I.

15. The crosslinking compound of any one of claims 1, 2, 10 and 11, wherein only four of $R^2, R^4, R^7, R^9, R^{12}, R^{14}, R^{17}, R^{19}$ are selected from the group consisting of Cl, Br, and I.

16. The crosslinking compound of any one of claims 1, 2, 10 and 11, wherein only five of $R^2, R^4, R^7, R^9, R^{12}, R^{14}, R^{17}, R^{19}$ are selected from the group consisting of Cl, Br, and I.

17. The crosslinking compound of any one of claims 1, 2, 10 and 11, wherein only five of $R^2, R^4, R^7, R^9, R^{12}, R^{14}, R^{17}, R^{19}$ are selected from the group consisting of Br, and I.

18. The crosslinking compound of any one of claims 1, 2, 10 and 11, wherein only six of $R^2, R^4, R^7, R^9, R^{12}, R^{14}, R^{17}, R^{19}$ are selected from the group consisting of Cl, Br, and I.

19. The crosslinking compound of any one of claims 1, 2, 10 and 11, wherein only seven of $R^2, R^4, R^7, R^9, R^{12}, R^{14}, R^{17}, R^{19}$ are selected from the group consisting of Cl, Br, and I.

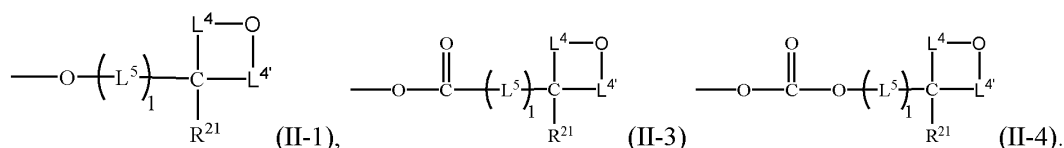
20. The crosslinking compound of any one of claims 1, 2, 10 and 11, wherein $R^2, R^4, R^7, R^9, R^{12}, R^{14}, R^{17}, R^{19}$ are all eight are selected from the group consisting of Cl, Br, and I.

21. The crosslinking compound of any one of claim 1, 2, 10 to 20, wherein said halogen is Cl.

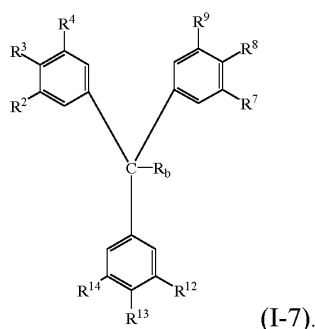
22. The crosslinking compound of any one of claim 1, 2, 10 to 20, wherein said halogen is Br.

23. The crosslinking compound of any one of claim 1, 2, 10 to 20, wherein said halogen is I.

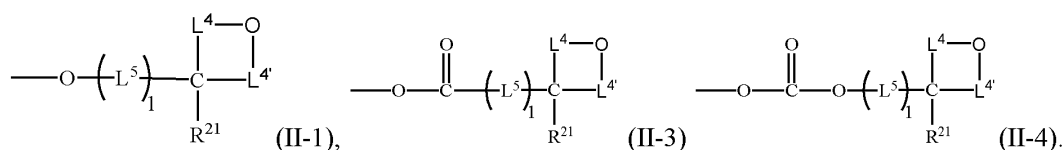
24. The crosslinking compound of any one of claim 1, 2, 10 to 22, wherein R^3, R^8, R^{13} , and R^{18} are individually selected from structure (II-1), structure (II-3) or structure (II-4), where L^4 is a C_{1-2} linear -chain alkylene, $L^{4'}$ is either a direct valence bond or a C_1 straight chain alkylene, and L^5 is a C_{1-5} linear chain alkylene or a C_{3-5} branched alkylene, and R^{21} is H, C_{1-8} linear alkyl, C_{3-8} branched alkyl, or $-CH_2OH$,



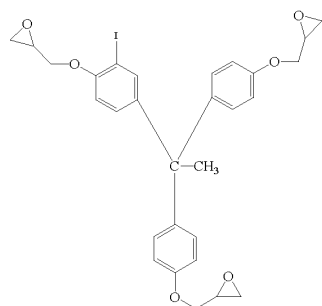
25. The crosslinking compound of any one of claims 1, 2 and 10, wherein said compound has structure (I-7), wherein R_b is selected from the group consisting of a C_{1-6} straight-chain alkyl or C_{3-15} branched alkyl, and further wherein R^3, R^8 and R^{13} are individually selected from Y, where $R^2, R^4, R^7, R^9, R^{12}, R^{14}$, are selected from the group consisting of, H, Cl, Br, and I, and at least one of $R^2, R^4, R^7, R^9, R^{12}, R^{14}$ is a halogen selected from the group consisting of, Cl, Br, and I,



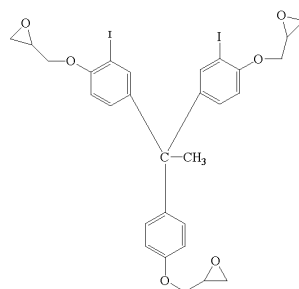
26. The crosslinking compound of any one of claims 1, 2, 10, and 25, wherein only one of R^2 , R^4 , R^7 , R^9 , R^{12} , and R^{14} is selected from the group consisting of Cl, Br, I.
27. The crosslinking compound of any one of claims 1, 2, 10, and 25, wherein only two of R^2 , R^4 , R^7 , R^9 , R^{12} , and R^{14} are selected from the group consisting of Cl, Br, I.
28. The crosslinking compound of any one of claims 1, 2, 10, and 25, wherein only three of R^2 , R^4 , R^7 , R^9 , R^{12} , and R^{14} are selected from the group consisting of Cl, Br, I.
29. The crosslinking compound of any one of claims 1, 2, 10, and 25, wherein only four of R^2 , R^4 , R^7 , R^9 , R^{12} , and R^{14} are selected from the group consisting of Cl, Br, I.
30. The crosslinking compound of any one of claims 1, 2, 10, and 25, wherein only five of R^2 , R^4 , R^7 , R^9 , R^{12} , and R^{14} are selected from the group consisting of Cl, Br, I.
31. The crosslinking compound of any one of claims 1, 2, 10, and 25, wherein only five of R^2 , R^4 , R^7 , R^9 , R^{12} , and R^{14} are selected from the group consisting of Br, I.
32. The crosslinking compound of any one of claims 1, 2, 10, and 25, wherein R^2 , R^4 , R^7 , R^9 , R^{12} , and R^{14} are all selected from the group consisting of Cl, Br, I.
33. The crosslinking compound of any one of claims 1, 2, 10, and 25, wherein said halogen is Cl.
34. The crosslinking compound of any one of claims 1, 2, 10, and 25, wherein said halogen is Br.
35. The crosslinking compound of any one of claims 1, 2, 10, and 25, wherein said halogen is I.
36. The crosslinking compound of any one of claim 1, 2, 10, 25 to 35, wherein R^3 , R^8 and R^{13} are individually selected from structure (II-1), structure (II-3) or structure (II-4), where L^4 is a C_{1-2} linear -chain alkylene, L^4 is either a direct valence bond or a C_1 straight chain alkylene, and L^5 is a C_{1-5} linear chain alkylene or a C_{3-5} branched alkylene, and R^{21} is H, C_{1-8} linear alkyl, C_{3-8} branched alkyl, or $-CH_2OH$,



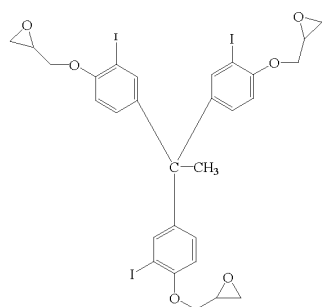
37. The crosslinking compound of claim 36, wherein R^3 , R^8 and R^{13} all have structure (II-1).
38. The crosslinking compound of claim 36, wherein R^3 , R^8 and R^{13} all have structure (II-3).
39. The crosslinking compound of claim 36, wherein R^3 , R^8 and R^{13} all have structure (II-4).
40. The crosslinking compound of claim 36, wherein R^3 , has structure (II-1) and R^8 and R^{13} all have structure (II-3).
41. The crosslinking compound of claim 36, wherein R^3 , has structure (II-1) and R^8 and R^{13} all have structure (II-4).
42. The crosslinking compound of claim 36, wherein R^3 , has structure (II-3) and R^8 and R^{13} all have structure (II-4).
43. The crosslinking compound of claim 36, wherein R^3 , has structure (II-4) and R^8 and R^{13} all have structure (II-3).
44. The crosslinking compound of claim 36, wherein R^3 , has structure (II-3) and R^8 and R^{13} all have structure (II-1).
45. The crosslinking compound of claim 36, wherein R^3 , has structure (II-4) and R^8 and R^{13} all have structure (II-1).
46. The crosslinking compound of any one of claim 25 to 45, wherein L^4 is $-\text{CH}_2-$, $L^{4'}$ is a direct valence bond and R_{21} is H.
47. The crosslinking compound of any one of claim 25 to 45, wherein L^4 is $-\text{CH}_2-$, $L^{4'}$ is $-\text{CH}_2-$ and R_{21} is a C_1 to C_4 linear alkyl.
48. The crosslinking compound of any one of claim 25 to 45, wherein L^4 is $-\text{CH}_2-$, $L^{4'}$ is $-\text{CH}_2-$ and R_{21} is a $-\text{CH}_2\text{-OH}$.
49. The crosslinking compound of claim 25, wherein said crosslinking compound is selected from the group consisting of the following structures:



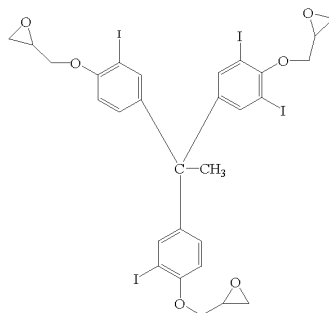
(I-7a),



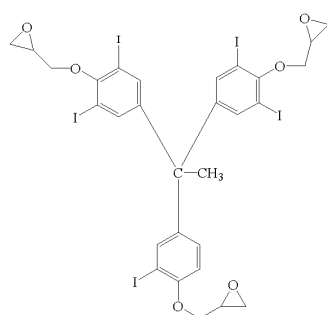
(I-7b),



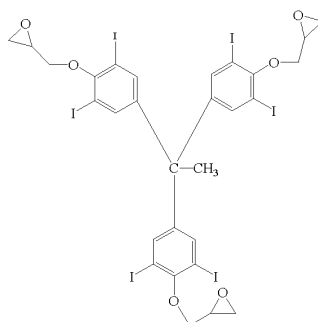
(I-7c),



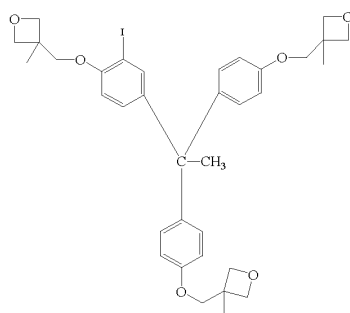
(I-7d),



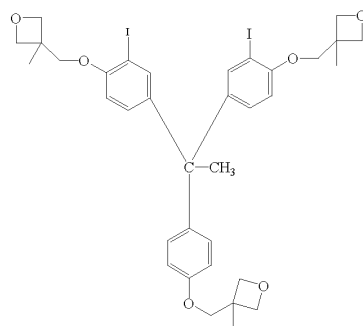
(I-7e),



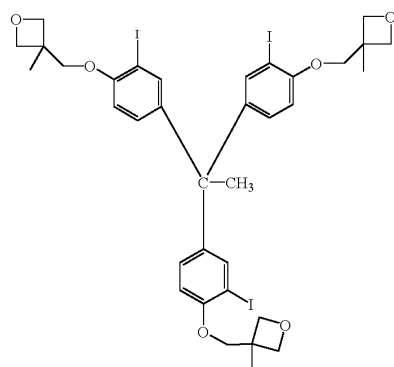
(I-7f),



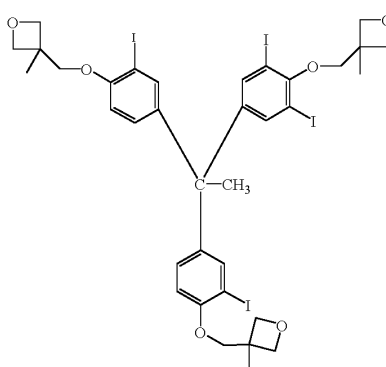
(I-7g),



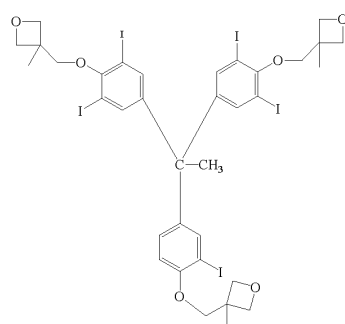
(I-7h),



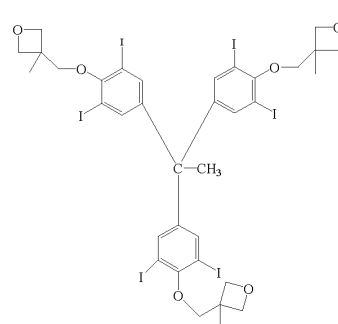
(I-7i),



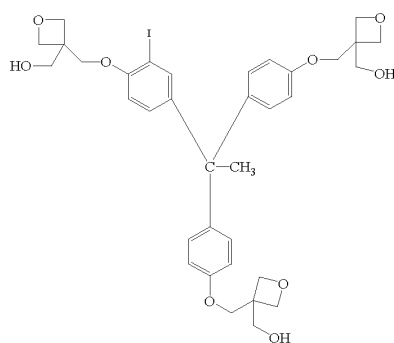
(I-7j),



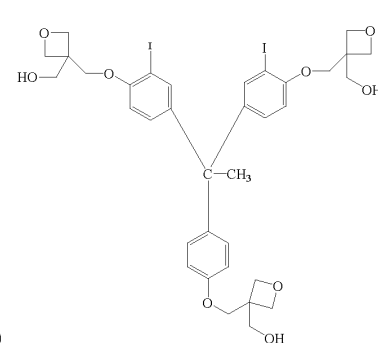
(I-7k),



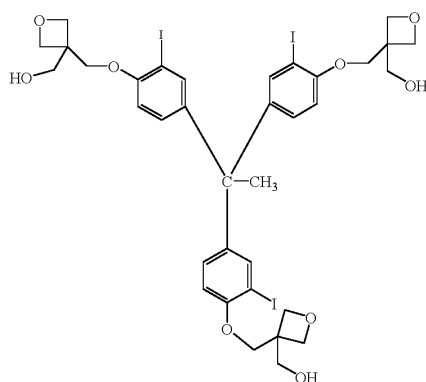
(I-7l),



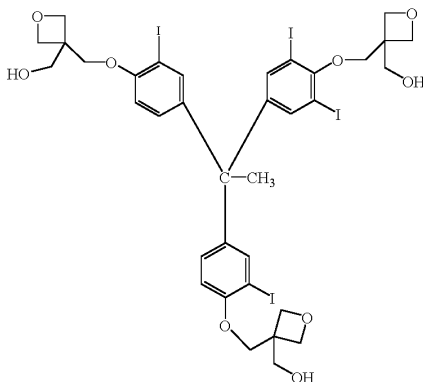
(I-7m),



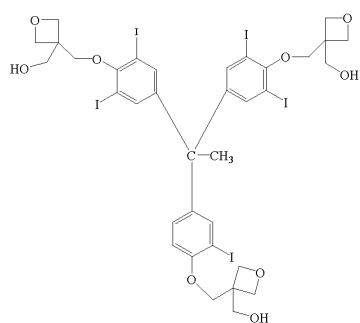
(I-7n),



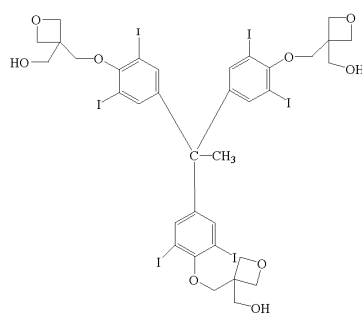
(I-7o),



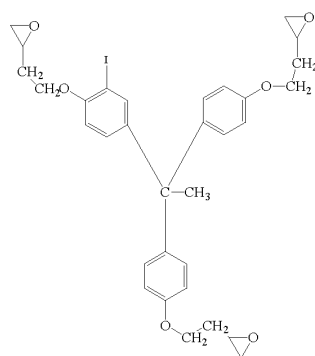
(I-7p),



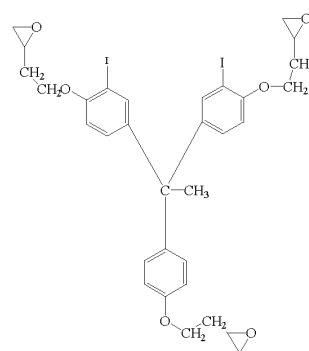
(I-7q),



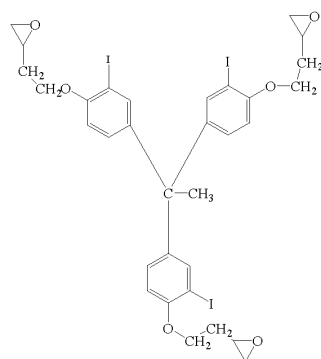
(I-7r),



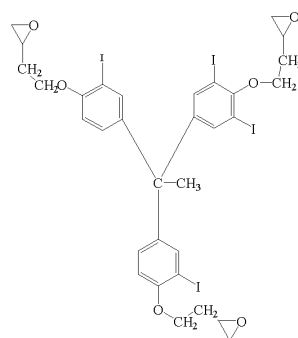
(I-7s),



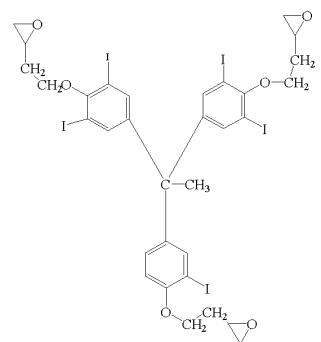
(I-7t),



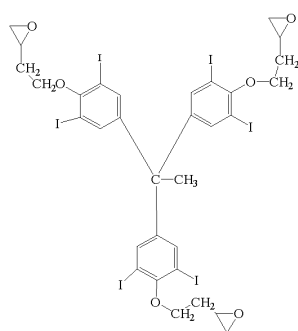
(I-7u),



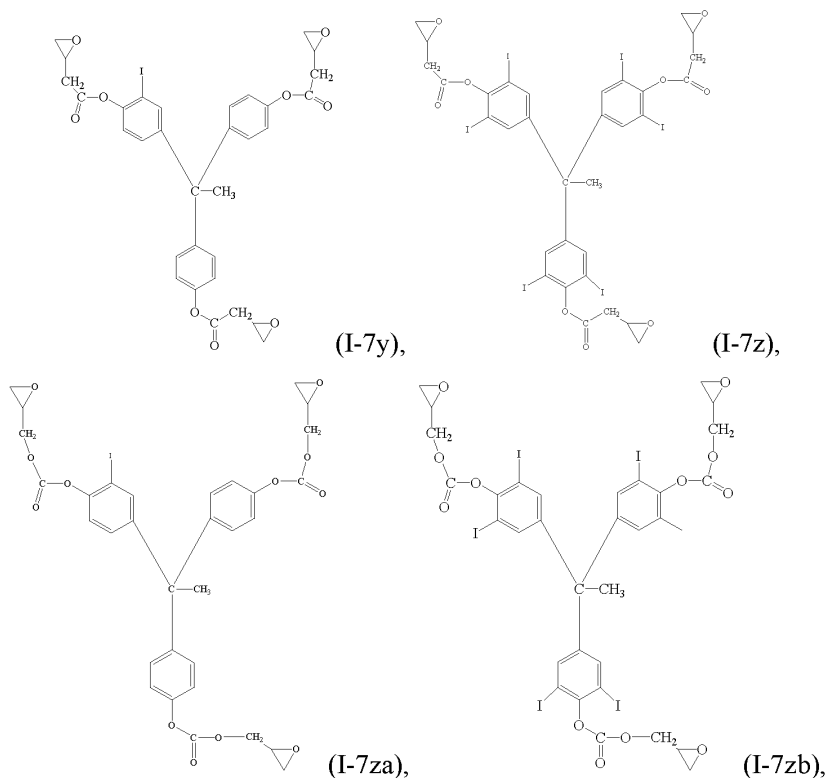
(I-7v),



(I-7w),



(I-7x),



- 50.** A composition comprising at least one crosslinking compound of any one of claims 1 to 49, and an acid generating agent.
- 51.** The composition of claim 50 comprising at least two different crosslinking compounds and an acid generating agent.
- 52.** The composition of claim 50 comprising at least one crosslinking compound of any one of claims 3 to 9.
- 53.** The composition of claim 50 comprising at least one crosslinking compound of any one of claims 10 to 49.
- 54.** The composition of claim 50 comprising at least one crosslinking compound of any one of claims 3 to 9 and at least one crosslinking compound of any one of claims 10 to 49.
- 55.** The composition of any one of claim 50 to 54, wherein said acid generator contains a photoacid generator.
- 56.** The composition of claim 55, wherein said photoacid generator are selected from the group consisting of iodonium salts, tetrahydrothiophenium salts, sulfonium salts, diazonium salts

pyridinium salts.

57. The composition of claim 55 or 56, wherein the molar ratio of the photoacid generator to the compound represented by structure (I) (the molar number of the photoacid generator/ the molar number of the compound represented by structure (I)) is 0.66 or less.

58. The composition as stated in any one of Claims 55 to 57 where at least two acid generators are present.

59. The composition of any one of claims 50 to 58, including additional solvents.

60. The composition of any one of claim 50 to 58, wherein it is a photoresist composition.

61. The composition of claim 60, wherein said photoresist composition where said crosslinking compound which is a crosslinker of any one of claims 3 to 9.

62. The composition of claim 60, wherein said photoresist composition where said crosslinking compound which is a crosslinker of any one of claims 10 to 49.

63. The composition of claim 60, wherein said photoresist composition where said crosslinking compound is a mixture of a crosslinker of any one of claims 3 to 9 and a crosslinker of any one of claims 10 to 49.

64. The composition of any one of claim 50 to 63, wherein it is negative photoresist composition.

65. The composition of claim 64, wherein said negative chemically is a chemically amplified EUV or e-beam photoresist composition comprising,

Component (A) a crosslinking compound of any one of claims 1 to 49,

Component (B) a photoacid generator

Component (C) an optional additional crosslinking component,

Component (D) an optional acid quencher component,

Component (E) an organic spin coating solvent.

66. The composition of claim 65, where component (D) is not an optional component.

67. The composition of claim 65 where component (A) comprises at least one crosslinking compound of any one of claims 3 to 9.

68. The composition of claim 65 where component (A) comprises at least one crosslinking compound of any one of claims 10 to 49.

69. The composition of claim 65 where component (A) comprises at least one compound of any one of claims 3 to 9 and at least one crosslinking compound of any one of claims 10 to 49.

70. A process of forming negative image with a negative photoresist by EUV or e beam exposure, comprising step ia) to va)

- i) coating the negative chemically amplified EUV photoresist or beam composition of any one of claims 65 to 69 on a substrate, to form a coated film,
- ii) baking said coated film to form a baked coated film,
- iii) exposing regions of the baked coated film through a mask with EUV or e-beam radiation, forming exposed and unexposed regions,
- iv) an optional post exposure baking step,
- v) developing away the unexposed regions with an organic solvent developer forming a negative image pattern in said coated photoresist on the substrate,
- vi) etching the substrate with a plasma or a chemical etchant using said negative image pattern as a mask, forming a negative image in the substrate.

71. A method for producing a resist film comprising:

applying the composition according to any one of claims 65 to 69 as resist film on a substrate.

72. A method for producing a resist pattern comprising:

- producing a resist film by the method according to claim 71;
- exposing the resist film;
- optionally, heating the exposed resist film; and
- developing the exposed resist film.

73. A method for producing a processed substrate comprising:

- producing a resist pattern by the method according to claim 72; and processing a substrate by using the resist pattern as a mask.

74. The method according to claim 73, further comprising the step of forming wiring on the processed substrate.

75. A method for the selective iodination of a multi-phenolic compound of structure (I-8) which employs both a reagent comprising a 1-iodopyrrolidine-2,5-dione moiety and a reagent comprising an aryl sulfonic acid moiety, to selectively effect iodination at position R^2 , R^4 , R^9 , R^7 , R^{12} , R^{14} , R^{17} , or R^{19} , originally substituted by H, where single iodination or multiple iodination may be selected by increasing the molar amount of these reagents relative to the number of these positions to be iodinated, where in structure (I-8), n_1 and n_2 are each independently 1 or 0, X is $C_pH_{2p-n_1-n_2}$ or $C_{6+4(q-1)}H_{4+2(q-1)-n_1-n_2}$, p is 1 to 6, q is 1 to 3, where said method comprises the steps

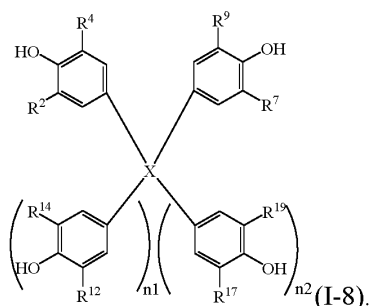
a. to d.

a. dissolving the phenolic compound of structure (I-8) where the group R^2 , R^4 , R^7 , R^9 , R^{12} , R^{14} , R^{17} or R^{19} to be iodinated is H and the reagent comprising an aryl sulfonic acid in an alkylcyano solvent with stirring at temperature of about -5°C to about 5°C ,

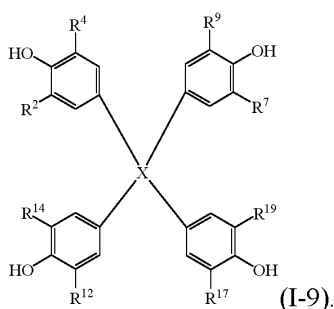
b. keeping the temperature of the stirred reaction solution at about -5°C to about 5°C , adding to it said reagent comprising a 1-iodopyrrolidine-2,5-dione moiety dissolved in an alkylcyano solvent,

c. stirring the resultant reaction mixture at a temperature of about -5°C to about 5°C , until the reaction is complete,

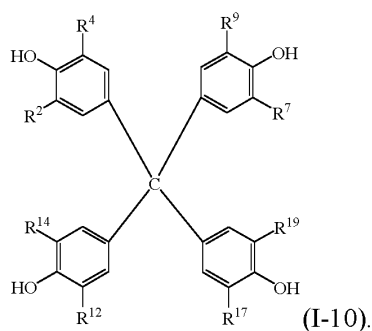
d. isolating the resultant iodinated phenolic compound,



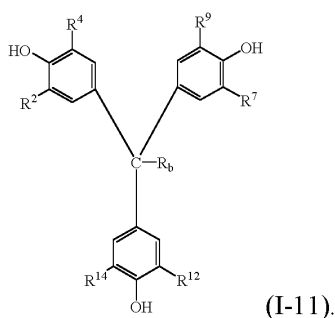
76. The method of claim 75, wherein said multi-phenolic compound more specifically has structure (I-9), where R^2 , R^4 , R^9 , R^7 , R^{12} , R^{14} , R^{17} , or R^{19} , are positions to selectively effect iodination at position, originally substituted by H,



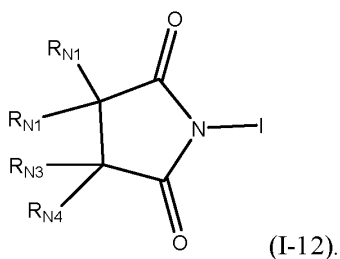
77. The method of claim 75, wherein said multi-phenolic compound more specifically has structure (I-10), where R^2 , R^4 , R^9 , R^7 , R^{12} , R^{14} , R^{17} , or R^{19} , are positions to selectively effect iodination, originally substituted by H,



78. The method of claim 75, wherein said multi-phenolic compound more specifically has structure (I-11), where R^2 , R^4 , R^9 , R^7 , R^{12} , R^{14} , are positions to selectively effect iodination, originally substituted by H, and R_b is selected from the group consisting of a C_{1-6} straight-chain alkyl or C_{3-15} branched alkyl,



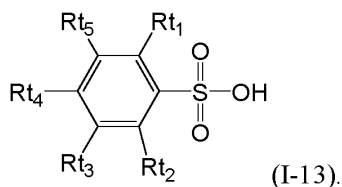
79. The method of any one of claims 75 to 78, wherein said reagent comprising a 1-iodopyrrolidine-2,5-dione moiety has structure (I-12), where R_{N1} , R_{N2} , R_{N3} , and R_{N4} are individually selected from H, a C_{1-5} straight-chain alkyl or C_{3-5} branched alkyl,



80. The method of any one of claims 75 to 79, wherein said reagent comprising a 1-iodopyrrolidine-2,5-dione moiety is 1-iodopyrrolidine-2,5-dione.

81. The method of any one of claims 75 to 80, wherein said reagent comprising an aryl sulfonic acid has structure (I-13), wherein substituents R_{t1} to R_{t5} are individually selected from H, a C_{1-5}

straight-chain alkyl or C₃₋₅ branched alkyl, C₁₋₅ straight-chain alkoxy or C₃₋₅ branched alkoxy, a halide, a C₁₋₅ straight-chain fluorinated alkyl or C₃₋₅ branched fluorinated alkyl, and nitro,



82. The method of any one of claim 75 to 81 wherein said reagent comprising an aryl sulfonic acid moiety is toluene sulfonic acid.

83. The method of any one of claim 75 to 82, when said alkylcyano solvent is one where the alkyl moiety is a C₁₋₅ straight-chain alkyl or C₃₋₅ branched alkyl.

84. The method of any one of claim 75 to 83, when said alkylcyano solvent is acetonitrile.

85. The use of the crosslinking compound of any one of claims 1 to 49 or the composition of any one of claims 50 to 69 for coating a substrate.