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(54) Title: POLYCYCLIC AROMATIC COMPOUNDS CONTAINING AN S ATOM OR $S(=O)_2$ GROUP AND THEIR USE AS DYES

$$(P—O)_x—Q—Y_w \qquad (1)$$

(57) Abstract: Polycyclic aromatic hydrocarbon compounds of formula (I) having an S atom or $S(=O)_2$ moiety incorporated in their basic polycyclic structure that can have a nitrogen-containing heterocycloaliphatic group and/or a substituted or unsubstituted phenoxy group and/or a polymeric moiety bonded to the polycyclic structure and to compositions such as, e.g., printing inks which comprise these polycyclic aromatic hydrocarbons as colorants.

POLYCYCLIC AROMATIC COMPOUNDS CONTAINING AN S ATOM OR $S(=0)_2$ GROUP AND THEIR USE AS DYES

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to novel polycyclic aromatic hydrocarbon compounds having an S atom or $S(=O)_2$ moiety incorporated in their basic polycyclic structure that can have a nitrogen-containing heterocycloaliphatic group and/or a substituted or unsubstituted phenoxy group and/or a polymeric moiety bonded to the polycyclic structure and to compositions such as, e.g., printing inks which comprise these polycyclic aromatic hydrocarbons as colorants.

2. Discussion of Background Information

[0002] Counterfeiting and market diversion of mass produced goods are facilitated if the products are handled on a lot base rather than on an individual item base. In such case counterfeit or diverted products are easily introduced into the supply chain. Producers and retailers would like to be in a position to distinguish their original products from such counterfeit or diverted (parallel imported or smuggled) products at the level of the individual unit that is sold.

[0003] Further, secure documents such as currency, passports, or identity cards are increasingly counterfeit around the world. This situation is a very critical issue for governments and society in general. For example criminal organizations may use fake passports or identity cards for human beings traffic. As reprographic technologies become more and more sophisticated, it becomes even more difficult to make a clear distinction between a fake document and the original. Document security has therefore a considerable impact on the economy of the countries and also on the victims of illicit traffic involving counterfeit documents.

[0004] In an attempt to prevent counterfeiting marking is currently used extensively for the recognition, identification and authentication of individual items. The marking may be applied, for example, in the form of indicia such as 1-dimensional barcodes, stacked 1-dimensional barcodes, 2-dimensional barcodes, 3-dimensional barcodes, a data matrix. and the like. The application of markings is frequently carried out by a printing process which uses a printing ink

with specific optical properties that are imparted to the ink by one or more substances contained therein such as, e.g., luminescent dyes, pigments, or cholesteric liquid crystal compounds.

[0005] A class of compounds which is suitable for use in, e.g., printing inks for marking purposes are compounds having a perylene, terrylene or quaterrylene skeleton. Perylene, terrylene and quaterrylene display fluorescence and there are many derivatives of these compounds which are known and may theoretically be employed as pigments in compositions for marking such as printing inks and the like. However, a drawback of these compounds is their often unsatisfactorily low solubility or dispersibility in liquid media such as those which are useful in printing inks. This low solubility/dispersibility limits the suitability of these compounds as colorants for liquid compositions in general. It would thus, be advantageous to be able to increase the solubility and/or dispersibility of perylene, terrylene and quaterrylene dyes in liquid media and in particular, liquid media for use in printing inks. See Application No. 13/115,602, filed May 25, 2011, and Provisional Application No. 61/558,236, filed November 10, 2011 which are incorporated by reference herein in their entireties.

SUMMARY OF THE INVENTION

[0006] The present invention provides polycyclic aromatic hydrocarbon compounds of general formula (1):

$$(P—O)_x—Q—Y_w$$

(1)

wherein P represents a polymeric moiety having at least three repeating units which comprise an optionally substituted phenyl ring;

Q represents a polycyclic aromatic hydrocarbon moiety containing an S atom or $S(=O)_2$ moiety (i.e., a polycyclic aromatic hydrocarbon skeleton having an S atom or a $S(=O)_2$ moiety incorporated in its basic structure which may optionally comprise one or more substituents in addition to the substituents Y and/or P-O);

Y is selected from (i) halogen, (ii) optionally substituted N-heterocycloaliphatic groups having from 3 to about 8 ring members and which are bonded to Q through an N atom, and (iii) optionally substituted phenoxy groups;

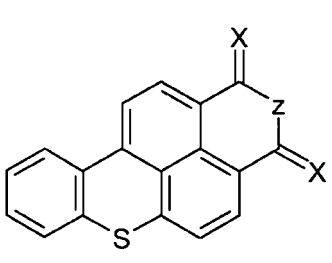
x represents an integer of from 0 to 4; and w represents an integer of from 0 to 4,

and wherein w and x are not simultaneously 0,

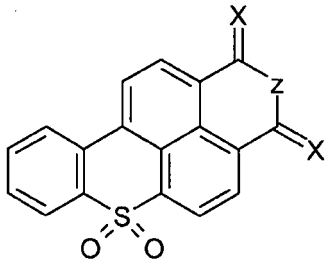
provided that when x = 0, at least one Y is selected from (ii) and (iii).

[0007] In one aspect of the compound of formula (1), x may be 1 and/or (x + w) may not be higher than about 6.

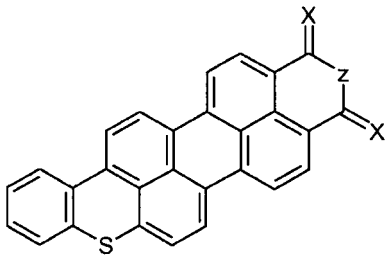
[0008] In another aspect, Q may be a moiety having a basic structure (i.e., without optionally present substituents) of formula (A) or (B) or (A') or (B'):



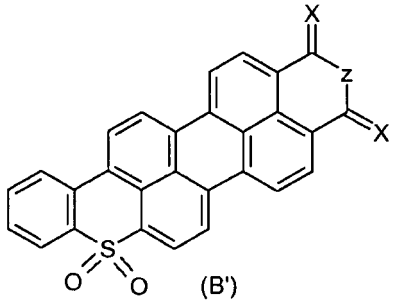
(A)



(A')



(B)



(B')

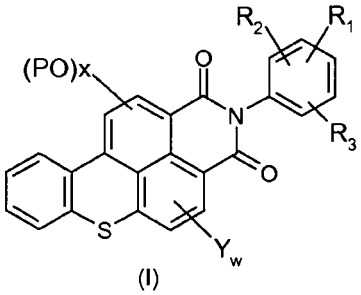
wherein Z represents O, S or N-R, and X, which can be the same or different, represents O, S, or NR'. Thus, the group formed by Z and X can be represented, for example, by -CO-Z-CO- (may be replaced by [–COOH HOOC-] (i.e., the dicarboxylic acid instead of the anhydride)), –CS-Z-CO-, -CS-Z-CS-, or –C(=NR')-NR-CO-; and

R and R' independently represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms; and R and R' may also be combined to form, together with the N atoms to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring.

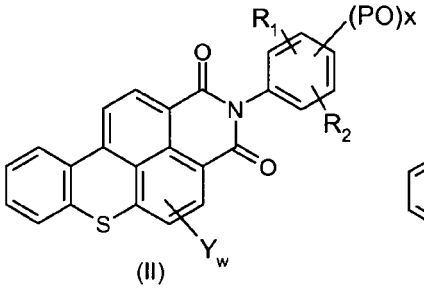
[0009] In one aspect of the compounds of the above formulae (A), (B), (A') and (B'), for the group Z = N-R, R may be selected, for example, from optionally substituted alkyl having from 1 to about 6 carbon atoms, optionally substituted alkylaryl or arylalkyl having from 7 to about 12 carbon atoms, optionally substituted aryl having from about 6 to about 20 carbon atoms, and optionally substituted heteroaryl having from about 3 to about 20 carbon atoms such as, e.g., from optionally substituted alkyl having from 1 to about 4 carbon atoms, optionally substituted phenyl, or optionally substituted benzyl. By way of non-limiting example, R may represent phenyl substituted with from 1 to about 3 groups selected from halogen and alkyl having from 1 to about 6 carbon atoms such as, e.g., a phenyl group substituted by at least two alkyl groups which comprise a secondary or tertiary carbon atom, examples of which include isopropyl and tert.-butyl groups.

[0010] In another aspect of the compounds of the above formulae (A), (B), (A') and (B'). the group Z represents O or N-R (including compounds wherein each group Z is O, compounds wherein each group Z is N-R (with the groups R being the same or different), and compounds wherein one group Z is O and the other group Z is N-R).

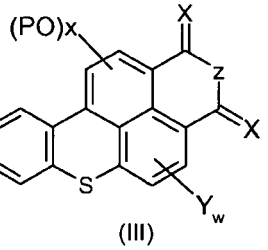
[0011] For example, compounds of the instant invention include compounds of formulae (I) or (II) or (III) or (IV) or (V) or (VI) which can include $(PO)_x$ and/or Y_w:



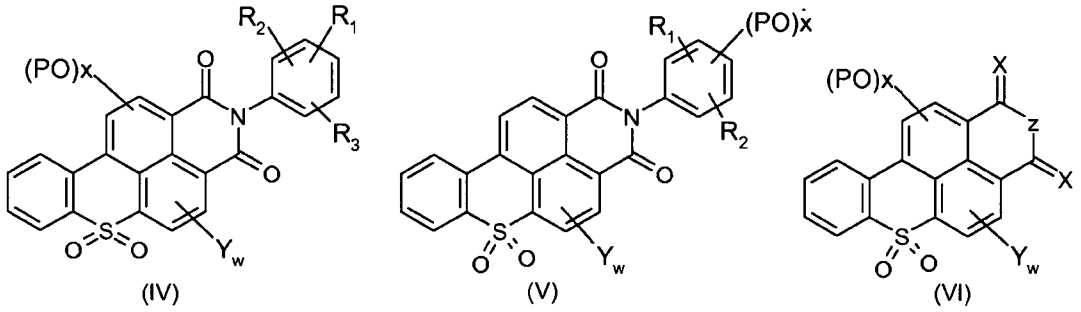
(I)



(II)



(III)



wherein in the case of formula (III) and (VI), the group Z, represents O, S or N-R, and X, which can be the same or different, represents O, S, or NR'. Thus, the group formed by Z and X can be represented, for example, by -CO-Z-CO- (may be replaced by [–COOH HOOC-] (i.e., the dicarboxylic acid instead of the anhydride)), –CS-Z-CO-, -CS-Z-CS-, or –C(=NR')-NR-CO-;

R and R' independently represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms; and R and R' may be combined to form, together with the N atoms to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring;

R_1, R_2 and R_3 are independently selected from hydrogen, C_1-C_4 alkyl, C_1-C_4 alkyl-COOH, C_1-C_4 alkyl-SO_3H, C_1-C_4 alkoxy, mono(C_1-C_4)alkylamino, di(C_1-C_4)alkylamino, C_1-C_4 aminoalkyl, halogen, cyano, nitro, and SO_3H, the alkyl groups being optionally substituted;

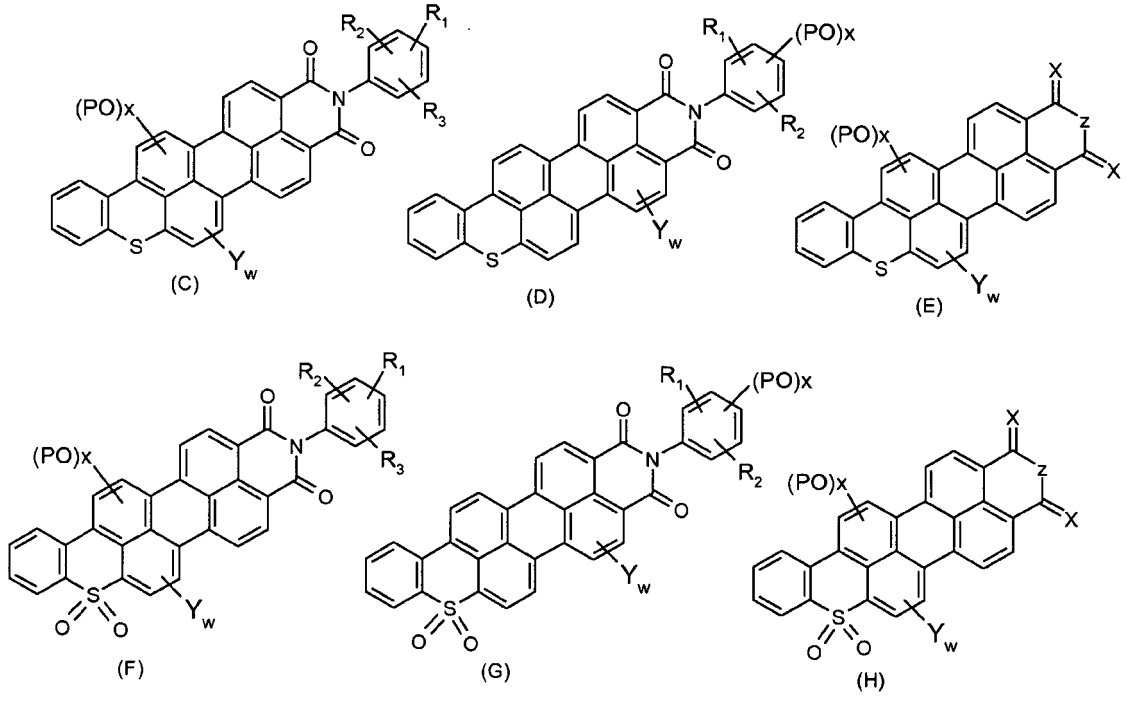
Y is selected from (i) halogen, (ii) optionally substituted N-heterocycloaliphatic groups having from 3 to about 8 ring members and which are bonded to an aromatic ring through an N atom, (for example, at least one group Y may be selected from heterocycloaliphatic groups having from 3 to about 8 ring members, which ring members may comprise from 1 to about 3 heteroatoms (e.g., 1, 2 or 3 heteratoms) selected from N, S, and O, provided that at least one ring member is N and/or the heterocycloaliphatic groups may be substituted by one or more substituents selected from alkyl and alkoxy groups comprising up to about 10 carbon atoms) and (iii) optionally substituted phenoxy groups which are bonded to an aromatic ring through an O atom, the phenoxy group may be substituted by one or more (e.g., 1, 2 or 3 identical or different) substituents selected from halogen (e.g., F, Cl, Br and I), nitro, cyano, NRR', SO_3H

and COOH and salts and derivatives of these sulfonic and carboxylic acid groups (e.g., salts of alkali and alkaline earth metals such as Na, K, Ca, and Mg , esters such as C1-C4 alkyl esters, and amides such as amides with NRR' as amido moiety), OH, heterocycloalkyl comprising up to three heteroatoms selected from O, N and S as ring members and from 3 to about 8 ring members, and alkyl (including cycloalkyl) and alkoxy (including cycloalkoxy) groups comprising from 1 to about 10 carbon atoms (e.g., 1, 2, 3, 4, 5 or 6 carbon atoms);

P represents a polymeric moiety having at least three repeating units which comprise an optionally substituted phenyl ring;

and x is an integer of from 0 to 4, w is an integer of from 0 to 4.

[0012] In yet another aspect of the compounds of the present invention, Q may be a moiety having a basic structure (i.e., without optionally present substituents) of formula (C) or (D) or (E) or (F) or (G) or (H) which can include $(PO)_x$ and/or Y_w :



wherein in the case of formula (E) and (H), Z represents O, S or N-R, and X, which can be the same or different, represents O, S, or NR'. Thus, the group formed by Z and X can be represented, for example, by -CO-Z-CO- (may be replaced by [–COOH HOOC-] (i.e., the dicarboxylic acid instead of the anhydride)), –CS-Z-CO-, -CS-Z-CS-, or –C(=NR')-NR-CO-;

R and R' independently represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms; and R and R' may be combined to form, together with the N atoms to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring;

R_1, R_2 and R_3 are independently selected from hydrogen, C_1-C_4 alkyl, C_1-C_4 alkyl-COOH, C_1-C_4 alkyl-SO_3H, C_1-C_4 alkoxy, mono(C_1-C_4)alkylamino, di(C_1-C_4)alkylamino, C_1-C_4 aminoalkyl, halogen, cyano, nitro, and SO_3H, the alkyl groups being optionally substituted;

Y is selected from (i) halogen, (ii) optionally substituted N-heterocycloaliphatic groups having from 3 to about 8 ring members and which are bonded to an aromatic ring through an N atom,; (for example, at least one group Y may be selected from heterocycloaliphatic groups having from 3 to about 8 ring members, which ring members may comprise from 1 to about 3 heteroatoms (e.g., 1, 2 or 3 heteratoms) selected from N, S, and O, provided that at least one ring member is N and/or the heterocycloaliphatic groups may be substituted by one or more substituents selected from alkyl and alkoxy groups comprising up to about 10 carbon atoms) and (iii) optionally substituted phenoxy groups which are bonded to an aromatic ring through an O atom, the phenoxy group may be substituted by one or more (e.g., 1, 2 or 3 identical or different) substituents selected from halogen (e.g., F, Cl, Br and I), nitro, cyano, NRR', SO_3H and COOH and salts and derivatives of these sulfonic and carboxylic acid groups (e.g., salts of alkali and alkaline earth metals such as Na, K, Ca, and Mg , esters such as C_1-C_4 alkyl esters, and amides such as amides with NRR' as amido moiety), OH, heterocycloalkyl comprising up to three heteroatoms selected from O, N and S as ring members and from 3 to about 8 ring members, and alkyl (including cycloalkyl) and alkoxy (including cycloalkoxy) groups comprising from 1 to about 10 carbon atoms (e.g., 1, 2, 3, 4, 5 or 6 carbon atoms);

P represents a polymeric moiety having at least three repeating units which comprise an optionally substituted phenyl ring;

and x represents an integer of from 0 to 4; and w is an integer of from 0 to 4.

Thus, for formula (C) or (D) or (E) or (F) or (G) or (H), each of x and w can both be 0, either x and w can be 0, and x can be 0, 1, 2, 3 or 4, and w can be 0, 1, 2, 3 or 4.

[0013] Additionally, the present invention provides compounds of Formula (B) and (B') as set forth above that are completely unsubstituted or carry one or more (e.g., 1, 2, 3, 4, 5, or 6) substituents (which may be the same or different). Non-limiting examples of substituents include halogen (e.g., F, Cl, Br and I), nitro, cyano, NRR', SO_3H and COOH and salts and derivatives of these sulfonic and carboxylic acid groups (e.g., salts of alkali and alkaline earth metals such as Na, K, Ca, and Mg , esters such as C1-C4 alkyl esters, and amides such as amides with NRR' as amido moiety), OH, heterocycloalkyl comprising up to three heteroatoms selected from O, N and S as ring members and from 3 to about 8 ring members, alkyl (including cycloalkyl) and alkoxy (including cycloalkoxy) groups comprising from 1 to about 10 carbon atoms (e.g., 1, 2, 3, 4, 5 or 6 carbon atoms), and optionally substituted aryl (e.g. phenyl) and aralkyl (e.g., benzyl) groups having up to about 20 carbon atoms.

[0014] In one aspect of these compounds of the present invention, the group Z represents N-R wherein R may be selected, for example, from optionally substituted alkyl having from 1 to about 6 carbon atoms, optionally substituted alkylaryl or arylalkyl having from 7 to about 12 carbon atoms, optionally substituted aryl having from about 6 to about 20 carbon atoms, and optionally substituted heteroaryl having from about 3 to about 20 carbon atoms such as, e.g., from optionally substituted alkyl having from 1 to about 4 carbon atoms, optionally substituted phenyl, or optionally substituted benzyl. By way of non-limiting example, R may represent phenyl substituted with from 1 to about 3 groups selected from halogen and alkyl having from 1 to about 6 carbon atoms such as, e.g., a phenyl group substituted by at least two alkyl groups which comprise a secondary or tertiary carbon atom, non-limiting examples of which include isopropyl and tert.-butyl groups.

[0015] In a still further aspect, at least one group Y of the compounds of disclosed herein, such as the compound of formula (1), may be selected from heterocycloaliphatic groups having from 3 to about 8 ring members, which ring members may comprise from 1 to about 3 heteroatoms

(e.g., 1, 2 or 3 heteratoms) selected from N, S, and O, provided that at least one ring member is N. Further, the heterocycloaliphatic groups may be substituted by one or more substituents selected from alkyl and alkoxy groups comprising up to about 10 carbon atoms.

[0016] For example, at least one group Y of the compounds disclosed herein, such as the compound of formula (1) or the compounds of the other formulas, may be the residue (i.e., without a hydrogen atom bonded to the N atom) of a heterocyclic compound selected from optionally substituted azacyclooctane, optionally substituted azepane, optionally substituted piperidine, optionally substituted piperazine, optionally substituted pyrrolidine, optionally substituted azetidine, optionally substituted aziridine, optionally substituted morpholine, optionally substituted oxazolidine, optionally substituted pyrazolidine, optionally substituted isopyrazolidine, optionally substituted isoxazolidine, and optionally substituted thiazolidine. The optional substituents on the rings may preferably be independently selected from C_1-C_4 alkoxy and C_1-C_6 alkyl groups. Of course, a compound may comprise two or more different heterocycloaliphatic groups Y.

[0017] In a still further aspect, at least one group Y, when present, of the compounds disclosed herein, such as the compound of formula (1) or compounds of the other formulas, may be selected from optionally substituted phenoxy groups, wherein the phenoxy group may be substituted by one or more (e.g., 1, 2 or 3 identical or different) substituents selected from halogen (e.g., F, Cl, Br and I), nitro, cyano, NRR', SO_3H and COOH and salts and derivatives of these sulfonic and carboxylic acid groups (e.g., salts of alkali and alkaline earth metals such as Na, K, Ca, and Mg , esters such as C_1-C_4 alkyl esters, and amides such as amides with NRR' as amido moiety), OH, heterocycloalkyl comprising up to three heteroatoms selected from O, N and S as ring members and from 3 to about 8 ring members, and alkyl (including cycloalkyl) and alkoxy (including cycloalkoxy) groups comprising from 1 to about 10 carbon atoms (e.g., 1, 2, 3, 4, 5 or 6 carbon atoms).

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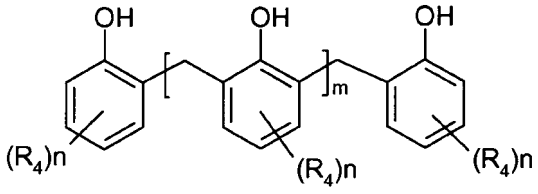
[0018] In another aspect of the compounds set forth above, P-O, when present, may be the residue (i.e., without hydrogen atom of one of the phenolic hydroxy groups) of a compound of general formula (2):



(2)

wherein the groups R_4, the same or different from each other, are selected from C_1-C_{10} alkyl and C_1-C_4 alkoxy; m represents an integer of from 1 to about 30; and n represents an integer of from 1 to about 3. For example, m may represent an integer of from 1 to 10 and/or n may be 1 or 2 and/or the groups R_4 may independently be selected from C_1-C_{10} alkyl such as, e.g., isopropyl, tert-butyl, tert-octyl, n-nonyl and branched nonyl.

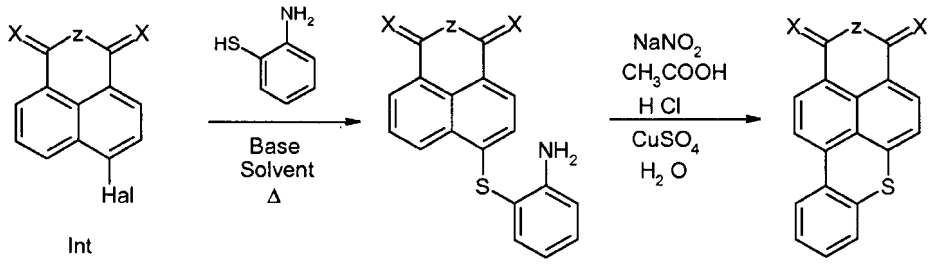
[0019] The present invention also provides a process for making compounds disclosed herein, such as the compound of formula (1). The process comprises reacting in an aprotic polar organic solvent a compound of formula $Q\text{-}(Hal)_v$ wherein Hal represents halogen and v represents an integer of from 1 to 8, with an N-containing cycloaliphatic compound and/or a polymeric compound of formula P-OH and/or an optionally substituted phenolic compound. If two or more different compounds are to be reacted with a compound of formula $Q\text{-}(Hal)_v$ the reactions are preferably carried out successively (with or without isolating the intermediate) in order to be able to better control the composition of the mixture of reaction products obtained. One of skill in the art will appreciate that depending on the reaction conditions individual compounds or a mixture of positional isomers may be obtained if v is 2 or higher.

[0020] The process for preparing compounds $Q\text{-}(Hal)_v$ wherein Hal represents halogen and v represents an integer of from 1 to 8 may be performed as follows by reacting compounds Q as above-mentioned, such as represented by formula (A), (A'), (B) or (B') free of halogen. Q compounds can be reacted in AcOH as a solvent with about 5 equivalent of SO_2Cl_2 in the presence of I_2 and iodobenzene as catalyst, the whole composition can be heated between 70 to

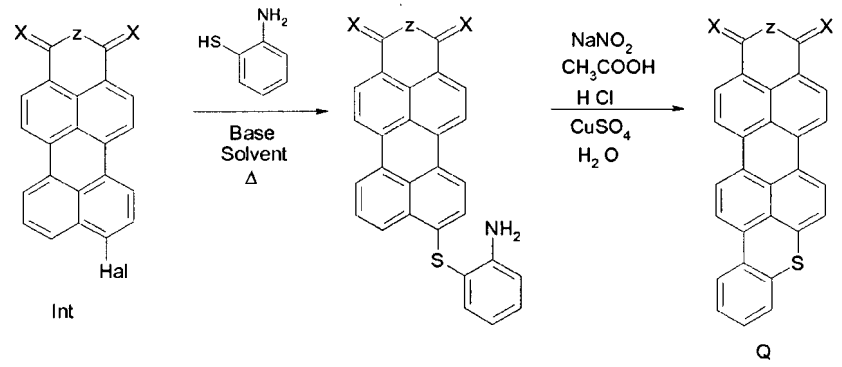
90°C during about three or to four hours or over night depending on the initial compounds used. The resulting mixtures can be washed with a mixture of water and organic solvent. The organic phase can be obtained after extraction of the organic solvent from water, the solvent can then be evaporated and the resulting crude oil can be subject to separation and purification with techniques of purification known by one skilled in the art, such as chromatography.

[0021] The process for preparing the molecule (A), (A'), (B) or (B') can comprise the following step (a) or (b):

(a)



(b)



wherein X and Z are the same as above defined and Hal represents halogen such as Cl or Br, various bases can be used such as K_2CO_3 and the solvent is for example a polar solvent such as N-methyl-2-pyrrolidone (NMP). The temperature of reaction represented by Δ can be between 80 to 120°C, and the preparation of compounds Int (also named intermediate of synthesis leading

to preparation of molecule Q) is well known by one skilled in the art or are also commercially available.

[0022] In one aspect of the process, at least the reaction involving the N-containing cycloaliphatic compound (and usually also the reaction involving the reaction comprising the polymeric compound and/or the optionally substituted phenolic compound) may be carried out in the presence of an inorganic base and/or a strong organic non-nucleophilic base.

[0023] In another aspect of the process, at least the reaction involving the optionally substituted phenolic compound (and usually also the reaction involving the reaction comprising the polymeric compound or the optionally phenolic compound) may be carried out in the presence of an inorganic base and/or a strong organic non-nucleophilic base.

[0024] In another aspect of the process, from about 0.5 to about 10 g of compound of formula Q-$(Hal)_v$ may be employed per 100 g of polymeric compound of formula P-OH. In another aspect of the process, from about 0.5 to about 10 g of compound of formula Q-$(Hal)_v$ may be reacted with from about 2 to 3 equivalent of optionally substituted phenolic compound. In another aspect of the process, from about 0.5 to about 10 g of compound of formula Q-$(Hal)_v$ may be reacted with 5 to 10 equivalents of N-containing cycloaliphatic compound or the reaction can be made for example with the N-containing cycloaliphatic compound as a co-solvent together with the one needed for carrying out the process according to the invention.

[0025] In yet another aspect, the polar solvent may comprise at least one solvent in which the polymeric compound, if used, is soluble and/or may be at least one of N-methylpyrrolidone, dimethyl formamide, dimethyl acetamide, and dimethylsulfoxide.

[0026] The present invention also provides a printing ink composition. The composition comprises a polar liquid medium and at least one compound of formula (1) or (A) or (A') or (B) or (B') or (C) or (D) or (E) or (F) or (G) or (H) or (I) or (II) or (III) or (IV) or (V) or (VI) disclosed herein, such as the compound of formula (1) or compounds of the other formulas dissolved or dispersed in the medium. Such medium for non limiting example may be methyl ethyl ketone (MEK) or dimethylketone.

[0027] In one aspect, the composition may comprise from about 0.01 % to about 40 %, e.g., from about 0.05 % to about 10 %, or from about 0.1 % to about 5 % by weight of at least one compound disclosed herein, such as the compound of formula (1) or compounds of the other formulas, based on the total weight of the composition

[0028] In another aspect, the composition may further comprise at least one conductivity imparting substance (such as, e.g., a salt).

[0029] The present invention further provides a marking or security feature which is made with the printing ink composition of the present invention as set forth above and/or comprises at least one compound disclosed herein, such as the compound of formula (1) or compounds of the other formulas.

[0030] In one aspect, the marking or security feature may comprise at least one of a thread, a label, a barcode, a 2D code, a pattern, indicia, a data matrix, a stamp, a tax stamp, a stamp, a tax stamp, a digital stamp, and a cloud of dots (visible or invisible) which supports data information.

[0031] The present invention also provides an article which comprises the marking or security feature set forth above. For example, the marking or security feature may be present as a layer on the article.

[0032] In one aspect, the article may be at least one of a label such as, e.g., a tax label, packaging, a can, a metal, an aluminum foil, a cartridge, a closed cartridge (e.g., a capsule) that contains, e.g., a pharmaceutical, a nutraceutical, a foodstuff or a beverage (such as, e.g., coffee, tea, milk, chocolate, etc.), an article made of glass, an article made of ceramic, a banknote, a stamp, a security document, an identity card, a passport, a driver's license, a credit card, an access card, a ticket such as, e.g., a transportation ticket or an event ticket, a voucher, a value document, an ink-transfer film, a reflective film, a thread, a commercial good, and a cigarette packaging carrying or not carrying coded or encrypted information.

[0033] The present invention also provides a method of authenticating an article. The method comprises providing the article with the marking or security feature set forth above (including the various aspects thereof) and/or comprises applying onto the article the printing ink composition set forth above (including the various aspects thereof).

[0034] In one aspect of the method, the article may be at least one of a tax label, packaging, a can, a metal, an aluminum foil, a cartridge, a closed cartridge (e.g., a capsule) that contains, e.g., a pharmaceutical, a nutraceutical, a foodstuff or a beverage (such as, e.g., coffee, tea, milk, chocolate, etc.), an article made of glass, an article made of ceramic, a banknote, a stamp, a security document, an identity card, a passport, a driver's license, a credit card, an access card, a ticket such as, e.g., a transportation ticket or an event ticket, a voucher, a value document, an ink-transfer film, a reflective film, a thread, a commercial good, and a cigarette packaging carrying or not carrying coded or encrypted information.

[0035] The present invention also provides a polymer wherein at least about 0.1 % of the polymer molecules have bonded thereto 1 to 4 residues (e.g., 1, 2 or 3 residues) of formula —Q—$(Y)_w$ wherein

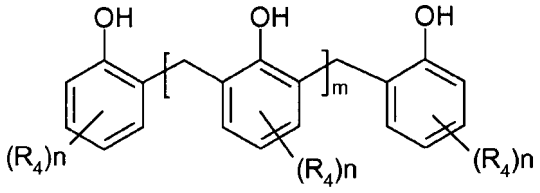
Q represents an A or B or (A') or (B') moiety;

Y is selected from (i) halogen (e.g., F, Cl, Br and I),

(ii) optionally substituted N-heterocycloaliphatic groups having from 3 to about 8 ring members, at least one of which is N, which are bonded to Q through an N atom, and (iii) optionally substituted phenoxy groups bonded to Q through the O atom;

w represents an integer of from 1 to 4; and further provided that Q may at the same time be bonded to up to 4 polymer molecules (e.g., to 1, 2, 3 or 4 different polymer molecules).

[0036] In one aspect of the polymer, the polymer may be a compound of general formula (2):



(2)

wherein the groups R_4, the same or different from each other, are selected from C_1-C_{10} alkyl and C_1-C_4 alkoxy; m represents an integer of from 1 to about 30; and n represents an integer of from 1 to about 3.

[0037] Regarding x and w, examples of combinations thereof include wherein x is 1 and w = 0; wherein x is 0 and w is 2 or not higher than 4; and wherein (x + w) is not higher than about 4.

[0038] In yet another aspect, the polymer may be obtainable by the process set forth above (including the various aspects thereof).

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0039] The particulars shown herein are by way of example and for purposes of illustrative discussion of the embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the present invention. In this regard, no attempt is made to show structural details of the present invention in more detail than is necessary for the fundamental understanding of the present invention, the description making apparent to those skilled in the art how the several forms of the present invention may be embodied in practice.

[0040] Regarding the meanings of the groups R, R', R", R_1, R_2, R_3 and R_4 mentioned herein, the following applies throughout the present specification and the appended claims (it being understood that throughout the present specification and the appended claims the indicated number of carbon atoms invariably refers to the respective unsubstituted group):

[0041] An "optionally substituted aliphatic" or "optionally substituted alkyl" group includes linear and branched alkyl groups which preferably have from 1 to about 12 carbon atoms, e.g., from 1 to about 8 carbon atoms, from 1 to about 6 carbon atoms, or from 1 to about 4 carbon atoms. Specific non-limiting examples thereof include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, sec-butyl, linear or branched pentyl (e.g., 2-methylbutyl, 2-ethylpropyl and 2,2-dimethylpropyl), linear or branched hexyl (e.g., 2-ethylbutyl, 3-ethylbutyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, and 2,3-dimethylbutyl), linear or branched heptyl, linear or branched octyl (e.g., 2-ethylhexyl), and linear or branched nonyl. The alkyl groups may be substituted with one or more substituents (e.g., one, two, three, four, etc.). Non-limiting

examples of these substituents include OH, halogen such as, e.g., F, Cl, Br, and I (as in, e.g., trifluoromethyl, trichloromethyl, pentafluorethyl and 2,2,2-trifluoroethyl), alkoxy having from 1 to about 6 carbon atoms, e.g., from 1 to about 4 carbon atoms, such as, e.g., methoxy, ethoxy, propoxy and butoxy, acyloxy having from 1 to about 4 carbon atoms such as, e.g., acetoxy and propionyloxy, aryloxy having from about 6 to about 10 carbon atoms such as, e.g., (optionally substituted) phenoxy, aroyloxy having from about 6 to about 10 carbon atoms such as, e.g., benzoyloxy, -COOH (including partially or completely salified forms thereof), alkoxycarbonyl having from 1 to about 4 carbon atoms in the alkyl groups such as, e.g., methoxycarbonyl and ethoxycarbonyl, $-SO_3H$, alkylsulfonyl, arylsulfonyl, alkylsulfonylamino, nitro, cyano, amino, monoalkylamino and dialkylamino wherein the alkyl groups have from 1 to about 6 carbon atoms, e.g., from 1 to about 4 carbon atoms, such as, e.g., methylamino, dimethylamino, ethylamino, diethylamino, propylamino and dipropylamino. The alkyl groups may also be substituted by one or more optionally substituted cycloalkyl groups (preferably having from 3 to about 8 ring carbon atoms) as further set forth below. Preferred substituents for the alkyl groups include F, Cl, Br, OH, methoxy, ethoxy, -COOH, $-SO_3H$, amino, methylamino, ethylamino, dimethylamino and diethylamino. If more than one substituent is present, the substituents may be the same or different. Also, one or more (e.g., one or two) of the C atoms of the alkyl group may be replaced by a heteroatom such as, e.g., O, S and NR'" (with R'" representing, for example, H or alkyl having from 1 to about 4 carbon atoms). Further, the alkyl group may have one or more carbonyl groups (C=O) incorporated therein and/or may comprise one or more carbon-carbon double and/or triple bonds (such as in, e.g., vinyl, allyl and propargyl).

[0042] An "optionally substituted cycloaliphatic" or "optionally substituted cycloalkyl" group preferably comprises from about 3 to about 12 ring carbon atoms, more preferably from about 5 to about 8 ring carbon atoms such as, e.g., cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl. The cycloalkyl groups may be substituted with one or more substituents (e.g., one, two, three, four, etc). Non-limiting examples of these substituents include OH, halogen such as, e.g., F, Cl, Br, and I, alkoxy having from 1 to about 6 carbon atoms, e.g., from 1 to about 4 carbon atoms, such as, e.g., methoxy, ethoxy, propoxy and butoxy, acyloxy having from 1 to about 4 carbon atoms such as, e.g., acetoxy and propionyloxy, aryloxy having from about 6 to about 10 carbon atoms such as, e.g., (optionally substituted) phenoxy, aroyloxy

having from about 6 to about 10 carbon atoms such as, e.g., benzoyloxy, -COOH (including partially or completely salified forms thereof), alkoxycarbonyl having from 1 to about 4 carbon atoms in the alkyl groups such as, e.g., methoxycarbonyl and ethoxycarbonyl, $-SO_3H$, alkylsulfonyl, arylsulfonyl, alkylsulfonylamino, nitro, cyano, amino, monoalkylamino and dialkylamino wherein the alkyl groups have from 1 to about 6 carbon atoms, e.g., from 1 to about 4 carbon atoms, such as, e.g., methylamino, dimethylamino, ethylamino, diethylamino, propylamino and dipropylamino. The cycloalkyl groups may also be substituted by one or more optionally substituted alkyl groups (preferably having from 1 to about 4 carbon atoms) as set forth above. Preferred substituents for the alkyl groups include F, Cl, Br, OH, methoxy, ethoxy, -COOH, $-SO_3H$, amino, methylamino, ethylamino, dimethylamino and diethylamino. If more than one substituent is present, the substituents may be the same or different. Further, the cycloalkyl group may have one or more carbonyl groups (C=O) incorporated therein and/or may comprise one or more carbon-carbon double bonds (such as in, e.g., cyclopentenyl and cyclohexenyl).

[0043] An "optionally substituted aryl (aromatic)" group and an "optionally substituted heteroaryl (heteroaromatic" group denote optionally fused aryl and heteroaryl groups which preferably comprise from about 5 to about 15 ring members, e.g., from about 6 to about 10 ring members. The heteroaryl groups will usually comprise from 1 to about 3 ring members selected from O, S and N and may be partially or fully hydrogenated. Specific examples of these aryl and heteroaryl groups include phenyl, naphthyl, anthranyl, phenanthryl, 2- or 3-furyl, 2- or 3-thienyl, 1-, 2- or 3-pyrrolyl, 1-, 2-, 4- or 5-imidazolyl, 1-, 3-, 4- or 5-pyrazolyl, 2-, 4- or 5-oxazolyl, 3-, 4- or 5-isoxazolyl, 2-, 4- or 5-thiazolyl, 3-, 4- or 5-isothiazolyl, 2-, 3- or 4-pyridyl, 2-, 4-, 5- or 6-pyrimidinyl, 1,2,3-triazol- 1-, -4- or -5-yl, 1,2,4-triazol-1-, -3- or -5-yl, 1 - or 5-tetrazolyl, 1,2,3-oxadiazol-4- or -5-yl, 1,2,4-oxadiazol-3- or -5-yl, 1,3,4-thiadiazol-2- or -5-yl, 1,2,4-thiadiazol-3- or -5-yl, 1,2,3-thiadiazol-4- or -5-yl, 3- or 4-pyridazinyl, pyrazinyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-indolyl, indazolyl, 4- or 5-isoindolyl, 1-, 2-, 4- or 5-benzimidazolyl, 1-, 3-, 4-, 5-, 6- or 7-benzopyrazolyl, 2-, 4-, 5-, 6- or 7-benzoxazolyl, 3-, 4-, 5-, 6- or 7-benzisoxazolyl, 2-, 4-, 5-, 6- or 7-benzothiazolyl, 2-, 4-, 5-, 6- or 7-benzisothiazolyl, 4-, 5-, 6- or 7-benz-2,1,3-oxadiazolyl, 2-, 3, 4-, 5-, 6-, 7- or 8-quinolyl, 1-, 3-, 4-, 5-, 6-, 7- or 8-isoquinolyl, 3-, 4-, 5-, 6-, 7- or 8-cinnolinyl, 2-, 4-, 5-, 6-, 7- or 8-quinazolinyl, 5- or 6-quinoxalinyl, 2-, 3-, 5-, 6-, 7- or 8-2H- benzo-1,4-

oxazinyl, 1,3-benzodioxol-5-yl, 1,4-benzo-dioxane-6-yl, 2,1,3-benzothiadiazol-4- or -5-yl or 2,1,3-benzoxadiazol-5-yl, 2,3-dihydro-2-, -3-, -4- or -5-furyl, 2,5-dihydro-2-, -3-, -4- or -5-furyl, tetrahydro-2- or -3-furyl, 1,3-dioxolan-4-yl, tetrahydro-2- or -3-thienyl, 2,3-dihydro-1-, -2-, -3-, 4- or -5-pyrrolyl, 2,5-dihydro-1-, -2-, -3-, -4- or -5-pyrrolyl, 1-, 2- or 3-pyrrolidinyl, tetrahydro-1-, -2- or -4-imidazolyl, 2,3-dihydro-1-, -2-, -3-, -4- or -5-pyrazolyl, tetrahydro-1-, -3- or -4-pyrazolyl, 1,4-dihydro-1-, -2-, -3- or -4-pyridyl, 1,2,3,4-tetrahydro-1-, -2-, -3-, -4-, -5- or -6-pyridyl, 1-, 2-, 3- or 4-piperidinyl, 2-, 3- or 4-morpholinyl, tetrahydro-2-, -3- or -4-pyranyl, 1 ,4-dioxaneyl, 1,3-dioxane-2-, -4- or -5-yl, hexahydro-1-, -3- or -4-pyridazinyl, hexahydro-1-, -2-, -4- or -5-pyrimidinyl, 1 -, 2- or 3-piperazinyl, 1 ,2,3,4-tetrahydro-1 -, -2-, -3-, -4-, -5-, -6-, -7- or -8-quinolyl, 1,2,3,4-tetrahydro-1-, -2-, -3-, -4-, -5-, -6-, -7- or -8-isoquinolyl, 2-, 3-, 5-, 6-, 7- or 8-3,4-dihydro-2H-benzo-1,4-oxazinyl, 2,3-methylenedioxyphenyl, 3,4-methylenedioxyphenyl, 2,3-ethylenedioxyphenyl, 3,4-ethylenedioxyphenyl, 3,4-(difluoromethylenedioxy)phenyl, 2,3-dihydrobenzofuran-5- or -6-yl, 2,3-(2-oxomethylenedioxy)phenyl, 3,4-dihydro-2H-1,5-benzodioxepin-6- or -7-yl, 2,3-dihydrobenzofuranyl, 2,3-dihydro-2-oxofuranyl. The aryl and heteroaryl groups may be substituted with one or more (e.g., one, two, three, four, etc.) substituents which are preferably selected from halogen such as, e.g., F, Cl, Br, and I, OH, -COOH (including partially or completely salified forms thereof), $-SO_3H$, nitro, cyano, alkoxy having from 1 to about 4 carbon atoms such as, e.g., methoxy and ethoxy, acyloxy having from 1 to about 4 carbon atoms such as, e.g., acetoxy and propionyloxy, aryloxy having from about 6 to about 10 carbon atoms such as, e.g., phenoxy, aroyloxy having from about 6 to about 10 carbon atoms such as, e.g., benzoyloxy, amino, monoalkylamino and dialkylamino wherein the alkyl groups have from 1 to about 6 carbon atoms, e.g., from 1 to about 4 carbon atoms, such as, e.g., methylamino, dimethylamino, ethylamino, diethylamino, propylamino and dipropylamino, acylamino having from 1 to about 8 carbon atoms such as, e.g., acetylamino and propionylamino, aminocarbonyl, monoalkylaminocarbonyl, diaminocarbonyl and alkoxycarbonyl having from 1 to about 4 carbon atoms in the alkyl groups such as, e.g., methoxycarbonyl and ethoxycarbonyl, optionally substituted acyl having from 2 to about 8 carbon atoms such as acetyl and propionyl, alkylsulfonyl, arylsulfonyl and alkylsulfonylamino. If more than one substituent is present, the substituents may be the same or different. Also, the aryl and heteroaryl groups may be substituted by aryl groups and/or alkylaryl groups. Specific and

non-limiting examples of substituted aryl groups include chlorophenyl, dichlorophenyl, fluorophenyl, bromophenyl, phenoxyphenyl, hydroxyphenyl, dihydroxyphenyl, methoxyphenyl, aminophenyl, dimethylaminophenyl and biphenylyl.

[0044] An "optionally substituted alkylaryl" group and an "optionally substituted alkylheteroaryl" group denote optionally substituted aryl groups and optionally substituted heteroaryl groups as set forth above which are (further) substituted by at least one optionally substituted alkyl group (preferably comprising from 1 to about 6, e.g., from 1 to about 4 carbon atoms) as set forth above. Specific examples thereof include tolyl, xylyl, mesityl, ethylphenyl, cumyl, trifluormethylphenyl, hydroxytolyl, chlorotolyl, methylpyridyl, methylfuryl, methylthienyl, diisopropylphenyl, di(tert-butyl)phenyl, and methylnaphthyl.

[0045] An "optionally substituted arylalkyl" group and an "optionally substituted heteroarylalkyl" group denote optionally substituted alkyl groups (preferably comprising from 1 to about 6, e.g., from 1 to about 4 carbon atoms) as set forth above which are (further) substituted by at least one optionally substituted aryl group and/or optionally substituted heteroaryl group as further set forth above. Specific examples thereof include benzyl, methylbenzyl, chlorobenzyl, dichlorbenzyl, hydroxybenzyl, 1-phenylethyl, 2-phenylethyl, pyridylmethyl, thienylmethyl, furylmethyl, and naphthylmethyl.

[0046] An "optionally substituted and/or fused 5- to 7-membered ring" denotes a saturated, partially unsaturated or aromatic N-heterocyclic ring which in addition to the one or two N atoms already present therein may comprise one or two additional heteroatoms which are selected from O, N and S. The ring will usually have five or six ring members. Also, the ring will often comprise no additional heteroatom. Further, the ring may have one or two aromatic and/or heteroaromatic rings (e.g., benzene rings) fused to it and/or may be substituted with one or more (e.g., one, two, three, four, etc.) substituents which are preferably selected from F, Cl, Br, and I, OH, -COOH (including partially or completely salified forms thereof), $-SO_3H$, cyano, nitro, alkoxy having from 1 to about 4 carbon atoms such as, e.g., methoxy and ethoxy, acyloxy having from 1 to about 4 carbon atoms such as, e.g., acetoxy and propionyloxy, aryloxy having from about 6 to about 10 carbon atoms such as, e.g., phenoxy, aroyloxy having from about 6 to about 10 carbon atoms such as, e.g., benzoyloxy, amino, monoalkylamino and dialkylamino wherein

the alkyl groups have from 1 to about 6 carbon atoms, e.g., from 1 to about 4 carbon atoms, such as, e.g., methylamino, dimethylamino, ethylamino, diethylamino, propylamino and dipropylamino, acylamino having from 1 to about 8 carbon atoms such as, e.g., acetylamino and propionylamino, aminocarbonyl, monoalkylaminocarbonyl, diaminocarbonyl and alkoxycarbonyl having from 1 to about 4 carbon atoms in the alkyl groups such as, e.g., methoxycarbonyl and ethoxycarbonyl, optionally substituted acyl having from 2 to about 8 carbon atoms such as acetyl and propionyl, alkylsulfonyl, arylsulfonyl and alkylsulfonylamino, optionally substituted alkyl having from 1 to about 6 carbon atoms such as, e.g., methyl, ethyl, hydroxymethyl and hydroxyethyl, optionally substituted (hetero)aryl such as, e.g., phenyl, tolyl, xylyl, hydroxyphenyl, pyridinyl and pyrrolyl, and optionally substituted alkylaryl such as, e.g., benzyl. If more than one substituent is present, the substituents may be the same or different. Non-limiting examples of unsubstituted N-containing 5- to 7- membered rings include pyrrolyl, pyrrolidinyl, pyridinyl, pyrimidinyl, piperidinyl, morpholinyl, piperazinyl, thienyl, pyrazolyl, pyrazolidinyl, oxazolyl and oxazolidinyl.

[0047] As set forth above, the compounds of the present invention include general formula (1):

$$(P—O)_x—Q—Y_w$$

(1)

wherein P represents a polymeric moiety having at least three repeating units which comprise an optionally substituted phenyl ring;

Q represents a polycyclic aromatic hydrocarbon moiety containing an S atom or $S(=O)_2$ moiety (i.e., a polycyclic aromatic hydrocarbon skeleton containing an S atom or $S(=O)_2$ moiety incorporated in its basic structure which may optionally comprise one or more substituents in addition to the substituents Y and/or P-O) ;

Y is selected from (i) halogen, (ii) optionally substituted N-heterocycloaliphatic groups having from 3 to about 8 ring members and which are bonded to Q through an N atom, and (iii) optionally substituted phenoxy groups;

x represents an integer of from 0 to 4;

w represents an integer of from 0 to 4

and wherein w and x are not simultaneously 0;

provided that when x = 0 at least one Y is selected from (ii) and (iii).

[0048] If more than one halogen is present (i.e., if w is at least 3), the halogen atoms may be the same or different and are preferably the same. Further, if more than one optionally substituted N-heterocycloaliphatic group having from 3 to about 8 ring members is present, the groups may be the same or different as well (and preferably are the same). Further, if more than one optionally substituted phenoxy group is present, the groups may be the same or different as well (and preferably are the same). Further, x will often be 1 or 2, more preferably 1, and the sum (x + w) will often not exceed 6, e.g., not exceed 5, or not exceed 4.

[0049] It also is to be appreciated that while a group (P-O)- will usually be bonded directly to the moiety Q, it may also be bonded to an aromatic group (in particular, a phenyl group) which is not part of the Q skeleton but is (a part of) a substituent thereof. In this regard, the above formulae (II), (V), (D) and (G) may be referred to. In the case of compounds of formulae (II), (V), (D) and (G), the group (P-O)- is bonded to the optionally substituted phenyl ring of a group -CO-NR-CO- (which is one of the meanings of Z and X in formulae (A), (B), (E) and (H)) wherein R represents an optionally substituted phenyl group. It is also possible for bonding to –C(=NR')-NR-CO- wherein (P-O)- may be bonded to an aromatic group R and/or R').

[0050] Group Y can be selected from N-heterocycloaliphatic groups having from 3 to about 8 ring members (e.g., 3, 4, 5, 6, 7 or 8 ring members), which ring members may comprise from 1 to about 3 heteroatoms (e.g., 1, 2 or 3 heteratoms) selected from N, S, and O, provided that at least one ring member is N. At least one (and preferably at least two) of the ring members are carbon atoms. By way of non-limiting example, a heterocycloaliphatic group Y may have 5, 6 or 7 ring members (preferably 5 or 6 ring members) and contain 1 or 2 heteroatoms, at least one of them being an N atom. If two heteroatoms are present, the second heteroatom may be N, S or O. If three heteroatoms are present, the second or third heteroatom may be the same or different and be selected from N, O and S. For example, a heterocycloaliphatic group Y containing 3 heteroatom ring members may contain 3 N atoms, or 2 N atoms and one O atom or one S atom.

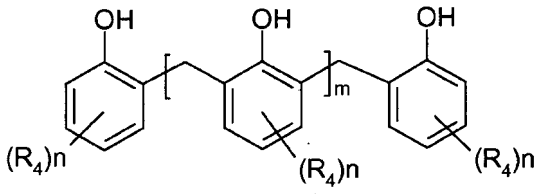
[0051] The heterocycloaliphatic groups Y may further be substituted by one or more substituents (e.g., 1, 2, 3 or 4 substituents and preferably not more than 3, or not more than 2 substituents) selected from alkyl and alkoxy groups comprising up to about 10 carbon atoms (e.g., 1, 2, 3, 4, 5 or 6 carbon atoms). Non-limiting examples of corresponding substituents include ethyl, methyl, n-propyl, i-propyl, n-butyl, sec.-butyl, and tert.-butyl and the corresponding alkoxy groups.

[0052] For example, group Y may be a group that is the residue of a compound (i.e., without H atom bonded to the nitrogen atom) selected from optionally substituted azacyclooctane, optionally substituted azepane, optionally substituted piperidine, optionally substituted piperazine, optionally substituted pyrrolidine, optionally substituted azetidine, optionally substituted aziridine, optionally substituted morpholine, optionally substituted oxazolidine, optionally substituted pyrazolidine, optionally substituted isopyrazolidine, optionally substituted isoxazolidine, and optionally substituted thiazolidine. The optional substituents on the heterocyclic rings (e.g., 1, 2, 3 or 4 substituents) may be the same or different and may preferably be selected from C_1-C_4 alkoxy and C_1-C_6 alkyl groups. A specific and non-limiting example of a correspondingly substituted group is 3,5-dimethyl-1-piperidinyl.

[0053] Group Y may be additionally selected from optionally substituted phenoxy group, wherein the phenoxy groups may be substituted by one or more (e.g., 1, 2 or 3 identical or different) substituents selected from halogen (e.g., F, Cl, Br and I), nitro, cyano, NRR', SO_3H and COOH and salts and derivatives of these sulfonic and carboxylic acid groups (e.g., salts of alkali and alkaline earth metals such as Na, K, Ca, and Mg , esters such as C_1-C_4 alkyl esters, and amides such as amides with NRR' as amido moiety), OH, heterocycloalkyl comprising up to three heteroatoms selected from O, N and S as ring members and from 3 to about 8 ring members, and alkyl (including cycloalkyl) and alkoxy (including cycloalkoxy) groups comprising from 1 to about 10 carbon atoms (e.g., 1, 2, 3, 4, 5 or 6 carbon atoms). Specifics and non-limiting example of a correspondingly substituted phenoxy group are 2,6-di-tert-butyl-4-methylphenoxy, p-cresyl, and o-cresyl.

[0054] A polymeric moiety P in a polymer-bonded compound of general formula (1) preferably comprises only carbon atoms (i.e., no heteroatoms such as O, N or S) in the backbone thereof. Also, the polymeric moiety preferably comprises at least three aromatic rings (e.g., phenyl rings)

in the backbone thereof. These aromatic rings (which may be the same or different and preferably are the same) may be connected to each other either directly or through one or more atoms, preferably carbon atoms. At least some (and preferably all) of these aromatic rings may carry one or more (e.g., 1, 2 or 3) polar (heteroatom containing) substituents that increase the solubility of the polymeric moiety in polar media (such as, e.g., alcohol, etc.) compared to the polymeric moiety without polar substituent(s). If more than one polar substituent is present, the substituents may be the same or different. Of course, one or more additional (non-polar) substituents may be present on an aromatic ring as well. By way of non-limiting example, the polymeric moiety may be derived from a phenolic resin such as, e.g., a novolac resin and in particular, a phenolic resin having at least about 3 hydroxy groups and/or a (weight) average molecular weight of at least about 300, e.g., at least about 350, and not higher than about 3,000, e.g., not higher than about 1,500. For example, P may be derived from (be the residue of) a compound of general formula (2):

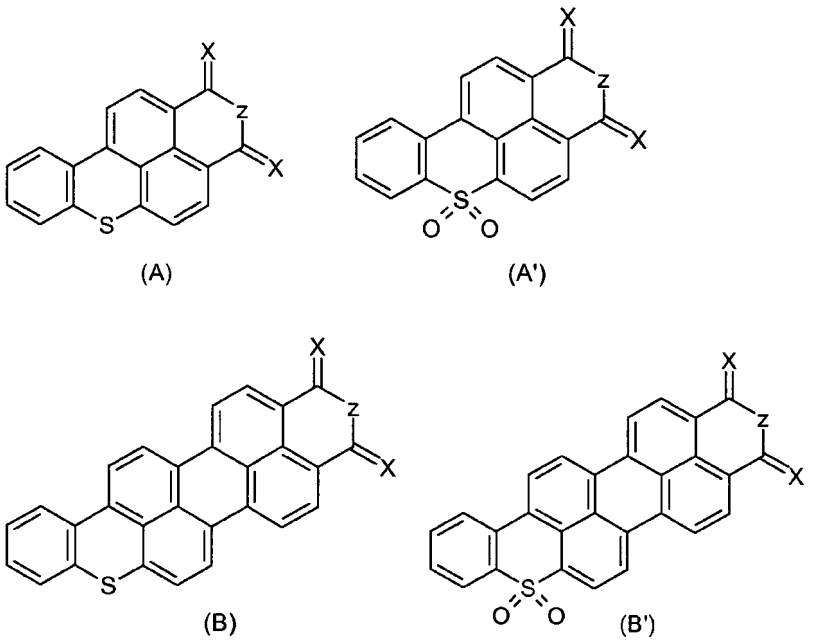


(2)

wherein the groups R_4, the same or different from each other, are selected from C_1-C_{10} alkyl and C_1-C_4 alkoxy; m represents an integer of from 1 to about 30, e.g., from 1 to 25, from 1 to 15, from 1 to 10, from 1 to 5, from 1 to 3, from 5 to 15, from 5 to 10, from 10 to 20, or from 20 to 30; and n represents an integer of from 1 to 3 (e.g., 1, 2 or 3). For example, m may represent an integer of from 1 to 10 and/or n may be 1 or 2 and/or the groups R_4 may independently be selected from C_1-C_{10} alkyl such as, e.g., isopropyl, tert-butyl, tert-octyl, n-nonyl and branched nonyl. Further, a group R_4 may be in the meta- or para-position with respect to the OH group. For example, if two groups R_4 are present on a phenyl ring (the same or different, preferably the same groups R_4) they may be present in any of the available positions on the phenyl ring, such as, e.g., meta/para or meta/meta with respect to the OH group.

[0055] One of skill in the art will appreciate that compounds of general formula (2) will often be present as a mixture of compounds with different values of m. In this case, the average value of m in the general formula (2) will often be at least about 1, e.g., at least about 2, e.g., at least about 3, or at least about 4, and will also often be not higher than about 30, e.g., not higher than about 20, not higher than about 15, or not higher than about 10.

[0056] As also set forth above, Q may be a moiety having a basic structure of formula (A) or (B) or (A') or (B'):

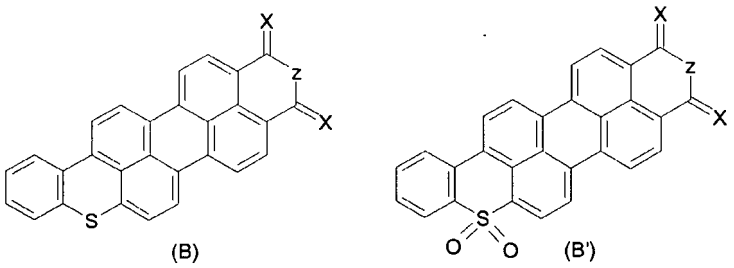


[0057] In the above formulae (A) and (B) or (A') or (B'), Z represents O, S or N-R, and X, which can be the same or different, represents O, S, or NR'. Thus, the group formed by Z and X can be represented, for example, by -CO-Z-CO- (may be replaced by [–COOH HOOC-] (i.e., the dicarboxylic acid instead of the anhydride)), –CS-Z-CO-, -CS-Z-CS-, or –C(=NR')-NR-CO-.

[0058] The groups R and R' in the above formulae independently represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms. Additionally, R and

R' may be combined to form, together with the N atoms to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring.

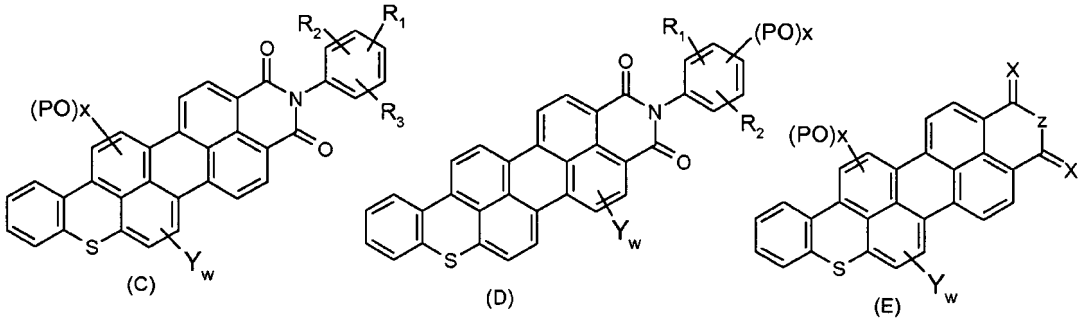
[0059] There are also provided optionally substituted compounds of formula (B) or (B')

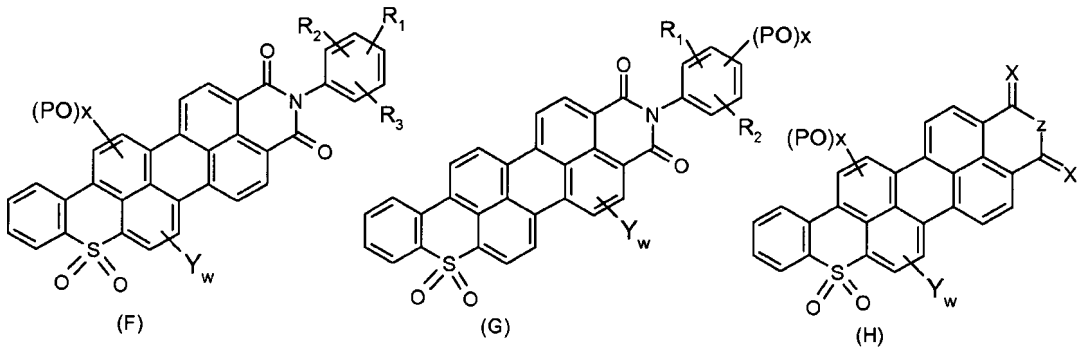


wherein Z represents O, S or N-R, and X, which can be the same or different, represents O, S, or NR'. Thus, the group formed by Z and X can be represented, for example, by -CO-Z-CO- (may be replaced by [–COOH HOOC-] (i.e., the dicarboxylic acid instead of the anhydride)), –CS-Z-CO-, -CS-Z-CS-, or –C(=NR')-NR-CO-; and

R and R' independently represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms; and R and R' may also be combined to form, together with the N atoms to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring.

These compounds can include compounds of formulae (C), (D) or (E) or (F) or (G) or (H):





wherein in the case of formula (E) and (H), Z represents O, S or N-R; and X, which can be the same or different, represents O, S, or NR'; and

R and R' independently represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms; and R and R' may be combined to form, together with the N atoms to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring;

R_1, R_2 and R_3 are independently selected from hydrogen, C_1-C_4 alkyl, C_1-C_4 alkyl-COOH, C_1-C_4 alkyl-SO_3H, C_1-C_4 alkoxy, mono(C_1-C_4)alkylamino, di(C_1-C_4)alkylamino, C_1-C_4 aminoalkyl, halogen, cyano, nitro, and SO_3H, the alkyl groups being optionally substituted;

Y is selected from (i) halogen and (ii) optionally substituted N-heterocycloaliphatic groups having from 3 to about 8 ring members and which are bonded to an aromatic ring through an N atom; and (iii) optionally substituted phenoxy groups which are bonded to an aromatic ring through an O atom, the phenoxy group may be substituted by one or more substituents selected from halogen, nitro, cyano, NRR', SO_3H and COOH and salts and derivatives of these sulfonic and carboxylic acid groups, OH, heterocycloalkyl comprising up to three heteroatoms selected from O, N and S as ring members and from 3 to about 8 ring members, and alkyl (including cycloalkyl) and alkoxy (including cycloalkoxy) groups comprising from 1 to about 10 carbon atoms;

P represents a polymeric moiety having at least three repeating units which comprise an optionally substituted phenyl ring;

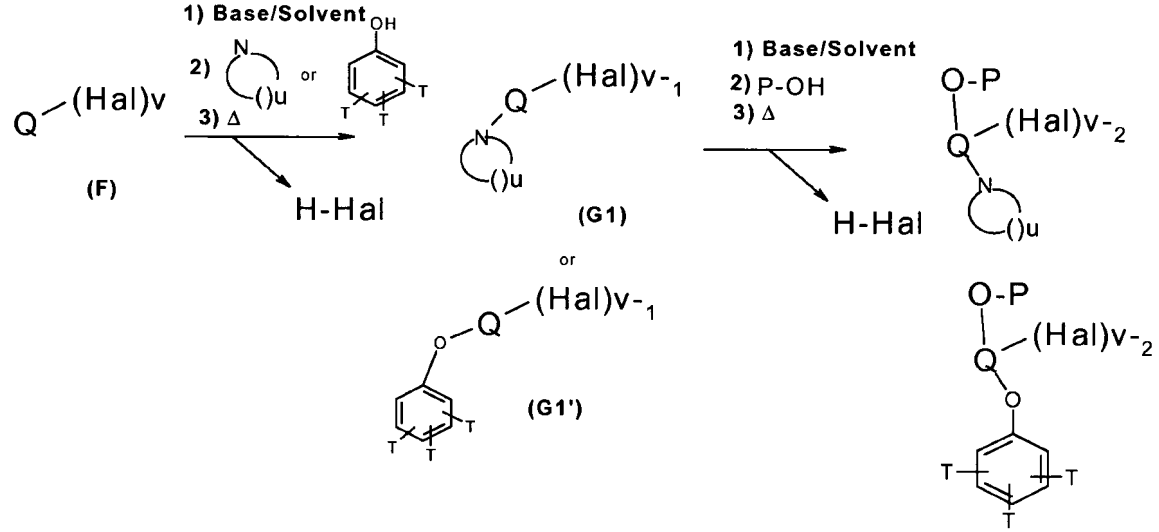
and x is an integer of from 0 to 4; and w is an integer of from 0 to 4.

[0060] The compounds formula (B) or (B') can be unsubstituted.

[0061] Compounds of general formula (1) may be made, for example, by a process which comprises reacting in an aprotic polar organic solvent a compound of formula $Q-(Hal)_v$ wherein Hal represents halogen (e.g., F, Cl, Br or I) and v represents an integer of from 1 to 8 (e.g., 1, 2, 3, 4, or 5), with a compound selected from (a) N-containing cycloaliphatic compounds, (b) polymeric compounds of formula P-OH, and (c) optionally substituted phenolic compounds or by reacting a compound of formula $Q-(Hal)_v$ successively with two (if v is at least 2) or three (if v is at least 3) or even more compounds which are independently selected from compounds (a), (b) and (c). In the latter case the at least two compounds which are reacted successively with a compound of formula $Q-(Hal)_v$ may belong to the same group or a different group. For example, the compound of formula $Q-(Hal)_v$ may successively be reacted with two different compounds (a) or a compound (a) and a compound (b) in any order. Usually at least the reaction involving the N-containing cycloaliphatic compound (and usually also the reaction involving the reaction comprising the polymeric compound and/or the phenolic compound) may be carried out in the presence of an inorganic base and/or a strong organic non-nucleophilic base. The polar solvent usually comprises at least one solvent in which the polymeric compound, if used, is soluble and/or is at least one of N-methylpyrrolidone, dimethyl formamide, dimethyl acetamide, and dimethylsulfoxide.

[0062] A corresponding process may, for example, be represented by the following reaction schemes (1) or (2) or (3) or (4):

(1)



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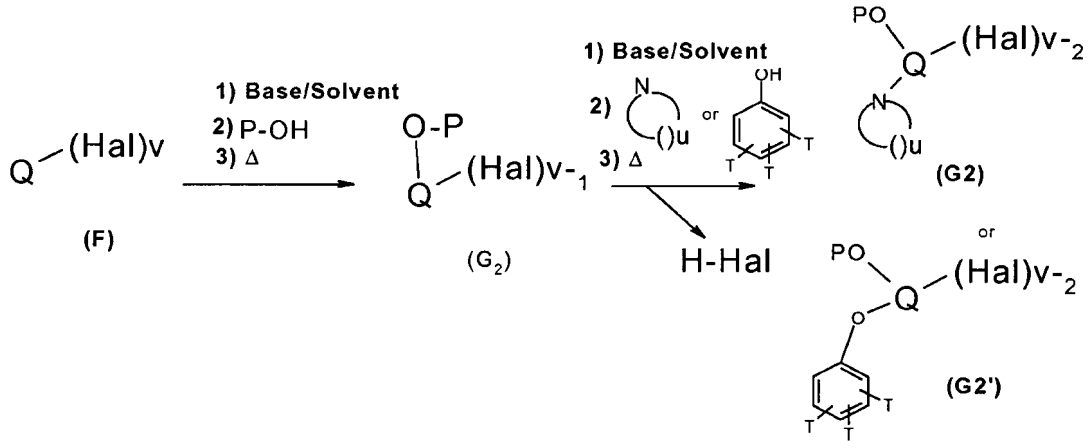
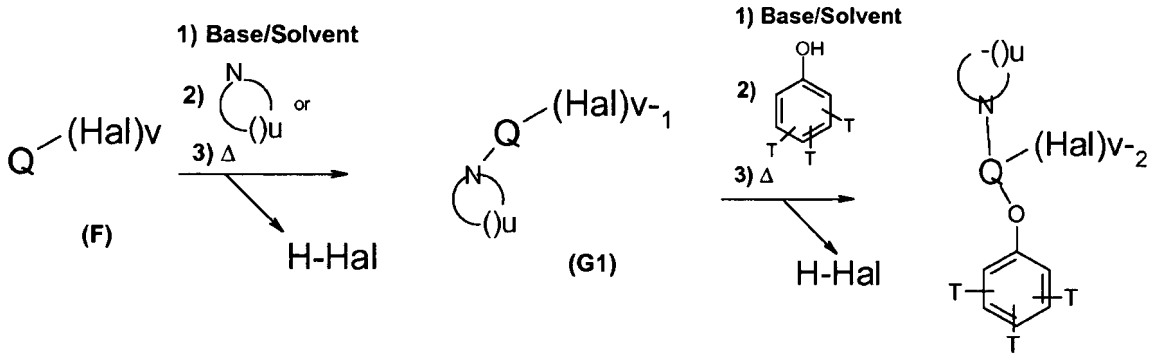
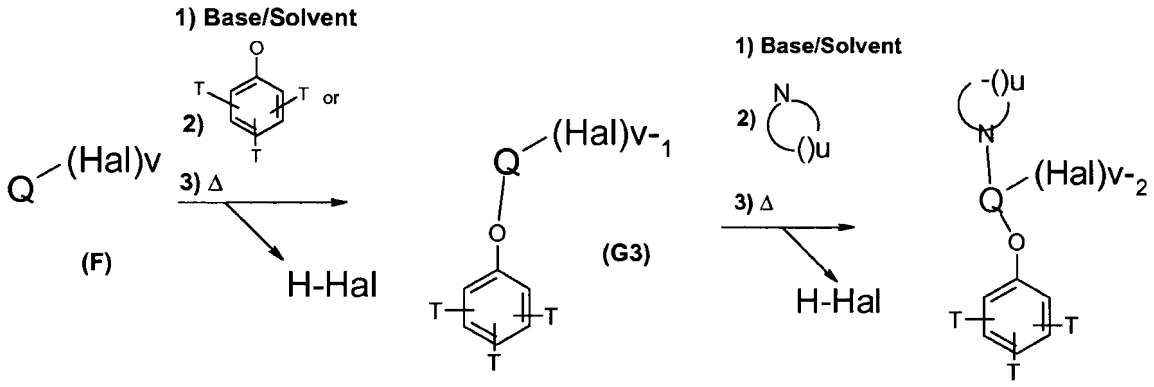


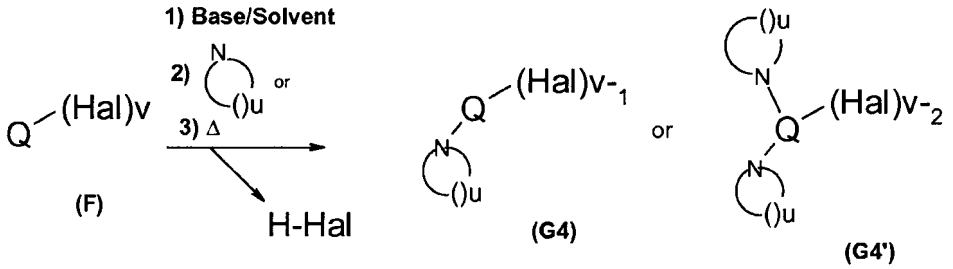
(3)


1) Base/Solvent
2)
or
3) Δ
(F)
H-Hal
(G1)
1) Base/Solvent
2)
3) Δ
H-Hal

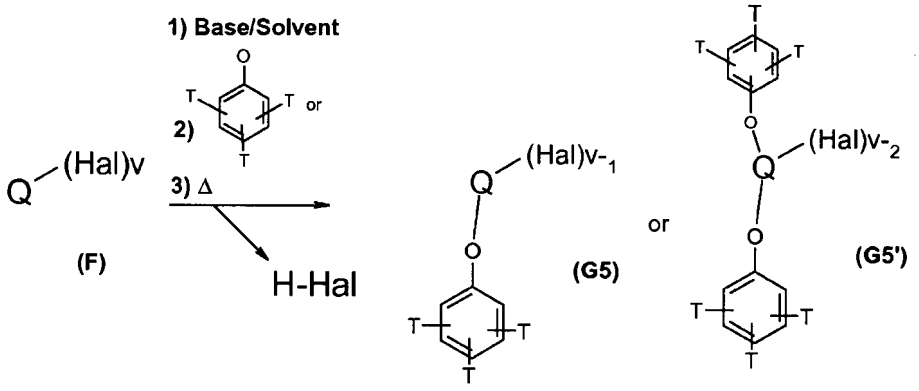
(4)


1) Base/Solvent
2)
or
3) Δ
(F)
H-Hal
(G3)
1) Base/Solvent
2)
3) Δ
H-Hal

(5)


1) Base/Solvent
2)
or
3) Δ
(F)
H-Hal
(G4)
or
(G4')

(6)



wherein P and Q are defined as above;

wherein T is selected from, but not limited to, halogen (e.g., F, Cl, Br and I), nitro, cyano, NRR', SO_3H and COOH and salts and derivatives of these sulfonic and carboxylic acid groups (e.g., salts of alkali and alkaline earth metals such as Na, K, Ca, and Mg , esters such as C_1-C_4 alkyl esters, and amides such as amides with NRR' as amido moiety), OH, heterocycloalkyl comprising up to three heteroatoms selected from O, N and S as ring members and from 3 to about 8 ring members, and alkyl (including cycloalkyl) and alkoxy (including cycloalkoxy) groups comprising from 1 to about 10 carbon atoms (e.g., 1, 2, 3, 4, 5 or 6 carbon atoms);

Hal represents halogen;

() represents CH_2 wherein at least one CH_2 group can be replaced by O, NH or S;

u is from 2 to 7;

v is an integer of from 2 to 8;

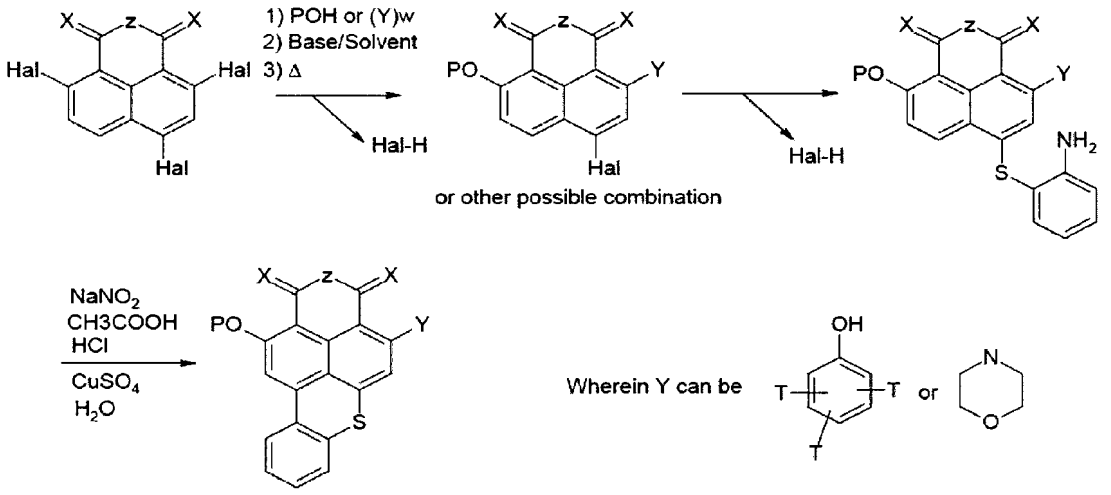
and the symbol "Δ" represents the application of heat (heating).

F is the halogenated compound having a Q core as defined above. G1 or G2 or (G3) are the intermediates of reaction, when running the processes (1) or (2) or (3) or (4).

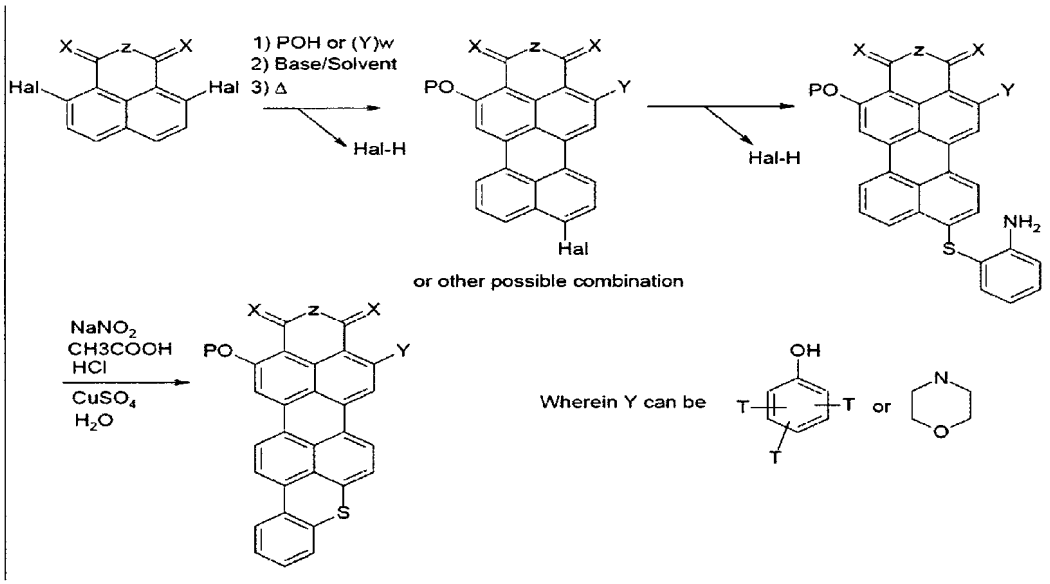
In the case of when running the process (5) and (6) which lead to compounds (G4) or (G5) or (G4') or (G5') v is an integer from 1 to 8.

Other alternatives processes are also possible to obtain the compounds according to formula (1) such as processes (7) or (8):

(7)



(8)



wherein the definitions of T, Hal, X, Z, POH, Y and w are the same as above defined.

[0063] It is to be appreciated that while the above reaction schemes show reactions wherein the compound obtained after the first step is reacted with one or more additional compounds these reaction schemes also illustrate processes for making compounds of the present invention such as those of formula (1) wherein only one halogen atom of a compound of formula $Q\text{-}(Hal)_v$ is replaced by a compound selected from N-containing cycloaliphatic compounds, polymeric compounds of formula P-OH, and optionally substituted phenolic compounds, i.e., wherein the process is complete after the first step (i.e., no further reactions will take place).

[0064] If one of the above processes is to be selected, it will usually be preferred to employ the process that will afford the intermediate (after the first step) that exhibits the higher solubility.

[0065] Examples of inorganic and organic bases suitable for catalyzing nucleophilic substitution reactions are well known to those of skill in the art. An example of a suitable inorganic base is K_2CO_3. Reaction temperatures will often range from about 50° C to about 140° C, also depending on the boiling point of the solvent used. It further will often be desirable to employ an anti-foam agent such as, e.g., a polyethylene glycol or derivative thereof. The reaction product (e.g., polymer-bonded compound of formula (1)) can usually be isolated from the resultant reaction mixture and optionally purified by conventional means such as, e.g., filtration, centrifugation, extraction, chromatographic methods, etc.

[0066] The weight ratio of compound(s) of formula $Q\text{-}(Hal)_v$ (or similar compounds) to polymeric compound(s) of formula P-OH (or a similar polymeric compounds) depends on several factors such as, e.g., the molecular weight(s) of compound(s) of formula $Q\text{-}(Hal)_v$, the average number of compound(s) of formula $Q\text{-}(Hal)_v$ that is/are to be bonded to a single polymer molecule or the average number of polymer molecules that are to be bonded to a single compound of formula $Q\text{-}(Hal)_v$ (or a similar compound). In particular, in a polymer-bonded compound of the present invention a single polymer molecule P may have one or more than one unit Q (e.g., an average of 1, 2, 3, 4 of units Q) bonded thereto. Conversely, one or more than one polymer molecule (e.g., an average of 1, 2, 3, 4, or more polymer molecules) may be bonded to a single unit Q. It also is to be appreciated that it is possible to employ as starting materials

and intermediates in the reactions represented by the above reaction schemes not only individual compounds but also mixtures of compounds with different values of v (and even different values of u). For example, a starting material of formula Q-(Hal)$_v$ may be a mixture of two compounds (not taking into account positional isomers) wherein v represents 5 or 6. Likewise, even if a single compound of formula Q-(Hal)$_v$ also named (G) is employed as starting material, depending on the reaction conditions the intermediate obtained after the first reaction may be a single compound or a mixture of compounds such as, e.g., a mixture of three compounds (not taking into account positional isomers) wherein, for example, 1, 2 or 3 halogen atoms are replaced by a group P-O- or an N- heterocycloaliphatic ring.

[0067] It further is possible (and sometimes preferred) to employ a relatively large stoichiometric excess of polymer(s) with respect to compound(s) of formula Q-(Hal)$_v$ (or similar compounds). This will result in a polymer wherein only a small fraction (e.g., not more than about 0.1%, not more than about 0.5 %, not more than about 1 %, or not more than about 2 %, not more than about 4%, not more than about 6%, not more than about 8%, not more than about 10%) of the polymer molecules have at least one unit Q bonded thereto, thereby affording a doped polymer of the present invention. The doped polymer can be used for the same purposes for which the polymer-bonded compound of the present invention is employable such as, e.g., as a component of a printing ink composition.

[0068] It is, of course, possible to react one compound of formula Q-(Hal)$_v$ (or a similar compound) with more than one (or more than one type of) polymer. By way of non-limiting example, a compound of formula Q-(Hal)$_v$ (or a similar compound) may be reacted with a mixture of polymers of the above formula (2). Conversely, two or more different compounds of formula Q-(Hal)$_v$ (e.g., two or more compounds with different values for v and/or different meanings of Hal) may be reacted with (bonded to) a single (type of) polymer. Finally, two or more different compounds of formula Q-(Hal)$_v$ (or similar compounds) may be reacted with two or more different (types of) polymers, although this will usually result in difficult to control product mixtures.

[0069] A printing ink composition in accordance with the present invention comprises a (preferably polar) liquid medium and one or more (types of) compounds of general formula (1)

and/or compounds of the other formulas as set forth above (e.g., a mixture of one, two or three different compounds of general formula (1)) or any of the other formulas) dissolved or dispersed in the medium. The concentration of the compound(s) of general formula (1) and/or compounds of the other formulas in the medium depends on several factors such as, e.g., the polymer(s) to which the Q-containing compounds is/are bonded, the desired color intensity, the liquid medium, the remaining (optional) components of the composition, the intended purpose of the printing ink composition, and the substrate onto which the printing ink composition is to be applied. Often the (total) concentration of the one or more compound(s) of general formula (1) and/or compounds of the other formulas in the printing ink composition will be at least about 0.01 %, at least about 0.02 %, or at least 0.05 % by weight, and will usually be not higher than about 40 % by weight, e.g. not higher than about 20 %, not higher than about 10 %, or not higher than about 5 % by weight based on the total weight of the composition. The use of a mixture of different compounds permits for complex marking to provide an advantageous composition to render documents difficult to forge. Thus, for example, a mixture of different compounds in a printing ink composition permits the making of unique "chemical keys" that can be fine tuned by varying the concentrations and/or the compounds included in the composition.

[0070] The intended purpose of the printing ink composition is one of several factors which determines suitable and desirable concentration ranges for the compounds of general formula (1) and/or compounds of the other formulas as well as the types and concentration ranges of suitable or desirable optional components of the composition. There are many different types of printing processes. Non-limiting examples thereof include inkjet printing (thermal, piezoelectric, continuous, etc.), flexography, intaglio printing (e.g., gravure printing), screen printing, letterpress printing, offset printing, pad printing, relief printing, planographic printing and rotogravure printing. In a preferred embodiment, a printing ink composition in accordance with the present invention is suitable (at least) for inkjet printing. Industrial inkjet printers, commonly used for numbering, coding and marking applications on conditioning lines and printing presses, are particularly suitable. Preferred ink-jet printers include single nozzle continuous ink-jet printers (also called raster or multi level deflected printers) and drop-on-demand ink-jet printers, in particular valve-jet printers. Accordingly, the following discussion of printing ink compositions relates primarily to compositions for inkjet printing. However, it is to be kept in

mind that the present invention is not limited to printing ink compositions for inkjet printing but rather encompasses all printing ink compositions in which compounds of the present invention can be employed. Accordingly, the following considerations and statements apply *mutatis mutandis* to all printing ink compositions in which the compounds in accordance with the teaching of the present invention are useful.

[0071] Printing inks in general comprise coloring agents and liquid vehicles which comprise solutions of resinous binders in solvents. The specific choice of binders and solvents depends on several factors, such as, for example, the compound(s), the remaining components that are to be present, and the nature of the substrate to be printed. Non-limiting examples of suitable binders for use in the ink compositions for inkjet printing include binders which are conventionally used in inkjet printing inks, including resins such as nitrocellulose, acrylate resins and polyester resins (such as, e.g., DYNAPOL® L 1203 , L 205, L 206, L 208, L 210, L 411, L 651, L658, L 850, L 912, L 952, LH 530, LH 538, LH 727, LH 744, LH 773, LH 775, LH 818, LH 820, LH 822, LH 912, LH 952, LH 530, LH 538, LH 727, LH 744, LH 773, LH 775, LH 818, LH 820, LH 822, LH 823, LH 826, LH 828, LH 830, LH 831, LH 832, LH 833, LH 838, LH898, LH 908, LS436, LS615, P1500, S1218, S1227, S1247, S1249, S1252, S1272, S1401, S1402, S1426, S1450, S1510, S1606, S1611, S243, S320, S341, S361, S394, and S EP1408 from Evonik). Of course, other suitable resins known to those of skill in the art may be used as well. A typical (total) concentration of the one or more binders in the printing ink composition is from about 0.5 % to about 10 % by weight, based on the total weight of the composition. In this regard, it further is to be taken into account that typical viscosity values for inkjet printing inks are in the range of from about 4 to about 30 mPa.s at 25°C.

[0072] It further is to be appreciated that the polymer which has one or more units Q bonded thereto (and in the case of the doped polymer of the present invention as set forth above, also the polymer which is not bonded to any Q-containing molecule but is present in admixture with polymer that has a Q-containing unit bonded thereto) may also act as a binder for the composition. At any rate, the (principal) binder of the ink composition must be compatible with the polymer which a Q-containing unit bonded thereto, e.g., must not result in the formation of any insoluble substance, etc. when combined with the later.

[0073] Suitable solvents for inkjet printing inks are known to those of skill in the art. Non-limiting examples thereof include low-viscosity, slightly polar and aprotic organic solvents, such as, e.g., methyl ethyl ketone (MEK), acetone, ethyl acetate, ethyl 3-ethoxypropionate, toluene and mixtures of two or more thereof.

[0074] In particular if the printing ink composition of the present invention is to be applied by continuous inkjet printing the composition will usually also comprise at least one conductivity imparting agent (for example, a salt). The conductivity imparting agent will have a non-negligible solubility in the composition. Non-limiting examples of suitable conductivity imparting agents include salts such as, e.g., tetraalkyl ammonium salts (e.g., tetrabutyl ammonium nitrate, tetrabutyl ammonium perchlorate and tetrabutyl ammonium hexafluorophosphate), alkali metal thiocyanates such as potassium thiocyanate, akali potassium salts such as KPF_6 and alkali metal perchlorates such as lithium perchlorate. The conductivity imparting agent will be present in a concentration which is sufficient to provide the conductivity which is required or desirable. Of course, mixtures of two or more different conductivity imparting agents (salts) can be used. Often the one or more conductivity imparting agents will be present in a total concentration of from about 0.1 % to 2 % by weight, based on the total weight of the composition.

[0075] The printing ink composition according to the present invention may furthermore comprise one or more customary additives, such as, for example, fungicides, biocides, surfactants, sequestering agents, pH adjusters, etc. in the amounts customary for these additives. Further, the printing ink composition may comprise one or more additional colorants and/or components which impart a specific optical property (i.e., components which are different from the polymer-bonded compounds of the present invention). These additional components may be selected from, for example, conventional pigments and dyes, luminescent (e.g., fluorescent) pigments and dyes, and cholesteric and/or nematic liquid crystals. Examples of luminescent pigments include certain classes of inorganic compounds such as the sulphides, oxysulphides, phosphates, vanadates, garnets, spinels, etc. of non luminescent cations, which are doped with at least one luminescent transition-metal or a rare-earth metal cation. In order to strengthen the security of the ink composition may further comprise one or more pigments and/or dyes which

absorb in the visible or invisible region of the electromagnetic spectrum and/or may further comprise one or more pigments and/or dyes which are luminescent. Non-limiting examples of suitable pigments and/or dyes which absorb in the visible or invisible region of the electromagnetic spectrum include phthalocyanine derivatives. Non-limiting examples of suitable luminescent pigments and/or dyes include lanthanide derivatives. The presence of pigment(s) and/or dye(s) will enhance and reinforce the security of the marking against counterfeiting.

[0076] The substrate or article which is to be provided with a marking and/or security feature in accordance with the present invention is not particularly limited and can be of various types. The substrate or article may, for example, consist (essentially) of or comprise one or more of a metal (for example, in the form of a container such as a can for holding various items such as, e.g., beverages or foodstuffs), optical fibers, a woven, a coating, and equivalents thereof, a plastic material, a ceramic material, glass (for example, in the form of a capsule or container such as a bottle for holding various items such as, e.g., beverages or foodstuffs), cardboard, packaging, paper, and a polymeric material. It is pointed out that these substrate materials are given exclusively for exemplifying purposes, without restricting the scope of the invention.

[0077] The substrate may furthermore already carry at least one marking or security element which comprises a substance selected from, e.g., inorganic luminescent compounds, organic luminescent compounds, IR-absorbers, magnetic materials, forensic markers, and combinations thereof. The marking or security element can be present in the form of indicia or a data matrix. on the substrate surface or be incorporated (embedded) in the substrate itself. The marking can be present also in the form of a cloud of dots or a specific pattern visible and/or invisible to the naked eye, randomly or not distributed in the item or article or goods or security documents or what is described above to be intended to be protected and/or authenticated.

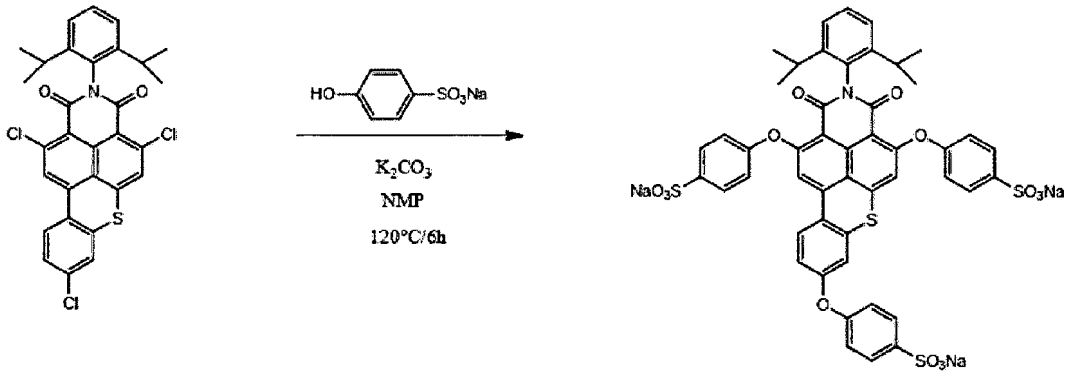
[0078] The present invention will be more specifically explained with reference to examples.

However, the scope of the present invention is not limited to the following examples.

EXAMPLES

[0079] Preparation of 4,4',4"-((2-(2,6-diisopropylphenyl)-1,3-dioxo-2,3-dihydro-1H-thioxantheno[2,1,9-def]isoquinoline-4,8,12-triyl)tris(oxy))tribenzenesulfonate. The orange solid of sodium 4,4',4"-((2-(2,6-diisopropylphenyl)-1,3-dioxo-2,3-dihydro-1H-thioxantheno[2,1,9-def]isoquinoline-4,8,12-triyl)tris(oxy))tribenzenesulfonate.

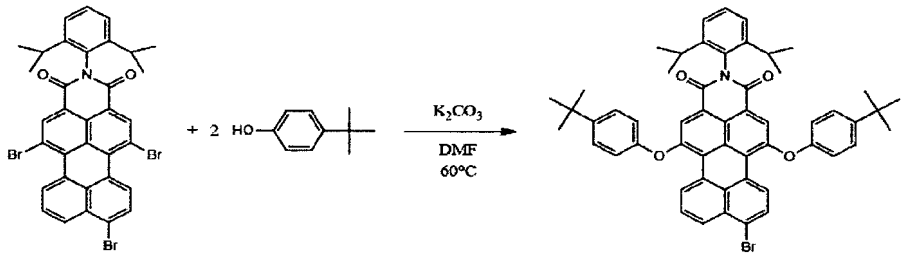
Compound 4,8,12-trichloro-2-(2,6-diisopropylphenyl)-1H-thioxantheno[2,1,9-def]isoquinoline-1,3(2H)-dione (0.3g), sodium 4-hydroxybenzenesulfonate (0.41g) and anhydrous potassium carbonate (0.73g) were added to 10mL of N-methyl-2-pyrrolidinone (NMP). The solution was heated at 130°C with good stirring within 4 hours. After boiling a further 4 hours, the solution was cooled at room temperature, after a minute the liquor was added to dichloromethane (100ml) and the precipitate was filtered and dried at 60°C to give a orange solid of sodium 4,4',4"-((2-(2,6-diisopropylphenyl)-1,3-dioxo-2,3-dihydro-1H-thioxantheno[2,1,9-def]isoquinoline-4,8,12-triyl)tris(oxy))tribenzenesulfonate. The orange solid of sodium 4,4',4"-((2-(2,6-diisopropylphenyl)-1,3-dioxo-2,3-dihydro-1H-thioxantheno[2,1,9-def]isoquinoline-4,8,12-triyl)tris(oxy))tribenzenesulfonate (0.1g) was given with a nominal yield of 18.0%. MS: base peak 1046



[0080] Preparation of 8-bromo-5,12-bis(4-(tert-butyl)phenoxy)-2-(2,6-diisopropylphenyl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione.

Compound 8,5,8,12-tribromo-2-(2,6-diisopropylphenyl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (5.0g), 4-(tert-butyl)phenol (2.09g) and anhydrous potassium

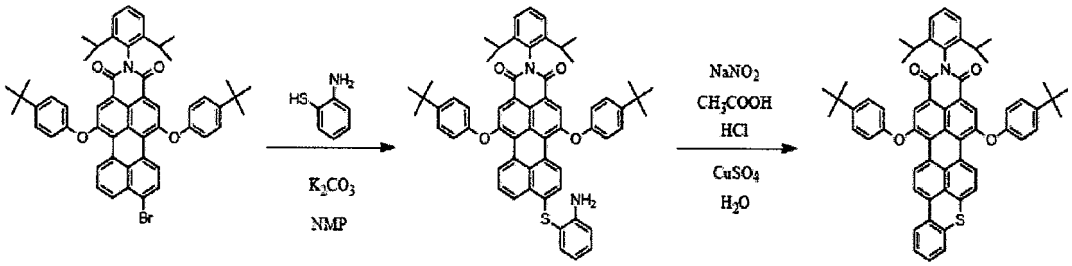
carbonate (2.18g) were added to 166mL of N,N-dimethylformamide (DMF).The solution was heated at 60°C with good stirring within 4 hours. After boiling a further 4 hours, the solution was cooled at room temperature, after a minute the liquor was added to 30% aqueous hydrochloride acid (600ml) filtered and dried at 60°C to give a red solid of 8-bromo-5,12-bis(4-(tert-butyl)phenoxy)-2-(2,6-diisopropylphenyl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione The solid was purified on Chromatography Column to eliminate by-products. The red solid of 8-bromo-5,12-bis(4-(tert-butyl)phenoxy)-2-(2,6-diisopropylphenyl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (4.24g) was given with a nominal yield of 71.1%. RMN-H (CDCl3) MS: base peak 855.



[0081] Preparation of 5,15-bis(4-(tert-butyl)phenoxy)-2-(2,6-diisopropylphenyl)-1H-thioxantheno[2',1',9':10,5,6]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione.

Compound 8-bromo-5,12-bis(4-(tert-butyl)phenoxy)-2-(2,6-diisopropylphenyl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (3.0g), 2-aminobenzenthiol (0.48g, 10% excess) and anhydrous potassium carbonate (0.24g) were added to 30mL of N-methyl-2-pyrrolidinone (NMP). The solution was heated rapidly and refluxed for 30min. After a minute the liquor was added to 2% aqueous hydrochloride acid (250ml) and after standing overnight, filtered and dried at 105°C to give a red-blue solid of 8-((2-aminophenyl)thio)-5,12-bis(4-(tert-butyl)phenoxy)-2-(2,6-diisopropylphenyl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (2.06g) with a nominal yield of 60.0%. 8-((2-aminophenyl)thio)-5,12-bis(4-(tert-butyl)phenoxy)-2-(2,6-diisopropylphenyl)-1H-benzo[5,10] anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (2.06g) was dissolved in warm glacial acetic (12mL) and concentration hydrochloride acid (1.3mL) giving a fine suspension. The suspension was cooled to 0°C and a solution of sodium nitrite (0.16g) in water (3.6mL) added and stirred continuously till clear. The prepared solution was added to a boiling solution of hydrated cupric sulphate (2.6g) in water

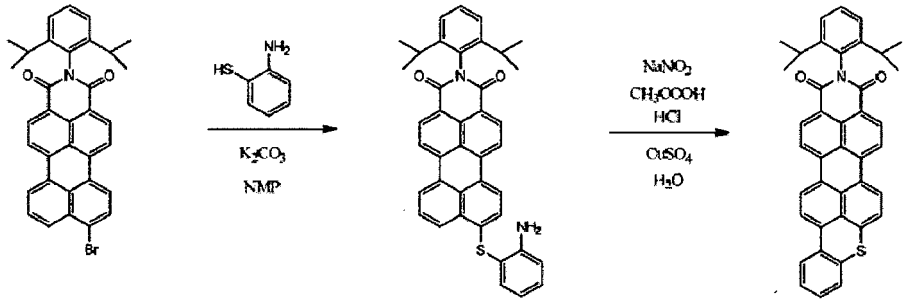
(60mL) with good stirring within 1 hour. After boiling a further 1hour, the solution was cooled, filtered and a blue-red solid was given. The solid was washed with a warm solution of sodium hydroxide (20mL, 3%) three times and purified on Chromatography Column to eliminate by-products. The blue solid of 5,15-bis(4-(tert-butyl)phenoxy)-2-(2,6-diisopropylphenyl)-1H-thioxantheno[2',1',9':10,5,6]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (0.69g) was given with a nominal yield of 34.2%. MS: base peak 884.



[0082] Preparation of 2-(2,6-diisopropylphenyl)-1H-thioxantheno[2',1',9':10,5,6]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione.

Compound 8-bromo-2-(2,6-diisopropylphenyl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (9.0g), 2-aminobenzenthiol (2.19g, 10% excess) and anhydrous potassium carbonate (1.10g) were added to 100mL of N-methyl-2-pyrrolidinone (NMP). The solution was heated rapidly and refluxed for 30min. After a minute the liquor was added to 2% aqueous hydrochloride acid (750ml) and after standing overnight, filtered and dried at 105°C to give a red-blue solid of 8-((2-aminophenyl)thio)-2-(2,6-diisopropylphenyl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (8.31g) with a nominal yield of 86.3%. 8-((2-aminophenyl)thio)-2-(2,6-diisopropylphenyl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (5.15g) was dissolved in warm glacial acetic (31mL) and concentration hydrochloride acid (3.1mL) giving a fine suspension. The suspension was cooled to 0°C and a solution of sodium nitrite (0.6g) in water (9mL) added and stirred continuously till clear. The prepared solution was added to a boiling solution of hydrated cupric sulphate (9.7g) in

water (150mL) with good stirring within 1hour. After boiling a further 1hour, the solution was cooled, filtered and a blue solid was given. The solid was washed with a warm solution of sodium hydroxide (50mL, 3%) three times and purified on chromatography column to eliminate by-products. The blue solid of 2-(2,6-diisopropylphenyl)-1H-thioxantheno[2',1',9':10,5,6]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (1.82g) was given with a nominal yield of 36.5%. MS: base peak 587.



[0083] The ink according to the present invention contains at least one compound of formula (1) and/or other formulas according to the present invention. Examples of such inks which can be used may have the following formulations and are suitable to be used with inkjet printers.

Ink Formulation 1

Component	Function	% b.w.
Nitrocellulose	Binder resin	1.5
Lithium Perchlorate	Salt for conductivity	0.5
5,15-bis(4-(tert-butyl)phenoxy)-2-(2,6-diisopropylphenyl)-1H-thioxantheno[2',1',9':10,5,6]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione	Dye	1.0
Acetone	Solvent	97.0

[0084] The ink according to the present invention is not only based with one dye according to formula (1) and/or other formulas according to the present invention, but could also be a mixture

of different dyes of formula (1) and/or the other formulas which leads to a complex ink, such as with multiple fluorescent properties, and is useful against forgery and/or counterfeiting.

[0085] It is noted that the foregoing examples have been provided merely for the purpose of explanation and are in no way to be construed as limiting of the present invention. While the present invention has been described with reference to exemplary embodiments, it is understood that the words which have been used herein are words of description and illustration, rather than words of limitation. Changes may be made, within the purview of the appended claims, as presently stated and as amended, without departing from the scope and spirit of the present invention in its aspects. Although the present invention has been described herein with reference to particular means, materials and embodiments, the present invention is not intended to be limited to the particulars disclosed herein; rather, the present invention extends to all functionally equivalent structures, methods and uses, such as are within the scope of the appended claims.

WHAT IS CLAIMED IS:

1. A polycyclic aromatic hydrocarbon compound of general formula (1):

$$(P—O)_x—Q—Y_w$$

(1)

wherein P represents a polymeric moiety having at least three repeating units which comprise an optionally substituted phenyl ring;

Q represents a polycyclic aromatic hydrocarbon moiety containing an S atom or $S(=O)_2$ moiety in its basic structure;

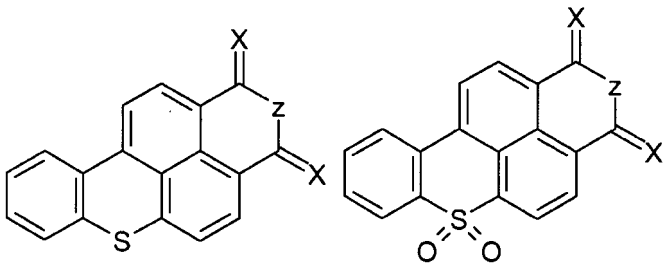
Y is selected from (i) halogen, (ii) optionally substituted N-heterocycloaliphatic groups having from 3 to about 8 ring members and which are bonded to Q through an N atom, and (iii) optionally substituted phenoxy groups;

x represents an integer of from 0 to 4; and w represents an integer of from 0 to 4

and wherein w and x are not simultaneously 0,

provided that when x = 0, at least one Y is selected from (ii) and (iii).

2. The compound of claim 1, wherein Q represents a moiety of formula (A) or (A'):



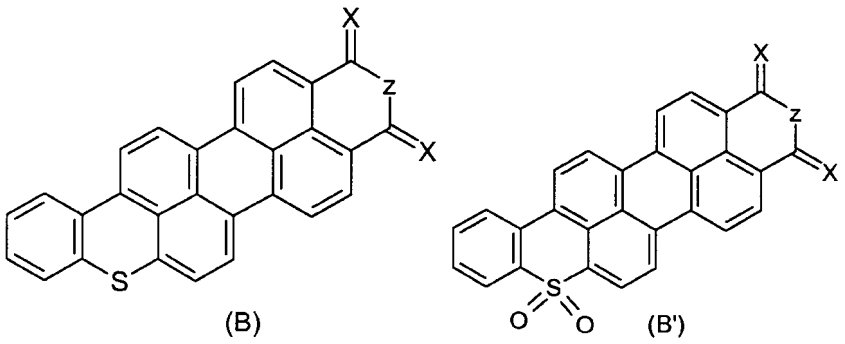
(A) (A')

wherein Z represents O, S or N-R;

wherein X, which can be the same or different, represents O, S, or NR'; and

R and R' independently represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms; and R and R' may also be combined to form, together with the N atoms to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring.

3. The compound of claim 1, wherein Q represents a moiety of formula (B) or (B'):



wherein Z represents O, S or N-R;

wherein X, which can be the same or different, represents O, S, or NR'; and

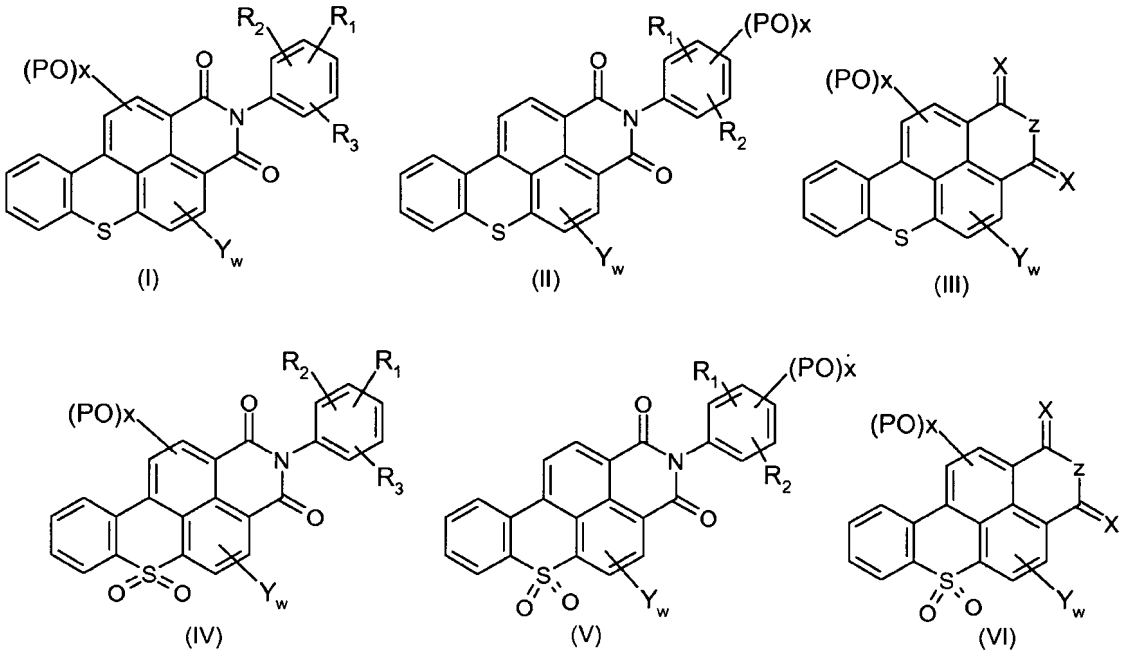
R and R' independently represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms; and R and R' may also be combined to form, together with the N atoms to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring.

4. The compound of claim 1 , wherein x is 1 and w = 0.

5. The compound of any one of claims 1 to 3, wherein x is 0 and w is 2 or not higher than 4.

6. The compound of any one of claims 1 to 4, wherein (x + w) is not higher than about 4.

7. The compound of any one of the preceding claims, wherein the compound is of formula (I) or (II) or (III) or (IV) or (V) or (VI):



wherein in the case of formula (III) and (VI), Z represents O, S or N-R; and X, which can be the same or different, represents O, S, or NR'; and

R and R' independently represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms; and R and R' may be combined to form, together with the N atoms to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring;

R_1, R_2 and R_3 are independently selected from hydrogen, C_1-C_4 alkyl, C_1-C_4 alkyl-COOH, C_1-C_4 alkyl-SO_3H, C_1-C_4 alkoxy, mono(C_1-C_4)alkylamino, di(C_1-C_4)alkylamino, C_1-C_4 aminoalkyl, halogen, cyano, nitro, and SO_3H, the alkyl groups being optionally substituted;

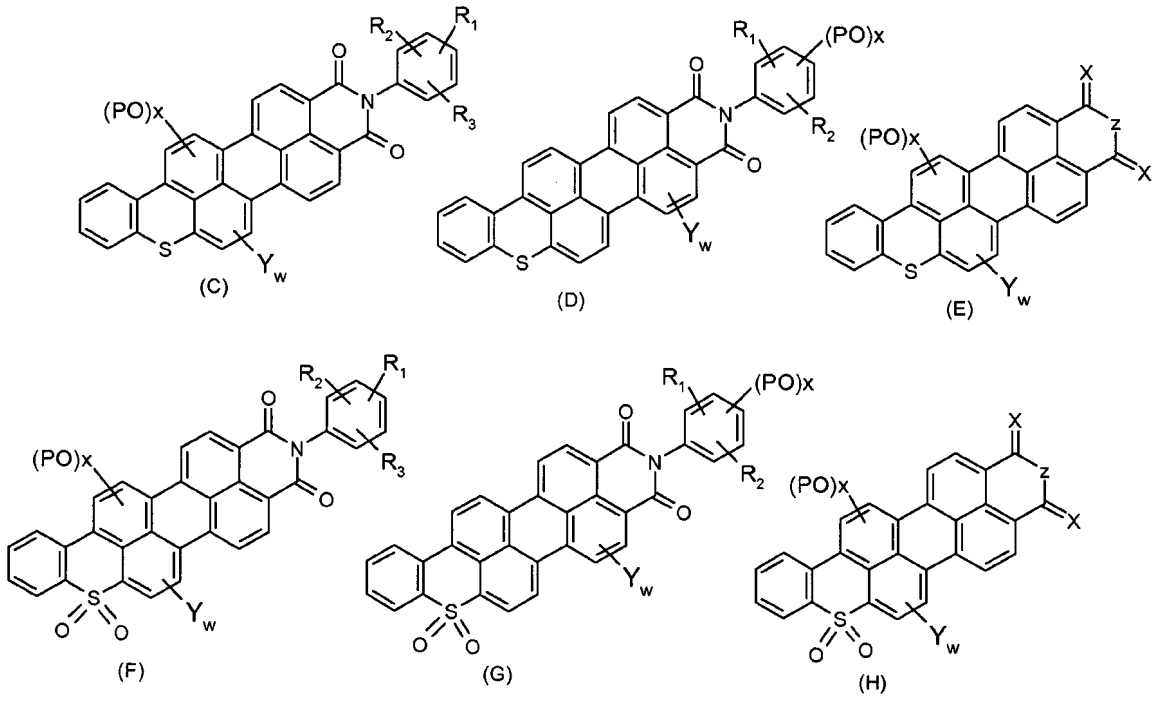
Y is selected from (i) halogen and (ii) optionally substituted N-heterocycloaliphatic groups having from 3 to about 8 ring members and which are bonded to an aromatic ring through an N atom, and (iii) optionally substituted phenoxy groups which are bonded to an aromatic ring

through an O atom, the phenoxy group may be substituted by one or more substituents selected from halogen, nitro, cyano, NRR', SO_3H and COOH and salts and derivatives of these sulfonic and carboxylic acid groups, OH, heterocycloalkyl comprising up to three heteroatoms selected from O, N and S as ring members and from 3 to about 8 ring members, and alkyl (including cycloalkyl) and alkoxy (including cycloalkoxy) groups comprising from 1 to about 10 carbon atoms;

P represents a polymeric moiety having at least three repeating units which comprise an optionally substituted phenyl ring; and

w is an integer of from 0 to 4.

8. The compound of any one of the preceding claims, wherein the compound is a compound of one of formulae (C), (D) or (E) or (F) or (G) or (H):



wherein in the case of formula (E) and (H), Z represents O, S or N-R; and X, which can be the same or different, represents O, S, or NR'; and

R and R' independently represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms; and R and R' may be combined to form, together with the N atoms to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring;

R_1, R_2 and R_3 are independently selected from hydrogen, C_1-C_4 alkyl, C_1-C_4 alkyl-COOH, C_1-C_4 alkyl-SO_3H, C_1-C_4 alkoxy, mono(C_1-C_4)alkylamino, di(C_1-C_4)alkylamino, C_1-C_4 aminoalkyl, halogen, cyano, nitro, and SO_3H, the alkyl groups being optionally substituted;

Y is selected from (i) halogen and (ii) optionally substituted N-heterocycloaliphatic groups having from 3 to about 8 ring members and which are bonded to an aromatic ring through an N atom,; and (iii) optionally substituted phenoxy groups which are bonded to an aromatic ring through an O atom, the phenoxy group may be substituted by one or more substituents selected from halogen, nitro, cyano, NRR', SO_3H and COOH and salts and derivatives of these sulfonic and carboxylic acid groups, OH, heterocycloalkyl comprising up to three heteroatoms selected from O, N and S as ring members and from 3 to about 8 ring members, and alkyl (including cycloalkyl) and alkoxy (including cycloalkoxy) groups comprising from 1 to about 10 carbon atoms;

P represents a polymeric moiety having at least three repeating units which comprise an optionally substituted phenyl ring;

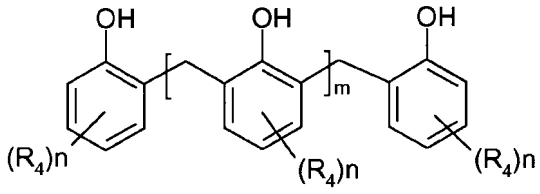
and x is an integer of from 0 to 4; and w is an integer of from 0 to 4.

9. The compound according to claim 8, wherein x is 0.

10. The compound of any one of the preceding claims wherein at least one group Y is selected from heterocycloaliphatic groups having from 3 to about 8 ring members, which ring members comprise from 1 to about 3 heteroatoms selected from N, S, and O, provided that at least one ring member is N, which heterocycloaliphatic compounds may be substituted by one or more substituents selected from alkyl and alkoxy groups each comprising up to about 10 carbon atoms.

11. The compound of any one of the preceding claims wherein at least one group Y is a residue of a heterocycloaliphatic compound selected from optionally substituted azacyclooctane, optionally substituted azepane, optionally substituted piperidine, optionally substituted piperazine, optionally substituted pyrrolidine, optionally substituted azetidine, optionally substituted aziridine, optionally substituted morpholine, optionally substituted oxazolidine, optionally substituted pyrazolidine, optionally substituted isopyrazolidine, optionally substituted isoxazolidine, and optionally substituted thiazolidine, one or more substituents each being selected from C_1-C_4 alkoxy and C_1-C_6 alkyl groups.

12. The compound of any one of claims 1to 4 and 6-11, wherein P is a residue of a polymeric compound of general formula (2):



(2)

wherein the groups R_4, the same or different from each other, are selected from C_1-C_{10} alkyl and C_1-C_4 alkoxy;

m represents an integer of from 1 to about 30;

n represents an integer of from 1 to about 3.

13. The compound of claim 12 wherein m represents an integer of from 1 to 10 and n is 1 or 2.

14. The compound of any one of claims 12 and 13 wherein the groups R_4 are independently selected from C_1-C_{10} alkyl.

15. The compound of any one of claims 12 to 14 wherein the groups R_4 are independently selected from isopropyl, tert-butyl, tert-octyl, n-nonyl, and branched nonyl.

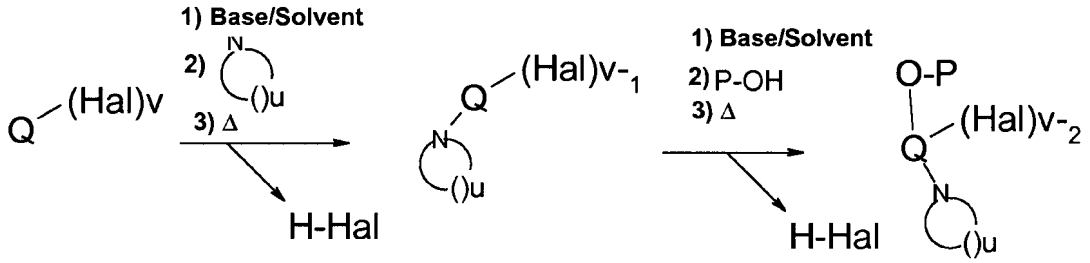
16. A process for making a compound of any one of the preceding claims wherein the process comprises reacting in a polar aprotic organic solvent a compound of formula $Q\text{-}(Hal)_v$ wherein Hal represents halogen and v represents an integer of from 2 to 8, successively with an N-containing cycloaliphatic compound and a polymeric compound of formula P-OH.

17. The process of claim 16 wherein at least a reaction involving the N-containing cycloaliphatic compound is carried out in the presence of at least one of an inorganic base and a strong organic non-nucleophilic base.

18. The process of any one of claims 16 or 17, wherein from about 0.5 to about 10 g of compound of formula $Q\text{-}(Hal)_v$ are employed per 100 g of polymeric compound of formula P-OH.

19. The process of any one of claims 16 to 18, wherein the polar solvent comprises at least one of N-methylpyrrolidone, dimethyl formamide, dimethyl acetamide, and dimethylsulfoxide.

20. The process of any one of claims 16 to 19 wherein the process is represented as follows:



wherein

() represents CH_2 wherein at least one CH_2 group can be replaced by O, NH or S;

u is from 2 to 7;

v is an integer of from 2 to 8.

21. A printing ink composition, wherein the composition comprises a polar liquid medium and at least one compound of any one of claims 1 to 15 dissolved or dispersed in the medium.

22. The printing ink composition of claim 21 wherein the composition comprises from about 0.01 % to about 40 % by weight of the at least one compound , based on a total weight of the composition.

23. The printing ink composition of any one of claims 21 or 22 wherein the printing ink composition further comprises at least one conductivity imparting substance.

24. A marking or security feature which is made with the printing ink composition of any one of claims 21 to 23.

25 A marking or security feature which comprises at least one compound of any one of the preceding claims 1 to 15.

26. The marking or security feature of any one of claims 24 or 25, wherein the marking or security feature comprises at least one of a thread, a label, a barcode, a 2D code, a pattern, indicia, and a data matrix.

27. An article which comprises the marking or security feature of any one of claims 24 to 26.

28. The article of claim 27 wherein the marking or security feature is present as a layer on the article.

29. The article of any one of claims 27 to 28 wherein the article is at least one of a can, a metal, an aluminum foil, a cartridge, a capsule, an article made of glass, an article made of ceramic, a packaging, a banknote, a passport, a security document, a value document, a ticket, a thread, a label, a card, a commercial good, and a cigarette packaging which may or may not carry coded or encrypted information.

30. A method of authenticating an article, wherein the method comprises providing the article with the marking or security feature of any one of claims 24 to 26.

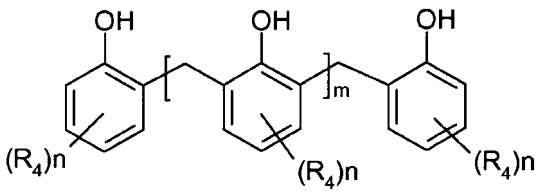
31. A method of authenticating an article, wherein the method comprises applying onto the article the printing ink composition of any one of claims 21 to 23.

32. The method of any one of claims 30 to 31, wherein the article is at least one of a can, a metal, an aluminum foil, a cartridge, a capsule, an article made of glass, an article made of ceramic, a packaging, a banknote, a passport, a security document, a value document, a ticket, a thread, a label, a card, a commercial good, and a cigarette packaging which may or may not carry coded or encrypted information.

33. A polymer, wherein at least about 0.1 % of polymer molecules have bonded thereto 1 to 4 residues of formula —Q—$(Y)_w$ wherein Q represents a moiety of formula (A) or (A') according to claim 2, or (B) or (B') according to claim 3; Y is selected from (i) halogen and (ii) optionally substituted N-heterocycloaliphatic groups having from 3 to about 8 ring members, at least one of which is N, which are bonded to Q through an N atom, and/or an optionally substituted phenol group which is bonded to Q through the O atom provided that at least one Y represents (ii);

w represents an integer of from 1 to 4; and further provided that Q may at the same time be bonded to up to 4 polymer molecules .

34. The polymer of claim 33, wherein the polymer is a compound of general formula (2):



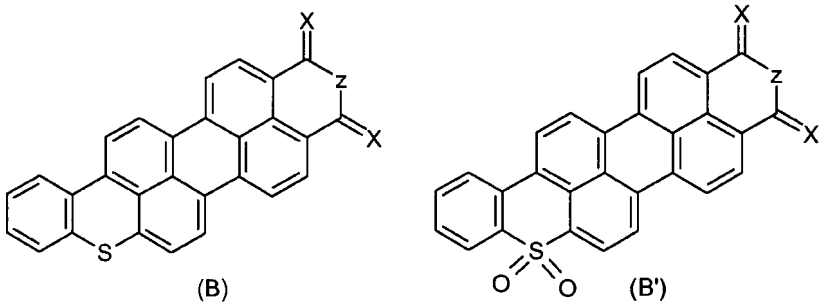
(2)

wherein the groups R_4, the same or different from each other, are selected from C_1-C_{10} alkyl and C_1-C_4 alkoxy;

m represents an integer of from 1 to about 30;

n represents an integer of from 1 to about 3.

35. Optionally substituted compound of formula (B) or (B'):

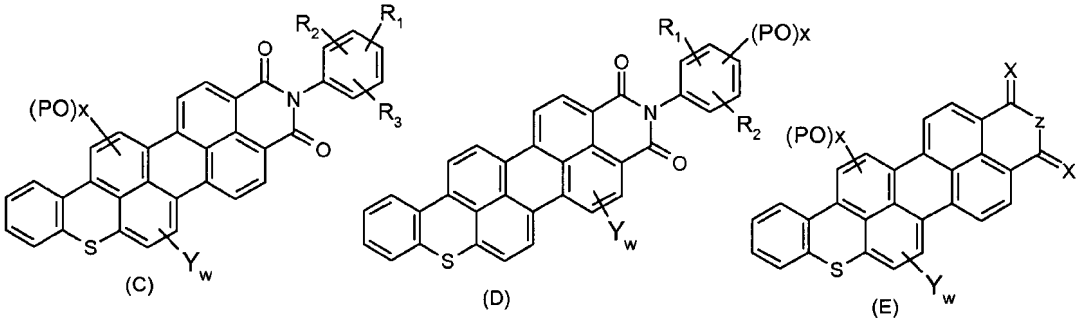


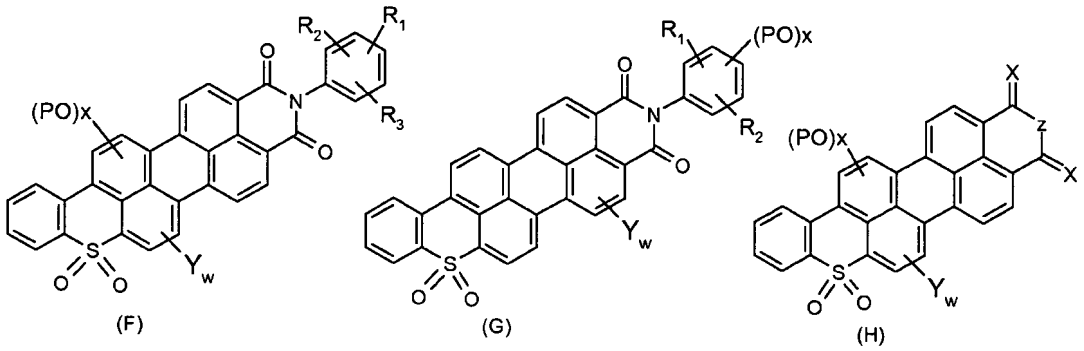
wherein Z represents O, S or N-R, and X, which can be the same or different, represents O, S, or NR';

R and R' independently represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms; and R and R' may also be combined to form, together with the N atoms to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring.

36. The compound of claim 35 which is unsubstituted.

37. The compound of claim 35, wherein the compound is a compound of one of formulae (C), (D) or (E) or (F) or (G) or (H):





wherein in the case of formula (E) and (H), Z represents O, S or N-R; and X, which can be the same or different, represents O, S, or NR'; and

R and R' independently represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms; and R and R' may be combined to form, together with the N atoms to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring;

R_1, R_2 and R_3 are independently selected from hydrogen, C_1-C_4 alkyl, C_1-C_4 alkyl-COOH, C_1-C_4 alkyl-SO_3H, C_1-C_4 alkoxy, mono(C_1-C_4)alkylamino, di(C_1-C_4)alkylamino, C_1-C_4 aminoalkyl, halogen, cyano, nitro, and SO_3H, the alkyl groups being optionally substituted;

Y is selected from (i) halogen and (ii) optionally substituted N-heterocycloaliphatic groups having from 3 to about 8 ring members and which are bonded to an aromatic ring through an N atom,; and (iii) optionally substituted phenoxy groups which are bonded to an aromatic ring through an O atom, the phenoxy group may be substituted by one or more substituents selected from halogen, nitro, cyano, NRR', SO_3H and COOH and salts and derivatives of these sulfonic and carboxylic acid groups, OH, heterocycloalkyl comprising up to three heteroatoms selected from O, N and S as ring members and from 3 to about 8 ring members, and alkyl (including cycloalkyl) and alkoxy (including cycloalkoxy) groups comprising from 1 to about 10 carbon atoms;

P represents a polymeric moiety having at least three repeating units which comprise an optionally substituted phenyl ring;

and x is an integer of from 0 to 4; and w is an integer of from 0 to 4.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/072514

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D495/16 C08G83/00 C09B57/14
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D C08G C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 194 828 A1 (HOECHST AG [DE]) 1 March 1974 (1974-03-01) examples 7, 46, 50 compounds 1-12	1,2,6,7
X	FR 1 489 487 A (HOECHST AG) 21 July 1967 (1967-07-21) examples 1,5 claim 1	1,6
X	FR 1 444 489 A (HOECHST AG) 1 July 1966 (1966-07-01) compounds 5, 10, 16-17 claim 2 page 1, lines 1-5	1,2,5-7

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 January 2013	16/01/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Marzi, Elena

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 367 937 A (OTTO FUCHS ET AL) 6 February 1968 (1968-02-06) claims 1, 5-6 compounds 5, 16, 17 -----	1,2,5-7
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X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; SHIROSAKI, TSUTOMU ET AL: "Dyes for hydrophobic fibers", XP002678127, retrieved from STN Database accession no. 1976:166255 abstract & JP 51 001778 A (NIPPON KAYAKU CO., LTD., JAPAN) 8 January 1976 (1976-01-08) abstract RN: 59025-18-2; 59025-19-3 -----	1,2,6,7 1,2,6,7
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; MIURA, KONOE ET AL: "Liquid crystal compositions", XP002678128, retrieved from STN Database accession no. 1986:470248 abstract RN: 103415-08-3 & JP 60 262887 A (MITSUBISHI CHEMICAL INDUSTRIES CO., LTD., JAPAN) 26 December 1985 (1985-12-26) ----- -/--	1,2,6,7

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; IMAHORI, SEIICHI ET AL: "Benzothioxanthene dyes for polyester fibers", XP002678129, retrieved from STN Database accession no. 1976:479687 abstract RN: 59917-56-5 & JP 51 035785 A (MITSUBISHI CHEMICAL INDUSTRIES CO., LTD., JAPAN) 26 March 1976 (1976-03-26) -----	1,2,6,7
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; IMAHORI, SEIICHI ET AL: "Coloring organic polymer materials", XP002678130, retrieved from STN Database accession no. 1976:407281 abstract RN: 59344-56-8; 59344-57-9 & JP 51 022736 A (MITSUBISHI CHEMICAL INDUSTRIES CO., LTD., JAPAN) 23 February 1976 (1976-02-23) -----	1,2,6,7
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; TOBA, YASUMASA ET AL: "Holographic recording material with chemical and environmental stability and manufacture of volume phase-type hologram by using same", XP002678131, retrieved from STN Database accession no. 1995:367471 abstract RN: 161055-15-8 & JP 6 175566 A (TOYO INK MFG CO, JAPAN) 24 June 1994 (1994-06-24) -----	1,5,6
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	& JP 60 221403 A (NIPPON KAYAKU CO., LTD., JAPAN) 6 November 1985 (1985-11-06) abstract RN: 102356-06-9	1,5,6
X	EP 0 999 239 A2 (CLARIANT FINANCE BVI LTD [VG]) 10 May 2000 (2000-05-10) claims 1-9 example 2 page 3, paragraph 21 page 4, paragraph 25	1-37
X	EP 1 172 418 A2 (CLARIANT FINANCE BVI LTD [VG]) 16 January 2002 (2002-01-16) claims 1-6	1-37
Y	WO 2008/001036 A2 (FUJIFILM IMAGING COLORANTS LTD [GB]; JAMES RACHEL ANNE [GB]) 3 January 2008 (2008-01-03) claims 1-14	1-37
Y	MARECHAL E: "Polymeric Dyes - Synthesis, Properties and Uses", PROGRESS IN ORGANIC COATING, ELSEVIER, NL, vol. 10, 1 January 1982 (1982-01-01), pages 251-287, XP002651835, ISSN: 0033-0655 paragraph [03.4]	1-37

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/072514

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		WO 2008001036 A2	03-01-2008

(19)中华人民共和国国家知识产权局

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WO2013/075980 EN 2013.05.30
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代理人 彭立兵 林柏楠
(51)Int.Cl.
C07D 495/16(2006.01)
C08G 83/00(2006.01)
C09B 57/14(2006.01)

权利要求书7页 说明书26页

(54)发明名称

在其基础结构中含有S原子或S(=O)2基团的多环芳烃化合物

(57)摘要

具有并入其基础多环结构中的S原子或S(=O)2部分的多环芳烃化合物，所述基础多环结构可以具有含氮杂脂环基和/或取代或未取代的苯氧基和/或键合到该多环结构上的聚合部分，并涉及包含这些多环芳烃作为着色剂的组合物如印刷油墨。$(P—O)_x—Q—Y_w$ (1)

CN 103958522 A

1. 通式 (1) 的多环芳烃化合物：

$$(P—O)_x—Q—Y_w$$

(1)

其中 P 代表具有至少三个包含任选取代的苯环的重复单元的聚合部分；

Q 代表在其基础结构中含有 S 原子或 $S(=O)_2$ 部分的多环芳烃部分；

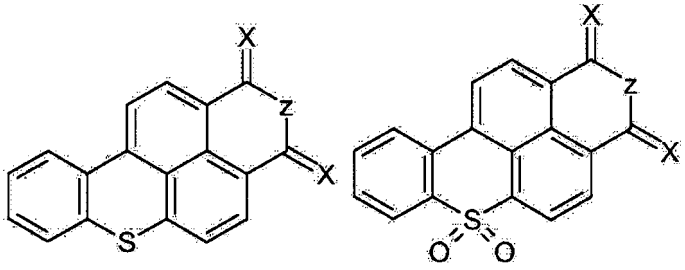
Y 选自 (i) 卤素、(ii) 具有 3 至大约 8 个环成员并经 N 原子键合到 Q 上的任选取代的 N- 杂脂环基，和 (iii) 任选取代的苯氧基；

x 代表 0 至 4 的整数；且 w 代表 0 至 4 的整数，

并且其中 w 和 x 不同时为 0，

条件是当 x = 0 时，至少一个 Y 选自 (ii) 和 (iii)。

2. 根据权利要求 1 所述的化合物，其中 Q 代表式 (A) 或 (A') 的部分：



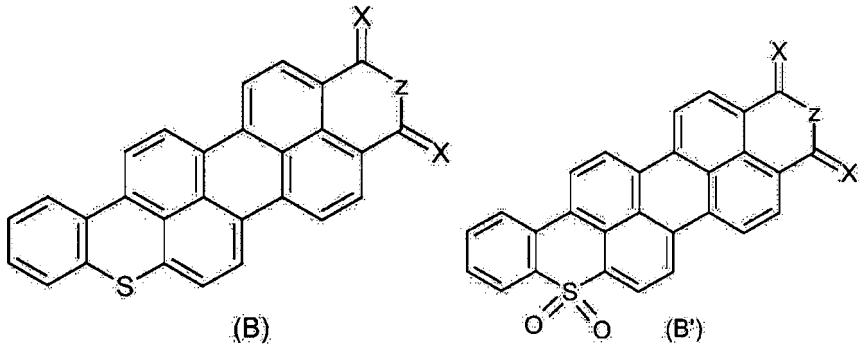
(A)　　(A')

其中 Z 代表 O、S 或 N-R；

其中 X，其可以相同或不同，代表 O、S 或 NR'；和

R 和 R' 独立地代表任选取代的具有 1 至大约 20 个碳原子的脂族、脂环族、芳族、杂芳族、烷芳基、烷基杂芳基、芳烷基或杂芳基烷基基团；并且 R 和 R' 也可以组合以便与它们连接于其上的 N 原子一起形成任选取代的和 / 或稠合的 5- 至 7- 员环。

3. 根据权利要求 1 所述的化合物，其中 Q 代表式 (B) 或 (B') 的部分：



(B)　　(B')

其中 Z 代表 O、S 或 N-R；

其中 X，其可以相同或不同，代表 O、S 或 NR'；和

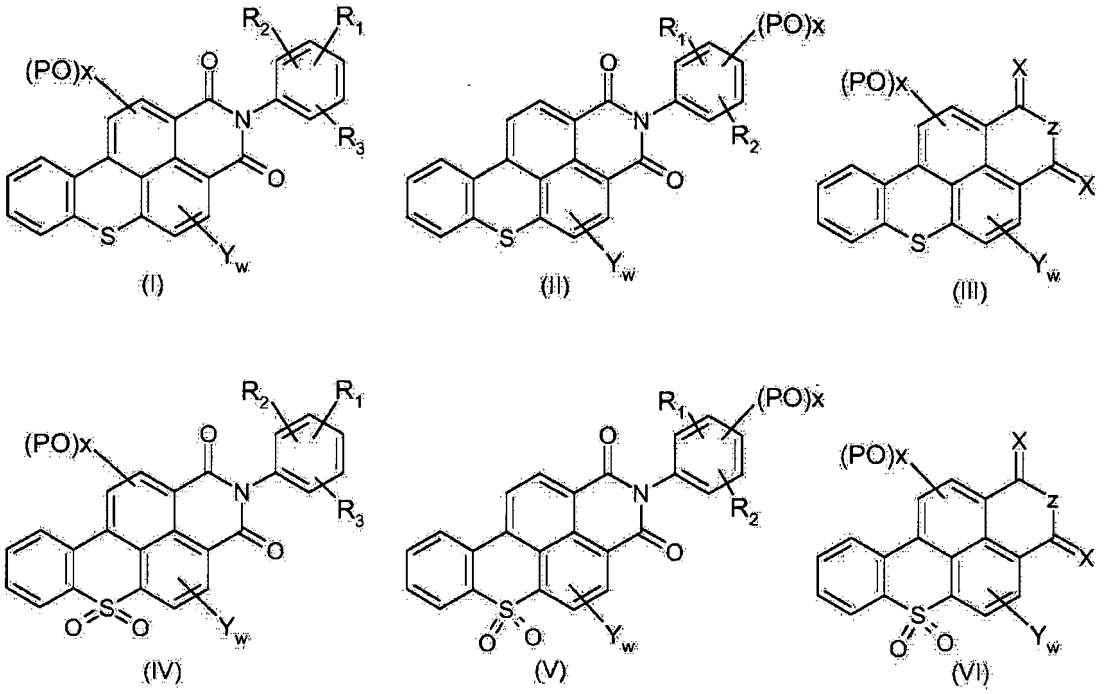
R 和 R' 独立地代表任选取代的具有 1 至大约 20 个碳原子的脂族、脂环族、芳族、杂芳族、烷芳基、烷基杂芳基、芳烷基或杂芳基烷基基团；并且 R 和 R' 也可以组合以便与它们连接于其上的 N 原子一起形成任选取代的和 / 或稠合的 5- 至 7- 员环。

4. 根据权利要求 1 所述的化合物，其中 x 为 1 且 w = 0。

5. 根据权利要求 1 至 3 任一项所述的化合物，其中 x 为 0 且 w 为 2 或不高于 4。

6. 根据权利要求 1 至 4 任一项所述的化合物，其中 (x+w) 不高于大约 4。

7. 根据前述权利要求任一项所述的化合物，其中所述化合物具有式 (I) 或 (II) 或 (III) 或 (IV) 或 (V) 或 (VI)：



其中在式 (III) 和 (VI) 的情况下，基团 Z 代表 O、S 或 N-R，并且 X，其可以相同或不同，代表 O、S 或 NR'；和

R 和 R' 独立地代表任选取代的具有 1 至大约 20 个碳原子的脂族、脂环族、芳族、杂芳族、烷芳基、烷基杂芳基、芳烷基或杂芳基烷基基团；并且 R 和 R' 可以组合以便与它们连接于其上的 N 原子一起形成任选取代的和 / 或稠合的 5- 至 7- 员环；

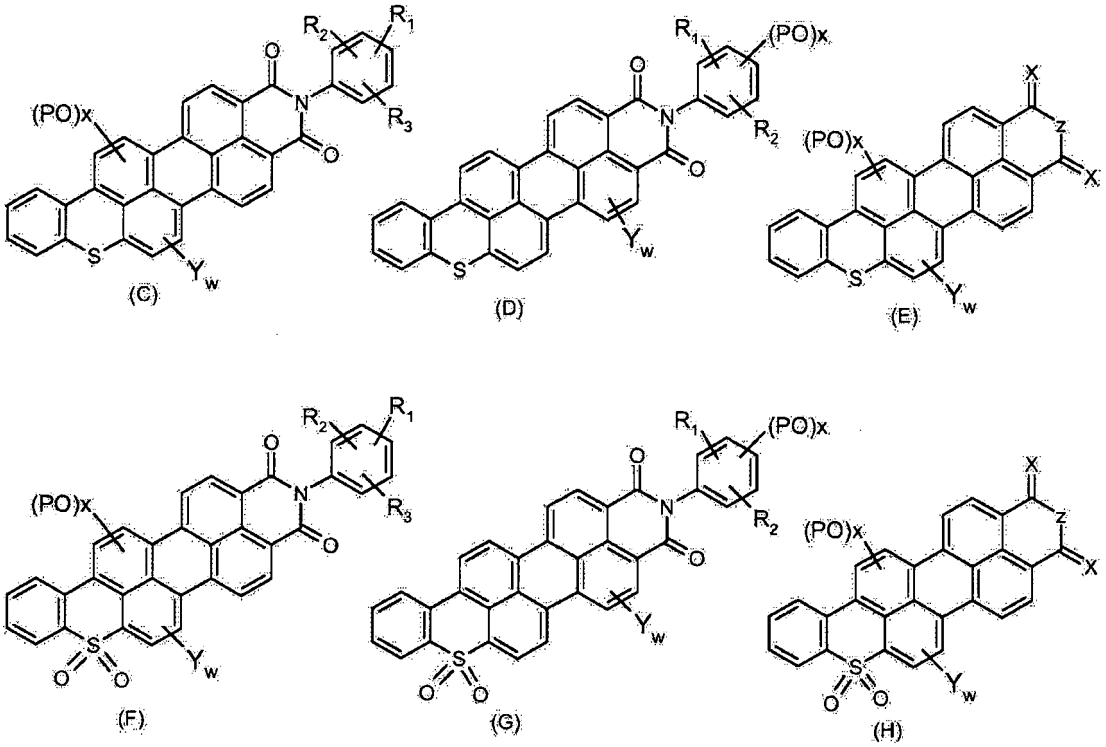
R_1、R_2 和 R_3 独立地选自氢、C_1-C_4 烷基、C_1-C_4 烷基 -COOH、C_1-C_4 烷基 -SO_3H、C_1-C_4 烷氧基、单 (C_1-C_4) 烷基氨基、二 (C_1-C_4) 烷基氨基、C_1-C_4 氨基烷基、卤素、氰基、硝基和 SO_3H，所述烷基是任选取代的；

Y 选自 (i) 卤素、(ii) 具有 3 至大约 8 个环成员并经 N 原子键合到芳族环上的任选取代的 N- 杂脂环基，和 (iii) 任选取代的苯氧基，其经 O 原子键合到芳族环上，该苯氧基可以被一个或多个取代基取代，所述取代基选自卤素、硝基、氰基、NRR'、SO_3H 和 COOH 以及这些磺酸和羧酸基团的盐和衍生物、OH、包含最多三个作为环成员的选自 O、N 和 S 的杂原子和 3 至大约 8 个环成员的杂环烷基、包含 1 至大约 10 个碳原子的烷基（包括环烷基）和烷氧基（包括环烷氧基）；

P 代表具有至少三个包含任选取代的苯环的重复单元的聚合部分；和

w 为 0 至 4 的整数。

8. 根据前述权利要求任一项所述的化合物，其中所述化合物是式 (C) 或 (D) 或 (E) 或 (F) 或 (G) 或 (H) 之一的化合物：



其中在式 (E) 和 (H) 的情况下，Z 代表 O、S 或 N-R，并且 X，其可以相同或不同，代表 O、S 或 NR'；和

R 和 R' 独立地代表任选取代的具有 1 至大约 20 个碳原子的脂族、脂环族、芳族、杂芳族、烷芳基、烷基杂芳基、芳烷基或杂芳基烷基基团；并且 R 和 R' 也可以组合以便与它们连接于其上的 N 原子一起形成任选取代的和 / 或稠合的 5- 至 7- 员环；

R_1、R_2 和 R_3 独立地选自氢、C_1-C_4 烷基、C_1-C_4 烷基 -COOH、C_1-C_4 烷基 -SO_3H、C_1-C_4 烷氧基、单 (C_1-C_4) 烷基氨基、二 (C_1-C_4) 烷基氨基、C_1-C_4 氨基烷基、卤素、氰基、硝基和 SO_3H，所述烷基是任选取代的；

Y 选自 (i) 卤素、(ii) 具有 3 至大约 8 个环成员并经 N 原子键合到芳族环上的任选取代的 N- 杂脂环基，和 (iii) 任选取代的苯氧基，其经 O 原子键合到芳族环上，该苯氧基可以被一个或多个取代基取代，所述取代基选自卤素、硝基、氰基、NRR'、SO_3H 和 COOH 以及这些磺酸和羧酸基团的盐和衍生物、OH、包含最多三个作为环成员的选自 O、N 和 S 的杂原子和 3 至大约 8 个环成员的杂环烷基、包含 1 至大约 10 个碳原子的烷基（包括环烷基）和烷氧基（包括环烷氧基）；

P 代表具有至少三个包含任选取代的苯环的重复单元的聚合部分；

并且 x 为 0 至 4 的整数；并且 w 为 0 至 4 的整数。

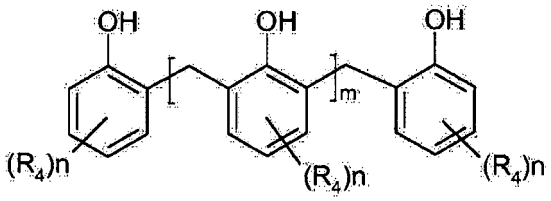
9. 根据权利要求 8 所述的化合物，其中 x 为 0。

10. 根据前述权利要求任一项所述的化合物，其中至少一个基团 Y 选自具有 3 至大约 8 个环成员的杂脂环基，其环成员包含 1 至大约 3 个选自 N、S 和 O 的杂原子，条件是至少一个环成员是 N，该杂脂环族化合物可以被一个或多个选自各自包含最多大约 10 个碳原子的烷基和烷氧基的取代基取代。

11. 根据前述权利要求任一项所述的化合物，其中至少一个基团 Y 是杂脂环族化合物

的残基，所述杂脂环族化合物选自任选取代的氮杂环辛烷、任选取代的氮杂环庚烷、任选取代的哌啶、任选取代的哌嗪、任选取代的吡咯烷、任选取代的氮杂环丁烷、任选取代的氮杂环丙烷、任选取代的吗啉、任选取代的噁唑烷、任选取代的吡唑烷、任选取代的异吡唑烷、任选取代的异噁唑烷和任选取代的噻唑烷，一个或多个取代基各自选自 C_1-C_4 烷氧基和 C_1-C_6 烷基。

12. 根据权利要求 1 至 4 和 6-11 任一项的化合物，其中 P 是通式 (2) 的聚合化合物的残基：



(2)

其中基团 R_4 彼此相同或不同，选自 C_1-C_{10} 烷基和 C_1-C_4 烷氧基；

m 代表 1 至大约 30 的整数；

n 代表 1 至大约 3 的整数。

13. 根据权利要求 12 所述的化合物，其中 m 代表 1 至 10 的整数且 n 为 1 或 2。

14. 根据权利要求 12 和 13 任一项所述的化合物，其中所述基团 R_4 独立地选自 C_1-C_{10} 烷基。

15. 根据权利要求 12 至 14 任一项所述的化合物，其中所述基团 R_4 独立地选自异丙基、叔丁基、叔辛基、正壬基和支化壬基。

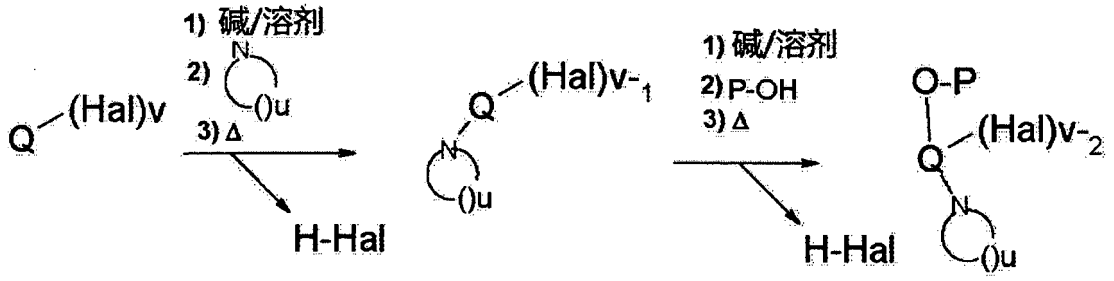
16. 制造根据前述权利要求任一项所述的化合物的方法，其中所述方法包括在极性非质子有机溶剂中令式 $Q-(Hal)_v$ 的化合物，其中 Hal 代表卤素且 v 代表 2 至 8 的整数，与含 N 的脂环族化合物和式 P-OH 的聚合化合物依次反应。

17. 根据权利要求 16 所述的方法，其中至少涉及该含 N 脂环族化合物的反应在无机碱和强有机非亲核碱的存在下进行。

18. 根据权利要求 16 或 17 任一项所述的方法，其中每 100 克式 P-OH 的聚合化合物使用大约 0.5 至大约 10 克的式 $Q-(Hal)_v$ 的化合物。

19. 根据权利要求 16 至 18 任一项所述的方法，其中所述极性溶剂包含 N- 甲基吡咯烷酮、二甲基甲酰胺、二甲基乙酰胺和二甲亚砜的至少一种。

20. 根据权利要求 16 至 19 任一项所述的方法，其中该方法表示如下：



其中

() 代表 CH_2，其中至少一个 CH_2 基团可以被 O、NH 或 S 替代；

u 为 2 至 7 ;

v 为 2 至 8 的整数。

21. 一种印刷油墨组合物，其中所述组合物包含极性液体介质和溶解或分散在所述介质中的至少一种根据权利要求 1 至 15 任一项所述的化合物。

22. 根据权利要求 21 所述的印刷油墨组合物，其中所述组合物包含所述组合物总重量的大约 0.01 重量%至大约 40 重量%的所述至少一种化合物。

23. 根据权利要求 21 或 22 任一项所述的印刷油墨组合物，其中所述印刷油墨组合物进一步包含至少一种导电性赋予物质。

24. 一种标识或防伪标记，其用根据权利要求 21 至 23 任一项所述的印刷油墨组合物制得。

25. 一种标识或防伪标记，其包含根据前述权利要求 1 至 15 任一项所述的至少一种化合物。

26. 根据权利要求 24 或 25 任一项所述的标识或防伪标记，其中所述标识或防伪标记包含线、标签、条形码、二维码、图案、标记和数据矩阵的至少一种。

27. 一种制品，其包含根据权利要求 24 至 26 任一项所述的标识或防伪标记。

28. 根据权利要求 27 所述的制品，其中所述标识或防伪标记以层的形式存在于所述制品上。

29. 根据权利要求 27 至 28 任一项所述的制品，其中所述制品是以下的至少一种 :罐头、金属、铝箔、盒、胶囊、玻璃制成的制品、陶瓷制成的制品、包装、钞票、护照、安全文件、有价值的文件、票、线、标签、卡、商品和卷烟包装，其携带或不携带编码或加密信息。

30. 一种验证制品的方法，其中所述方法包括提供具有根据权利要求 24 至 26 任一项所述的标识或防伪标记的所述制品。

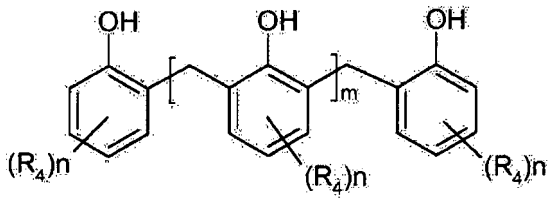
31. 一种验证制品的方法，其中所述方法包括将根据权利要求 21 至 23 任一项所述的印刷油墨组合物施加到所述制品上。

32. 根据权利要求 30 至 31 任一项所述的方法，其中所述制品是以下的至少一种 :罐头、金属、铝箔、盒、胶囊、玻璃制成的制品、陶瓷制成的制品、包装、钞票、护照、安全文件、有价值的文件、票、线、标签、卡、商品和卷烟包装，其携带或不携带编码或加密信息。

33. 一种聚合物，其中至少大约 0.1%的聚合物分子具有键合于其上的 1 至 4 个式—Q—$(Y)_w$ 的残基，其中 Q 代表根据权利要求 2 所述的式 (A) 或 (A') 或根据权利要求 3 所述的式 (B) 或 (B') 的部分 ;Y 选自 (i) 卤素和 (ii) 具有 3 至大约 8 个环成员的任选取代的 N- 杂脂环基，该环成员的至少一个是 N，该 N- 杂脂环基经 N 原子键合到 Q 上，和 / 或 (iii) 经 O 原子键合到 Q 上的任选取代的酚基，条件是至少一个 Y 代表 (ii) ;

w 代表 1 至 4 的整数 ;并且进一步的条件是 Q 可以同时键合到最多 4 个聚合物分子上。

34. 根据权利要求 33 所述的聚合物，其中所述聚合物是通式 (2) 的化合物 :



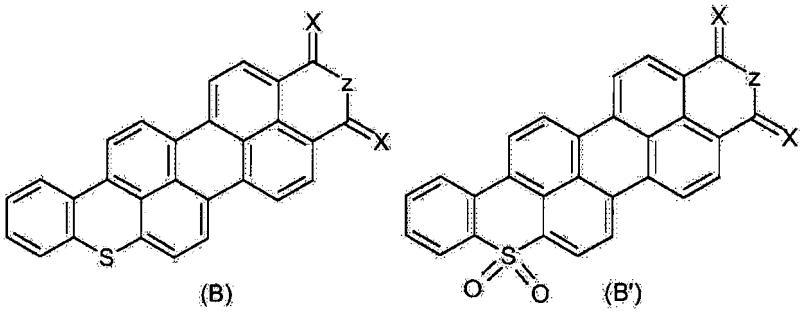
(2)

其中彼此相同或不同的基团 R_4 选自 C_1-C_{10} 烷基和 C_1-C_4 烷氧基；

m 代表 1 至大约 30 的整数；

n 代表 1 至大约 3 的整数。

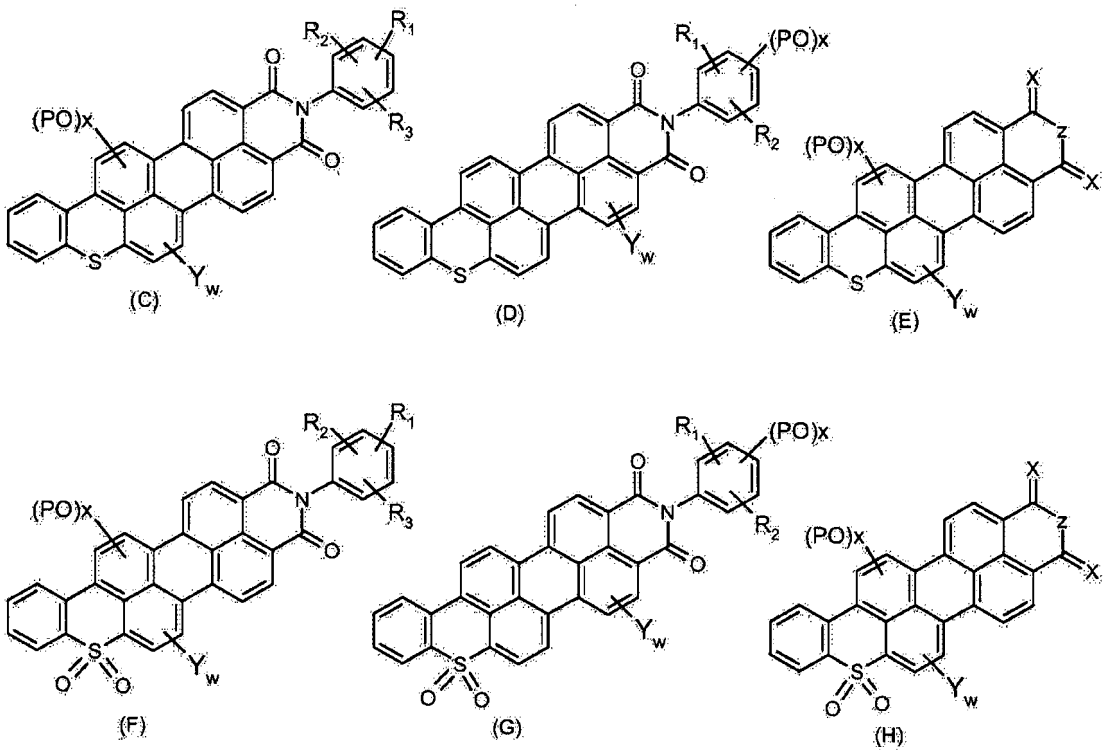
35. 任选取代的式 (B) 或 (B') 的化合物：



其中 Z 代表 O、S 或 N-R，并且 X，其可以相同或不同，代表 O、S 或 NR'；R 和 R' 独立地代表任选取代的具有 1 至大约 20 个碳原子的脂族、脂环族、芳族、杂芳族、烷芳基、烷基杂芳基、芳烷基或杂芳基烷基基团；并且 R 和 R' 也可以组合以便与它们连接于其上的 N 原子一起形成任选取代的和 / 或稠合的 5- 至 7- 员环。

36. 根据权利要求 35 所述的化合物，其是未取代的。

37. 根据权利要求 35 所述的化合物，其中所述化合物是式 (C)、(D) 或 (E) 或 (F) 或 (G) 或 (H) 之一的化合物：



其中在式 (E) 和 (H) 的情况下，Z 代表 O、S 或 N-R，并且 X，其可以相同或不同，代表 O、S 或 NR'；并且

R 和 R' 独立地代表任选取代的具有 1 至大约 20 个碳原子的脂族、脂环族、芳族、杂芳族、烷芳基、烷基杂芳基、芳烷基或杂芳基烷基基团；并且 R 和 R' 也可以组合以便与它们连接于其上的 N 原子一起形成任选取代的和 / 或稠合的 5- 至 7- 员环；

R_1、R_2 和 R_3 独立地选自氢、C_1-C_4 烷基、C_1-C_4 烷基 -COOH、C_1-C_4 烷基 -SO_3H、C_1-C_4 烷氧基、单 (C_1-C_4) 烷基氨基、二 (C_1-C_4) 烷基氨基、C_1-C_4 氨基烷基、卤素、氰基、硝基和 SO_3H，所述烷基是任选取代的；

Y 选自 (i) 卤素、(ii) 具有 3 至大约 8 个环成员并经 N 原子键合到芳族环上的任选取代的 N- 杂脂环基；和 (iii) 任选取代的苯氧基，其经 O 原子键合到芳族环上，该苯氧基可以被一个或多个取代基取代，所述取代基选自卤素、硝基、氰基、NRR'、SO_3H 和 COOH 以及这些磺酸和羧酸基团的盐和衍生物、OH、包含最多三个作为环成员的选自 O、N 和 S 的杂原子和 3 至大约 8 个环成员的杂环烷基、包含 1 至大约 10 个碳原子的烷基（包括环烷基）和烷氧基（包括环烷氧基）；

P 代表具有至少三个包含任选取代的苯环的重复单元的聚合部分；并且 x 为 0 至 4 的整数，w 为 0 至 4 的整数。

在其基础结构中含有S原子或S(=O)2基团的多环芳烃化合物

技术领域

[0001] 本发明涉及具有并入其基础多环结构中的S原子或$S(=O)_2$部分的新型多环芳烃化合物，所述基础多环结构可以具有含氮杂脂环基和/或取代或未取代的苯氧基和/或键合到该多环结构上的聚合部分，本发明还涉及包含这些多环芳烃作为着色剂的组合物如印刷油墨。

背景技术

[0002] 如果基于批号而不是基于各个物品处理产品的话，会便于大规模生产的商品的假冒与市场转移。在此情况下，可以容易地将伪造或转移的产品引入到供应链中。生产商和零售商都希望能够以销售的各个单位的水平区分他们的原始产品与此类假冒或转移（平行进口或走私）的产品。

[0003] 此外，安全文件如货币、护照或身份证在世界各地越来越多地被假冒。这种情况通常对政府和社会是非常危险的问题。例如犯罪组织可能会使用假护照或身份证用于贩卖人口。由于复制技术变得越来越复杂，甚至更难以清楚地区分假文件与原始文件。文件安全因此对国家经济也对涉及伪造文件的非法贩卖的受害者具有显著的影响。

[0004] 在防止假冒的努力中，标识目前被广泛用于各个物品的识别、鉴定与验证。该标识例如可以诸如一维条形码、层叠一维条形码、二维条形码、三维条形码、数据矩阵等标记形式施加。标记的施加通常通过印刷方法来进行，该印刷方法采用具有由一种或多种包含在油墨中的物质（如荧光染料、颜料或胆甾型液晶化合物）赋予该油墨的特定光学性质的印刷油墨。

[0005] 适用于例如用于标识目的的印刷油墨的一类化合物是具有芘、三萘嵌二苯(terrylene)或四萘嵌三苯(quaterrylene)骨架的化合物。芘、三萘嵌二苯和四萘嵌三苯显示荧光，并存在许多这些化合物的衍生物，这些衍生物是已知的并在理论上可以用作标识用组合物如印刷油墨等等中的颜料。但是，这些化合物的缺点是它们在液体介质（如可用于印刷油墨中的那些）中通常不令人满意的低溶解性或分散性。这种低溶解性/分散性通常限制了这些化合物作为液体组合物的着色剂的适用性。由此有利的是能够提高芘、三萘嵌二苯和四萘嵌三苯染料在液体介质，特别是用于印刷油墨的液体介质中的溶解性和/或分散性。参见2011年5月25日提交的申请13/115,602和2011年11月10日提交的临时申请61/558,236，其内容经此引用全文并入本文。

发明内容

[0006] 本发明提供通式(1)的多环芳烃化合物：

[0007]

$$(P—O)_x—Q—Y_w$$

(1)

[0008] 其中 P 代表具有至少三个包含任选取代的苯环的重复单元的聚合部分；

[0009] Q 代表含有 S 原子或 $S(=O)_2$ 部分的多环芳烃部分（即具有并入其基础结构中的 S 原子或 $S(=O)_2$ 部分的多环芳烃骨架，该基础结构除取代基 Y 和 / 或 P-O 外任选包含一个或多个取代基）；

[0010] Y 选自 (i) 卤素、(ii) 具有 3 至大约 8 个环成员并经 N 原子键合到 Q 上的任选取代的 N- 杂脂环基，和 (iii) 任选取代的苯氧基；

[0011] x 代表 0 至 4 的整数；且 w 代表 0 至 4 的整数，

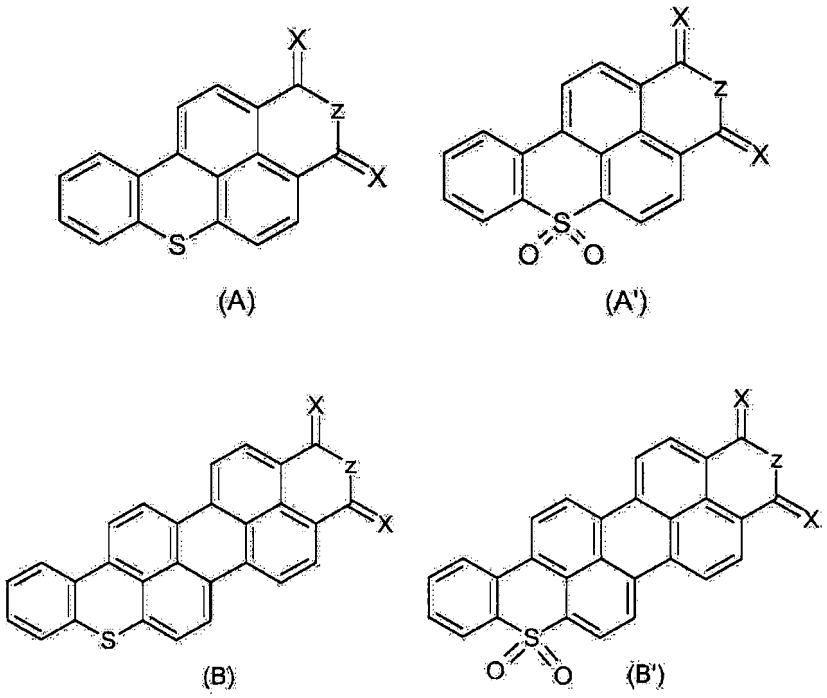
[0012] 并且其中 w 和 x 不同时为 0，

[0013] 条件是当 x = 0 时，至少一个 Y 选自 (ii) 和 (iii)。

[0014] 在式 (1) 的化合物的一个方面中，x 可以是 1 和 / 或 (x+w) 可以不高于大约 6。

[0015] 在另一方面，Q 可以是具有式 (A) 或 (B) 或 (A') 或 (B') 的基础结构（即不具有任选存在的取代基）的部分：

[0016]



[0017] 其中 Z 代表 O、S 或 N-R，并且 X，其可以相同或不同，代表 O、S 或 NR'。因此，Z 和 X 形成的基团可以表示为例如 -CO-Z-CO-（可以替换为 [- COOH HOOC-]（即二羧酸而非酸酐））、- CS-Z-CO-、-CS-Z-CS- 或 - C(=NR')-NR-CO-；并且

[0018] R 和 R' 独立地代表任选取代的具有 1 至大约 20 个碳原子的脂族、脂环族、芳族、杂芳族、烷芳基、烷基杂芳基、芳烷基或杂芳基烷基基团；并且 R 和 R' 也可以组合以便与它们连接于其上的 N 原子一起形成任选取代的和 / 或稠合的 5- 至 7- 员环。

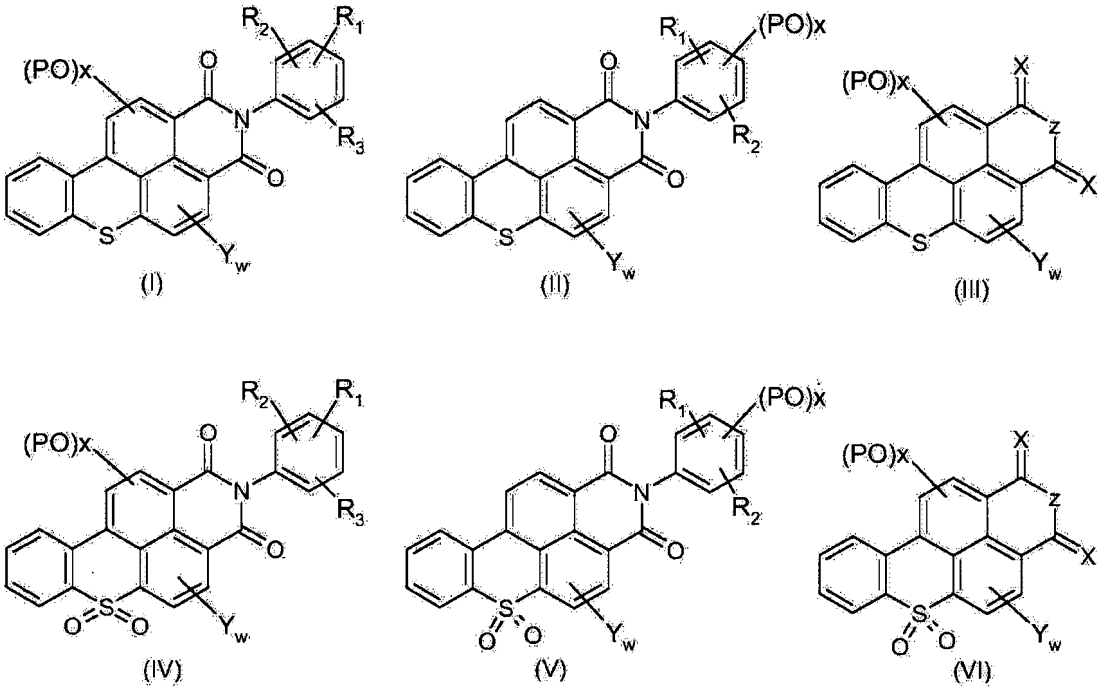
[0019] 在上式 (A)、(B)、(A') 和 (B') 的化合物的一个方面中，对于基团 Z = N-R，R 可以例如选自任选取代的具有 1 至大约 6 个碳原子的烷基、任选取代的具有 7 至大约 12 个碳原子的烷芳基或芳烷基、任选取代的具有大约 6 至大约 20 个碳原子的芳基和任选取代的具有大约 3 至大约 20 个碳原子的杂芳基，例如选自任选取代的具有 1 至大约 4 个碳原子的烷基、任选取代的苯基或任选取代的苄基。作为非限制性实例，R 可以代表用 1 至大约 3 个选

自卤素和具有 1 至大约 6 个碳原子的烷基的基团取代的苯基，例如被至少两个包含仲或叔碳原子的烷基取代的苯基，所述包含仲或叔碳原子的烷基的实例包括异丙基和叔丁基。

[0020] 在上式 (A)、(B)、(A') 和 (B') 的化合物的另一方面中，基团 Z 代表 O 或 N-R（包括其中各基团 Z 为 O 的化合物、其中各基团 Z 为 N- 的化合物（基团 R 相同或不同），以及其中一个基团 Z 是 O 且另一基团 Z 是 N-R 的化合物）。

[0021] 例如，本发明的化合物包括式 (I) 或 (II) 或 (III) 或 (IV) 或 (V) 或 (VI) 的化合物，其可以包括 $(PO)_x$ 和 / 或 Y_w：

[0022]



[0023] 其中在式 (III) 和 (VI) 的情况下，基团 Z 代表 O、S 或 N-R，并且 X，其可以相同或不同，代表 O、S 或 NR'。因此，由 Z 和 X 构成的基团可以例如表示为 -CO-Z-CO-（可以替换为 [-COOH HOOC-]（即二羧酸而非酸酐））、-CS-Z-CO-、-CS-Z-CS- 或 -C(=NR')-NR-CO-；

[0024] R 和 R' 独立地代表任选取代的具有 1 至大约 20 个碳原子的脂族、脂环族、芳族、杂芳族、烷芳基、烷基杂芳基、芳烷基或杂芳基烷基基团；并且 R 和 R' 也可以组合以便与它们连接于其上的 N 原子一起形成任选取代的和 / 或稠合的 5- 至 7- 员环；

[0025] R_1、R_2 和 R_3 独立地选自氢、C_1-C_4 烷基、C_1-C_4 烷基 -COOH、C_1-C_4 烷基 $-SO_3H$、C_1-C_4 烷氧基、单 (C_1-C_4) 烷基氨基、二 (C_1-C_4) 烷基氨基、C_1-C_4 氨基烷基、卤素、氰基、硝基和 SO_3H，该烷基是任选取代的；

[0026] Y 选自 (i) 卤素、(ii) 具有 3 至大约 8 个环成员并经 N 原子键合到芳族环上的任选取代的 N- 杂脂环基（例如至少一个基团 Y 选自具有 3 至大约 8 个环成员的杂脂环基，该环成员可以包含 1 至大约 3 个选自 N、S 和 O 的杂原子（例如 1、2 或 3 个杂原子），条件是至少一个环成员是 N 和 / 或杂脂环基被一个或多个选自包含最多大约 10 个碳原子的烷基和烷氧基的取代基取代）和 (iii) 任选取代的苯氧基，其经 O 原子键合到芳族环上，该苯氧基可以被一个或多个（例如 1、2 或 3 个相同或不同的）取代基取代，所述取代基选自卤素（例如 F、Cl、Br 和 I）、硝基、氰基、NRR'、SO_3H 和 COOH 以及这些磺酸和羧酸基团的盐和衍生

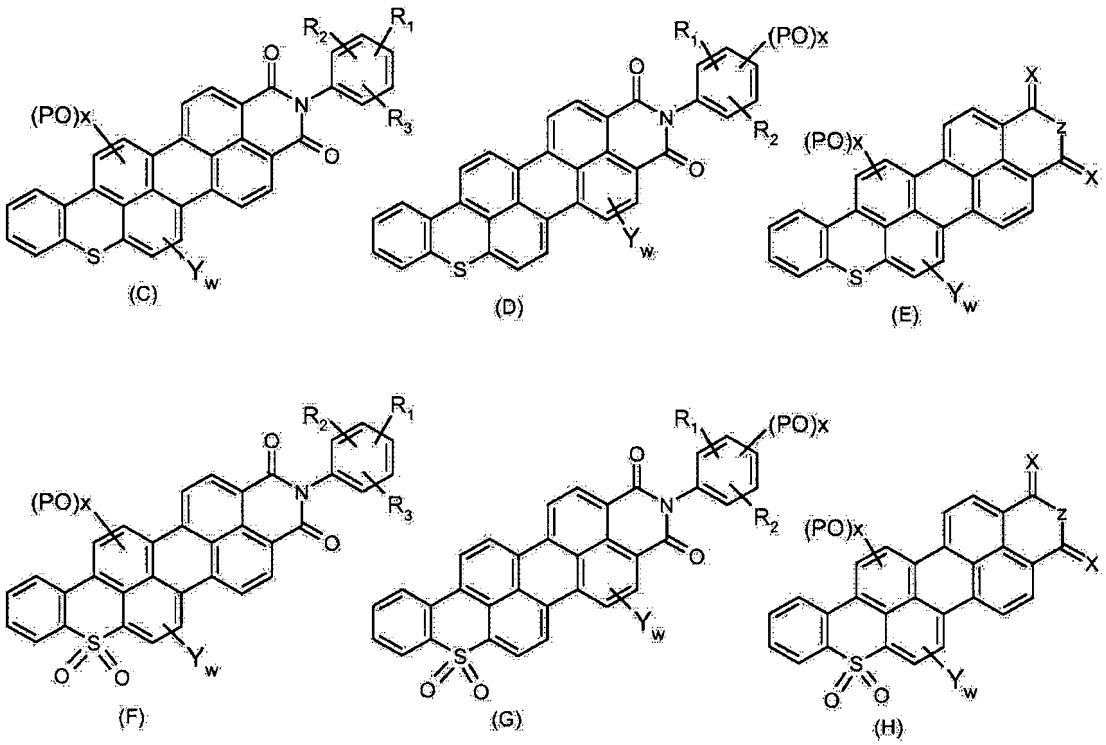
物（例如碱金属与碱土金属如Na、K、Ca和Mg的盐，酯，如C_1-C_4烷基酯，和酰胺，如具有NRR'作为酰胺基部分的酰胺）、OH、包含最多三个作为环成员的选自O、N和S的杂原子和3至大约8个环成员的杂环烷基、包含1至大约10个碳原子（例如1、2、3、4、5或6个碳原子）的烷基（包括环烷基）和烷氧基（包括环烷氧基）；

[0027] P代表具有至少三个包含任选取代的苯环的重复单元的聚合部分；

[0028] 并且x为0至4的整数，w为0至4的整数。

[0029] 在本发明的化合物的再一方面，Q可以是具有式(C)或(D)或(E)或(F)或(G)或(H)的基础结构（即不具有任选存在的取代基）的部分，其可以包括$(PO)_x$和/或Y_w：

[0030]



[0031] 其中在式(E)和(H)的情况下，Z代表O、S或N-R，并且X，其可以相同或不同，代表O、S或NR'。因此，由Z和X构成的基团可以例如表示为-CO-Z-CO-（可以替换为[-COOHHOOC-]（即二羧酸而非酸酐））、-CS-Z-CO-、-CS-Z-CS-或-C(=NR')-NR-CO-；

[0032] R和R'独立地代表任选取代的具有1至大约20个碳原子的脂族、脂环族、芳族、杂芳族、烷芳基、烷基杂芳基、芳烷基或杂芳基烷基基团；并且R和R'也可以组合以便与它们连接于其上的N原子一起形成任选取代的和/或稠合的5-至7-员环；

[0033] R_1、R_2和R_3独立地选自氢、C_1-C_4烷基、C_1-C_4烷基-COOH、C_1-C_4烷基-SO_3H、C_1-C_4烷氧基、单(C_1-C_4)烷基氨基、二(C_1-C_4)烷基氨基、C_1-C_4氨基烷基、卤素、氰基、硝基和SO_3H，该烷基是任选取代的；

[0034] Y选自(i)卤素、(ii)具有3至大约8个环成员并经N原子键合到芳族环上的任选取代的N-杂脂环基（例如至少一个基团Y选自具有3至大约8个环成员的杂脂环基，该环成员可以包含1至大约3个选自N、S和O的杂原子（例如1、2或3个杂原子），条件是至少一个环成员是N和/或杂脂环基被一个或多个选自包含最多大约10个碳原子的烷基和烷氧基的取代基取代）和(iii)任选取代的苯氧基，其经O原子键合到芳族环上，该苯氧

基可以被一个或多个（例如 1、2 或 3 个相同或不同的）取代基取代，所述取代基选自卤素（例如 F、Cl、Br 和 I）、硝基、氰基、NRR'、SO_3H 和 COOH 以及这些磺酸和羧酸基团的盐和衍生物（例如碱金属与碱土金属如 Na、K、Ca 和 Mg 的盐，酯，如 C_1-C_4 烷基酯，和酰胺，如具有 NRR' 作为酰胺基部分的酰胺）、OH、包含最多三个作为环成员的选自 O、N 和 S 的杂原子和 3 至大约 8 个环成员的杂环烷基、包含 1 至大约 10 个碳原子（例如 1、2、3、4、5 或 6 个碳原子）的烷基（包括环烷基）和烷氧基（包括环烷氧基）；

[0035] P 代表具有至少三个包含任选取代的苯环的重复单元的聚合部分；

[0036] 并且 x 为 0 至 4 的整数，w 为 0 至 4 的整数。

[0037] 因此，对于式 (C) 或 (D) 或 (E) 或 (F) 或 (G) 或 (H)，x 与 w 各自可以均为 0，x 或 w 为 0，以及 x 可以为 0、1、2、3 或 4 和 w 可以为 0、1、2、3 或 4。

[0038] 此外，本发明提供如上所述的式 (B) 和 (B') 的化合物，其是完全未取代的或带有一个或多个（例如 1、2、3、4、5 或 6 个）取代基（其可以相同或不同）。取代基的非限制性实例包括卤素（例如 F、Cl、Br 和 I）、硝基、氰基、NRR'、SO_3H 和 COOH 以及这些磺酸和羧酸基团的盐和衍生物（例如碱金属与碱土金属如 Na、K、Ca 和 Mg 的盐，酯，如 C_1-C_4 烷基酯，和酰胺，如具有 NRR' 作为酰胺基部分的酰胺）、OH、包含最多三个作为环成员的选自 O、N 和 S 的杂原子和 3 至大约 8 个环成员的杂环烷基、包含 1 至大约 10 个碳原子（例如 1、2、3、4、5 或 6 个碳原子）的烷基（包括环烷基）和烷氧基（包括环烷氧基），以及具有最多大约 20 个碳原子的任选取代的芳基（例如苯基）和芳烷基（例如苄基）。

[0039] 在本发明的这些化合物的一个方面中，基团 Z 代表 N-R，其中 R 可以例如选自任选取代的具有 1 至大约 6 个碳原子的烷基、任选取代的具有 7 至大约 12 个碳原子的烷芳基或芳烷基、任选取代的具有大约 6 至大约 20 个碳原子的芳基和任选取代的具有大约 3 至大约 20 个碳原子的杂芳基，例如选自任选取代的具有 1 至大约 4 个碳原子的烷基、任选取代的苯基或任选取代的苄基。作为非限制性实例，R 可以代表用 1 至大约 3 个选自卤素和具有 1 至大约 6 个碳原子的烷基的基团取代的苯基，例如被至少两个包含仲或叔碳原子的烷基取代的苯基，所述包含仲或叔碳原子的烷基的实例包括异丙基和叔丁基。

[0040] 在再一方面，本文中公开的化合物、如式 (1) 的化合物的至少一个基团 Y 可以选自具有 3 至大约 8 个环成员的杂脂环基，其环成员可以包含 1 至大约 3 个选自 N、S 和 O 的杂原子（例如 1、2 或 3 个杂原子），条件是至少一个环成员是 N。此外，该杂脂环基可以被一个或多个选自包含最多大约 10 个碳原子的烷基和烷氧基的取代基取代。

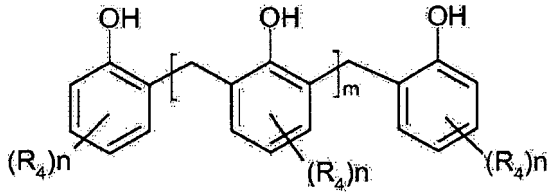
[0041] 例如，本文中公开的化合物、如式 (1) 的化合物或其它式的化合物的至少一个基团 Y 可以是杂环化合物的残基（即不具有键合到 N 原子上的氢原子），所述杂环化合物选自任选取代的氮杂环辛烷、任选取代的氮杂环庚烷 (azepane)、任选取代的哌啶、任选取代的哌嗪、任选取代的吡咯烷、任选取代的氮杂环丁烷、任选取代的氮杂环丙烷、任选取代的吗啉、任选取代的噁唑烷、任选取代的吡唑烷、任选取代的异吡唑烷、任选取代的异噁唑烷和任选取代的噻唑烷。该环上的任选取代基可以优选独立地选自 C_1-C_4 烷氧基和 C1-C6 烷基。当然，化合物可以包含两个或多个不同的杂脂环基 Y。

[0042] 在又一方面，本文中公开的化合物、如式 (1) 的化合物或其它式的化合物的至少一个基团 Y 当存在时可以选自任选取代的苯氧基，其中该苯氧基可以被一个或多个（例如 1、2 或 3 个相同或不同的）取代基取代，所述取代基选自卤素（例如 F、Cl、Br 和 I）、硝基、

氰基、NRR'、SO_3H 和 COOH 以及这些磺酸和羧酸基团的盐和衍生物（例如碱金属与碱土金属如 Na、K、Ca 和 Mg 的盐，酯，如 C_1-C_4 烷基酯，和酰胺，如具有 NRR' 作为酰胺基部分的酰胺）、OH、包含最多三个作为环成员的选自 O、N 和 S 的杂原子和 3 至大约 8 个环成员的杂环烷基、包含 1 至大约 10 个碳原子（例如 1、2、3、4、5 或 6 个碳原子）的烷基（包括环烷基）和烷氧基（包括环烷氧基）。

[0043] 在上述化合物的另一方面，P-O 当存在时可以是通式 (2) 的化合物的残基（即不具有酚羟基之一的氢原子）：

[0044]



(2)

[0045] 其中基团 R_4 彼此相同或不同，选自 C_1-C_{10} 烷基和 C_1-C_4 烷氧基；m 代表 1 至大约 30 的整数；n 代表 1 至大约 3 的整数。例如，m 可以代表 1 至 10 的整数和 / 或 n 可以是 1 或 2 和 / 或基团 R_4 可以独立地选自 C_1-C_{10} 烷基如异丙基、叔丁基、叔辛基、正壬基和支化壬基。

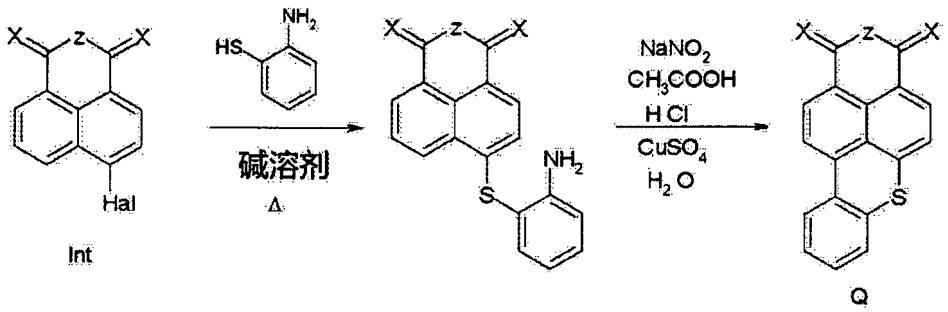
[0046] 本发明还提供制造本文中公开的化合物如式 (1) 的化合物的方法。该方法包括在非质子极性有机溶剂中令式 Q-$(Hal)_v$ 的化合物，其中 Hal 代表卤素且 v 代表 1 至 8 的整数，与含 N 的脂环族化合物和 / 或式 P-OH 的聚合化合物和 / 或任选取代的酚类化合物反应。如果两种或多种不同的化合物要与式 Q-$(Hal)_v$ 的化合物反应，该反应优选依次进行（分离或不分离中间体）以便能够更好地控制获得的反应产物混合物的组成。本领域技术人员将理解取决于反应条件，如果 v 为 2 或更高，可能获得各个化合物或位置异构体的混合物。

[0047] 制备其中 Hal 代表卤素和 v 代表 1 至 8 的整数的化合物 Q-$(Hal)_v$ 的方法可以如下进行：令不含卤素的如上所述的化合物 Q、如式 (A)、(A')、(B) 或 (B') 所代表的化合物反应。Q 化合物可以在作为溶剂的 AcOH 中与大约 5 当量的 SO_2Cl_2 在作为催化剂的 I_2 和碘代苯的存在下反应，取决于所用的初始化合物，整个组合物可以在大约 3 至 4 小时过程中加热或加热过夜至 70 至 90℃。所得混合物可以用水和有机溶剂的混合物洗涤。从水中萃取有机溶剂后获得有机相，随后蒸发该溶剂，所得粗油用本领域技术人员已知的提纯技术、如色谱法施以分离和提纯。

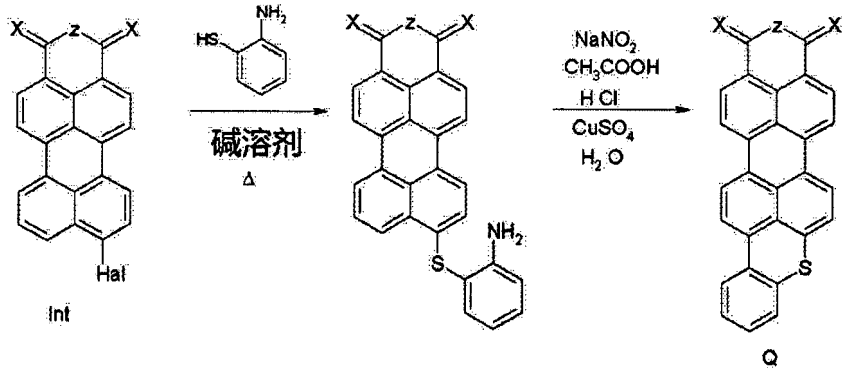
[0048] 制备分子 (A)、(A')、(B) 或 (B') 的方法可以包括下列步骤 (a) 或 (b)：

[0049]

(a)



(b)



[0050] 其中 X 和 Z 与上文定义的相同，并且 Hal 代表卤素如 Cl 或 Br，可以使用各种碱如 K_2CO_3，溶剂是例如极性溶剂如 N- 甲基 -2- 吡咯烷酮 (NMP)。Δ 表示的反应温度可以为 80 至 120℃，化合物 Int（也称为通向制备分子 Q 的合成的中间体）的制备是本领域技术人员公知的，或可以购得。

[0051] 在该方法的一个方面，至少涉及含 N 脂环族化合物的反应（以及通常还有涉及该聚合化合物和 / 或任选取代的酚类化合物的反应）可以在无机碱和 / 或强有机非亲核碱的存在下进行。

[0052] 在该方法的另一方面，至少涉及任选取代的酚类化合物的反应（以及通常还有涉及该聚合化合物或任选取代的酚类化合物的反应）可以在无机碱和 / 或强有机非亲核碱的存在下进行。

[0053] 在该方法的另一方面，每 100 克式 P-OH 的聚合化合物使用大约 0.5 至大约 10 克式 $Q-(Hal)_v$ 的化合物。在该方法的另一方面，大约 0.5 至大约 10 克式 $Q-(Hal)_v$ 的化合物可以与大约 2 至 3 当量的任选取代的酚类化合物反应。在该方法的另一方面，大约 0.5 至大约 10 克式 $Q-(Hal)_v$ 的化合物可以与 5 至 10 当量的含 N 脂环族化合物反应，或者可以用该含 N 脂环族化合物作为共溶剂 (co-solvent) 与进行本发明的方法所需溶剂一起制造该反应。

[0054] 在再一方面，该极性溶剂可以包含至少一种其中该聚合化合物（如果使用的话）可溶的溶剂和 / 或可以是 N- 甲基吡咯烷酮、二甲基甲酰胺、二甲基乙酰胺和二甲亚砜的至少一种。

[0055] 本发明还提供一种印刷油墨组合物。该组合物包含极性液体介质和至少一种本文

中公开的式 (1) 或 (A) 或 (A') 或 (B) 或 (B') 或 (C) 或 (D) 或 (E) 或 (F) 或 (G) 或 (H) 或 (I) 或 (II) 或 (III) 或 (IV) 或 (V) 或 (VI) 的化合物，如溶解或分散在该介质中的式 (1) 的化合物或其它式的化合物。作为非限制性实例的此类介质可以是甲乙酮 (MEK) 或二甲酮。

[0056] 在一方面，该组合物可以包含该组合物总重量的大约 0.01 重量％至大约 40 重量％，例如大约 0.05 重量％至大约 10 重量％，或大约 0.1 重量％至大约 5 重量％的至少一种本文中公开的化合物，如式 (1) 的化合物或其它式的化合物。

[0057] 在另一方面，该组合物可以进一步包含至少一种导电性赋予物质（例如盐）。

[0058] 本发明进一步提供用如上所述的本发明的印刷油墨制造和 / 或包含至少一种本文中公开的化合物、如式 (1) 的化合物或其它式的化合物的标识或防伪标记。

[0059] 在一方面，该标识或防伪标记可以包含承载数据信息的线 (thread)、标签、条形码、二维码、图案、标记、数据矩阵、邮票、税票、邮票、税票、数字印章和云点（可见或不可见）的至少一种。

[0060] 本发明还提供一种包含如上所述的标识或防伪标记的制品。例如，该标识或防伪标记可以以层的形式存在于该制品上。

[0061] 在一方面，该制品可以是以下的至少一种：标签如税务标签、包装、罐头、金属、铝箔、盒、含有例如药物、营养品、食品或饮料（例如咖啡、茶、牛奶、巧克力等）的封闭的盒（例如胶囊）、玻璃制成的制品、陶瓷制成的制品、钞票、邮票、安全文件、身份证、护照、驾驶执照、信用卡、门禁卡、票（例如交通票或活动门票）、凭单、有价值的文件、油墨转印膜、反射膜、线、商品和卷烟包装，其携带或不携带编码或加密信息。

[0062] 本发明还提供验证制品的方法。该方法包括提供具有如上所述的标识或防伪标记的制品（包括其各个方面）和 / 或包括向制品上施加如上所述的印刷油墨组合物（包括其各个方面）。

[0063] 在该方法的一个方面，该制品可以是以下的至少一种：税务标签、包装、罐头、金属、铝箔、盒、含有例如药物、营养品、食品或饮料（例如咖啡、茶、牛奶、巧克力等）的封闭的盒（例如胶囊）、玻璃制成的制品、陶瓷制成的制品、钞票、邮票、安全文件、身份证、护照、驾驶执照、信用卡、门禁卡、票（例如交通票或活动门票）、凭单、有价值的文件、油墨转印膜、反射膜、线、商品和卷烟包装，其携带或不携带编码或加密信息。

[0064] 本发明还提供一种聚合物，其中该聚合物分子的至少大约 0.1％具有键合于其上的 1 至 4 个式—Q—$(Y)_w$ 的残基（例如 1、2 或 3 个残基），其中：

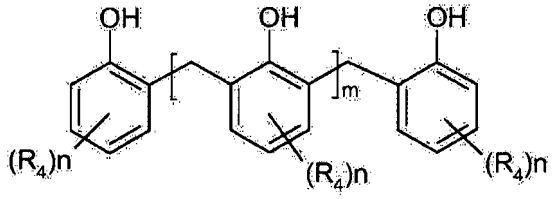
[0065] Q 代表 (A) 或 (B) 或 (A') 或 (B') 部分；

[0066] Y 选自 (i) 卤素（例如 F、Cl、Br 和 I），(ii) 具有 3 至大约 8 个环成员的任选取代的 N- 杂脂环基，该环成员的至少一个是 N，该 N- 杂脂环基经 N 原子键合到 Q 上，和 (iii) 经 O 原子键合到 Q 上的任选取代的苯氧基；

[0067] w 代表 1 至 4 的整数；并且进一步的条件是 Q 可以同时键合到最多 4 个聚合物分子上（例如键合到 1、2、3 或 4 个不同的聚合物分子上）。

[0068] 在该聚合物的一个方面，该聚合物可以是通式 (2) 的化合物：

[0069]



(2)

[0070] 其中彼此相同或不同的基团 R_4 选自 C_1-C_{10} 烷基和 C_1-C_4 烷氧基；m 代表 1 至大约 30 的整数；并且 n 代表 1 至大约 3 的整数。

[0071] 关于 x 和 w，其组合的实例包括其中 x 为 1 且 w = 0；其中 x 为 0 且 w 为 2 或不高于 4；以及其中 (x+w) 不高于大约 4。

[0072] 在又一方面，该聚合物可以通过上述方法（包括其各个方面）获得。

具体实施方式

[0073] 本文中所示的细节是通过举例的方式并仅用于示例性描述本发明的实施方案，并为了提供据信是最有用和容易理解的本发明的原则与概念方面而呈现。在这方面，并未试图超越基本理解本发明所需地更详细显示本发明的结构细节，该描述令本领域技术人员明白如何在实践中实现本发明的几种形式。

[0074] 关于本文中提及的基团 R、R'、R"、R_1、R_2、R_3 和 R_4 的含义，下面的含义在本说明书和所附权利要求书中通篇适用（应当理解，在本说明书和所附权利要求书中通篇显示的碳原子数总是指各未取代的基团）：

[0075] "任选取代的脂族"或"任选取代的烷基"基团包括直链和支化烷基，其优选具有 1 至大约 12 个碳原子，例如 1 至大约 8 个碳原子、1 至大约 6 个碳原子或 1 至大约 4 个碳原子。其具体的非限制性实例包括甲基、乙基、正丙基、异丙基、正丁基、异丁基、叔丁基、仲丁基、直链或支化戊基（例如 2- 甲基丁基、2- 乙基丙基和 2,2- 二甲基丙基）、直链或支化己基（例如 2- 乙基丁基、3- 乙基丁基、2,2- 二甲基丁基、3,3- 二甲基丁基和 2,3- 二甲基丁基）、直链或支化庚基、直链或支化辛基（例如 2- 乙基己基）和直链或支化壬基。该烷基可以被一个或多个取代基（例如一个、两个、三个、四个等）取代。这些取代基的非限制性实例包括 OH，卤素如 F、Cl、Br 和 I（如在例如三氟甲基、三氯甲基、五氟乙基和 2,2,2- 三氟乙基中），具有 1 至大约 6 个碳原子、例如 1 至大约 4 个碳原子的烷氧基，如甲氧基、乙氧基、丙氧基和丁氧基，具有 1 至大约 4 个碳原子的酰氧基，如乙酰氧基和丙酰氧基，具有大约 6 至大约 10 个碳原子的芳氧基，例如（任选取代的）苯氧基，具有大约 6 至大约 10 个碳原子的芳酰氧基，如苯甲酰氧基，-COOH（包括其部分或完全盐化的形式），在烷基中具有 1 至大约 4 个碳原子的烷氧基羰基如甲氧基羰基和乙氧基羰基，$-SO_3H$，烷基磺酰基、芳基磺酰基、烷基磺酰基氨基、硝基、氰基、氨基、单烷基氨基和二烷基氨基，其中该烷基具有 1 至大约 6 个碳原子，例如 1 至大约 4 个碳原子，如甲基氨基、二甲基氨基、乙基氨基、二乙基氨基、丙基氨基和二丙基氨基。如下文中进一步陈述的那样，该烷基还可以被一个或多个任选取代的环烷基（优选具有 3 至大约 8 个环碳原子）取代。该烷基的优选取代基包括 F、Cl、Br、OH、甲氧基、乙氧基、-COOH、$-SO_3H$、氨基、甲基氨基、乙基氨基、二甲基氨基和二乙基氨基。如果存在超过一个取代基，该取代基可以相同或不同。同样，该烷基基团的一个或多个（例如一个

或两个）C 原子可以被杂原子如 O、S 和 NR'"（其中 R'"代表例如 H 或具有 1 至大约 4 个碳原子的烷基）替代。此外，该烷基可以具有一个或多个并入其中的羰基（C = O）和 / 或可以包含一个或多个碳 - 碳双键和 / 或三键（如在例如乙烯基、烯丙基和炔丙基中那样）。

[0076] "任选取代的脂环族"或"任选取代的环烷基"基团优选包含大约 3 至大约 12 个环碳原子，更优选大约 5 至大约 8 个环碳原子如环丙基、环丁基、环戊基、环己基、环庚基和环辛基。该环烷基可以被一个或多个取代基（例如一个、两个、三个、四个等）取代。这些取代基的非限制性实例包括 OH，卤素如 F、Cl、Br 和 I，具有 1 至大约 6 个碳原子、例如 1 至大约 4 个碳原子的烷氧基，如甲氧基、乙氧基、丙氧基和丁氧基，具有 1 至大约 4 个碳原子的酰氧基，如乙酰氧基和丙酰氧基，具有大约 6 至大约 10 个碳原子的芳氧基，例如（任选取代的）苯氧基，具有大约 6 至大约 10 个碳原子的芳酰氧基，如苯甲酰氧基，-COOH（包括其部分或完全盐化的形式），在烷基中具有 1 至大约 4 个碳原子的烷氧基羰基如甲氧基羰基和乙氧基羰基，$-SO_3H$，烷基磺酰基、芳基磺酰基、烷基磺酰基氨基、硝基、氰基、氨基、单烷基氨基和二烷基氨基，其中该烷基具有 1 至大约 6 个碳原子，例如 1 至大约 4 个碳原子，如甲基氨基、二甲基氨基、乙基氨基、二乙基氨基、丙基氨基和二丙基氨基。如下文中进一步陈述的那样，该环烷基还可以被一个或多个任选取代的烷基（优选具有 1 至大约 4 个碳原子）取代。该烷基的优选取代基包括 F、Cl、Br、OH、甲氧基、乙氧基、-COOH、$-SO_3H$、氨基、甲基氨基、乙基氨基、二甲基氨基和二乙基氨基。如果存在超过一个取代基，该取代基可以相同或不同。此外，该环烷基可以具有一个或多个并入其中的羰基（C = O）和 / 或可以包含一个或多个碳 - 碳双键（如在例如环戊烯基和环己烯基中那样）。

[0077] "任选取代的芳基（芳族）"基团和"任选取代的杂芳基（杂芳族）"基团表示优选包含大约 5 至大约 15 个环成员，例如大约 6 至大约 10 个环成员的任选稠合的芳基和杂芳基。该杂芳基通常包含 1 至大约 3 个选自 O、S 和 N 的环成员并可以部分或完全氢化。这些芳基和杂芳基的具体事例包括苯基，萘基，蒽基，菲基，2- 或 3- 呋喃基，2- 或 3- 噻吩基，1-、2- 或 3- 吡咯基，1-、2-，4- 或 5- 咪唑基，1-、3-、4- 或 5- 吡唑基，2-、4- 或 5- 噁唑基，3-、4- 或 5- 异噁唑基，2-、4- 或 5- 噻唑基，3-、4- 或 5- 异噻唑基，2-、3- 或 4- 吡啶基，2-、4-、5- 或 6- 嘧啶基，1，2，3- 三唑 -1-、-4- 或 -5- 基，1，2，4- 三唑 -1-、-3- 或 -5- 基，1- 或 5- 四唑基，1，2，3- 噁二唑 -4- 或 -5- 基，1，2，4- 噁二唑 -3- 或 -5- 基，1，3，4- 噻二唑 -2- 或 -5- 基，1，2，4- 噻二唑 -3- 或 -5- 基，1，2，3- 噻二唑 -4- 或 -5- 基，3- 或 4- 哒嗪基，吡嗪基，1-、2-、3-、4-、5-、6- 或 7- 吲哚基，吲唑基，4- 或 5- 异吲哚基，1-、2-、4- 或 5- 苯并咪唑基，1-、3-、4-、5-、6- 或 7- 苯并吡唑基，2-、4-、5-、6- 或 7- 苯并噁唑基，3-、4-、5-、6- 或 7- 苯并异噁唑基，2-、4-、5-、6- 或 7- 苯并噻唑基，2-、4-、5-、6- 或 7- 苯并异噻唑基，4-、5-、6- 或 7- 苯并 -2，1，3- 噁二唑基，2-、3-、4-、5-、6-、7- 或 8- 喹啉基，1-、3-、4-、5-、6-、7- 或 8- 异喹啉基，3-、4-、5-、6-、7- 或 8- 噌啉基，2-、4-、5-、6-、7- 或 8- 喹唑啉基，5- 或 6- 喹噁啉基，2-、3-、5-、6-、7- 或 8-2H- 苯并 -1，4- 噁嗪基，1，3- 苯并二氧戊环 -5- 基，1，4- 苯并 - 二氧杂环己烷 -6- 基，2，1，3- 苯并噻二唑 -4- 或 -5- 基或 2，1，3- 苯并噁二唑 -5- 基，2，3- 二氢 -2-、-3-、-4- 或 -5- 呋喃基，2，5- 二氢 -2-、-3-、-4- 或 -5- 呋喃基，四氢 -2- 或 -3- 呋喃基，1，3- 二氧戊环 -4- 基，四氢 -2- 或 -3- 噻吩基，2，3- 二氢 -1-、-2-、-3-、4- 或 -5- 吡咯基，2，5- 二氢 -1-、-2-、-3-、-4- 或 -5- 吡咯基，1-、2- 或 3- 吡咯烷基，四氢 -1-、-2- 或 -4- 咪唑基，2，3- 二氢 -1-、-2-、-3-、-4- 或 -5- 吡唑基，四氢 -1-、-3- 或 -4- 吡

唑基，1,4-二氢-1-、-2-、-3-或-4-吡啶基，1,2,3,4-四氢-1-、-2-、-3-、-4-、-5-或-6-吡啶基，1-、2-、3-或4-哌啶基，2-、3-或4-吗啉基，四氢-2-、-3-或-4-吡喃基，1,4-二氧杂环己烷基，1,3-二氧杂环己烷-2-、-4-或-5-基，六氢-1-、-3-或-4-哒嗪基，六氢-1-、-2-、-4-或-5-嘧啶基，1-、2-或3-哌嗪基，1,2,3,4-四氢-1-、-2-、-3-、-4-、-5-、-6-、-7-或-8-喹啉基，1,2,3,4-四氢-1-、-2-、-3-、-4-、-5-、-6-、-7-或-8-异喹啉基，2-、3-、5-、6-、7-或8-3,4-二氢-2H-苯并-1,4-噁嗪基，2,3-亚甲二氧基苯基、3,4-亚甲二氧基苯基、2,3-亚乙二氧基苯基、3,4-亚乙二氧基苯基、3,4-(二氟代亚甲二氧基)苯基、2,3-二氢苯并呋喃-5-或-6-基，2,3-(2-氧代亚甲二氧基)苯基、3,4-二氢-2H-1,5-苯并二氧杂庚英(dioxepin)-6-或-7-基，2,3-二氢苯并呋喃基，2,3-二氢-2-氧代呋喃基。该芳基和杂芳基可以被一个或多个取代基(例如一个、两个、三个、四个等)取代，该取代基优选选自卤素如F、Cl、Br和I，OH，-COOH(包括其部分或完全盐化的形式)，$-SO_3H$，硝基，氰基，具有1至大约4个碳原子的烷氧基，如甲氧基和乙氧基，具有1至大约4个碳原子的酰氧基，如乙酰氧基和丙酰氧基，具有大约6至大约10个碳原子的芳氧基，如苯氧基，具有大约6至大约10个碳原子的芳酰氧基，如苯甲酰氧基，氨基，单烷基氨基和二烷基氨基，其中该烷基具有1至大约6个碳原子，例如1至大约4个碳原子，如甲基氨基、二甲基氨基、乙基氨基、二乙基氨基、丙基氨基和二丙基氨基，具有1至大约8个碳原子的酰基氨基，如乙酰基氨基和丙酰基氨基，氨基羰基，单烷基氨基羰基，二氨基羰基和在烷基中具有1至大约4个碳原子的烷氧基羰基，如甲氧基羰基和乙氧基羰基，具有2至大约8个碳原子的任选取代的酰基，如乙酰基和丙酰基，烷基磺酰基，芳基磺酰基和二氨基磺酰基氨基。如果存在超过一个取代基，该取代基可以相同或不同。同样，该芳基和杂芳基可以被芳基和/或烷芳基取代。取代芳基的具体和非限制性实例包括氯苯基、二氯苯基、氟苯基、溴苯基、苯氧基苯基、羟基苯基、二羟基苯基、甲氧基苯基、氨基苯基、二甲基氨基苯基和联苯基。

[0078] “任选取代的烷芳基”基团和“任选取代的烷基杂芳基”基团表示如上所述的任选取代的芳基与任选取代的杂芳基，其(进一步)被至少一个如上所述的任选取代的烷基(优选包含1至大约6个，例如1至大约4个碳原子)取代。其具体实例包括甲苯基、二甲苯基、均三甲苯基、乙苯基、异丙苯基、三氟甲基苯基、羟基甲苯基、氯甲苯基、甲基吡啶基、甲基呋喃基、甲基噻吩基、二异丙基苯基、二(叔丁基)苯基和甲基萘基。

[0079] “任选取代的芳烷基”基团和“任选取代的杂芳基烷基”基团表示如上所述的任选取代的烷基(优选包含1至大约6个，例如1至大约4个碳原子)，其(进一步)被至少一个如上所述的任选取代的芳基和/或任选取代的杂芳基取代。其具体实例包括苄基、甲基苄基、氯苄基、二氯苄基、羟基苄基、1-苯基乙基、2-苯基乙基、吡啶基甲基、噻吩基甲基、呋喃基甲基和萘基甲基。

[0080] “任选取代的和/或稠合的5-至7-员环”表示饱和的、部分不饱和的或芳族的N-杂环环，其除了已经存在于其中的一个或两个N原子之外可以包含一个或多个选自O、N和S的附加杂原子。该环通常具有五个或六个环成员。同样，该环将通常不包含附加的杂原子。此外，该环可以具有一个或两个与之稠合的芳族和/或杂芳族环(例如苯环)和/或可以被一个或多个(例如一个、两个、三个、四个等等)取代基取代，所述取代基优选选自F、Cl、Br和I，OH，-COOH(包括其部分或完全盐化形式)，$-SO_3H$，氰基，硝基，具有1至大约4个碳原子的烷氧基，如甲氧基和乙氧基，具有1至大约4个碳原子的酰氧基，如乙酰氧基和

丙酰氧基，具有大约6至大约10个碳原子的芳氧基，如苯氧基，具有大约6至大约10个碳原子的芳酰氧基，如苯甲酰氧基，氨基，单烷基氨基和二烷基氨基，其中该烷基具有1至大约6个碳原子，例如1至大约4个碳原子，如甲基氨基、二甲基氨基、乙基氨基、二乙基氨基、丙基氨基和二丙基氨基，具有1至大约8个碳原子的酰基氨基，如乙酰基氨基和丙酰基氨基，氨基羰基，单烷基氨基羰基，二氨基羰基和在烷基中具有1至大约4个碳原子的烷氧基羰基，如甲氧基羰基和乙氧基羰基，具有2至大约8个碳原子的任选取代的酰基，如乙酰基和丙酰基，烷基磺酰基，芳基磺酰基和烷基磺酰基氨基，具有1至大约6个碳原子的任选取代的烷基，如甲基、乙基、羟甲基和羟乙基，任选取代的（杂）芳基，如苯基、甲苯基、二甲苯基、羟基苯基、吡啶基和吡咯基，以及任选取代的烷芳基，如苄基。如果存在超过一个取代基，该取代基可以相同或不同。未取代的含N的5-至7-员环的非限制性实例包括吡咯基、吡咯烷基、吡啶基、嘧啶基、哌啶基、吗啉基、哌嗪基、噻吩基、吡唑基、吡唑烷基、噁唑基和噁唑烷基。

[0081] 如上所述，本发明的化合物包括通式（1）：

[0082]

$$(P—O)_x—Q—Y_w$$

(1)

[0083] 其中P代表具有至少三个包含任选取代的苯环的重复单元的聚合部分；

[0084] Q代表含有S原子或$S(=O)_2$部分的多环芳烃部分（即具有并入其基础结构中的S原子或$S(=O)_2$部分的多环芳烃骨架，该基础结构除取代基Y和/或P-O外任选包含一个或多个取代基）；

[0085] Y选自（i）卤素、（ii）具有3至大约8个环成员并经N原子键合到Q上的任选取代的N-杂脂环基，和（iii）任选取代的苯氧基；

[0086] x代表0至4的整数；

[0087] w代表0至4的整数，

[0088] 并且其中w和x不同时为0；

[0089] 条件是当x＝0时，至少一个Y选自（ii）和（iii）。

[0090] 如果存在超过一个卤素（即如果w为至少3），该卤素原子可以相同或不同并优选是相同的。此外，如果存在超过一个任选取代的具有3至大约8个环成员的N-杂脂环基，该基团也可以相同或不同（并优选是相同的）。此外，如果存在超过一个任选取代的苯氧基，该基团也可以相同或不同（并优选是相同的）。此外，x通常为1或2，更优选为1，并且(x+w)和通常不超过6，例如不超过5，或不超过4。

[0091] 还应该意识到，虽然基团(P-O)-通常直接键合到Q部分上，其还可以键合到并非Q骨架的一部分而是其取代基（的一部分）的芳族基团（特别是苯基）上。在这方面，可以提及上式(II)、(V)、(D)和(G)。在式(II)、(V)、(D)和(G)的化合物的情况下，基团(P-O)-键合到基团-CO-NR-CO-（其是式(A)、(B)、(E)和(H)中Z和X的含义之一）的任选取代的苯环上，其中R代表任选取代的苯基。还有可能键合到 -C(＝NR')-NR-CO-上，其中(P-O)-可以键合到芳族基团R和/或R'上。

[0092] 基团Y可以选自具有3至大约8个环成员（例如3、4、5、6、7或8个环成员）的N-杂脂环基，其环成员可以包含1至大约3个选自N、S和O的杂原子（例如1、2或3个杂原子），条件是至少一个环成员是N。该环成员的至少一个（优选至少两个）是碳原子。作

为非限制性实例，杂脂环基 Y 可以具有 5、6 或 7 个环成员（优选 5 或 6 个环成员）并含有 1 或 2 个杂原子，它们的至少一个是 N 原子。如果存在两个杂原子，第二杂原子可以是 N、S 或 O。如果存在三个杂原子，第二或第三杂原子可以相同或不同，并选自 N、O 和 S。例如，含有 3 个杂原子环成员的杂脂环基 Y 可以含有 3 个 N 原子，或 2 个 N 原子和一个 O 原子或一个 S 原子。

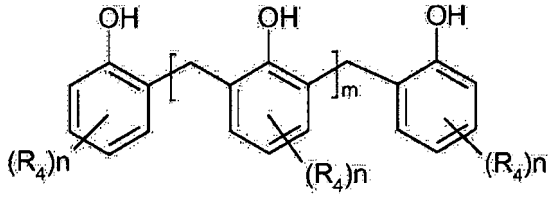
[0093] 该杂脂环基 Y 可以进一步被一个或多个取代基（例如 1、2、3 或 4 个取代基，并优选不超过 3 个，或不超过 2 个取代基）取代，所述取代基选自包含最多大约 10 个碳原子（例如 1、2、3、4、5 或 6 个碳原子）的烷基和烷氧基。相应取代基的非限制性实例包括乙基、甲基、正丙基、异丙基、正丁基、仲丁基和叔丁基以及相应的烷氧基。

[0094] 例如，基团 Y 可以是作为选自以下的化合物的残基的基团（即不具有键合到氮原子上的 H 原子），所述化合物选自：任选取代的氮杂环辛烷、任选取代的氮杂环庚烷、任选取代的哌啶、任选取代的哌嗪、任选取代的吡咯烷、任选取代的氮杂环丁烷、任选取代的氮杂环丙烷、任选取代的吗啉、任选取代的噁唑烷、任选取代的吡唑烷、任选取代的异吡唑烷、任选取代的异噁唑烷和任选取代的噻唑烷。该杂环环上的任选取代基（例如 1、2、3 或 4 个取代基）可以相同或不同并优选选自 C_1-C_4 烷氧基和 C_1-C_6 烷基。相应取代的基团的具体和非限制性实例是 3,5- 二甲基 -1- 哌啶基。

[0095] 基团 Y 可以额外地选自任选取代的苯氧基，其中该苯氧基可以被一个或多个（例如 1、2 或 3 个相同或不同的）取代基取代，所述取代基选自卤素（例如 F、Cl、Br 和 I）、硝基、氰基、NRR'、SO_3H 和 COOH 及这些磺酸和羧酸基团的盐和衍生物（例如碱金属与碱土金属如 Na、K、Ca 和 Mg 的盐，酯，如 C_1-C_4 烷基酯，和酰胺，如具有 NRR' 作为酰胺基部分的酰胺）、OH、包含最多三个作为环成员的选自 O、N 和 S 的杂原子和 3 至大约 8 个环成员的杂环烷基、以及包含 1 至大约 10 个碳原子（例如 1、2、3、4、5 或 6 个碳原子）的烷基（包括环烷基）和烷氧基（包括环烷氧基）。相应取代的苯氧基的具体和非限制性实例是 2,6- 二 - 叔丁基 -4- 甲基苯氧基、对甲酚基和邻甲酚基。

[0096] 通式 (1) 的聚合物键合的化合物的聚合部分 P 优选在其骨架中仅包含碳原子（即没有杂原子如 O、N 或 S）。同样，该聚合部分优选在其骨架中包含至少三个芳族环（例如苯环）。这些芳族环（其可以相同或不同并优选是相同的）可以直接或通过一个或多个原子（优选碳原子）彼此连接。这些芳族环的至少一些（优选全部）可以带有一个或多个（例如 1、2 或 3）与不具有极性取代基的聚合部分相比提高该聚合部分在极性介质（如醇等）中溶解度的极性（含杂原子的）取代基。如果存在超过一个极性取代基，该取代基可以相同或不同。当然，在芳族环上还可以存在一个或多个附加（非极性）取代基。作为非限制性实例，该聚合部分可以衍生自酚醛树脂、如酚醛清漆树脂，特别是具有至少大约 3 个羟基和 / 或至少大约 300，例如至少大约 350，且不高于大约 3,000，例如不高于大约 1,500 的（重量）平均分子量的酚醛树脂。例如，P 可以衍生自通式 (2) 的化合物（是其残基）：

[0097]



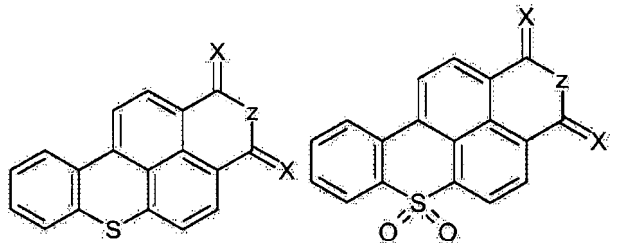
(2)

[0098] 其中基团 R_4 彼此相同或不同，选自 C_1-C_{10} 烷基和 C_1-C_4 烷氧基；m 代表 1 至大约 30 的整数，例如 1 至 25、1 至 15、1 至 10、1 至 5、1 至 3、5 至 15、5 至 10、10 至 20 或 20 至 30；并且 n 代表 1 至 3 的整数（例如 1、2 或 3）。例如，m 可以代表 1 至 10 的整数和 / 或 n 可以是 1 或 2 和 / 或基团 R_4 可以独立地选自 C_1-C_{10} 烷基如异丙基、叔丁基、叔辛基、正壬基和支化壬基。此外，基团 R_4 可以相对于 OH 基团处于间位或对位。例如，如果在苯基环上存在两个基团 R_4（相同或不同，优选相同的基团 R_4），它们可以存在于该苯基环上的任意可用位置，例如相对于 OH 基团的间 / 对位或间 / 间位。

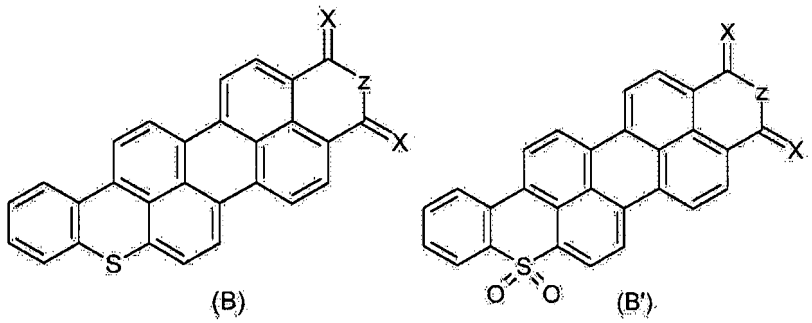
[0099] 本领域技术人员将认识到，通式 (2) 的化合物通常以具有不同 m 值的化合物的混合物形式存在。在这种情况下，通式 (2) 中 m 的平均值通常为至少大约 1，例如至少大约 2，例如至少大约 3 或至少大约 4，并通常不高于大约 30，例如不高于大约 20，不高于大约 15 或不高于大约 10。

[0100] 同样如上所述，Q 可以是具有式 (A) 或 (B) 或 (A') 或 (B') 的基础结构的部分：

[0101]



(A) (A')



(B) (B')

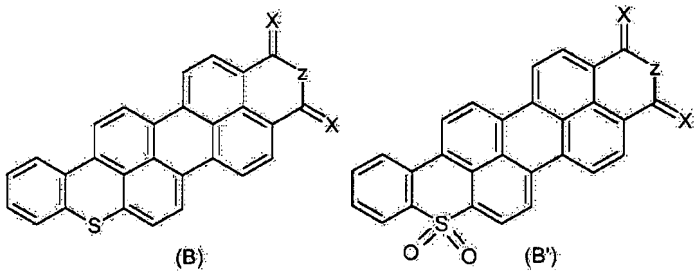
[0102] 在上式 (A) 和 (B) 或 (A') 或 (B') 中，Z 代表 O、S 或 N-R，并且 X，其可以相同或不同，代表 O、S 或 NR'。因此，Z 和 X 形成的基团可以表示为例如 -CO-Z-CO-（可以替换为 [-COOH HOOC-]（即二羧酸而非酸酐））、-CS-Z-CO-、-CS-Z-CS- 或 -C(=NR')-NR-CO-。

[0103] 上式中的基团 R 和 R' 独立地代表任选取代的具有 1 至大约 20 个碳原子的脂族、脂环族、芳族、杂芳族、烷芳基、烷基杂芳基、芳烷基或杂芳基烷基基团。此外，R 和 R' 也可

以组合以便与它们连接于其上的 N 原子一起形成任选取代的和 / 或稠合的 5- 至 7- 员环。

[0104] 还提供了式 (B) 或 (B') 的任选取代的化合物 :

[0105]

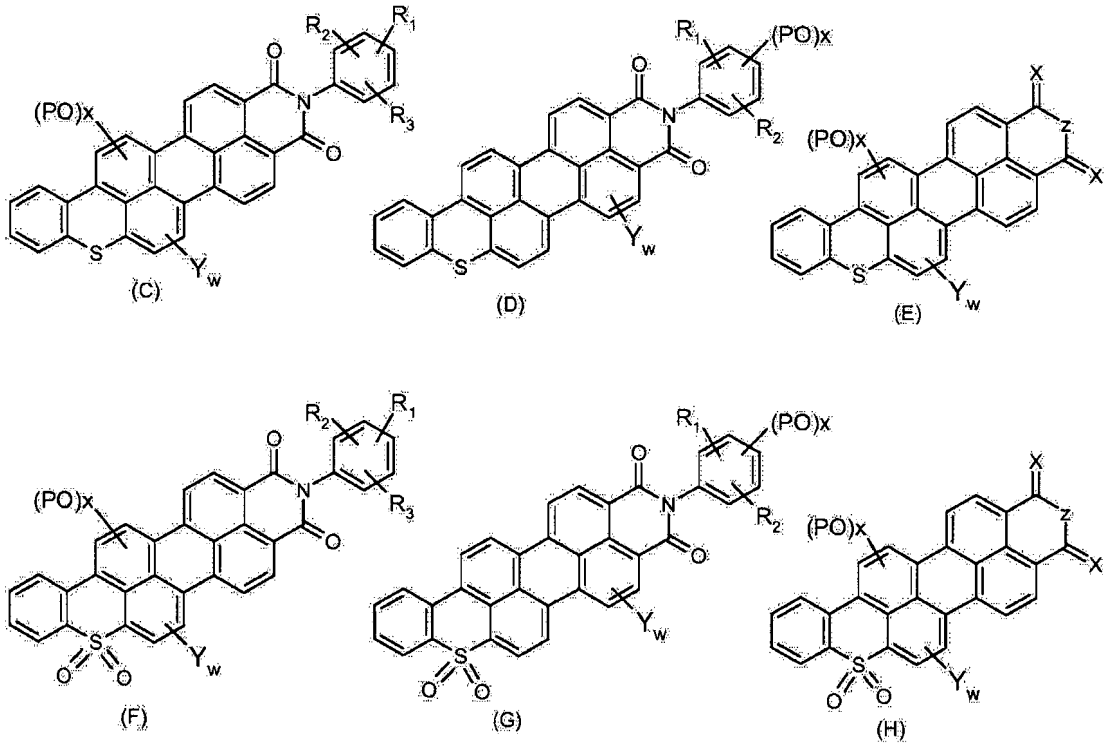


[0106] 其中 Z 代表 O、S 或 N-R,并且 X,其可以相同或不同,代表 O、S 或 NR'。因此,Z 和 X 形成的基团可以表示为例如 -CO-Z-CO-(可以替换为 [- COOH HOOC-](即二羧酸而非酸酐))、- CS-Z-CO-、-CS-Z-CS- 或 - C(= NR')-NR-CO- ;并且

[0107] R 和 R' 独立地代表任选取代的具有 1 至大约 20 个碳原子的脂族、脂环族、芳族、杂芳族、烷芳基、烷基杂芳基、芳烷基或杂芳基烷基基团 ;并且 R 和 R' 也可以组合以便与它们连接于其上的 N 原子一起形成任选取代的和 / 或稠合的 5- 至 7- 员环。

[0108] 这些化合物可以包括式 (C)、(D) 或 (E) 或 (F) 或 (G) 或 (H) 的化合物 :

[0109]



[0110] 其中在式 (E) 和 (H) 的情况下,Z 代表 O、S 或 N-R ;并且 X,其可以相同或不同,代表 O、S 或 NR' ;且

[0111] R 和 R' 独立地代表任选取代的具有 1 至大约 20 个碳原子的脂族、脂环族、芳族、杂芳族、烷芳基、烷基杂芳基、芳烷基或杂芳基烷基基团 ;并且 R 和 R' 也可以组合以便与它们连接于其上的 N 原子一起形成任选取代的和 / 或稠合的 5- 至 7- 员环 ;

[0112] R_1、R_2 和 R_3 独立地选自氢、C_1-C_4 烷基、C_1-C_4 烷基 -COOH、C_1-C_4 烷基 -SO_3H、C_1-C_4 烷氧基、单 (C_1-C_4) 烷基氨基、二 (C_1-C_4) 烷基氨基、C_1-C_4 氨基烷基、卤素、氰基、硝基和 SO_3H，该烷基是任选取代的；

[0113] Y 选自 (i) 卤素、(ii) 具有 3 至大约 8 个环成员并经 N 原子键合到芳族环上的任选取代的 N- 杂脂环基；和 (iii) 任选取代的苯氧基，其经 O 原子键合到芳族环上，该苯氧基可以被一个或多个取代基取代，所述取代基选自卤素、硝基、氰基、NRR'、SO_3H 和 COOH 以及这些磺酸和羧酸基团的盐和衍生物、OH、包含最多三个作为环成员的选自 O、N 和 S 的杂原子和 3 至大约 8 个环成员的杂环烷基、包含 1 至大约 10 个碳原子的烷基（包括环烷基）和烷氧基（包括环烷氧基）；

[0114] P 代表具有至少三个包含任选取代的苯环的重复单元的聚合部分；

[0115] 并且 x 为 0 至 4 的整数，w 为 0 至 4 的整数。

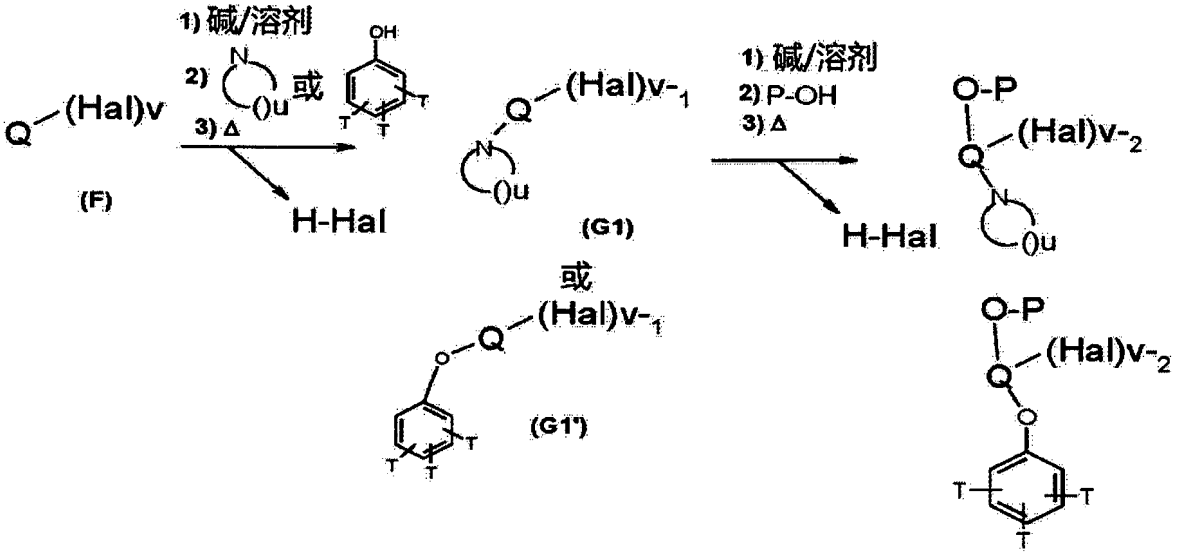
[0116] 式 (B) 或 (B') 的化合物可以是未取代的。

[0117] 通式 (1) 的化合物可以例如通过以下方法制造，该方法包括在非质子极性有机溶剂中令式 Q-$(Hal)_v$ 的化合物，其中 Hal 代表卤素（例如 F、Cl、Br 或 I）且 v 代表 1 至 8 的整数（例如 1、2、3、4 或 5），与选自 (a) 含 N 脂环族化合物、(b) 式 P-OH 的聚合化合物和 (c) 任选取代的酚类化合物的化合物反应，或通过令式 Q-$(Hal)_v$ 的化合物依次与两种（如果 v 为至少 2）或三种（如果 v 为至少 3）或甚至更多种独立地选自化合物 (a)、(b) 和 (c) 的化合物反应。在后一种情况下，依次与式 Q-$(Hal)_v$ 的化合物反应的至少两种化合物可以属于相同或不同的类别。例如，式 Q-$(Hal)_v$ 的化合物可以以任何次序依次与两种不同的化合物 (a) 或化合物 (a) 与化合物 (b) 反应。通常，至少涉及含 N 脂环族化合物的反应（通常还有涉及聚合化合物和 / 或酚类化合物的反应）可以在无机碱和 / 或强有机非亲核碱的存在下进行。该极性溶剂通常包括至少一种该聚合物化合物（如果使用的话）可溶于其中的溶剂和 / 或可以是 N- 甲基吡咯烷酮、二甲基甲酰胺、二甲基乙酰胺和二甲亚砜的至少一种。

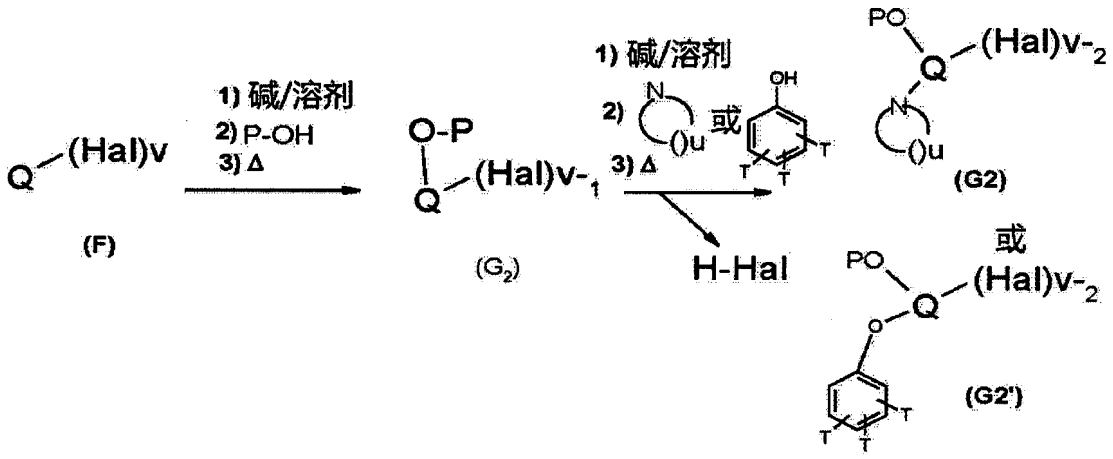
[0118] 相应的方法可以例如表示为以下反应图示 (1) 或 (2) 或 (3) 或 (4)：

[0119]

(1)

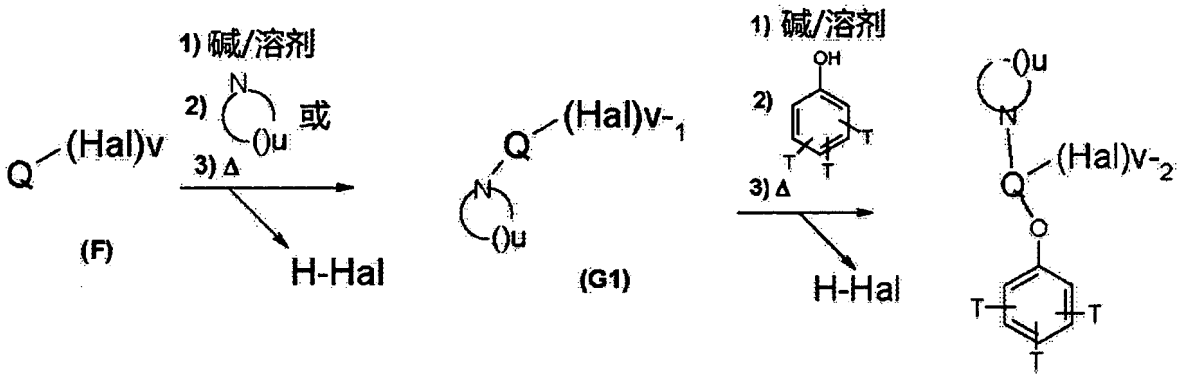

1) 碱/溶剂
2)
或
3) Δ
(F)
H-Hal
(G1)
1) 碱/溶剂
2) P-OH
3) Δ
H-Hal
或
(G1')

(2)

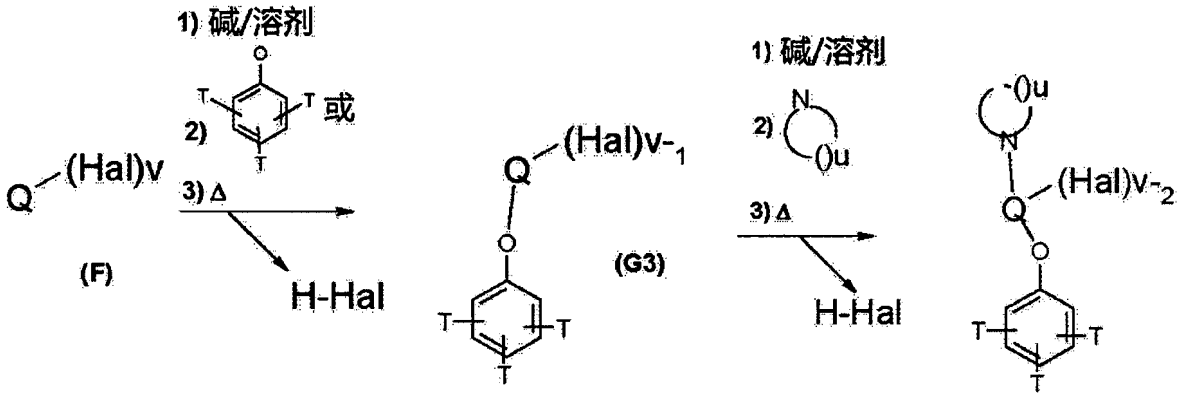

1) 碱/溶剂
2) P-OH
3) Δ
(F)
(G2)
1) 碱/溶剂
2)
或
3) Δ
H-Hal
或
(G2')

[0120]

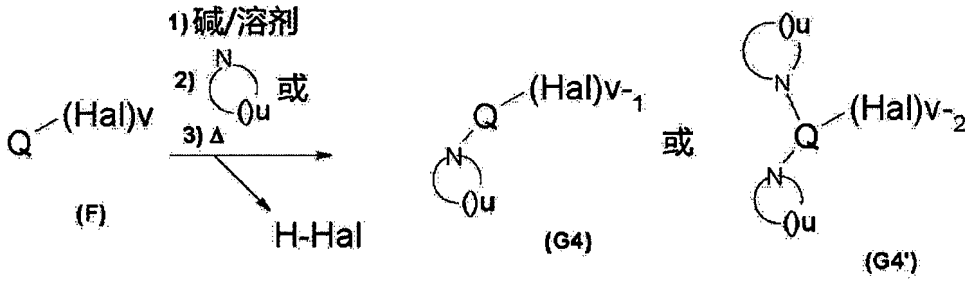
(3)


1) 碱/溶剂
2)
或
3) Δ
Q
(Hal)v
(F)
H-Hal
(Hal)v-1
(G1)
1) 碱/溶剂
2)
3) Δ
H-Hal
(Hal)v-2

(4)

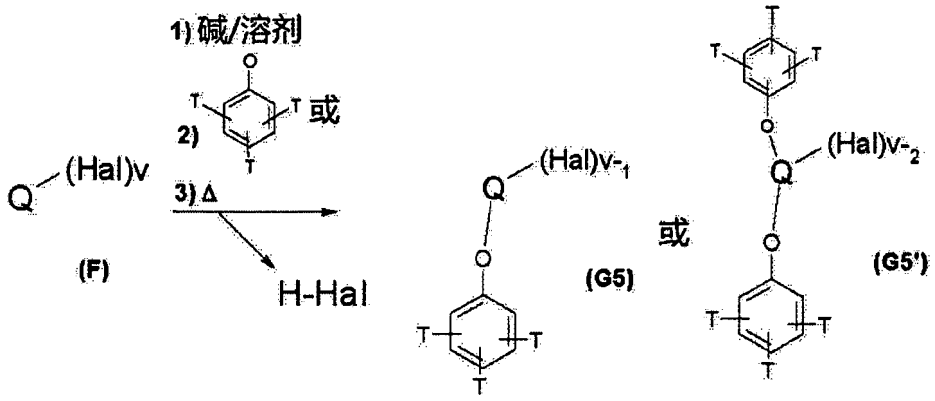

1) 碱/溶剂
2)
或
3) Δ
Q
(Hal)v
(F)
H-Hal
(Hal)v-1
(G3)
1) 碱/溶剂
2)
3) Δ
H-Hal
(Hal)v-2

(5)


1) 碱/溶剂
2)
或
3) Δ
Q
(Hal)v
(F)
H-Hal
(Hal)v-1
(G4)
或
(Hal)v-2
(G4')

[0121]

(6)



[0122] 其中 P 和 Q 如上定义；

[0123] 其中 T 选自但不限于卤素（例如 F、Cl、Br 和 I）、硝基、氰基、NRR'、SO_3H 和 COOH 以及这些磺酸和羧酸基团的盐和衍生物（例如碱金属与碱土金属如 Na、K、Ca 和 Mg 的盐，酯，如 C_1-C_4 烷基酯，和酰胺，如具有 NRR' 作为酰胺基部分的酰胺）、OH、包含最多三个作为环成员的选自 O、N 和 S 的杂原子和 3 至大约 8 个环成员的杂环烷基、以及包含 1 至大约 10 个碳原子（例如 1、2、3、4、5 或 6 个碳原子）的烷基（包括环烷基）和烷氧基（包括环烷氧基）；

[0124] Hal 代表卤素；

[0125] () 代表 CH_2，其中至少一个 CH_2 基团可以被 O、NH 或 S 替代；

[0126] u 为 2 至 7；

[0127] v 为 2 至 8 的整数；

[0128] 并且符号“Δ”代表施加热（加热）。

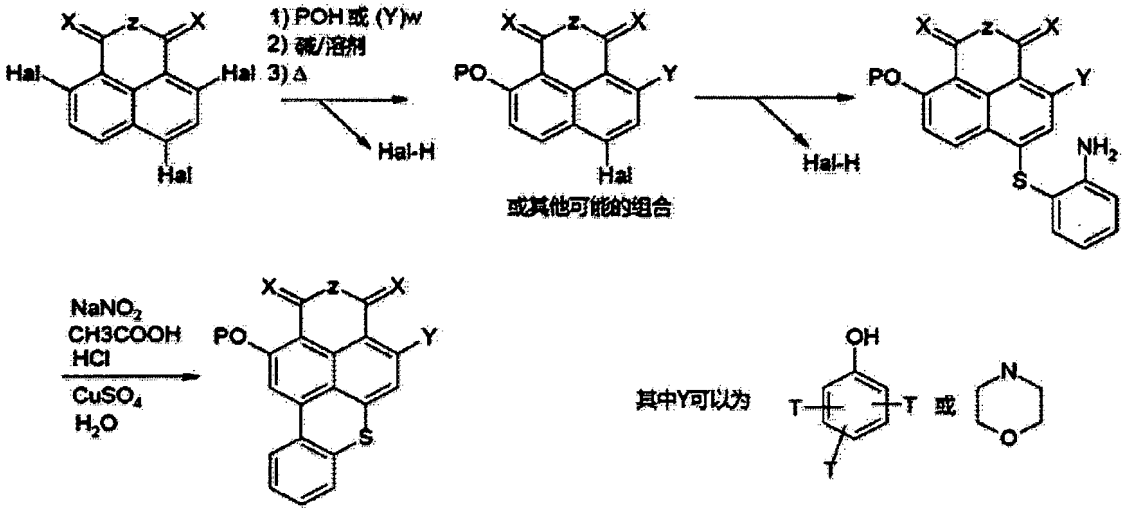
[0129] F 是具有如上定义的 Q 核心的卤化化合物。G1 或 G2 或 (G3) 是运行方法 (1) 或 (2) 或 (3) 或 (4) 时反应的中间产物。

[0130] 在运行导致化合物 (G4) 或 (G5) 或 (G4') 或 (G5') 的方法 (5) 和 (6) 的情况下，v 为 1 至 8 的整数。

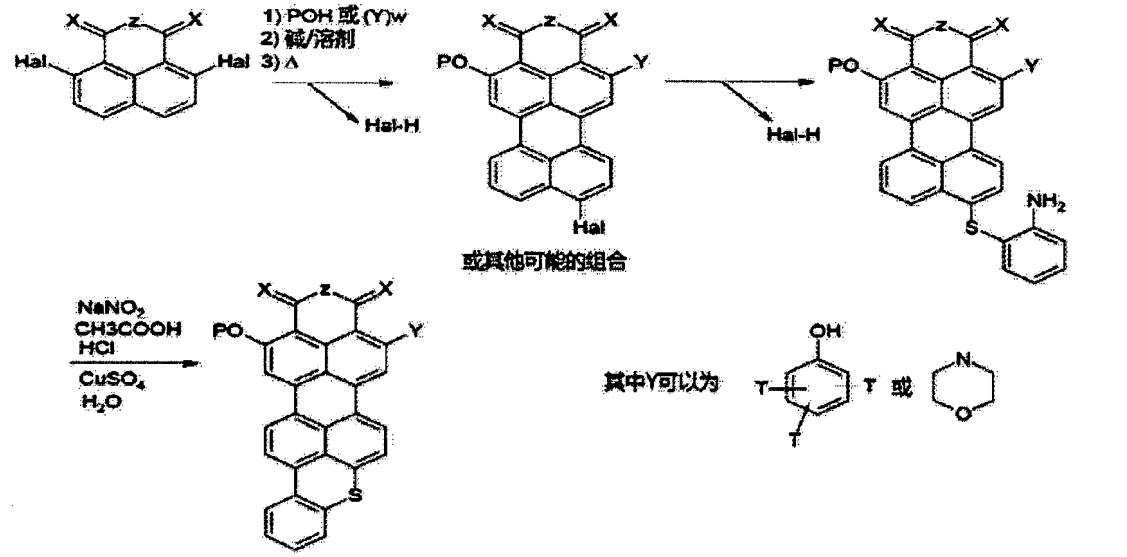
[0131] 其它替代方法也可能获得式 (1) 的化合物，如方法 (7) 或 (8)：

[0132]

(7)



(8)



[0133] 其中 T、Hal、X、Z、POH、Y 和 w 的定义与上文定义的相同。

[0134] 要理解的是，虽然上述反应图示显示了其中在第一步骤后获得的化合物与一种或多种附加化合物反应的反应，这些反应图示还显示了其中式 Q-(Hal)$_v$ 的化合物的仅一个卤素原子被选自含 N 脂环族化合物、式 P-OH 的聚合化合物和任选取代的酚类化合物所替代的本发明的化合物、如式 (1) 的那些的制造方法，即，其中该方法在第一步骤后完成（即将不发生进一步的反应）。

[0135] 如果要选择上述方法中的一种，通常优选采用提供表现出更高溶解度的中间产物（在第一步骤后）的方法。

[0136] 适用于催化亲核取代反应的无机和有机碱的实例对本领域技术人员而言是公知的。合适的无机碱的实例是 K_2CO_3。反应温度通常为大约 50℃至大约 140℃，取决于所用溶剂的沸点。通常进一步合意的是采用消泡剂如聚乙二醇或其衍生物。反应产物（例如式 (1) 的聚合物键合的化合物）通常可以从所得反应混合物中分离并任选通过常规手段如过

滤、离心、萃取、色谱方法等等来提纯。

[0137] 式 Q-(Hal)$_v$ 的化合物（或类似化合物）对式 P-OH 的聚合化合物（或类似聚合化合物）的重量比取决于几个因素，如式 Q-(Hal)$_v$ 的化合物的分子量、键合到单个聚合物分子上的式 Q-(Hal)$_v$ 的化合物的平均数量或键合到单个式 Q-(Hal)$_v$ 的化合物（或类似化合物）上的聚合物分子的平均数量。特别地，在本发明的聚合物键合的化合物中，单个聚合物分子 P 可以具有一个或超过一个键合于其上的单元 Q（例如平均 1、2、3、4 个单元 Q）。相反，一个或超过一个聚合物分子（例如平均 1、2、3、4 或更多聚合物分子）可以键合到单个单元 Q 上。还要理解的是，不仅可以使用单一化合物，还可以使用具有不同 v 值（甚至不同 u 值）的化合物的混合物作为上述反应图示所代表的反应中的原材料和中间产物。例如，式 Q-(Hal)$_v$ 的原材料可以是其中 v 代表 5 或 6 的两种化合物的混合物（未考虑位置异构体）。同样，如果使用也称为 (G) 的单一的式 Q-(Hal)$_v$ 的化合物，取决于反应条件，在第一反应后获得的中间产物可以是单一化合物或化合物的混合物，如其中例如 1、2 或 3 个卤素原子被基团 P-O- 或 N- 杂脂环族环所替代的三种化合物的混合物（未考虑位置异构体）。

[0138] 进一步有可能（有时优选）的是相对于式 Q-(Hal)$_v$ 的化合物（或类似化合物）使用相对大的化学计量过量的聚合物。这会获得其中仅少部分（例如不超过大约 0.1%、不超过大约 0.5%、不超过大约 1% 或不超过大约 2%，，不超过大约 4%，不超过大约 6%，不超过大约 8%，不超过大约 10%）具有至少一个键合于其上的单元 Q 的聚合物分子，由此提供本发明的掺杂聚合物。该掺杂聚合物可用于可采用本发明的聚合物键合的化合物相同的用途，例如用作印刷油墨组合物的组分。

[0139] 当然有可能令一种式 Q-(Hal)$_v$ 的化合物（或类似化合物）与超过一种（或超过一种类型的）聚合物反应。作为非限制性实例，式 Q-(Hal)$_v$ 的化合物（或类似化合物）可以与上述式 (2) 的聚合物的混合物反应。相反，两种或多种不同的式 Q-(Hal)$_v$ 的化合物（例如两种或多种具有不同的 v 值和 / 或不同的 Hal 含义的化合物）可以与单一（类型）的聚合物反应（键合于其上）。最后，两种或多种不同的式 Q-(Hal)$_v$ 的化合物（或类似化合物）可以与两种或多种（类型）聚合物反应，尽管这通常会导致难以控制反应混合物。

[0140] 本发明的印刷油墨组合物包含（优选极性的）液体介质和溶解或分散在该介质中的一种或多种（类型）的通式 (1) 的化合物和 / 或上述其它式的化合物（例如通式 (1) 或任何其它式的一种、两种或三种不同化合物的混合物）。该介质中通式 (1) 的化合物和 / 或其它式的化合物的浓度取决于几个因素，如含 Q 化合物键合于其上的聚合物、所需颜色强度、液体介质、组合物的其余（任选）组分、该印刷油墨组合物的预期用途、以及该印刷油墨要施加到其上的基底。通常，印刷油墨组合物中一种或多种通式 (1) 的化合物和 / 或其它式的化合物的（总）浓度为该组合物总重量的至少大约 0.01 重量%、至少大约 0.02 重量%、或至少 0.05 重量%，并通常不高于大约 40 重量%，例如不高于大约 20 重量%、不高于大约 10 重量% 或不高于大约 5 重量%。使用不同化合物的混合物允许复杂的标记以提供有利的组成，以使得文件难以被伪造。因此，例如，印刷油墨组合物中不同化合物的混合物允许具有独特的“化学密钥”的标记，该标记可以通过改变组合物中包含的浓度和 / 或化合物来进行微调。

[0141] 印刷油墨组合物的预期用途是确定通式 (1) 的化合物和 / 或其它式的化合物的合适且合意的浓度范围以及该组合物的合适或合意的任选组分的类型与浓度范围的多个因

素之一。存在许多不同类型的印刷工艺。其非限制性实例包括喷墨印刷（热、压电、连续等等）、苯胺印刷、雕刻印刷（例如凹版印刷）、丝网印刷、凸版印刷、胶版印刷、移印印刷、浮凸印刷、平版印刷和轮转凹版印刷。在一个优选实施方案中，本发明的印刷油墨组合物（至少）适于喷墨印刷。工业喷墨印刷机，通常用于调节线路 (conditioning lines) 与印刷机上的编号、编码与标记应用，是特别合适的。优选的喷墨印刷机包括单喷嘴连续喷墨印刷机（也称为逐线或多层偏离印刷机）及按需滴墨喷墨印刷机，特别是阀式喷墨印刷机。因此，印刷油墨组合物的以下讨论主要涉及用于喷墨印刷的组合物。但是，应当记住，本发明不限于用于喷墨印刷的印刷油墨组合物，而是涵盖了其中可以使用本发明的化合物的所有印刷油墨组合物。因此，以下注意事项和声明比照适用于其中根据本发明的教导可以使用该化合物的所有印刷油墨组合物。

[0142] 印刷油墨通常包含着色剂和液体载体 (vehicles)，其包含在溶剂中的树脂粘合剂溶液。粘合剂和溶剂的具体选择取决于多个因素，如该化合物、要存在的其余组分、以及待印刷的基底的性质。用于喷墨印刷的油墨组合物中使用的合适粘合剂的非限制性实例包括常规用于喷墨印刷油墨的粘合剂，包括树脂如硝化纤维素、丙烯酸酯树脂和聚酯树脂（如来自 Evonik 的 **DYNAPOL®** L1203、L205、L206、L208、L210、L411、L651、L658、L850、L912、L952、LH530、LH538、LH727、LH744、LH773、LH775、LH818、LH820、LH822、LH912、LH952、LH530、LH538、LH727、LH744、LH773、LH775、LH818、LH820、LH822、LH823、LH826、LH828、LH830、LH831、LH832、LH833、LH838, LH898、LH908、LS436、LS615、P1500、S1218、S1227、S1247、S1249、S1252、S1272、S1401、S1402、S1426、S1450、S1510、S1606、S1611、S243、S320、S341、S361、S394 和 S EP1408）。当然，也可以使用本领域技术人员已知的其它合适树脂。该印刷油墨组合物中一种或多种粘合剂的典型（总）浓度为该组合物总重量的大约 0.5 重量％至大约 10 重量％。在这方面，还应当考虑的是喷墨印刷油墨的典型粘度值为在 25℃下大约 4 至大约 30mPa. s。

[0143] 还要理解的是，具有一个或多个键合于其上的单元 Q 的聚合物（并且在如上所述的本发明的掺杂聚合物情况下，该聚合物没有键合到任何含 Q 分子上，而是以与具有键合于其上的任何含 Q 单元的聚合物的混合物形式存在）也可以充当用于该组合物的粘合剂。无论如何，该油墨组合物的（主要）粘合剂必须与具有键合于其上的含 Q 单元的聚合物相容，例如，在与后者混合时必须不会导致形成任何不溶性物质等等。

[0144] 适用于喷墨印刷油墨的溶剂是本领域技术人员已知的。其非限制性实例包括低粘度、略微极性和非质子的有机溶剂，例如甲基乙基酮 (MEK)、丙酮、乙酸乙酯、3- 乙氧基丙酸乙酯、甲苯及其两种或多种的混合物。

[0145] 特别地，如果本发明的印刷油墨组合物通过连续喷墨印刷施加的话，该组合物通常还包含至少一种导电性赋予剂（例如盐）。该导电性赋予剂将具有在组合物中不可忽略的溶解度。合适的导电性赋予剂的非限制性实例包括盐类，如四烷基铵盐（例如硝酸四丁基铵、高氯酸四丁基铵和六氟磷酸四丁基铵）、碱金属硫氰酸盐，如硫氰酸钾，碱性钾盐如 KPF_6 和碱金属高氯酸盐，如高氯酸锂。该导电性赋予剂将以足以提供所需或合意的导电性的浓度存在。当然，可以使用两种或多种不同的导电性赋予剂（盐）的混合物。通常，两种或多种导电性赋予剂将以该组合物总重量的大约 0.1 重量％至 2 重量％的总浓度存在。

[0146] 本发明的印刷油墨组合物可以进一步以其惯用量包含一种或多种惯用添加剂，如

杀真菌剂、杀生物剂、表面活性剂、螯合剂、pH 调节剂等。此外，该印刷油墨组合物可以包含一种或多种赋予特定光学性质的附加着色剂和 / 或组分（即不同于本发明的聚合物键合的化合物的组分）。这些附加组分可以选自例如常规颜料和染料、发光（例如荧光）颜料和染料、以及胆甾型和 / 或向列型液晶。发光颜料的实例包括某些种类的无机化合物，如非发光性阳离子的硫化物、氧硫化物、磷酸盐、钒酸盐、石榴石、尖晶石等等，其掺杂有至少一种发光的过渡金属或稀土金属阳离子。为了强化该油墨组合物的安全性，该油墨组合物可以进一步包含一种或多种在电磁波谱的可见或不可见区域中吸收的颜料和 / 或染料和 / 或可以进一步包含一种或多种发光性的颜料和 / 或染料。在电磁波谱的可见或不可见区域中吸收的合适的颜料和 / 或染料的非限制性实例包括酞菁衍生物。合适的发光颜料和 / 或染料的非限制性实例包括镧系元素衍生物。颜料和 / 或染料的存在将提高和强化该标识针对假冒的安全性。

[0147] 要提供本发明的标识和 / 或防伪标记的基底或制品没有特殊限制，可以具有多种类型。该基底或制品可以例如（基本）由以下的一种或多种组成或包含以下的一种或多种：金属（例如为容器形式，例如用于盛装各种物体如饮料或食品的罐头）、光学纤维、机织织物、涂层及其等同物、塑料材料、陶瓷材料、玻璃（例如为胶囊或容器形式，如用于盛装各种物体如饮料或食品的瓶子）、硬纸板、包装、纸张和聚合物材料。要指出的是，这些基底材料仅出于例示目的给出，而不限制本发明的范围。

[0148] 此外该基底可以已经带有至少一个标识或防伪元素，其包含选自以下的物质：例如无机发光化合物、有机发光化合物、IR 吸收剂、磁性材料、法医学标记及其组合。该标识或防伪元素可以以标记或数据矩阵形式存在，在基底表面上或并入（嵌入）基底本身中。该标识还可以以肉眼可见和 / 或不可见的云点或特定图案的形式存在，其随机或非随机地分布在该物体或制品或商品或安全文件或上述意在被保护和 / 或认证的物品中。

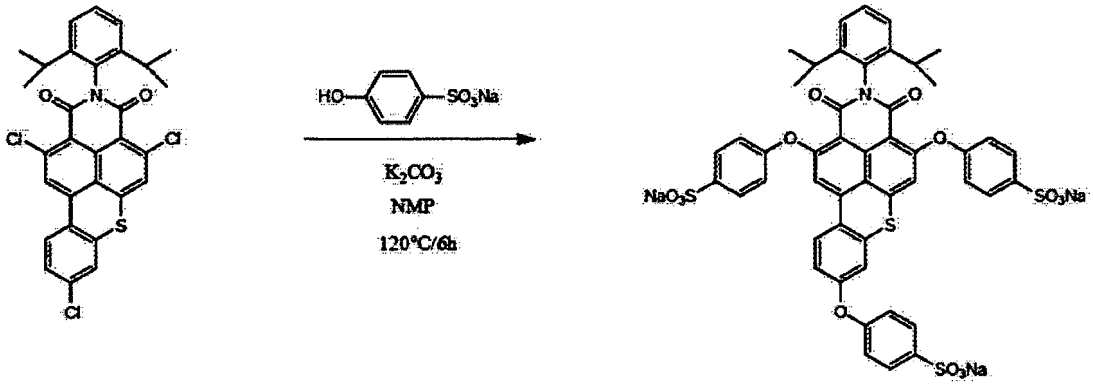
[0149] 将参照实施例更具体地解释本发明。但是，本发明的范围不限于下列实施例。

[0150] 实施例

[0151] 制备 4,4',4''-((2-(2,6- 二异丙基苯基)-1,3- 二氧代 -2,3- 二氢 -1H- 噻吨并 [2,1,9-def] 异喹啉 -4,8,12- 三基）三（氧基））三苯磺酸盐 (4,4',4''-((2-(2,6-diisopropylphenyl)-1,3-dioxo-2,3-dihydro-1H-thioxantheno[2,1,9-def]isoquinoline-4,8,12-triyl)tris(oxy))tribenzenesulfonate)。4,4',4''-((2-(2,6- 二异丙基苯基)-1,3- 二氧代 -2,3- 二氢 -1H- 噻吨并 [2,1,9-def] 异喹啉 -4,8,12- 三基）三（氧基））三苯磺酸钠的橙色固体。

[0152] 将化合物 4,8,12- 三氯 -2-(2,6- 二异丙基苯基)-1H- 噻吨并 [2,1,9-def] 异喹啉 -1,3(2H)- 二酮 (0.3 克）、4- 羟基苯磺酸钠 (0.41 克）和无水碳酸钾 (0.73 克）添加到 10 毫升 N- 甲基 -2- 吡咯烷酮 (NMP) 中。溶液在良好搅拌下在 130℃下加热 4 小时。在沸腾后再 4 小时，将溶液在室温下冷却，一分钟后将该液体添加到二氯甲烷 (100 毫升）中，将沉淀物过滤并在 60℃下加热以获得 4,4',4''-((2-(2,6- 二异丙基苯基)-1,3- 二氧代 -2,3- 二氢 -1H- 噻吨并 [2,1,9-def] 异喹啉 -4,8,12- 三基）三（氧基））三苯磺酸钠的橙色固体。4,4',4''-((2-(2,6- 二异丙基苯基)-1,3- 二氧代 -2,3- 二氢 -1H- 噻吨并 [2,1,9-def] 异喹啉 -4,8,12- 三基）三（氧基））三苯磺酸钠的橙色固体 (0.1 克）以 18.0％的标称产率获得。MS：基峰 (base peak)1046

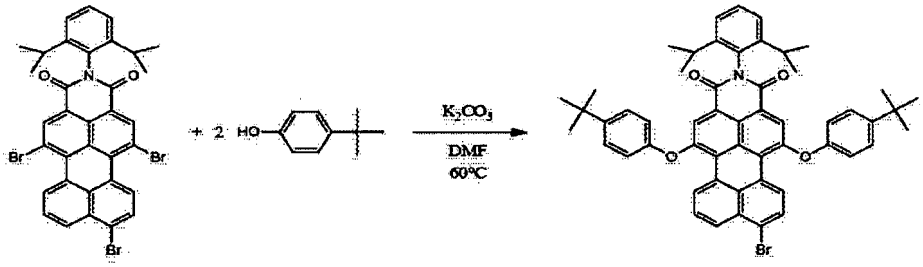
[0153]



[0154] 制备8-溴-5,12-双(4-(叔丁基)苯氧基)-2-(2,6-二异丙基苯基)-1H-苯并[5,10]蒽[2,1,9-def]异喹啉-1,3(2H)-二酮(8-bromo-5,12-bis(4-(tert-butyl)phenoxy)-2-(2,6-diisopropylphenyl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione)。

[0155] 将化合物8,5,8,12-三溴-2-(2,6-二异丙基苯基)-1H-苯并[5,10]蒽[2,1,9-def]异喹啉-1,3(2H)-二酮(5.0克)、4-(叔丁基)酚(2.09克)和无水碳酸钾(2.18克)添加到166毫升N,N-二甲基甲酰胺(DMF)中。溶液在良好搅拌下在60℃下加热4小时。在沸腾后再4小时,将溶液在室温下冷却,一分钟后将该液体添加到30%的盐酸水溶液(600毫升)中,过滤并在60℃下加热以获得8-溴-5,12-双(4-(叔丁基)苯氧基)-2-(2,6-二异丙基苯基)-1H-苯并[5,10]蒽[2,1,9-def]异喹啉-1,3(2H)-二酮的红色固体。固体在色谱柱上提纯以除去副产物。8-溴-5,12-双(4-(叔丁基)苯氧基)-2-(2,6-二异丙基苯基)-1H-苯并[5,10]蒽[2,1,9-def]异喹啉-1,3(2H)-二酮的红色固体(4.24克)以71.1%的标称产率获得。RMN-H(CDCl3)MS:基峰855。

[0156]

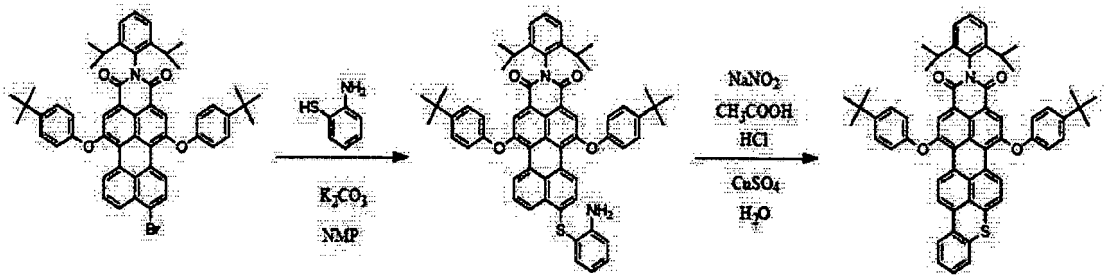


[0157] 制备5,15-双(4-(叔丁基)苯氧基)-2-(2,6-二异丙基苯基)-1H-噻吨并[2',1',9':10,5,6]蒽[2,1,9-def]异喹啉-1,3(2H)-二酮(5,15-bis(4-(tert-butyl)phenoxy)-2-(2,6-diisopropylphenyl)-1H-thioxantheno[2',1',9':10,5,6]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione)。

[0158] 将化合物8-溴-5,12-双(4-(叔丁基)苯氧基)-2-(2,6-二异丙基苯基)-1H-苯并[5,10]蒽[2,1,9-def]异喹啉-1,3(2H)-二酮(3.0克)、2-氨基苯硫醇(0.48克,过量10%)和无水碳酸钾(0.24克)添加到30毫升的N-甲基-2-吡咯烷酮(NMP)中。快速加热该溶液并回流30分钟。在一分钟后将该液体添加到2%的盐酸水溶液(250毫升)中,并随后静置过夜,过滤并在105℃下干燥以获得8-((2-氨基苯基)硫基)-5,12-双

(4-(叔丁基)苯氧基)-2-(2,6-二异丙基苯基)-1H-苯并[5,10]蒽[2,1,9-def]异喹啉-1,3(2H)-二酮的红蓝色固体(2.06克),标称产率为60.0%。将8-((2-氨基苯基)硫基)-5,12-双(4-(叔丁基)苯氧基)-2-(2,6-二异丙基苯基)-1H-苯并[5,10]蒽[2,1,9-def]异喹啉-1,3(2H)-二酮(2.06克)溶解在温暖的冰醋酸(12毫升)和浓盐酸(1.3毫升)中,获得细悬浮液。将该悬浮液冷却至0℃并加入亚硝酸钠(0.16克)在水(3.6毫升)中的溶液,继续搅拌直至澄清。在良好的搅拌下在1小时内将制备的溶液添加到水合硫酸铜(2.6克)在水(60毫升)中的沸腾溶液中。在沸腾后再1小时,将溶液冷却,过滤并获得蓝红色固体。用温暖的氢氧化钠溶液(20毫升,3%)洗涤该固体三次并在色谱柱上提纯以除去副产物。以34.2%的标称产率获得5,15-双(4-(叔丁基)苯氧基)-2-(2,6-二异丙基苯基)-1H-噻吨并[2',1',9':10,5,6]蒽[2,1,9-def]异喹啉-1,3(2H)-二酮(0.69克)的蓝色固体。MS:基峰884。

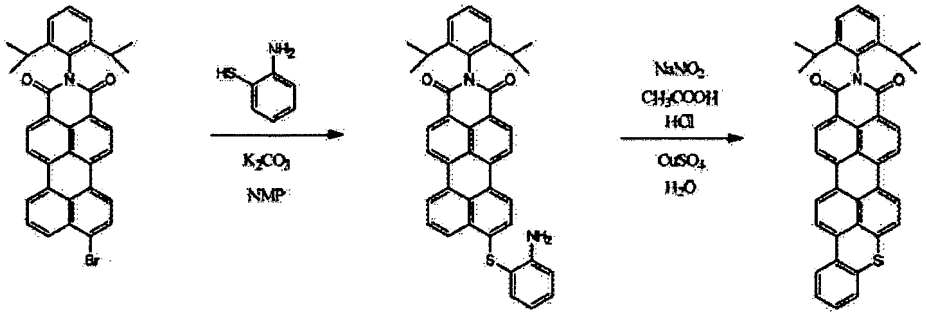
[0159]



[0160] 制备2-(2,6-二异丙基苯基)-1H-噻吨并[2',1',9':10,5,6]蒽[2,1,9-def]异喹啉-1,3(2H)-二酮(2-(2,6-diisopropylphenyl)-1H-thioxantheno[2',1',9':10,5,6]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione)。

[0161] 将化合物8-溴-2-(2,6-二异丙基苯基)-1H-苯并[5,10]蒽[2,1,9-def]异喹啉-1,3(2H)-二酮(9.0克)、2-氨基苯硫醇(2.19克,过量10%)和无水碳酸钾(1.10克)添加到100毫升的N-甲基-2-吡咯烷酮(NMP)中。快速加热该溶液并回流30分钟。在一分钟后将该液体添加到2%的盐酸水溶液(750毫升)中,并随后静置过夜,过滤并在105℃下干燥,以86.3%的标称产率获得8-((2-氨基苯基)硫基)-2-(2,6-二异丙基苯基)-1H-苯并[5,10]蒽[2,1,9-def]异喹啉-1,3(2H)-二酮的红蓝色固体(8.31克)。将8-((2-氨基苯基)硫基)-2-(2,6-二异丙基苯基)-1H-苯并[5,10]蒽[2,1,9-def]异喹啉-1,3(2H)-二酮(5.15克)溶解在温暖的冰醋酸(31毫升)和浓盐酸(3.1毫升)中,获得细悬浮液。将该悬浮液冷却至0℃并加入亚硝酸钠(0.6克)在水(9毫升)中的溶液,继续搅拌直至澄清。在良好的搅拌下在1小时内将制备的溶液添加到水合硫酸铜(9.7克)在水(150毫升)中的沸腾溶液中。在沸腾后再1小时,将溶液冷却,过滤并获得蓝色固体。用温暖的氢氧化钠溶液(50毫升,3%)洗涤该固体三次并在色谱柱上提纯以除去副产物。以36.5%的标称产率获得2-(2,6-二异丙基苯基)-1H-噻吨并[2',1',9':10,5,6]蒽[2,1,9-def]异喹啉-1,3(2H)-二酮的蓝色固体(1.82克)。MS:基峰587。

[0162]



[0163] 本发明的油墨含有至少一种本发明的式 (1) 和 / 或其它式的化合物。可以使用的此类油墨的实例具有下列配方并适用于喷墨印刷机。

[0164] 油墨配方 1

[0165]

组分	功能	重量%
硝化纤维素	粘合剂树脂	1.5
高氯酸锂	用于导电性的盐	0.5
5,15-双(4-(叔丁基)苯氧基)-2-(2,6-二异丙基苯基)-1H-噻吨并[2',1',9':10,5,6]蒽[2,1,9-def]异喹啉-1,3(2H)-二酮	染料	1.0
丙酮	溶剂	97.0

[0166] 本发明的油墨不仅是基于根据本发明的式 (1) 和 / 或其它式的一种染料，而可以是导致复合油墨的式 (1) 和 / 或其它式的不同染料的混合物，如具有多重荧光性质，并可用于防止伪造和 / 或假冒。

[0167] 要注意的是，前述实施例仅为说明目的提供，而不以任何方式解释为限制本发明。虽然已经参照示例性实施方案描述了本发明，要理解的是，本文中所用的言辞是说明和例示的言辞而非限制的言辞。在其方面内在不离开本发明的范围与精神的情况下，在所附权利要求的范围内可以进行修改，如目前的说明和修正的那样。尽管已经参照特定装置、材料和实施方案描述了本发明，并不欲将本发明限制于本文中公开的细节；相反，本发明延伸至所有功能上等效的结构、方法与用途，如在所附权利要求的范围内。

Abstract

Polycyclic aromatic hydrocarbon compounds of formula (I) having an S atom or $S(=O)_2$ moiety incorporated in their basic polycyclic structure that can have a nitrogen-containing heterocycloaliphatic group and/or a substituted or unsubstituted phenoxy group and/or a polymeric moiety bonded to the polycyclic structure and to compositions such as, e.g., printing inks which comprise these polycyclic aromatic hydrocarbons as colorants.