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(54) **OLIGOMERIC AND POLYMERIC OLED MATERIALS PRODUCED VIA ARYLATION OF QUINONES**

OLIGOMERE UND POLYMERE MATERIALIEN FÜR OLED'S HERGESTELLT DURCH ARYLIERUNG VON CHINON-DERIVATEN

MATERIAUX POUR SYSTEMES ILLUMINANTS ORGANIQUES OLIGOMERES ET POLYMERES PRODUITS PAR ARYLATION DE QUINONES

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(56) References cited:
EP-A- 0 130 056 **US-A- 4 814 403**
US-A- 5 585 454 **US-A- 5 646 232**

- **YAMAMOTO T ET AL: "PREPARATION OF PI-CONJUGATED POLY(HYDROQUINONE-2,5-DIYL) AND POLY(P-BENZOQUINONE-2,5-DIYL) AND THEIR ELECTROCHEMICAL BAHAVIOR" MACROMOLECULES, AMERICAN CHEMICAL SOCIETY. EASTON, US, vol. 31, no. 8, 21 April 1998 (1998-04-21), pages 2683-2685, XP000750172 ISSN: 0024-9297**
- **TOUR J M: "SOLUBLE OLIGO- AND POLYPHENYLENES" ADVANCED MATERIALS, VCH VERLAGSGESELLSCHAFT, WEINHEIM, DE, vol. 6, no. 3, 1 March 1994 (1994-03-01), pages 190-198, XP000429216 ISSN: 0935-9648**

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Description

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims the benefit of provisional U.S. application Serial No. 60/195,902, filed April 10, 2000, the disclosure of which is incorporated herein by reference.

STATEMENT AS TO RIGHTS TO INVENTIONS MADE UNDER FEDERALLY SPONSORED RESEARCH AND DEVELOPMENT

[0002] Not applicable

BACKGROUND OF THE INVENTION

[0003] Organic light emitting devices (OLEDs) are comprised of several thin layers of organic materials. These layers can be made to electroluminesce by applying a voltage across the device, and with sufficient brightness, range of color and operating lifetimes can be a practical alternative to LCD-based full color flat-panel displays. By placing red (R), green (G), and blue (B) emitting organic materials in a vertically stacked geometry with other transparent thin organic films, a new OLED display pixel is achieved which can be fabricated simply and provide a cost effective display panel.

[0004] In general, these OLED devices rely on a common mechanism leading to optical emission. Typically, this mechanism is based upon the radiative recombination of a trapped charge. Specifically, OLEDs will contain at least two thin organic layers separating the anode and cathode of the device. The material of one of these layers is specifically chosen based on the material's ability to transport holes, a "hole transporting layer" (HTL), and the material of the other layer is specifically selected according to its ability to transport electrons, an "electron transporting layer" (ETL). With such a construction, the device can be viewed as a diode with a forward bias when the potential applied to the anode is higher than the potential applied to the cathode. Under these bias conditions, the anode injects holes (positive charge carriers) into the hole transporting layer, while the cathode injects electrons into the electron transporting layer. The portion of the luminescent medium adjacent to the anode thus forms a hole injecting and transporting zone while the portion of the luminescent medium adjacent to the cathode forms an electron injecting and transporting zone. The injected holes and electrons each migrate toward the oppositely charged electrode. When an electron and hole localize on the same molecule, a Frenkel exciton is formed. Recombination of this short-lived state may be visualized as an electron dropping from its conduction potential to a valence band, with relaxation occurring, under certain conditions, preferentially via a photoemissive mechanism. Under this view of the mechanism of operation of typical thin-layer organic devices, the electroluminescent layer comprises a luminescence zone receiving mobile charge carriers (electrons and holes) from each electrode.

[0005] The materials that function as the electron transporting layer of the OLED are frequently the same materials that are incorporated into the OLED to produce the electroluminescent emission. Such devices in which the electron transporting layer functions as the emissive layer are referred to as having a single heterostructure. Alternatively, the electroluminescent material may be present in a separate emissive layer between the hole transporting layer and the electron transporting layer in what is referred to as a double heterostructure.

[0006] In addition to emissive materials that are present as the predominant component in the electron transporting layer, and that function both as the electron transporting material as well as the emissive material, the emissive material may itself be present in relatively low concentrations as a dopant in the electron transporting layer. Whenever a dopant is present, the predominant material in the electron transporting layer may be referred to as a host material. Materials that are present as host and dopant are selected so as to have a high level of energy transfer from the host to the dopant material. In addition, these materials need to be capable of producing acceptable electrical properties for the OLED. Furthermore, such host and dopant materials are preferably capable of being incorporated into the OLED using starting materials that can be readily incorporated into the OLED by using convenient fabrication techniques, in particular, by using vacuum-deposition techniques.

[0007] It is desirable for OLEDs to be fabricated using materials that provide electroluminescent emission in a relatively narrow band centered near selected spectral regions, which correspond to one of the three primary colors, red, green and blue so that they may be used as a colored layer in an OLED or stacked OLED. Additionally, the compounds should come from a class of compounds in which the emission may be varied by selectively varying the substituents or by modifying the structure of a base compound that produces emission from a charge transfer transition. Still further, the compounds should be capable of being readily deposited as a thin layer using vapor-phase or vacuum deposition techniques so that the compound can be readily incorporated into an OLED that is prepared entirely from, for example, vacuum-deposited organic materials. Still other considerations for new OEL materials involves considerations of environmental stability, cycle life and ease of fabrication. In order to ensure environmental stability and long cycle life, the

organic phosphors should be as inert to unwanted chemical and electrochemical reactions as possible.

[0008] A candidate structure in terms of stability would be polyparaphenylene (PPP), a polymer composed of a sequence of linearly connected benzene rings. PPP has excellent stability and luminescence properties, but is neither soluble in organic solvents nor volatile. As a result, PPP cannot be deposited as a thin film on a substrate surface to allow fabrication of a useful display device.

[0009] EP-A-0130056 discloses fluorinated polyphenylenes which may be used in a variety of applications, including as photoconducting polymers. However, the paraphenylene compounds disclosed in this document are insoluble in nonpolar organic solvents.

[0010] Other types of para-phenylene compounds are disclosed in US 5,646,232. In particular, rigid-rod and segmented rigid-rod polymers are disclosed in this document for a variety of applications focussed towards improving the strength of composite materials.

[0011] What is needed in the art are new polyparaphenylene materials that have suitable solubility and or deposition properties and further have the desired luminescence properties. Surprisingly, the present invention provides such compounds.

SUMMARY OF THE INVENTION

[0012] In one aspect, the present invention provides an oligomeric para-phenylene compound having the formula:

$$R^1\text{-}(Ar^i)_n\text{-}R^2$$

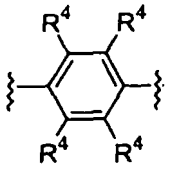
wherein the subscript n is an integer of from 5 to 15; the superscript i is an integer of from 1 to n and denotes the position downstream from R^1; each Ar^i is a substituted or unsubstituted aryl group; R^1 and R^2 are each substituents that increase the solubility of the para-phenylene compound in nonpolar organic solvents relative to the solubility of the corresponding compound wherein R^1 and R^2 are hydrogen; with the proviso that the Ar^i groups are linked together in a 1,4-paraphenylene manner.

[0013] The substituents R^1 and R^2 each independently have the formula:

$$R^3\text{-}(Ar^j)_m\text{-}$$

wherein the subscript m is an integer of from 1 to 5; the superscript j is an integer of from 1 to m and denotes the position of each Ar^j away from R^3. Each Ar^j is selected from:

a) a 1,4-phenylene group having the formula:



wherein each R^4 is independently selected from H, substituted or unsubstituted (C_1-C_{12})alkyl, substituted or unsubstituted (C_1-C_{12})alkoxy, substituted or unsubstituted (C_1-C_{12})alkylamino, substituted or unsubstituted (C_1-C_{12}) alkylthio, substituted or unsubstituted di(C_1-C_{12})alkylamino, substituted or unsubstituted arylamino, substituted or unsubstituted diarylamino and halogen, with the proviso that at least two of the four R^4 substituents are independently selected from substituted or unsubstituted (C_1-C_{12})alkyl and substituted or unsubstituted (C_1-C_{12})alkoxy, and

b) an aryl biradical selected from 1,4-naphthylene, 1,4-anthrylene, 9,10-anthrylene, 5,6,7,8-tetrahydronaphth-1,4-ylene, 9,9', 10,10'-tetra(C_1-C_{12})alkyl-9,10-dihydroanthr-1,4-ylene, 9,9'10,10'-tetraaryl-9,10-dihydroanthr-1,4-ylene, 9,9' 10,10'-tetra(C_1-C_{12})alkyl-9,10-dihydroanthr-2,6-ylene, and 9,9'10,10'-tetraaryl-9,10-dihydroanthr-1,4-ylene; and R^3 is selected from H, substituted or unsubstituted (C_1-C_{12})alkyl, substituted or unsubstituted (C_1-C_{12})alkoxy, substituted or unsubstituted (C_1-C_{12})alkylamino, substituted or unsubstituted (C_1-C_{12})alkylthio, substituted or unsubstituted di(C_1-C_{12})alkylamino, substituted or unsubstituted arylamino, substituted or unsubstituted diarylamino and halogen, with the proviso that the Ar^i groups are linked together in a 1,4-paraphenylene manner.

[0014] In another aspect, the present invention provides a method of forming a light emitting polymer, the method comprising exposing an oligomeric para-phenylene compound of claim 1 having attached acrylate ester groups to sufficient ultraviolet light to form a light emitting polymer comprising a plurality of oligomeric para-phenylene compounds

covalently attached to each other via ester and ether linkages.

[0015] In yet another aspect, the present invention provides a light emitting polymer, which comprises a plurality of oligomeric para-phenylene compounds covalently attached to each other via ester and ether linkages and which is obtained by a method as described above. An organic light emitting device (OLED) comprising a compound as defined above, is also provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016]

Figure 1 illustrates one scheme for preparing oligomeric para-phenylene compounds.
Figure 2 illustrates a scheme for preparing fluoro- and alkoxy-substituted para-phenylene oligomers.
Figures 3 and 4 illustrate schemes for preparing para-phenylene compounds having an even number of phenylene groups.
Figure 5 illustrates a scheme for preparing a para-phenylene oligomer having two diarylamino groups at the termini.
Figure 6 illustrates a scheme for the preparation of para-phenylene compounds on a solid support.
Figures 7 illustrate the preparation of polymerized light emitting polymers.

DETAILED DESCRIPTION OF THE INVENTION

Abbreviations and Definitions

[0017] The term "alkyl," by itself or as part of another substituent, means, unless otherwise stated, a straight or branched chain, or cyclic hydrocarbon radical, or combination thereof, which may be fully saturated, mono- or polyunsaturated and can include di- and multivalent radicals, having the number of carbon atoms designated *(i.e.* C_1-C_8 means one to eight carbons). Examples of saturated hydrocarbon radicals include groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, isobutyl, sec-butyl, cyclohexyl, (cyclohexyl)ethyl, cyclopropylmethyl, homologs and isomers of, for example, n-pentyl, n-hexyl, n-heptyl, n-octyl, and the like. An unsaturated alkyl group is one having one or more double bonds or triple bonds. Examples of unsaturated alkyl groups include vinyl, 2-propenyl, crotyl, 2-isopentenyl, 2-(butadienyl), 2,4-pentadienyl, 3-(1,4-pentadienyl), ethynyl, 1- and 3-propynyl, 3-butynyl, and the higher homologs and isomers. The term "alkyl," unless otherwise noted, is also meant to include those derivatives of alkyl defined in more detail below as "heteroalkyl," "cycloalkyl" and "alkylene." The term "alkylene" by itself or as part of another substituent means a divalent radical derived from an alkane, as exemplified by-$CH_2CH_2CH_2CH_2$-. Typically, an alkyl group will have from 1 to 24 carbon atoms, with those groups having 8 or fewer carbon atoms being preferred in the present invention.

[0018] The terms "alkoxy," "alkylamino" and "alkylthio" (or thioalkoxy) are used in their conventional sense, and refer to those alkyl groups attached to the remainder of the molecule via an oxygen atom, an amino group, or a sulfur atom, respectively. Similarly, the term dialkylamino (or diarylamino) refers to an amino group having two attached alkyl groups (or aryl groups) that can be the same or different.

[0019] The term "heteroalkyl," by itself or in combination with another term, means, unless otherwise stated, a stable straight or branched chain, or cyclic hydrocarbon radical, or combinations thereof, consisting of the stated number of carbon atoms and from one to three heteroatoms selected from the group consisting of O, N, Si and S, and wherein the nitrogen and sulfur atoms may optionally be oxidized and the nitrogen heteroatom may optionally be quatemized. The heteroatom(s) O, N and S may be placed at any interior position of the heteroalkyl group. The heteroatom Si may be placed at any position of the heteroalkyl group, including the position at which the alkyl group is attached to the remainder of the molecule. Examples include $-CH_2-CH_2-O-CH_3$, $-CH_2-CH_2-NH-CH_3$, $-CH_2-CH_2-N(CH_3)-CH_3$, $-CH_2-S-CH_2-CH_3$, $-CH_2-CH_2-S(O)-CH_3$, $-CH_2-CH_2-S(O)_2-CH_3$, $-CH=CH-O-CH_3$, $-Si(CH_3)_3$, $CH_2-CH=N-OCH_3$, and $-CH=CH-N(CH_3)-CH_3$. Up to two heteroatoms may be consecutive, such as, for example, $-CH_2-NH-OCH_3$ and $-CH_2-O-Si(CH_3)_3$.

[0020] The terms "cycloalkyl" and "heterocycloalkyl", by themselves or in combination with other terms, represent, unless otherwise stated, cyclic versions of "alkyl" and "heteroalkyl", respectively. Additionally, for heterocycloalkyl, a heteroatom can occupy the position at which the heterocycle is attached to the remainder of the molecule. Examples of cycloalkyl include cyclopentyl, cyclohexyl, 1-cyclohexenyl, 3-cyclohexenyl, cycloheptyl, and the like. Examples of heterocycloalkyl include 1 -(1,2,5,6-tetrahydropyridyl), 1-piperidinyl, 2-piperidinyl, 3-piperidinyl, 4-morpholinyl, 3-morpholinyl, tetrahydrofuran-2-yl, tetrahydrofuran-3-yl, tetrahydrothien-2-yl, tetrahydrothien-3-yl, 1-piperazinyl, 2-piperazinyl, and the like.

[0021] The terms "halo" or "halogen," by themselves or as part of another substituent, mean, unless otherwise stated, a fluorine, chlorine, bromine, or iodine atom.

[0022] The term "aryl," employed alone or in combination with other terms *(e.g.,* aryloxy, arylthioxy, arylalkyl) means, unless otherwise stated, an aromatic substituent which can be a single ring or multiple rings (up to three rings) which

are fused together or linked covalently. The rings may each contain from zero to four heteroatoms selected from N, O, and S, wherein the nitrogen and sulfur atoms are optionally oxidized, and the nitrogen atom(s) are optionally quatemized. The aryl groups that contain heteroatoms may be referred to as "heteroaryl" and can be attached to the remainder of the molecule through a heteroatom Non-limiting examples of aryl groups include phenyl, 1-naphthyl, 2-naphthyl, 4-biphenyl, pyrazinyl, 2-pyridyl, 3-pyridyl, 4-pyridyl, 2-pyrimidyl, 4-pyrimidyl, 1-isoquinolyl, 5-isoquinolyl, 5-quinoxalinyl and 5-quinolyl. Substituents for each of the above noted aryl ring systems are selected from the group of acceptable substituents described below. The term "arylalkyl" is meant to include those radicals in which an aryl group is attached to an alkyl group (e.g., benzyl, phenethyl, pyridylmethyl and the like) or a heteroalkyl group (e.g., phenoxymethyl, 2-pyridyloxymethyl, 3-(1-naphthyloxy)propyl, and the like). When the above-noted aryl groups occupy "interior" positions in an OLED material, one of skill in the art will understand that the linkage listed will also include the appropriate "para phenylene" position. For example, recitation above of 2-pyridyl will also include a pyridyl ring attached to other aryl rings via the 2- and 5-positions.

[0023] Each of the above terms (e.g.. "alkyl," "heteroalkyl" and "aryl") are meant to include both substituted and unsubstituted forms of the indicated radical. Preferred substituents for each type of radical are provided below.

[0024] Substituents for the alkyl and heteroalkyl radicals (including those groups often referred to as alkylene, alkenyl, heteroalkylene, heteroalkenyl, alkynyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, and heterocycloalkenyl) can be a variety of groups selected from: -OR', =O, =NR', =N-OR', -NR'R", -SR', -halogen, -SiR'R"R'", -OC(O)R', -C(O)R',-CO_2R', CONR'R", -OC(O)NR'R", -NR"C(O)R', -NR'-C(O)NR"R'", -NR"$C(O)_2$R', -NH-$C(NH_2)$=NH, -NR'$C(NH_2)$=NH, -NH-$C(NH_2)$=NR', -S(O)R', -$S(O)_2$R', -$S(O)_2$NR'R", -CN and -NO_2 in a number ranging from zero to (2N+ 1), where N is the total number of carbon atoms in such radical. One of skill in the art will appreciate that the extreme end, 2N+ 1, when N is 2 or more, is meant to include those polyhaloalkyl groups such as perfluoroethyl and the like. The groups R', R" and R'" each independently refer to hydrogen, unsubstituted(C_1-C_8)alkyl and heteroalkyl, unsubstituted aryl, aryl substituted with 1-3 halogens, unsubstituted alkyl, alkoxy or thioalkoxy groups, or aryl-(C_1-C_4)alkyl groups. When R' and R" are attached to the same nitrogen atom, they can be combined with the nitrogen atom to form a 5-, 6-, or 7-membered ring. For example, -NR'R" is meant to include 1-pyrrolidinyl and 4-morpholinyl. From the above discussion of substituents, one of skill in the art will understand that the term "alkyl" in its broadest sense is meant to include groups such as haloalkyl *(e.g.,* -CF_3 and -CH_2CF_3) and acyl *(e.g.,* -C(O)CH_3, -C(O)CF_3, - C(O)CH_2OCH_3, and the like). Preferably, the alkyl groups will have from 0-3 substituents, more preferably 0, 1, or 2 substituents, unless otherwise specified.

[0025] Similarly, substituents for the aryl and heteroaryl groups are varied and are selected from: -halogen, -OR', -OC(O)R', -NR'R", -SR', -R', -CN, -NO_2 -CO_2R', -CONR'R", -C(O)R', -OC(O)NR'R", -NR"C(O)R', -NR"$C(O)_2$R', ,-NR'-C(O)NR"R'", -NH-$C(NH_2)$=NH, -NR'$C(NH_2)$=NH, -NH-$C(NH_2)$=NR', -S(O)R', -$S(O)_2$R', -$S(O)_2$NR'R", - N_3, -$CH(Ph)_2$, perfluoro(C_1-C_4)alkoxy, and perfluoro(C_1-C_4)alkyl, in a number ranging from zero to the total number of open valences on the aromatic ring system; and where R', R" and R'" are independently selected from hydrogen, (C_1-C_8)alkyl and heteroalkyl, unsubstituted aryl and heteroaryl, (unsubstituted aryl)-(C_1-C_4)alkyl, and (unsubstituted aryl)oxy-(C_1-C_4)alkyl.

[0026] As used herein, the term "heteroatom" is meant to include oxygen (O), nitrogen (N), sulfur (S) and silicon (Si).

General

[0027] A polyphenylene oligomer, p-hexaphenyl (PHP) has poor solubility, but can be vacuum sublimed onto a substrate surface to produce a stable and highly efficient electroluminescent device. By selectively introducing substituents onto the polyphenylene oligomer, new OEL materials can be prepared which alter the emission spectrum and allow dissolution in common solvents.

[0028] The present invention provides compounds, compositions and methods for the preparation of OEL materials. In general, the materials can be constructed using an extension of the coupling of aryl diazonium salts with quinones (see, Koch, U.S. Patent No. 4,288,147). Thus, the linear non-condensed polycyclic quinone produced by Koch can provide a convenient synthetic pathway to a variety of substituted oligomeric paraphenylene compounds. Figure 1 provides a general method to the preparation of an alkoxy-substituted heptaphenylene compound. In this scheme, the alkoxy groups can be the same or different. Additionally, the chlorine substituents on benzoquinone (2,5-dichloro-1,4-benzoquinone) serve to direct the subsequent arylation reactions into a proper 1,4-paraphenylene substitution pattern, and can be further manipulated or reduced at a later stage of synthesis.

[0029] Other compositions of the invention include "branched" polymers of aryl groups, block copolymers, polyfurano ladder oligomers, as well as crosslinked oligomeric paraphenylene compounds.

Description of the Embodiments

Oligomeric Para-Phenylene Compounds

[0030] In one aspect, the present invention provides an oligomeric para-phenylene compound having the formula:

$$R^1\text{-}(Ar^i)_n\text{-}R^2 \qquad (I)$$

wherein the subscript n is an integer of from 5 to 15; the superscript i is an integer of from 1 to n and denotes the position downstream from R^1; each Ar^i is a substituted or unsubstituted aryl group; R^1 and R^2 are each substituents that increase the solubility of the para-phenylene compound in nonpolar organic solvents relative to the solubility of the corresponding compound wherein R^1 and R^2 are hydrogen; with the proviso that the Ar^i groups are linked together in a 1,4-paraphenylene manner. Thus, the formula above is meant to include compounds represented by, for example, $R^1\text{-}Ar^1\text{-}Ar^2\text{-}Ar^3\text{-}Ar^4\text{-}Ar^5\text{-}Ar^6\text{-}R^2$;
$R^1\text{-}Ar^1\text{-}Ar^2\text{-}Ar^3\text{-}Ar^4\text{-}Ar^5\text{-}Ar^6\text{-}Ar^7\text{-}Ar^8\text{-}Ar^9\text{-}R^2$; and
$R^1\text{-}Ar^1\text{-}Ar^2\text{-}Ar^3\text{-}Ar^4\text{-}Ar^5\text{-}Ar^6\text{-}Ar^7\text{-}Ar^8\text{-}Ar^9\text{-}Ar^{10}\text{-}Ar^{11}\text{-}R^2$, wherein each of the Ar groups can be the same or different, but wherein a coplanar arrangement is maintained.

[0031] Accordingly, in the present invention, the phrase "linked together in a 1,4-paraphenylene manner" refers to a linkage between aryl (or arylene) groups in which a coplanar orientation is maintained that allows cross conjugation and electron delocalization between rings. For example, phenyl (or phenylene) is linked in a 1,4 manner wherein adjacent Ar^i groups are attached at the 1- and 4-positions (relative to each other) on the phenyl or phenylene ring. Similarly, for fused polycyclic ring systems (e.g., naphthylene), the adjacent Ar^i groups are attached at the 2- and 6-positions and not the 1- and 4-positions. In this manner, electron flow is not interrupted by twisting of the naphthylene ring out of a coplanar arrangement with adjacent rings.

[0032] In one group of preferred embodiments, the Ar^i groups are independently selected from unsubstituted phenylene and phenylene having from 1 to 4 fluoro substituents. In another group of preferred embodiments, the Ar^i groups are independently selected from unsubstituted phenylene, phenylene having from 1 to 4 fluoro substituents; and substituted or unsubstituted fused polycyclic aryl with the proviso that any fused polycyclic aryl groups are linked in the compound in a manner that maintains a coplanar orientation relative to the adjacent Ar^i groups. More preferably, the fused polycyclic aryl groups are selected from substituted or unsubstituted 2,6-naphthylene, 2,7-phenanthrylene, 2,6-anthrylene, and 2,6-carbazolylidene, with the proviso that the substituents on the fused polycyclic rings do not disturb the coplanar arrangement of the Ar^i groups.

[0033] In another group of preferred embodiments, the subscript n is an integer of from 5 to 9. Still further preferred are those embodiments in which the subscript n is 7 and Ar^3 and Ar^5 are substituted or unsubstituted 2,6-naphthylene.

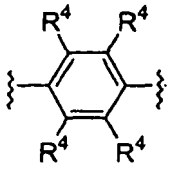
[0034] The substituents R^1 and R^2 are selected to increase the solubility of the oligomer in a nonpolar organic solvent such as toluene or xylene, relative to the solubility of the oligomer wherein R^1 and R^2 are each hydrogen.

[0035] R^1 and R^2 each independently have the formula:

$$R^3\text{-}(Ar^j)_m\text{-}$$

wherein the subscript m is an integer of from 1 to 5; the superscript j is an integer of from 1 to m and denotes the position downstream of (or away from) R^3 for each Ar^j; and each Ar^j is selected from:

a) a 1,4-phenylene group having the formula:

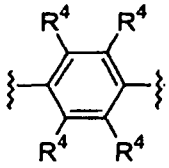


wherein each R^4 is independently selected from H, substituted or unsubstituted (C_1-C_{12})alkyl, substituted or unsubstituted (C_1-C_{12})alkoxy, substituted or unsubstituted (C_1-C_{12})alkylamino, substituted or unsubstituted (C_1-C_{12})alkylthio, substituted or unsubstituted di(C_1-C_{12})alkylamino, substituted or unsubstituted arylamino, substituted or unsubstituted diarylamino and halogen, with the proviso that at least two of the four R^4 substituents are independently selected from substituted or unsubstituted (C_1-C_{12})alkyl and substituted or unsubstituted (C_1-C_{12})alkoxy, and

b) an aryl biradical selected from 1,4-naphthylene, 1,4-anthrylene, 9,10-anthrylene, 5,6,7,8-tetrahydronaphth-1,4-ylene, 9,9',10,10'-tetra(C_1-C_{12})alkyl-9,10-dihydroanthr-1,4-ylene, 9,9'10,10'-tetraaryl-9,10-dihydroanthr-1,4-ylene, 9,9' 10,10'-tetra(C_1-C_{12})alkyl-9,10-dihydroanthr-2,6-ylene, and 9,9' 10,10'-tetraaryl-9,10-dihydroanthr-1,4-ylene; and R^3 is selected from H, substituted or unsubstituted (C_1-C_{12})alkyl, substituted or unsubstituted (C_1-C_{12})alkoxy, substituted or unsubstituted (C_1-C_{12})alkylamino, substituted or unsubstituted (C_1-C_{12})alkylthio, substituted or unsubstituted di(C_1-C_{12})alkylamino, substituted or unsubstituted arylamino, substituted or unsubstituted diarylamino

and halogen.

[0036] For these embodiments, the R^3 group and Ar^j groups are selected to interrupt the linear rod-like symmetry achieved with the oligomeric $(Ar^i)_n$ portion of the compound. Accordingly, for the aryl groups in this part of the molecule, substituents are selected and sites of attachment are selected that result in Ar^j groups twisting out of a coplanar arrangement and thereby increasing the solubility of the entire oligomer. In one group of preferred embodiments, each Ar^j is a 1,4-phenylene group having the formula:

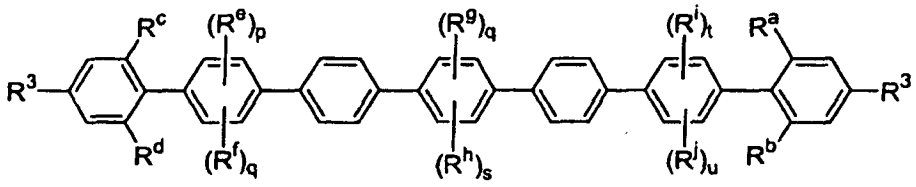


wherein each R^4 is independently selected from H, substituted or unsubstituted $(C_1\text{-}C_{12})$alkyl, substituted or unsubstituted $(C_1\text{-}C12)$alkoxy, substituted or unsubstituted $(C_1\text{-}C_{12})$alkylamino, substituted or unsubstituted $(C_1\text{-}C_{12})$alkylthio, substituted or unsubstituted di$(C_1\text{-}C_{12})$alkylamino, substituted or unsubstituted arylamino, substituted or unsubstituted diarylamino and halogen, with the proviso that at least two of the four R^4 substituents are independently selected from substituted or unsubstituted $(C_1\text{-}C_{12})$alkyl and substituted or unsubstituted $(C_1\text{-}C_{12})$alkoxy. More preferably, at least two of the four R^4 substituents are substituted or unsubstituted $(C_1\text{-}C_{12})$alkoxy.

[0037] In other preferred embodiments, m is an integer of from 1 to 3 and each Ar^j is a substituted or unsubstituted ring system selected from 1,4-naphthylene, 1,4-anthrylene, 9,10-anthrylene, 5,6,7,8-tetrahydronaphth-1,4-ylene, 9,9', 10,10'-tetra$(C_1\text{-}C_{12})$alkyl-9,10-dihydroanthr-1,4-ylene, 9,9' 10,10'-tetraaryl-9,10-dihydroanthr-1,4-ylene, 9,9' 10,10'-tetra$(C_1\text{-}C_{12})$alkyl-9,10-dihydroanthr-2,6-ylene, and 9,9'10,10'-tetraaryl-9,10-dihydroanthr-1,4-ylene. More preferably, m is one or two and each Ar^j is selected from substituted or unsubstituted 1,4-naphthylene, 1,4-anthrylene and 9,10-anthrylene.

[0038] In still other preferred embodiments, R^3 is selected from substituted or unsubstituted $(C_1\text{-}C_{12})$alkyl, substituted or unsubstituted $(C_1\text{-}C_{12})$alkoxy, substituted or unsubstituted $(C_1\text{-}C_{12})$alkylamino, substituted or unsubstituted di$(C_1\text{-}C_{12})$alkylamino, substituted or unsubstituted arylamino, and substituted or unsubstituted diarylamino.

[0039] In another group of particularly preferred embodiments, the oligomeric para-phenylene compound has the formula:

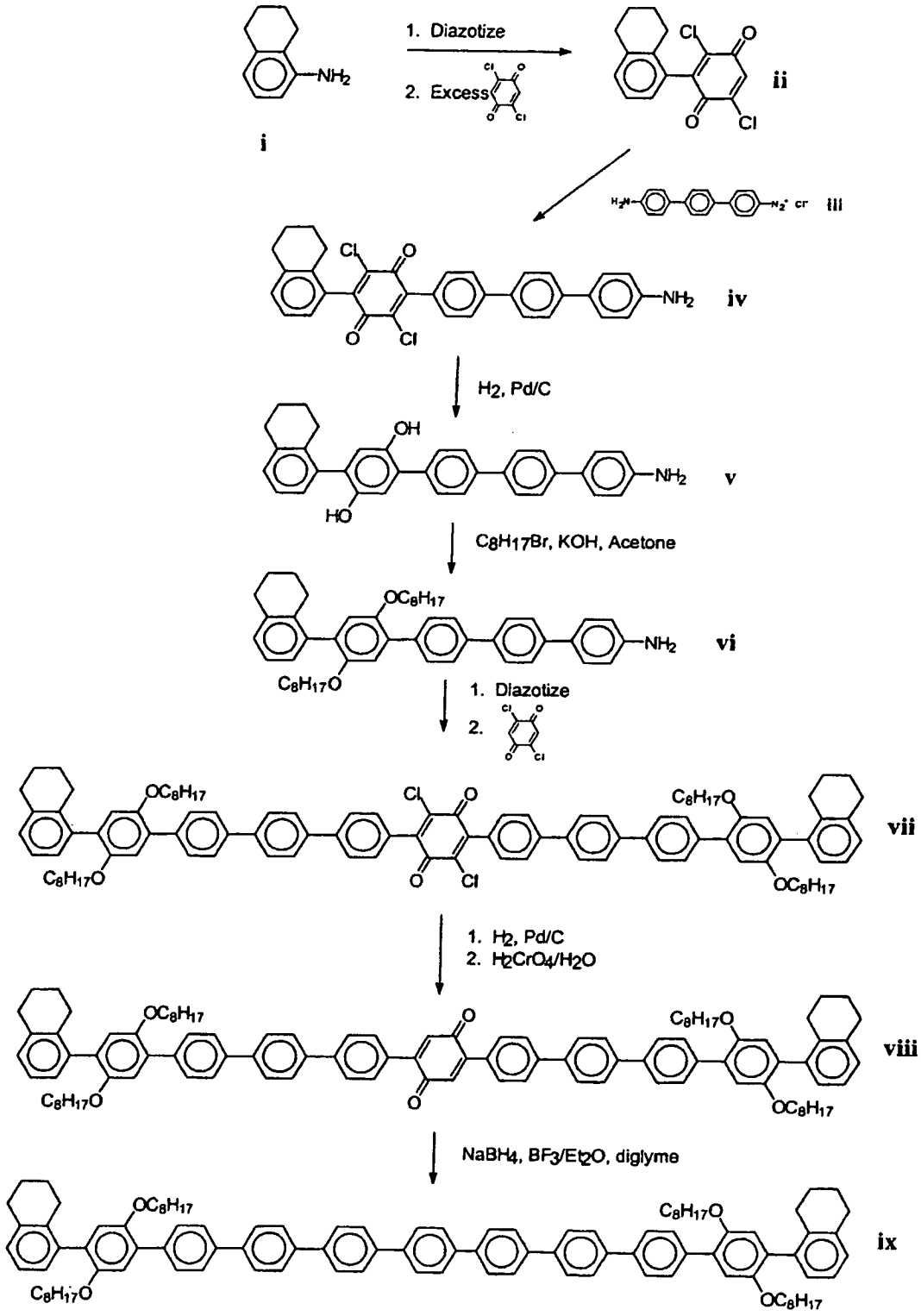


(II)

wherein each of R^a, R^b, R^c and R^d is independently selected from substituted or unsubstituted $(C_1\text{-}C_{12})$alkyl and substituted or unsubstituted $(C_1\text{-}C_{12})$alkoxy; the subscripts p, q, r, s, t and u are each independently integers of from 0 to 2; and each of R^e, R^f, R^g, R^h, R^i and R^j are independently a halogen, preferably fluorine. Still further preferred are those embodiments in which each of R^a, R^b, R^c and R^d is substituted or unsubstituted $(C_1\text{-}C_{12})$alkoxy, more preferably methoxy or ethoxy; the subscripts p, q, r, s, t and u are each 1; and each of R^e, R^f, R^g, R^h, R^i and R^j are halogen, preferably fluorine.

[0040] Scheme 1 is illustrative of methods useful in preparing compounds of this aspect of the invention.

Scheme 1



[0041] Synthesis in Scheme 1, begins with 5,6,7,8-tetrahydro-1-naphthylamine i (Aldrich Chemical Co., Milwaukee, Wisconsin, USA). Compound i can be converted to its corresponding diazonium salt according to established methods. Subsequent treatment of the diazonium salt with excess 2,5-dichloro-1,4-benzoquinone produces ii. Reaction of ii with iii (produced by diazotization of 4,4"-diamino-p-terphenyl (from Lancaster Synthesis, Inc.)) provides the adduct iv, which can be reduced to dihydroxy compound v and alkylated with, for example, octyl bromide in KOH and acetone, to provide

vi. Diazotization of vi and reaction with 0.5 equivalents of 2,5-dichloro-1,4-benzoquinone provides the bis-adduct, vii. The chloro groups of vii can be removed by hydrogenolysis over a palladium on carbon catalyst, and the resulting hydroquinone can be oxidized to the quinone viii using chromic acid. Reduction of viii to ix is accomplished, preferably using sodium borohydride in a solution of boron trifluoride etherate and diglyme.

[0042] Additional methodologies utilizing aryl diazonium couplings to produce para-phenylene oligomers of the present invention (and related derivatives) are provided in Figures 1-11. One of skill in the art will appreciate that the methods disclosed therein and described in further detail below can be adapted to the preparation of numerous substituted and unsubstituted versions of the claimed compounds, simply by small alterations in the starting materials used.

Methods of Preparing Oligomeric Para-Phenylene Compounds

[0043] The linear oligomers of the present invention can be prepared by a variety of methods.

[0044] Figure 1 illustrates one scheme toward the preparation of the subject compounds. In this Figure, an aryl diazonium salt (xxv) is combined with 2,5-dichloro-1,4-benzoquinone (Aldrich Chemical Co., Milwaukee, Wisconsin, USA) to produce an aryl substituted benzoquinone (xxvi). Treatment of xxvi with a second aryl diazonium salt (xxvii) provides comopund **xxviii**. To obtain symmetrical OEL materials, two equivalents of xxviii are oxidized to the corresponding diazonium salt and combined with another equivalent of 2,5-dichloro-1,4-benzoquinone to provide xxix. Hydrogenolysis removes the chloro substituents and provides a hydroquinone species which can then be oxidized to the quinone (chromic acid) and reduced to the target compound xxx with sodium borohydride and boron trifluoride etherate. In this scheme, the two O-alkyl groups (shown as OR) can be the same or different depending on diazonium salts used in the conversion of xxviii to xxix. A variety of starting aryl diazonium salts are known in the literature (see, Zollinger, DIAZO CHEMISTRY, VOL 1, AROMATIC AND HETEROAROMATIC COMPOUNDS, Wiley (1994)).

[0045] Other substituents can be introduced by means of arylation of quinones. For example, metathesis of 2,5-dichloro-1,4-benzoquinone provides 2,5-difluoro-1,4-benzoquinone xxxi in which the fluoro substituents are resistant to hydrogenolysis (see Figure 2). Proceeding with the scheme outlined in Figure 1, but substituting 2,5-difluoro-1,4-benzoquinone for 2,5-dichloro-1,4-benzoquinone, provides compounds of formula **xxxii**.

[0046] Generally, Figures 1 and 2 provide oligomeric para-phenylene compounds having odd numbers of phenyl rings. Alternative approaches (shown in Figures 3 and 4) result in oligomers of even numbered aryl rings.

[0047] In Figure 3, the diquinone 2,5,2',5'-tetrachlorobibenzoquinone (**xxxii**i, see Koch, U.S. Patent No. 4,288,147) can be treated with two equivalents of diazonium salt xxvii to provide **xxxiv**. Formation of the bis diazonium salt of **xxxiv** and reaction of that salt with a suitably blocked benzoquinone (**xxxv**) provides a compound of formula **xxxvi**, which upon hydrogenolysis and strong reduction provides the target compound **xxxvii**.

[0048] Figure 4 illustrates another approach for preparing oligomers having an even number ofphenylene groups. In this scheme, benzidene diamine is converted to the bis diazonium salt **xxxviii** for use as a starting material. The diazonium salt is reacted with two equivalents of **xxvi**, to produce intermediate **xxxix**. Again, hydrogenolysis and strong reduction of **xxxix** provides a target compound, **xl.**

[0049] In still other embodiments, the oligomeric para-phenylene compounds have diarylamino groups at each terminus. One route for the preparation of such compounds is illustrated in Figure 5. Here, triphenylamine (Aldrich Chemical Co.) is nitrated under conditions sufficient to product a mono-nitro product **xli**. Friedel-Crafts acylation of the two remaining para positions provides **xlii,** which can be reduced to the corresponding amine, and diazotized to provide **xliii.** Reaction of **xliii** with excess 2,5-dichloro-1,4-benzoquinone provides **xliv**. Coupling of two equivalents of **xliv** to the bis diazonium salt **xlv** provides intermediate **xlvi.** Hydrogenolysis and reduction of **xlvi** leads to compounds of formula **xlvii.**

Preparation of OEL materials on a solid surface

[0050] In addition to the methods for preparing oligomeric para-phenylene compounds described above, the present invention further provides methods for the preparation of such materials on a solid support. These methods are useful for preparing such oligomers that will ultimately be cleaved from the support, and also for preparing oligomers that are attached at the site of their utility.

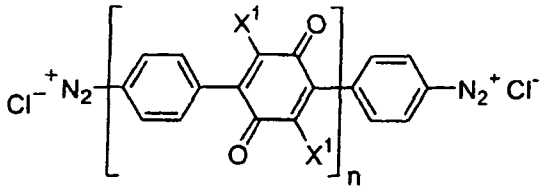
[0051] Figure 6 provides a general scheme for the preparation of oligomeric or polymeric para-phenylene compounds on a solid support. In this figure, a solid support (e.g., glass or an indium-tin oxide surface, lvi) is treated with an arylalkyl silane (e.g., triethoxy 4-(4-aminophenyl)butylsilane, lvii, from United Chemical Technologies, Bristol, Pennsylvania) to form a surface having a layer of attached aryl amine groups (lviii). Diazotization of the arylamines and reaction with 2,5-dichloro-1,4-benzoquinone provides a surface as shown in **lix.** Subesquent treatment of the derivatized surface **lix** with a diazonium species (e.g., **lx**) provides surface **lxi.** A second iteration of diazotization and subsequent reaction with 2,5-dichloro-1,4-benzoquinone provides surface **lxii.** Treatment of surface **lxii** with benzene diazonium chloride in aqueous ethanol provides surface **lxiii** which can be reduced and alkylated (e.g., with methyl iodide) to provide the surface **lxiv.** One of skill in the art will appreciate that the surface or support-bound chemistry can be modified to produce a variety

of surfaces having bound oligomeric or polymeric para-phenylene compounds using the reactions outlined in Figures 1-5 above.

[0052] Accordingly, a method of preparing a polymeric OLED material on a solid support, the method comprising:

(a) contacting a solid support-bound aryl diazonium salt with 3,6-dichloroquinone under conditions sufficient to form a solid support-bound aryl quinone derivative; and

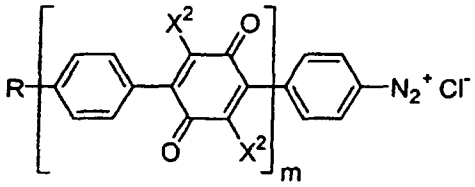
(b) contacting said solid support-bound aryl quinone derivative with a diazonium compound having the formula:



wherein each X^1 is a blocking group and the subscript n is an integer of from 0 to 4; under conditions sufficient to form an intermediate poly OLED material;

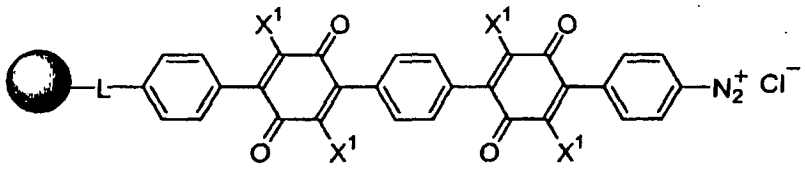
(c) repeating steps (a) and (b) from 2 to 70 times; and

(d) terminating the polymeric OLED material by contacting the product of step (c) with a terminating diazonium compound having the formula:



wherein each X^2 is a blocking group, R is a member selected from the group consisting of H, substituted or unsubstituted alkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted alkylamino, substituted or unsubstituted alkylthio, substituted or unsubstituted dialkylamino, substituted or unsubstituted arylamino and substituted or unsubstituted diarylamino; and m is an integer of from 0 to 3.

[0053] In one group of embodiments, an intermediate poly OLED material is produced having the formula:



wherein L is a linking group; the shaded sphere is a solid support; and X^1 is a member selected from the group consisting of halogen, substituted or unsubstituted alkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted alkylamino, substituted or unsubstituted alkylthio, and substituted or unsubstituted dialkylamino. Preferably, the solid support is selected from glass, tin oxide, indium oxide, and mixtures thereof.

[0054] A solid support-bound poly OLED material may also be formed by the methods above.

[0055] The solid supports used can be any of a variety of supports used and known in field of liquid-crystal display technology. Preferred supports include glass supports, tin oxide supports, indium oxide supports and tin oxide/indium oxide mixture supports.

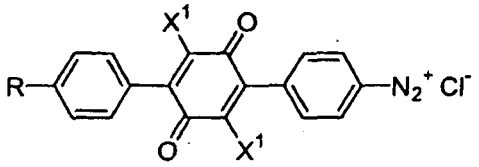
[0056] Similarly, the solid support-bound aryl diazonium salt of step (a) can encompass a variety of aryl diazonium salts which are covalently attached to the solid support. Typically, the covalent attachment is through a linking group which provides suitable spacing for the aryl diazonium salt to interact freely with molecules or reactive components exposed to the diazonium salt. The linking group is typically 6-50 atoms long and, prior to attachment to the support, will have a surface attaching portion and a longer chain portion. The surface attaching portion is that part of the linking group or spacer which is directly attached to the solid support. This portion can be attached to the solid support via

carbon-carbon bonds using, for example, supports having (poly)trifluorochloroethylene surfaces, or preferably, by siloxane bonds (using, for example, glass, silicon oxide, tin oxide or indium oxide as the solid support). Siloxane bonds with the surface of the support are formed in one embodiment via reactions of surface attaching portions bearing trichlorosilyl or trialkoxysilyl groups. At the distal end of the linking group is a site for attachment to the aryl diazonium salt component. For example, groups which are suitable for attachment to a longer chain portion would include amines, hydroxyl, thiol, and carboxyl. One of skill in the art will appreciate that cleavable linkages are preferred for those embodiments in which the poly OLED material is ultimately to be removed from the support. For those embodiments in which the poly OLED material is to remain attached to the support, a more robust linkage is preferred. For example, Figure 6 illustrates the attachment of an aryl amine (a diazonium salt precursor) to a solid support via a linking group that is covalently attached to the aryl amine through a stable carbon-carbon bond.

[0057] The solid support bound aryl diazonium salt is contacted with a substituted benzoquinone (e.g., 2,5-dichloro-1,4-benzoquinone or another suitably blocked benzoquinone) under conditions sufficient to form a solid support-bound aryl quinone derivative. The aryl quinone derivative is the species that is the result of covalent bond formation between the carbon atom bearing the diazonium moiety and a carbon atom (at a position α to a carbonyl group) of the substituted benzoquinone. A variety of conditions can be employed for forming the desired support-bound aryl quinone derivative. For example, the substituted benzoquinone can be contacted with the solid support bound aryl diazonium salt in the presence of an aqueous/organic solvent mixture (e.g., ethanol/water) at temperatures of from about 0°C to about room temperature, more preferably from about 0°C to about 10°C. The substituted benzoquinone is preferably a 2,5-disubstituted 1,4-benzoquinone, more preferably, 2,5-dichloro-1,4-benzoquinone, 2,5-dimethyl-1,4-benzoquinone, 2,5-diphenyl-1,4-benzoquinone, 2,5-dimethoxy-1,4-benzoquinone, or 4,8-dichloro-1,5-naphthoquinone, as well as related benzoquinones having alternative alkoxy, halogen or alkyl blocking groups at the 2- and 5-positions.

[0058] The aryl quinone derivative produced in step (a) is one in which a benzoquinone moiety is attached at the distal end of the nascent poly OLED material (see, for example, lix in Figure 6). Further elaboration of the poly OLED material is accomplished via reaction of a diazonium compound with the benzoquinone moiety to form a covalent linkage at the open carbon atom (see, for example, **lxi** in Figure 6). Essentially any of the diazonium salts provided in the Figures above and further referred to herein can be used.

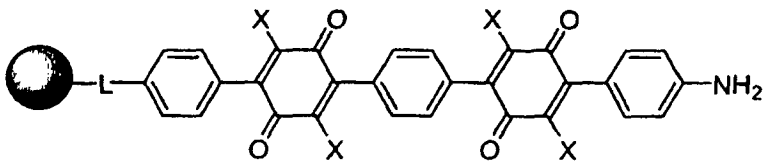
[0059] Preferably, the diazonium compound is one having the formula:



wherein the symbol R represents an amino, hydroxy, halogen, a substituted or unsubstituted alkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted alkylamino, substituted or unsubstituted alkylthio, substituted or unsubstituted dialkylamino, substituted or unsubstituted arylamino or a substituted or unsubstituted diarylamino. Protected forms of the above groups are also useful in the present invention. The letter X^1 represents a blocking group such as, for example, a halogen, substituted or unsubstituted alkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted dialkylamino, substituted or unsubstituted phenyl, and the like.

[0060] The conditions used to form the intermediate poly OLED material are essentially those conditions (solvent, temperature) described above for step (a). Preferably, the reaction is carried out in an aqueous ethanol mixture at a temperature of from 0°C to about room temperature.

[0061] In one group of particularly preferred embodiments, the intermediate poly OLED material has the formula:



wherein L is a linking group; the shaded sphere is a solid support; and X is selected from halogen, substituted or unsubstituted alkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted alkylamino, substituted or unsubstituted alkylthio, and substituted or unsubstituted dialkylamino.

Additional Uses of Condensed Poly Para-Phenylene Compounds

[0062] The arylation of quinones, described herein, can be used to prepare reactive monomers that also find utility in the preparation of crosslinked light-emitting polymers. For example, reactive monomers can be patterned like photoresists to allow patterning of red-green-blue (RGB) full-color light emitting pixels. An example of such a process is shown in Figure 7 (for poly para-phenylene compounds).

[0063] Turning first to Figure 7, alkylation of the phenolic hydroxy groups of 2,5-dihydroxyphenylene-1,4-diamine with the THP-protected form of 5-chloro-1-pentanol provides **lxv**. Oxidation of the diamine to a bis-diazonium salt and treatment of the product with excess 2,5-dichloro-1,4-benzoquinone provides lxvi. Reaction at the remaining benzoquinone centers with diazonium salt lxvii provides lxviii. Hydrogenolysis and reduction under mild conditions provides lxix. Alkylation of the hydroquinone hydroxy groups produced in the preceding step results in lxx. Removal of the THP protecting groups and acylation of the resultant hydroxyl groups with, for example, acryloyl chloride provides the diacrylate derivative **lxxi**. Exposure of the acrylate to UV light provides a crosslinked product **lxxii**.

[0064] All publications and patent applications cited in this specification are herein incorporated by reference as if each individual publication or patent application were specifically and individually indicated to be incorporated by reference. Although the foregoing invention has been described in some detail by way of illustration and example for purposes of clarity of understanding, it will be readily apparent to those of ordinary skill in the art in light of the teachings of this invention that certain changes and modifications may be made thereto without departing from the spirit or scope of the appended claims.

Claims

1. An oligomeric para-phenylene compound having the formula:

$$R^1\text{-}(Ar^i)_n\text{-}R^2$$

wherein

the subscript n is an integer of from 5 to 15;
the superscript i is an integer of from 1 to n and denotes the position downstream from R^1;

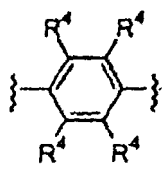
each Ar is a substituted or unsubstituted aryl group;
R^1 and R^2 are each substituents that increase the solubility of the para-phenylene compound in nonpolar organic solvents relative to the solubility of the corresponding compound wherein R^1 and R^2 are hydrogen; and each of R^1 and R^2 independently have the formula:

$$R^3\text{-}(Ar^j)_m\text{-}$$

wherein

the subscript m is an integer of from 1 to 5;
the subscript j is an integer of from 1 to m;
each Ar^j is selected from the group consisting of

a) a 1,4-phenylene group having the formula;



wherein each R^4 is a member independently selected from the group consisting of H, substituted or unsubstituted (C_1-C_{12})alkyl, substituted or unsubstituted (C_1-C_{12})alkoxy, substituted or unsubstituted (C_1-C_{12}) alkylamino, substituted or unsubstituted (C_1-C_{12})alkylthio, substituted or unsubstituted di(C_1-C_{12})alkylami-

no, substituted or unsubstituted arylamino, substituted or unsubstituted diarylamino and halogen, with the proviso that at least two of the four R^4 substituents are independently selected from substituted or unsubstituted (C_1-C_{12})alkyl and substituted or unsubstituted (C_1-C_{12})alkoxy, and
b) an aryl biradical selected from the group consisting of 1,4-naphthylene, 1,4-naphthylene, 9,10-anthrylene, 5,6,7,8-tetrahydropnaphth-1,4-ylene, 9,9',10,10'-tetra(C_1-C_{12})alkyl-9,10-dihydroanthr-1,4-ylene, 9,9', 10,10'-tetraayrl-9,10-dihydroanthr-1,4-ylene, 9,9',10,10'-tetra(C_1-C_{12})alkyl-9,10-dihydroanthr-2,6-ylene, 9,9',10,10'-tetraaryl-9,10-dihydroanthr-1,4-ylene; and

R^3 is selected from the group consisting of H, substituted or unsubstituted (C_1-C_{12})alkyl, substituted or unsubstituted (C_1-C_{12})alkoxy, substituted or unsubstituted (C_1-C_{12}) alkylamino, substituted or unsusbtituted (C_1-C_{12})alkylthio, substituted or unsubstituted di(C_1-C_{12})alkylamino, substituted or unsubstituted arylamino, substituted or unsubsituted diarylamino and halogen;
with the proviso that the Ar^i groups are linked together in a 1,4-paraphenylene manner.

2. A compound of claim 1, wherein n is an integer of from 5 to 9.

3. A compound of claim 1, wherein said Ar^i groups are independently selected from unsubstituted phenylene and phenylene having from 1 to 4 fluoro substituents.

4. A compound of claim 1, wherein m is an integer of from 1 to 3.

5. A compound of claim 1, wherein said Ar^i groups are independently selected from unsubstituted phenylene, phenylene having from 1 to 4 fluoro substituents; and substituted or unsubstituted fused polycyclic aryl with the proviso that any fused polycyclic aryl groups are linked in the compound in a manner that maintains a coplanar orientation relative to the adjacent Ar^i groups.

6. A compound of claim 5, wherein said fused polycyclic aryl groups are selected from the group consisting of 2,6-naphthylene, 2,7-phenanthyrlene, 2,6-anthrylene, and 2,6-carbazolylidene.

7. A compound of claim 1, wherein the subscript n is 7 and Ar^3 and Ar^5 are substituted and unsubstituted 2,6-naphthylene.

8. A compound of claim 1, wherein the subscript n is 7 and Ar^4 bears two substituted or unsubstituted phenyl ring substituents other than the remaining Ar^i groups.

9. An organic light emitting device (OLED) comprising a compound as defined in claim 1.

Patentansprüche

1. Oligomere para-Phenylenverbindung mit der Formel:

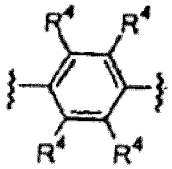
$$R^1\text{-}(Ar^i)_n\text{-}R^2$$

worin
das tiefgestellte Zeichen n für eine ganze Zahl von 5 bis 15 steht;
das hochgestellte Zeichen i für eine ganze Zahl von 1 bis n steht und die Position stromabwärts von R^1 angibt;
Ar jeweils für eine gegebenenfalls substituierte Arylgruppe steht;
R^1 und R^2 jeweils für Substituenten stehen, die die Löslichkeit der para-Phenylenverbindung in unpolaren organischen Lösungsmitteln gegenüber der Löslichkeit der entsprechenden Verbindung, in der R^1 und R^2 für Wasserstoff stehen, verbessern; und R^1 und R^2 jeweils unabhängig voneinander die Formel:

$$R^3\text{-}(Ar^j)_m\text{-}$$

aufweisen, worin
das tiefgestellte Zeichen m für eine ganze Zahl von 1 bis 5 steht;
das hochgestellte Zeichen j für eine ganze Zahl von 1 bis m steht;
Ar^j jeweils aus der Gruppe bestehend aus

a) einer 1,4-Phenylengruppe der Formel:



worin R^4 jeweils für ein unabhängig aus der Gruppe bestehend aus H, gegebenenfalls substituiertem (C_1-C_{12})-Alkyl, gegebenenfalls substituiertem (C_1-C_{12})-Alkoxy, gegebenenfalls substituiert e m (C_1-C_{12}) -Alkylamino, gegebenenfalls substituiertem (C_1-C_{12})-Alkylthio, gegebenenfalls substituiertem Di- (C_1-C_{12}) -alkylamino, gegebenenfalls substituiertem Arylamino, gegebenenfalls substituiertem Diarylamino und Halogen ausgewähltes Glied steht, mit der Maßgabe, dass mindestens zwei der vier R^4-Substituenten unabhängig voneinander aus gegebenenfalls substituiertem (C_1-C_{12})-Alkyl und gegebenenfalls substituiertem (C_1-C_{12})-Alkoxy ausgewählt sind, und

b) einem zweiwertigen Arylrest aus der Gruppe bestehend aus 1,4-Naphthylen, 1,4-Naphthylen, 9,10-Anthrylen, 5,6,7,8-Tetrahydronaphth-1,4-ylen, 9,9',10,10'-Tetra-(C_1-C_{12})-alkyl-9,10-dihydroanthr-1,4-ylen, 9,9',10,10'-Tetraaryl-9,10-dihydroanthr-1,4-ylen, 9,9',10,10'-Tetra-(C_1-C_{12})-alkyl-9,10-dihydroanthr-2,6-ylen, 9,9',10,10'-Tetraaryl-9,10-dihydroanthr-1,4-ylen,

ausgewählt ist; und

R^3 aus der Gruppe bestehend aus H, gegebenenfalls substituiert e m (C_1-C_{12}) -Alkyl, gegebenenfalls substituiertem (C_1-C_{12})-Alkoxy, gegebenenfalls substituiertem (C_1-C_{12})-Alkylamino, gegebenenfalls substituiertem (C_1-C_{12}) -Alkylthio, gegebenenfalls substituiertem Di- (C_1-C_{12}) -alkylamino, gegebenenfalls substituiertem Arylamino, gegebenenfalls substituiertem Diarylamino und Halogen ausgewählt ist;

mit der Maßgabe, dass die Ar^i-Gruppen in 1,4-para-Phenylen-Manier miteinander verknüpft sind.

2. Verbindung nach Anspruch 1, wobei n für eine ganze Zahl von 5 bis 9 steht.

3. Verbindung nach Anspruch 1, wobei die Ar^i-Gruppen unabhängig voneinander aus unsubstituiertem Phenylen und Phenylen mit 1 bis 4 Fluorsubstituenten ausgewählt sind.

4. Verbindung nach Anspruch 1, wobei m für eine ganze Zahl von 1 bis 3 steht.

5. Verbindung nach Anspruch 1, wobei die Ar^i-Gruppen unabhängig voneinander aus unsubstituiertem Phenylen, Phenylen mit 1 bis 4 Fluorsubstituenten und gegebenenfalls substituiertem kondensiertem polycyclischem Aryl ausgewählt sind, mit der Maßgabe, dass jegliche kondensierte polycyclische Arylgruppen in der Verbindung auf eine solche Weise verknüpft sind, dass eine coplanare Orientierung relativ zu den benachbarten Ar^i-Gruppen beibehalten wird.

6. Verbindung nach Anspruch 5, wobei die kondensierten polycyclischen Arylgruppen aus der Gruppe bestehend aus 2,6-Naphthylen, 2,7-Phenanthrylen, 2,6-Anthrylen und 2,6-Carbazolyliden ausgewählt sind.

7. Verbindung nach Anspruch 1, wobei das tiefgestellte Zeichen n für 7 steht und Ar^3 und Ar^5 für substituiertes und unsubstituiertes 2,6-Naphthylen stehen.

8. Verbindung nach Anspruch 1, wobei das tiefgestellte Zeichen n für 7 steht und Ar^4 neben den übrigen Ar^i-Gruppen zwei gegebenenfalls substituierte Phenylringsubstituenten trägt.

9. Organische lichtemittierende Vorrichtung (OLED), umfassend eine Verbindung gemäß Anspruch 1.

Revendications

1. Composé de para-phénylène oligomère ayant la formule:

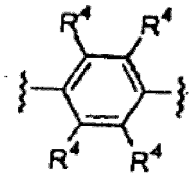
$$R^1\text{-}(Ar^i)_n\text{-}R^2$$

dans laquelle
l'indice n est un entier de 5 à 15;
l'exposant i est un entier de 1 à n et désigne la position en aval de R^1;
chaque Ar est un groupe aryle substitué ou non substitué ;
R^1 et R^2 sont chacun des substituants qui augmentent la solubilité du composé de para-phénylène dans des solvants organiques non polaires par rapport à la solubilité du composé correspondant dans lequel R^1 et R^2 sont hydrogène ;
et chaque R^1 et R^2 a indépendamment la formule:

$$R^3\text{-}(Ar^j)_m\text{-}$$

dans laquelle
l'indice m est un entier de 1 à 5;
l'exposant j est un entier de 1 à m;
chaque Ar^j est choisi dans le groupe constitué de

a) un groupe 1,4-phénylène ayant la formule:



dans laquelle chaque R^4 est un membre indépendamment choisi dans le groupe constitué de H, alkyle en C_1-C_{12} substitué ou non substitué, alcoxy en C_1-C_{12} substitué ou non substitué, alkylamino en C_1-C_{12} substitué ou non substitué, alkylthio en C_1-C_{12} substitué ou non substitué, di(alkylamino en C_1-C_{12}) substitué ou non substitué, arylamino substitué ou non substitué, diarylamino substitué ou non substitué et halogène, à condition qu'au moins deux des quatre substituants R^4 soient indépendamment choisis parmi alkyle en C_1-C_{12} substitué ou non substitué ou alcoxy en C_1-C_{12} substitué ou non substitué, et
b) un biradical aryle choisi dans le groupe constitué de 1 , 4-naphtylène, 1 , 4-naphtylène, 9 , 1 0-anthrylène, 5, 6, 7, 8-tétrahydropnapht-1,4-ylène, 9,9',10,10'-tétra(alkyle e n C_1-C_{12})-9,10-dihydroanthr-1,4-ylè n e , 9 , 9', 10,10' -tétraaryl-9,10-dihydroanthr-1,4-ylène, 9, 9', 1 0 , 10'-tétra(alkyle en C_1-C_{12})-9,10-dihydroanthr-2,6-ylène, 9,9',10,10'-tétraaryl-9,10-dihydroanthr-1,4-ylène ; et

R^3 est choisi dans le groupe constitué de H, alkyle en C_1-C_{12} substitué ou non substitué, alcoxy en C_1-C_{12} substitué ou non substitué, alkylamino en C_1-C_{12} substitué ou non substitué, alkylthio en C_1-C_{12} substitué ou non substitué, di(alkylamino en C_1-C_{12}) substitué ou non substitué, arylamino substitué ou non substitué, diarylamino substitué ou non substitué et halogène ;
à condition que les groupes Ar^i soient liés conjointement au moyen d'un 1,4-paraphénylène.

2. Composé de la revendication 1, dans lequel n est un entier de 5 à 9.

3. Composé de la revendication 1, dans lequel lesdits groupes Ar^i sont indépendamment choisis parmi phénylène non substitué et phénylène ayant de 1 à 4 substituants fluoro.

4. Composé de la revendication 1, dans lequel m est un entier de 1 à 3.

5. Composé de la revendication 1, dans lequel lesdits groupes Ar^i sont indépendamment choisis parmi phénylène non substitué, phénylène ayant de 1 à 4 substituants fluoro ; et aryle polycylique condensé substitué ou non substitué à condition que les groupes aryle polycycliques condensés éventuels soient liés dans le composé d'une façon qui maintient une orientation coplanaire par rapport aux groupes Ar^i adjacents.

6. Composé de la revendication 5, dans lequel lesdits groupes aryle polycycliques condensés sont choisis dans le

groupe constitué de 2,6-naphtylène, 2,7-phénanthrylène, 2 , 6-anthrylène et 2,6-carbazolylidène.

7. Composé de la revendication 1, dans lequel l'indice n est 7 et Ar^3 et Ar^5 sont 2,6-naphtylène substitué et non substitué.

8. Composé de la revendication 1, dans lequel l'exposant n est 7 et Ar^4 comporte deux substituants cycle phényle substitués ou non substitués autres que les groupes Ar^i restants.

9. Dispositif électroluminescent organique (OLED) comprenant un composé tel que défini dans la revendication 1.

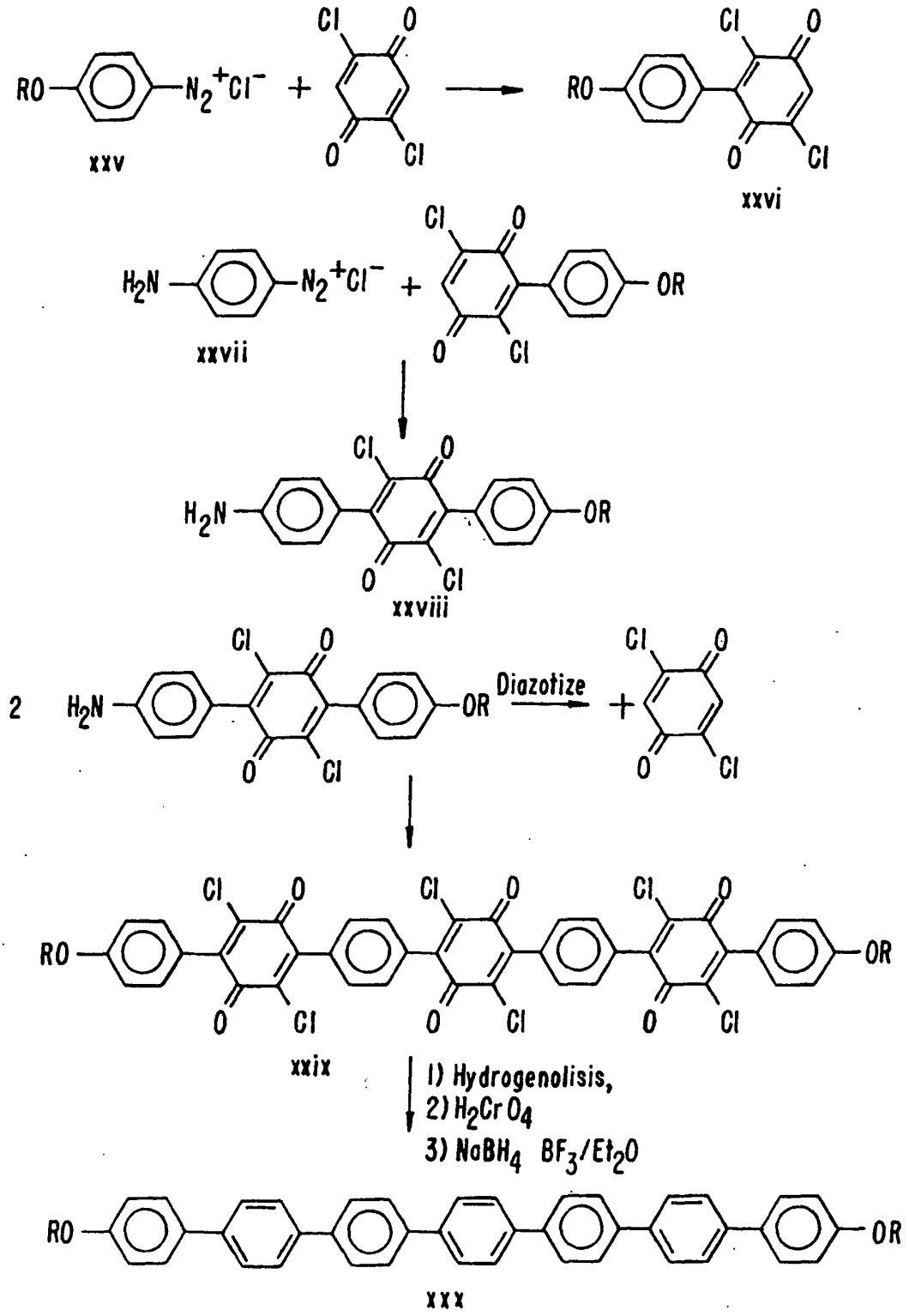

RO
$N_2^+Cl^-$
xxv
Cl
O
xxvi
H_2N
xxvii
OR
xxviii
2
Diazotize
xxix
1) Hydrogenolisis,
2) H_2CrO_4
3) $NaBH_4$ BF_3/Et_2O
xxx

FIG. 1.

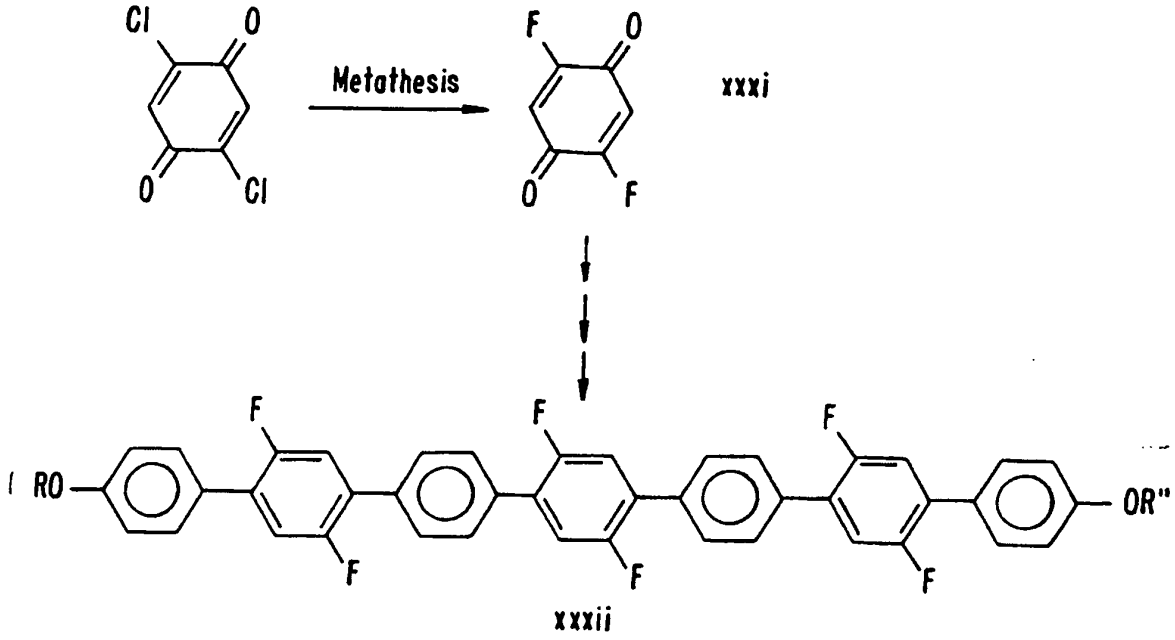


FIG. 2.

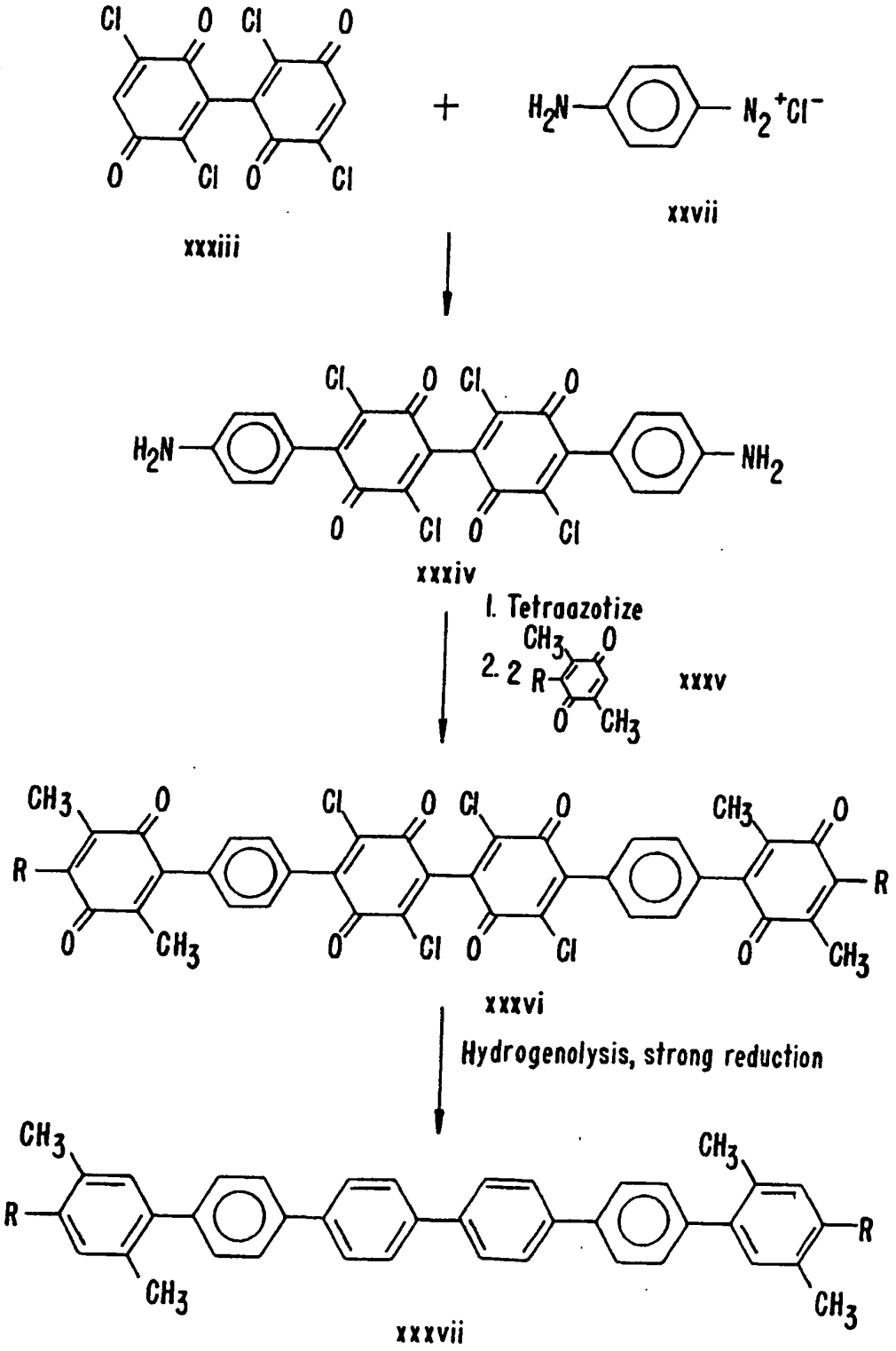

xxxiii
xxvii
xxxiv
1. Tetraazotize
2. 2
xxxv
xxxvi
Hydrogenolysis, strong reduction
xxxvii

FIG 3.

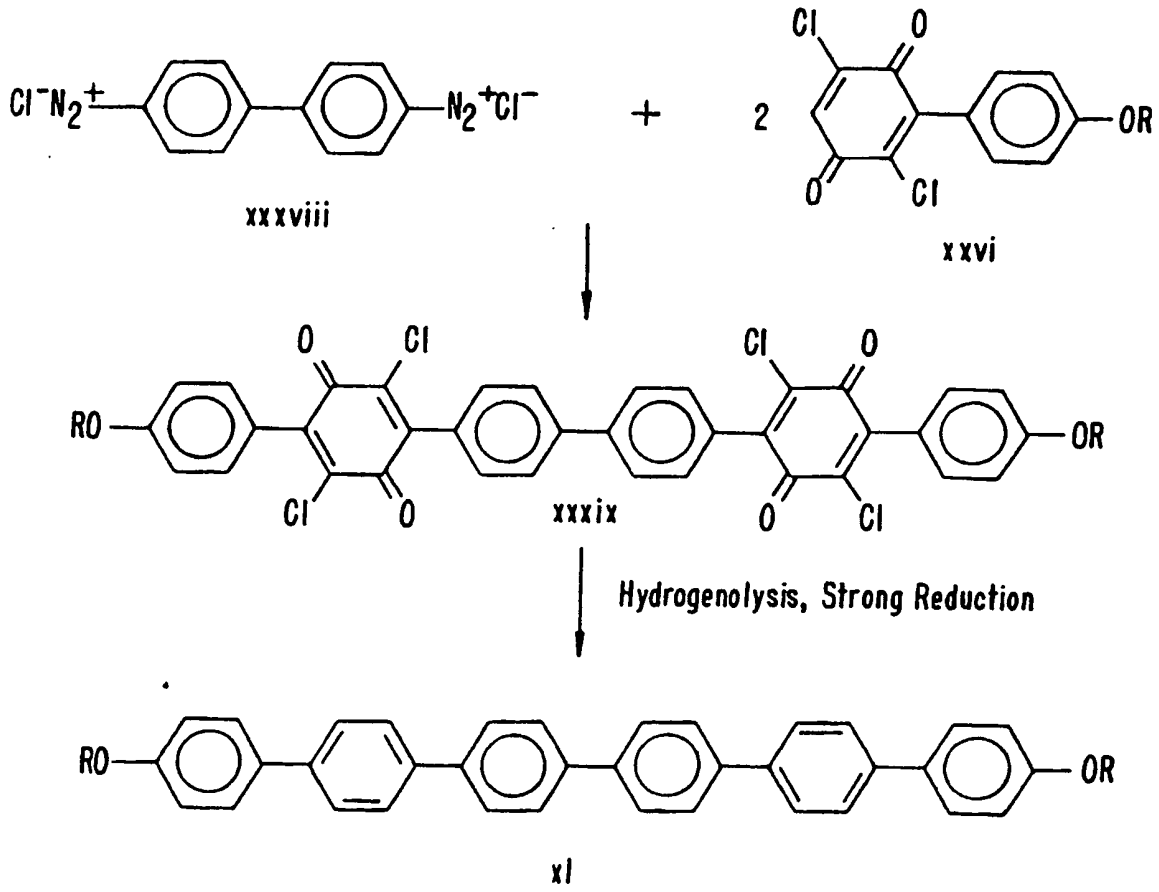

Cl⁻N₂⁺
N₂⁺Cl⁻
xxxviii
+
2
Cl
O
OR
O
Cl
xxvi
RO
O
Cl
Cl
O
OR
Cl
O
O
Cl
xxxix
Hydrogenolysis, Strong Reduction
RO
OR
xl

FIG. 4.

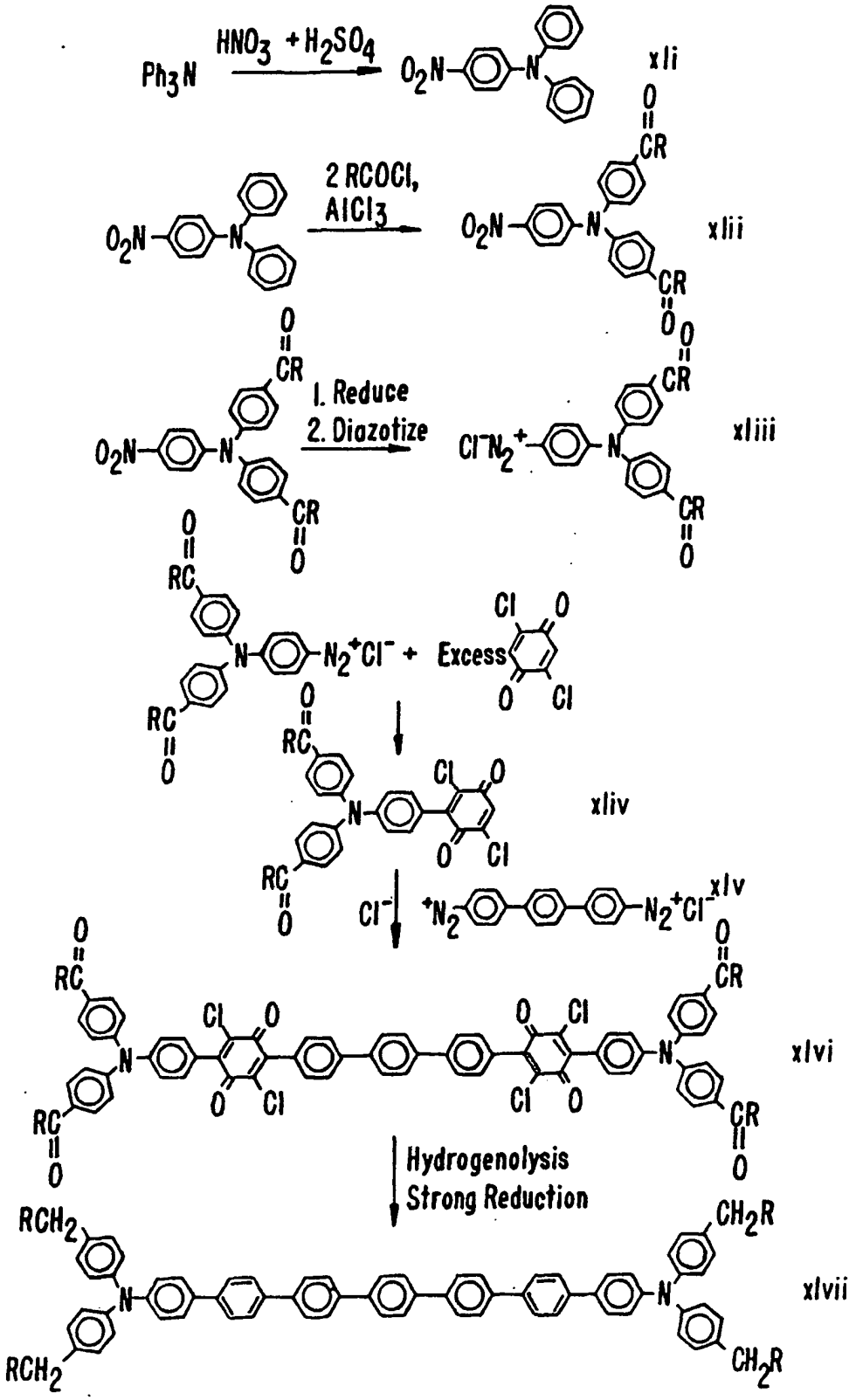

Ph3N
HNO3 + H2SO4
O2N
xli
2 RCOCl,
AlCl3
xlii
1. Reduce
2. Diazotize
Cl⁻N2⁺
xliii
Excess
xliv
xlv
xlvi
Hydrogenolysis
Strong Reduction
xlvii

FIG. 5.

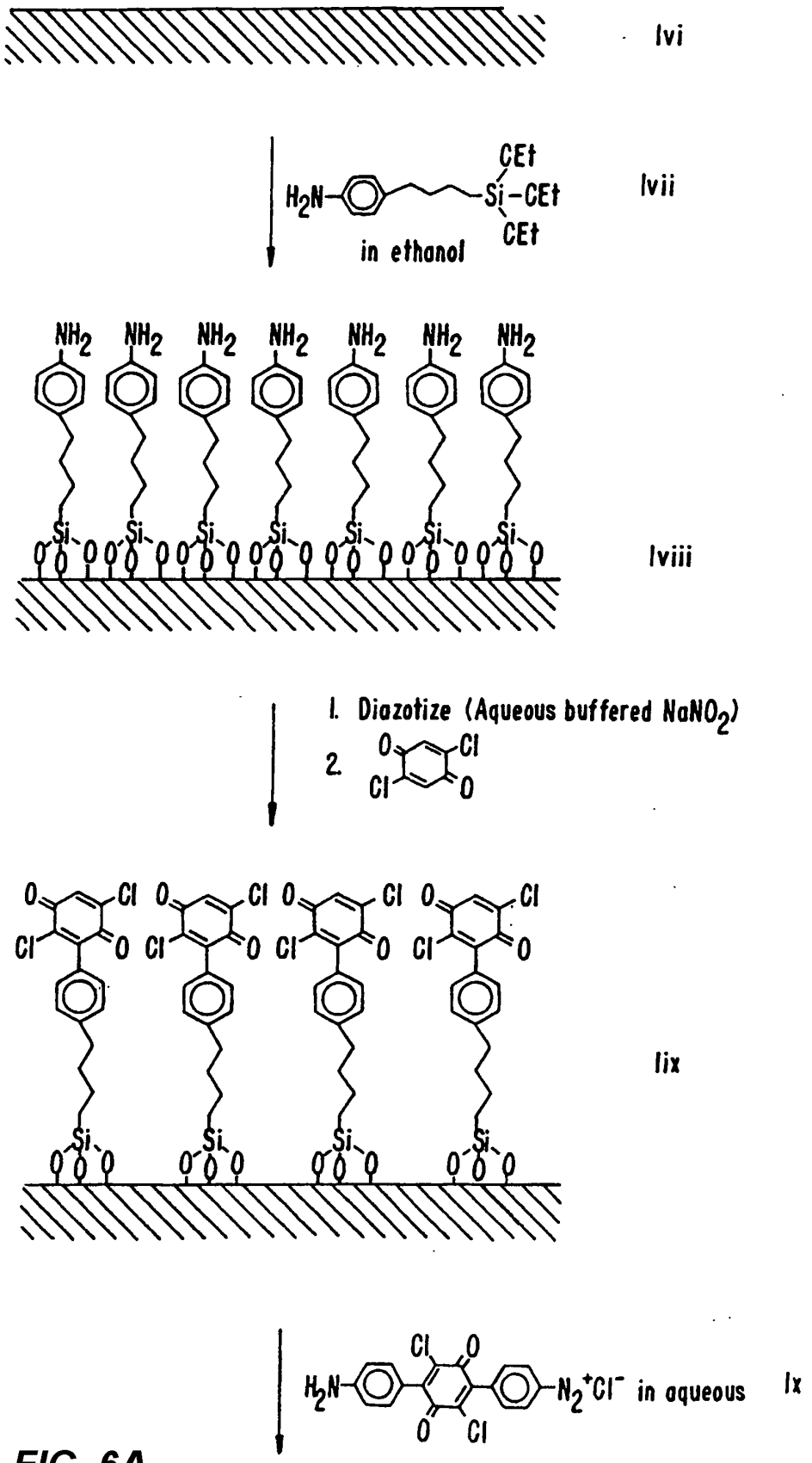

lvi
lvii
in ethanol
lviii
1. Diazotize (Aqueous buffered NaNO2)
2.
lix
in aqueous
lx

FIG. 6A.

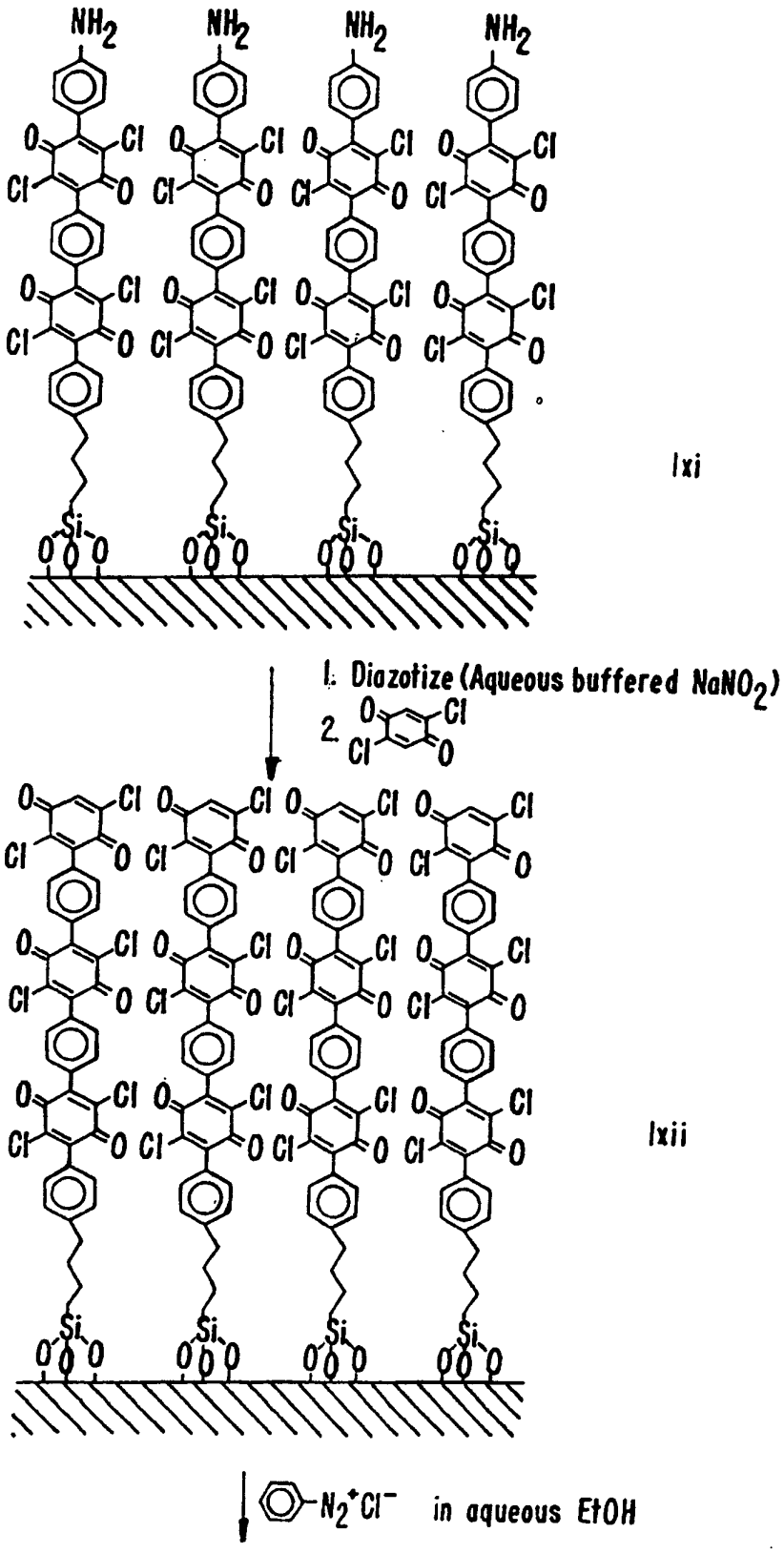

lxi
1. Diazotize (Aqueous buffered $NaNO_2$)
2.
lxii
$N_2^+Cl^-$ in aqueous EtOH

FIG. 6B.

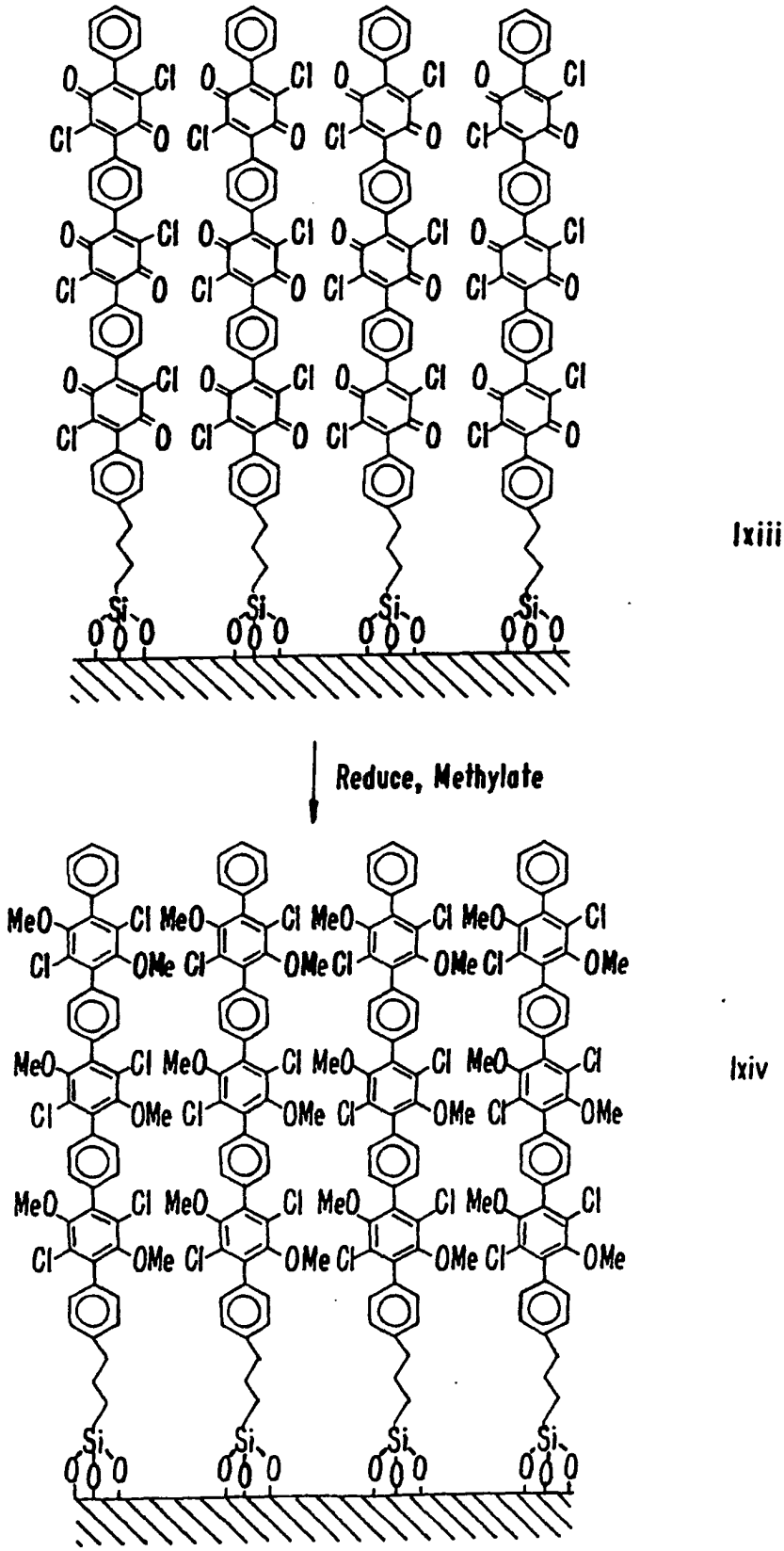


FIG. 6C.

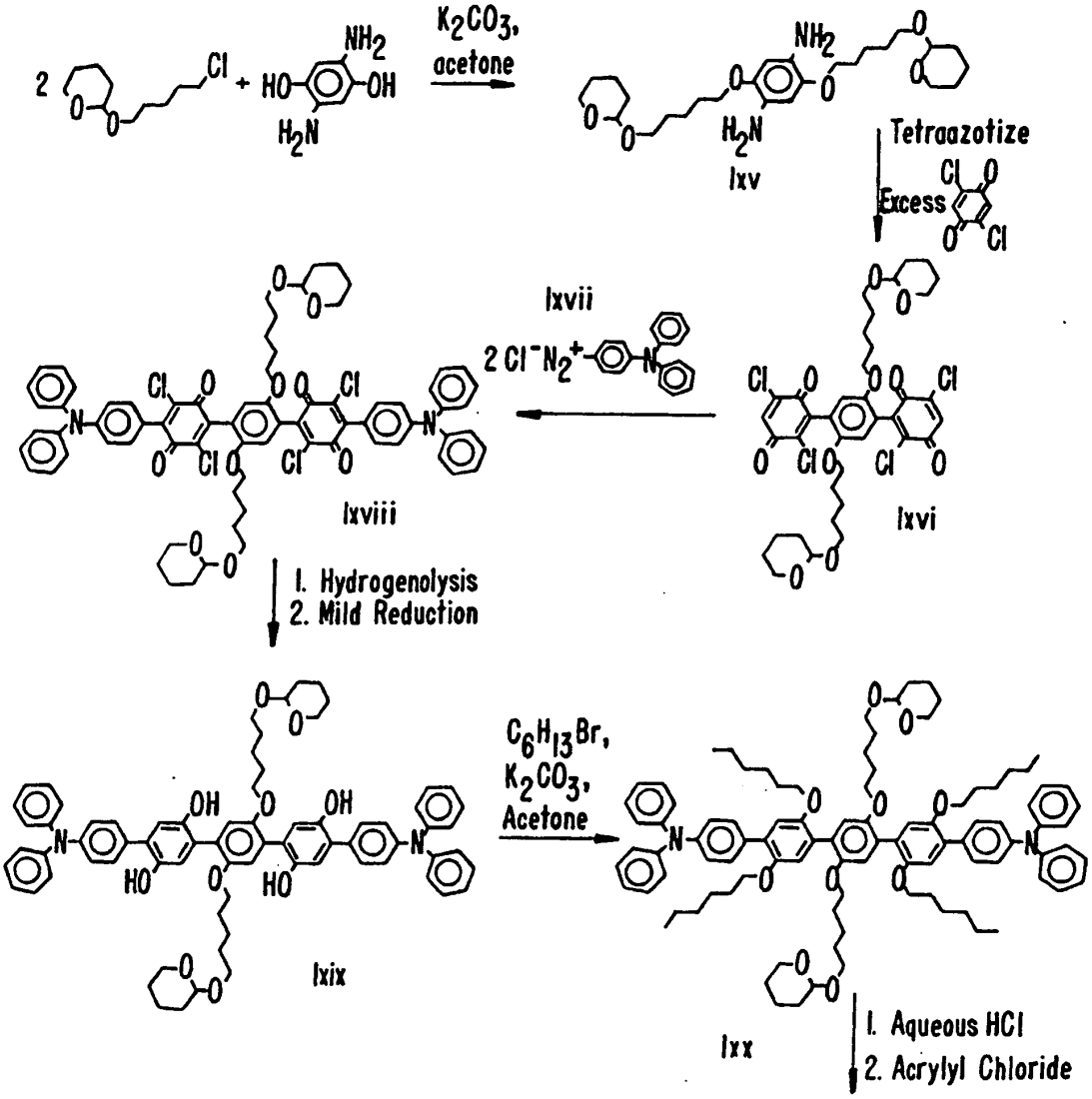
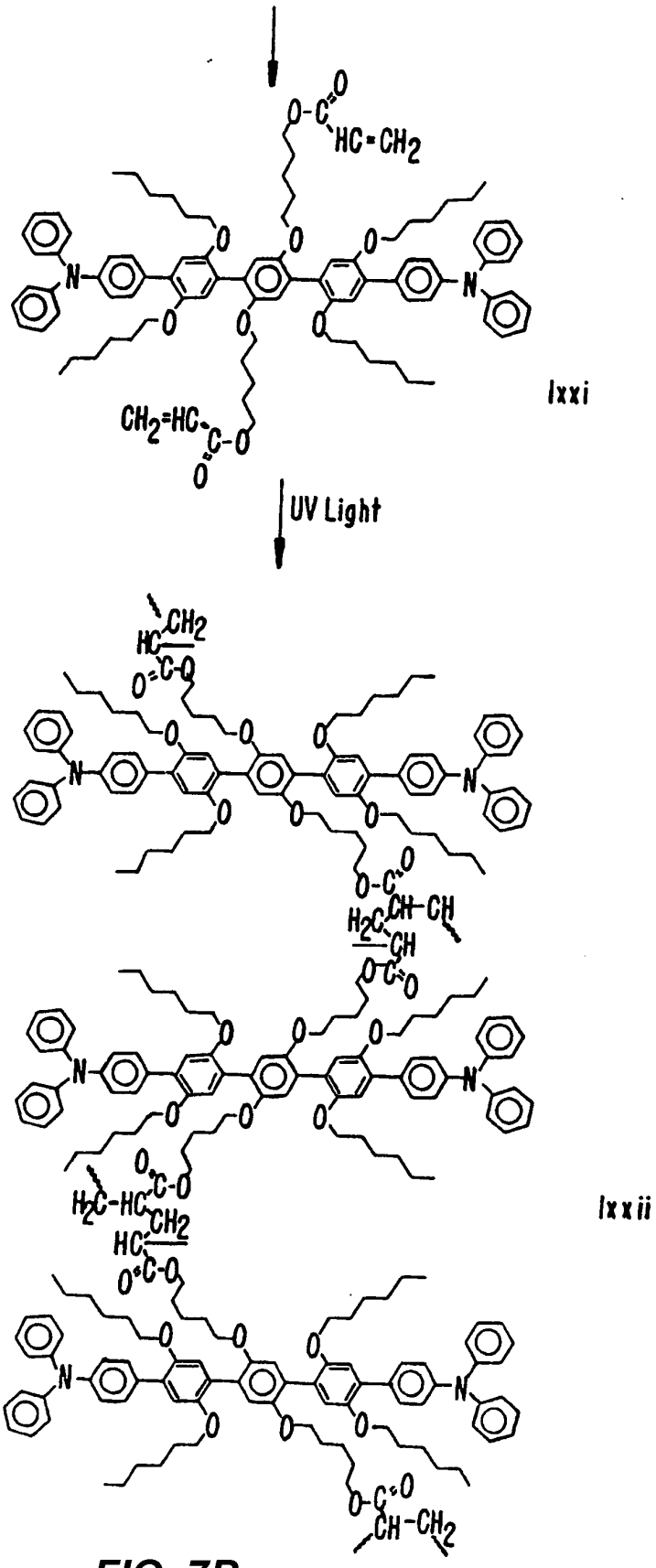

K2CO3, acetone
Ixv
Tetraazotize
Excess
Ixvii
Ixviii
Ixvi
1. Hydrogenolysis
2. Mild Reduction
Ixix
C6H13Br, K2CO3, Acetone
Ixx
1. Aqueous HCl
2. Acrylyl Chloride

FIG. 7A.



lxxi

lxxii

FIG. 7B.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 19590200 P **[0001]**
- EP 0130056 A **[0009]**
- US 5646232 A **[0010]**
- US 4288147 A, Koch **[0028] [0047]**

Non-patent literature cited in the description

- DIAZO CHEMISTRY. **ZOLLINGER.** AROMATIC AND HETEROAROMATIC COMPOUNDS. Wiley, 1994, vol. 1 **[0044]**

专利名称(译)	通过芳基化醌制备的低聚和聚合OLED材料		
公开(公告)号	EP1196956B1	公开(公告)日	2012-06-13
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[标]申请(专利权)人(译)	霍尼韦尔国际公司		
申请(专利权)人(译)	HONEYWELL INTERNATIONAL INC.		
当前申请(专利权)人(译)	HONEYWELL INTERNATIONAL INC.		
[标]发明人	KOCH GEORGE C		
发明人	KOCH, GEORGE, C.		
IPC分类号	H01L51/50 C08G61/10 C08G61/12 C07C15/14 C07C43/205 C07C43/21 C07C43/225 C07C50/30 C07C211/54 C07D493/22 C09K11/06		
CPC分类号	C08G61/10 C08G61/125		
优先权	60/195902 2000-04-10 US		
其他公开文献	EP1196956A2		
外部链接	Espacenet		

摘要(译)

提供具有以下通式的OLED材料：R 1 - （Ar 1）n -R 2其中下标n是5至15的整数;上标i是1至n的整数，表示R 1下游的位置;每个Ar是取代或未取代的芳基; R 1和R 2各自为相对于其中R 1和R 2为氢的相应化合物的溶解度而增加对苯撑化合物在非极性有机溶剂中的溶解度的取代基;条件是Ar基团以1,4-对苯撑的方式连接在一起。