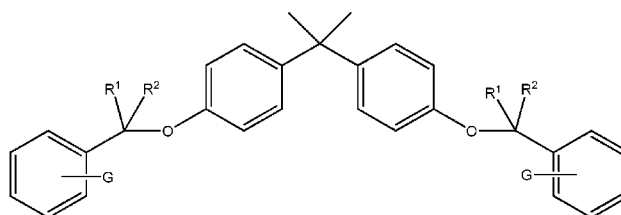


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(54) Title: BISPHENOL A COMPOUNDS USEFUL AS MARKERS FOR LIQUID HYDROCARBONS AND OTHER FUELS AND OILS



(I)

(57) Abstract: A compound having formula (I), wherein R^1 and R^2 independently represent hydrogen or C_1 - C_4 alkyl groups, and G represents hydrogen or at least one substituent selected from the group consisting of C_i - C_8 alkyl and C_1 - C_{18} alkoxy; provided that when R^1 and R^2 represent hydrogen, G does not represent hydrogen, 4-methyl, 4-methoxy, 3-methoxy, 2,6-dipropargyl, 4-vinyl, 4-ethynyl or 3-ethynyl.

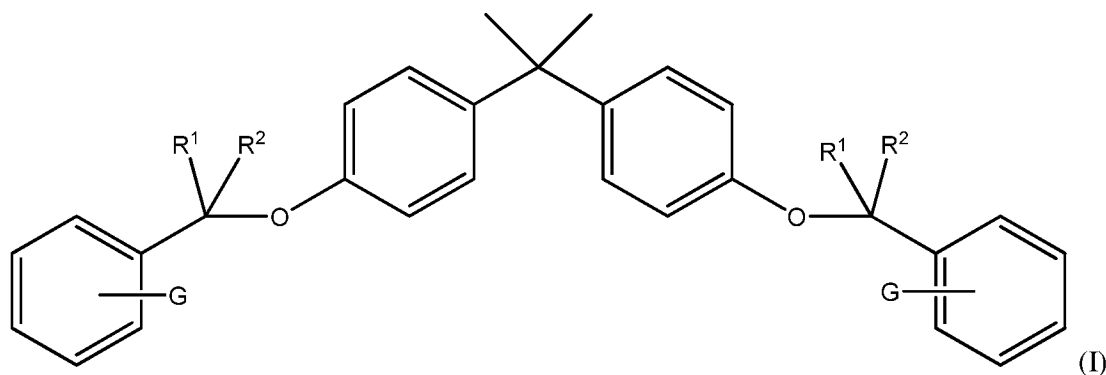
**BISPHENOL A COMPOUNDS USEFUL AS MARKERS
FOR LIQUID HYDROCARBONS AND OTHER FUELS AND OILS**

This invention relates to compounds useful in a method for marking liquid
5 hydrocarbons and other fuels and oils.

Marking of petroleum hydrocarbons and other fuels and oils with various kinds of
chemical markers is well known in the art. A variety of compounds have been used for this
purpose, as well as numerous techniques for detection of the markers, e.g., absorption
spectroscopy and mass spectrometry. For example, U.S. Pat. No. 7,858,373 discloses the use
10 of a variety of organic compounds for use in marking liquid hydrocarbons and other fuels and
oils. However, there is always a need for additional marker compounds for these products.
Combinations of markers can be used as digital marking systems, with the ratios of amounts
forming a code for the marked product. Additional compounds useful as fuel and lubricant
markers would be desirable to maximize the available codes. The problem addressed by this
15 invention is to find additional markers useful for marking liquid hydrocarbons and other fuels
and oils.

STATEMENT OF INVENTION

The present invention provides a compound having formula (I),



wherein R^1 and R^2 independently represent hydrogen or C_1 - C_4 alkyl groups, and G represents
hydrogen or at least one substituent selected from the group consisting of C_1 - C_{18} alkyl and
 C_1 - C_{18} alkoxy; provided that when R^1 and R^2 represent hydrogen, G does not represent
hydrogen, 4-methyl, 4-methoxy, 3-methoxy, 2,6-dipropargyl, 4-vinyl, 4-ethynyl or 3-ethynyl.

DETAILED DESCRIPTION

Percentages are weight percentages (wt%) and temperatures are in °C, unless specified otherwise. Concentrations are expressed either in parts per million (“ppm”) calculated on a weight/weight basis, or on a weight/volume basis (mg/L); preferably on a weight/volume basis. The term “petroleum hydrocarbon” refers to products having a predominantly hydrocarbon composition, although they may contain minor amounts of oxygen, nitrogen, sulfur or phosphorus; petroleum hydrocarbons include crude oils as well as products derived from petroleum refining processes; they include, for example, crude oil, lubricating oil, hydraulic fluid, brake fluid, gasoline, diesel fuel, kerosene, jet fuel and heating oil. Marker compounds of this invention can be added to a petroleum hydrocarbon or a liquid biologically derived fuel; examples of the latter are biodiesel fuel, ethanol, butanol, ethyl tert-butyl ether or mixtures thereof. A substance is considered a liquid if it is in the liquid state at 20°C. A biodiesel fuel is a biologically derived fuel containing a mixture of fatty acid alkyl esters, especially methyl esters. Biodiesel fuel typically is produced by transesterification of either virgin or recycled vegetable oils, although animal fats may also be used. An ethanol fuel is any fuel containing ethanol, in pure form, or mixed with petroleum hydrocarbons, e.g., “gasohol.” An “alkyl” group is a substituted or unsubstituted hydrocarbyl group having from one to twenty-two carbon atoms in a linear or branched arrangement. An “alkyl” group may have double or triple bonds. Substitution on alkyl groups of one or more hydroxy or alkoxy groups is permitted. Preferably, alkyl groups are saturated and unsubstituted. Preferably, the compounds of this invention contain elements in their naturally occurring isotopic proportions.

G represents hydrogen or at least one substituent selected from the group consisting of C₁-C₁₈ alkyl and C₁-C₁₈ alkoxy, i.e., each aromatic ring bearing a “G” substituent in formula (I) is unsubstituted or has at least one substituent selected from the group consisting of C₁-C₁₈ alkyl and C₁-C₁₈ alkoxy. Preferably, when G is not hydrogen it represents one to three substituents on each aromatic ring, which may be the same or different, preferably one or two substituents, preferably two or three substituents, preferably one or two identical substituents, preferably two or three identical substituents. However, the substituents represented by “G” are the same on the two aromatic rings substituted by G, i.e., the compound is symmetric with a plane of symmetry between the benzene rings of the central biphenyl moiety. Preferably, G represents hydrogen or at least one substituent selected from the group consisting of C₁-C₁₂ alkyl and C₁-C₁₂ alkoxy, preferably C₁-C₈ alkyl and C₁-C₈ alkoxy,

preferably C₁-C₆ alkyl and C₁-C₆ alkoxy, preferably C₁-C₆ saturated alkyl and C₁-C₆ saturated alkoxy, preferably C₁-C₄ saturated alkyl and C₁-C₄ saturated alkoxy, preferably C₁-C₄ saturated alkyl, preferably C₁-C₃ saturated alkyl, preferably methyl and ethyl. Preferably, R¹ and R² independently represent hydrogen, methyl or ethyl; preferably hydrogen or methyl.

- 5 Preferably, R¹ is methyl and R² is hydrogen, preferably R¹ and R² both are hydrogen. Preferably, G does not represent hydrogen. Preferably, G does not represent a single substituent in the 4-position. Preferably, when R¹ and R² represent hydrogen, G represents at least one saturated alkyl group, preferably not in the 4-position. Preferably, when R¹ and R² represent hydrogen, and G represents a single saturated alkyl group at the 4-position, the
- 10 saturated alkyl group is a C₃-C₈ alkyl group

In using the compounds of this invention as markers, preferably the minimum amount of each compound added to a liquid to be marked is at least 0.01 ppm, preferably at least 0.02 ppm, preferably at least 0.05 ppm, preferably at least 0.1 ppm, preferably at least 0.2 ppm.

Preferably, the maximum amount of each marker is 50 ppm, preferably 20 ppm, preferably 15

- 15 ppm, preferably 10 ppm, preferably 5 ppm, preferably 2 ppm, preferably 1 ppm, preferably 0.5 ppm. Preferably, the maximum total amount of marker compounds is 100 ppm, preferably 70 ppm, preferably 50 ppm, preferably 30 ppm, preferably 20 ppm, preferably 15 ppm, preferably 12 ppm, preferably 10 ppm, preferably 8 ppm, preferably 6 ppm, preferably 4 ppm, preferably 3 ppm, preferably 2 ppm, preferably 1 ppm. Preferably, a marker compound
- 20 is not detectable by visual means in the marked petroleum hydrocarbon or liquid biologically derived fuel, i.e., it is not possible to determine by unaided visual observation of color or other characteristics that it contains a marker compound. Preferably, a marker compound is one that does not occur normally in the petroleum hydrocarbon or liquid biologically derived fuel to which it is added, either as a constituent of the petroleum hydrocarbon or liquid
- 25 biologically derived fuel itself, or as an additive used therein.

Preferably, the marker compounds have a log P value of at least 3, where P is the 1-octanol/water partition coefficient. Preferably, the marker compounds have a log P of at least 4, preferably at least 5. Log P values which have not been experimentally determined and reported in the literature can be estimated using the method disclosed in Meylan, W.M &

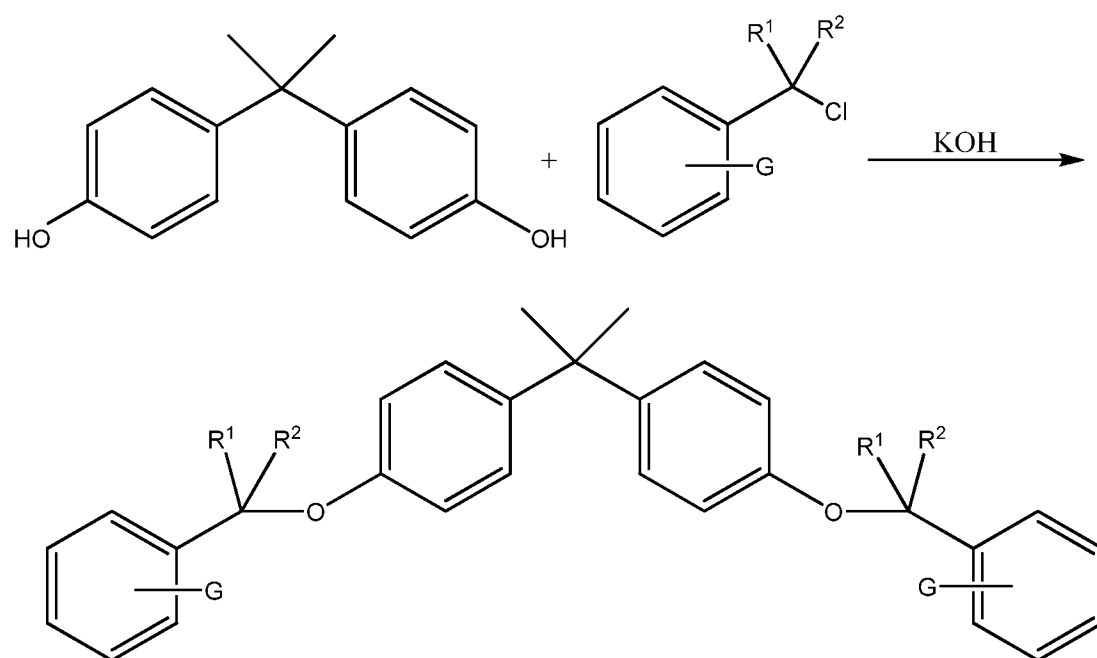
- 30 Howard, P.H., *J. Pharm. Sci.*, vol. 84, pp. 83-92 (1995). Preferably the petroleum hydrocarbon or liquid biologically derived fuel is a petroleum hydrocarbon, biodiesel fuel or ethanol fuel; preferably a petroleum hydrocarbon or biodiesel fuel; preferably a petroleum

hydrocarbon; preferably crude oil, gasoline, diesel fuel, kerosene, jet fuel or heating oil; preferably gasoline.

Preferably, the marker compounds are detected by at least partially separating them from constituents of the petroleum hydrocarbon or liquid biologically derived fuel using a chromatographic technique, e.g., gas chromatography, liquid chromatography, thin-layer chromatography, paper chromatography, adsorption chromatography, affinity chromatography, capillary electrophoresis, ion exchange and molecular exclusion chromatography. Chromatography is followed by at least one of: (i) mass spectral analysis, and (ii) FTIR. Identities of the marker compounds preferably are determined by mass spectral analysis. Preferably, mass spectral analysis is used to detect the marker compounds in the petroleum hydrocarbon or liquid biologically derived fuel without performing any separation. Alternatively, marker compounds may be concentrated prior to analysis, e.g., by distilling some of the more volatile components of a petroleum hydrocarbon or liquid biologically derived fuel.

Preferably, more than one marker compound is present. Use of multiple marker compounds facilitates incorporation into the petroleum hydrocarbon or liquid biologically derived fuel of coded information that may be used to identify the origin and other characteristics of the petroleum hydrocarbon or liquid biologically derived fuel. The code comprises the identities and relative amounts, e.g., fixed integer ratios, of the marker compounds. One, two, three or more marker compounds may be used to form the code. Marker compounds according to this invention may be combined with markers of other types, e.g., markers detected by absorption spectrometry, including those disclosed in U.S. Pat. No. 6,811,575; U.S. Pat. App. Pub. No. 2004/0250469 and EP App. Pub. No. 1,479,749. Marker compounds are placed in the petroleum hydrocarbon or liquid biologically derived fuel directly, or alternatively, placed in an additives package containing other compounds, e.g., antiwear additives for lubricants, detergents for gasoline, etc., and the additives package is added to the petroleum hydrocarbon or liquid biologically derived fuel.

The compounds of this invention may be prepared by methods known in the art. For example, substituted benzyl halides may react with Bisphenol A in the presence of base according to the following equation:



EXAMPLESExample 1: Preparation of Bisphenol A bis(2-methylbenzyl) ether:

Under an inert atmosphere, 5.23 g Bisphenol A (BPA) (22.9 mmol) and 2.83 g potassium hydroxide (50.4 mmol) were dissolved in 50 mL dimethylacetamide. Stirring was started at 500 rpm and the contents were warmed to 70 °C. After 30 minutes, 7.09 g 2-methylbenzyl chloride (50.4 mmol) dissolved in 50 mL dimethylacetamide was added to the reaction mixture. The mixture was then heated at 100 °C for 4 h until no 2-methylbenzyl chloride was noted in the GPC trace. During the course of the reaction, a white precipitate had formed. The reaction mixture was cooled to room temperature and then poured into a 1 L separatory funnel containing 200 mL deionized water. The aqueous layer immediately became opaque. The reaction flask was washed with 50 mL deionized water and this wash was added along with 150 mL toluene to the separatory funnel. The separatory funnel was shaken and the bilayer allowed to settle. The lower, aqueous layer appeared opaque while the upper, organic layer was clear and colorless. The organic layer was separated and the aqueous layer was washed 3 additional times with 100 mL toluene. The combined organic fractions were dried over 20 g magnesium sulfate and filtered into a 1 L round bottom flask. The solvent was removed from the filtered toluene solution on a rotary evaporator initially at room temperature then at 70 °C. Following solvent removal, a viscous oil remained in the round bottom flask. This crude product was recrystallized at 0 °C from an acetone solution. The crystalline white solid that had formed was filtered on a 7.0 cm Büchner funnel using Whatman 540 filter paper. The crystals were pulverized into a powder and washed with cold acetone. The white powder was transferred to a 75 °C vacuum oven and dried for 24 h. For Bisphenol A bis(2-methylbenzyl) ether: 52 % yield (5.2 g, 12 mmol); white powder; mp 117 °C. ¹H NMR (500.1 MHz, CD₂Cl₂, ppm, *J* = Hz): 7.40 (d, 7.2, 2H, Ph), 7.23 (m, 6H, Ph), 7.17 (m, 4H, Ph), 6.90 (m, 4H, Ph), 5.02 (s, 4H, -PhCH₂O-), 2.37 (s, 6H, -PhCH₃), 1.65 (s, 6H, -C(CH₃)₂).

Example 2: Preparation of Bisphenol A bis(3-methylbenzyl) ether:

Prepared according to the procedure of Example 1 from BPA and 3-methylbenzyl chloride - 21 % yield; colorless oil. ¹H NMR (500.1 MHz, CD₂Cl₂, ppm, *J* = Hz): 7.22 – 7.29 (m, 6H, Ph), 7.15 (m, 6H, Ph), 6.87 (m, 4H, Ph), 5.00 (s, 4H, -PhCH₂O-), 2.37 (s, 6H, -PhCH₃), 1.64 (s, 6H, -C(CH₃)₂).

Example 3: Preparation of Bisphenol A bis(4-methylbenzyl) ether (composition known, CAS# 87353-49-9):

Prepared according to the procedure of Example 1 from BPA and 4-methylbenzyl chloride - 61 % yield; white powder; mp 101 °C. ¹H NMR (500.1 MHz, CD₂Cl₂, ppm, *J* = Hz): 7.32 (d, 8.1, 4H, Ph), 7.20 (d, 7.9, 4H, Ph), 7.15 (m, 4H, Ph), 6.87 (m, 4H, Ph), 4.99 (s, 4H, -PhCH₂O-), 2.36 (s, 6H, -PhCH₃), 1.64 (s, 6H, -C(CH₃)₂).

Example 4: Preparation of Bisphenol A bis(alpha-methylbenzyl) ether:

Prepared according to the procedure of Example 1 from BPA and alpha-methylbenzyl chloride - 84 % yield; gold oil. ¹H NMR (500.1 MHz, (CD₃)₂CO, ppm, *J* = Hz): 7.42 (m, 4H, Ph), 7.33 (m, 4H, Ph), 7.24 (m, 2H, Ph), 7.01 (m, 4H, Ph), 6.76 (m, 4H, Ph), 5.39 (q, 6.5, 2H, PhCH(Me)O-), 1.52 – 1.57 (m, 12H, Me).

Example 5: Demonstration of GC-MS detectability

15 Method Evaluation for Ex. 1 Product in DCM:

Stock	Stock(mg/ml)	SubStock(μg/ml)
Ex. 1 product	1.13	11.300

11.3mg in 10 ml DCM, 0.25 ml Stock in 25ml DCM

Standard	1	2	3	4
Substock	200μl	400μl	600μl	800μl
Ex. 1 product (μg/L)	226	452	678	904

Linearity and Accuracy:

Standard	Conc(ppb)	Area	Conc.(ppb)	% Recovery
1	226	48058	239.8	106.1
1	226	47839	239.1	105.8
2	452	114210	445.2	98.5
2	452	110243	432.9	95.8
3	678	186029	668.3	98.6
3	678	183055	659.0	97.2
4	904	264936	913.3	101.0
4	904	267871	922.4	102.0

Plotting area against concentration gave a line with slope=321.9825, intercept= -29140 and $R^2=0.9968$

Repeatability and Accuracy:

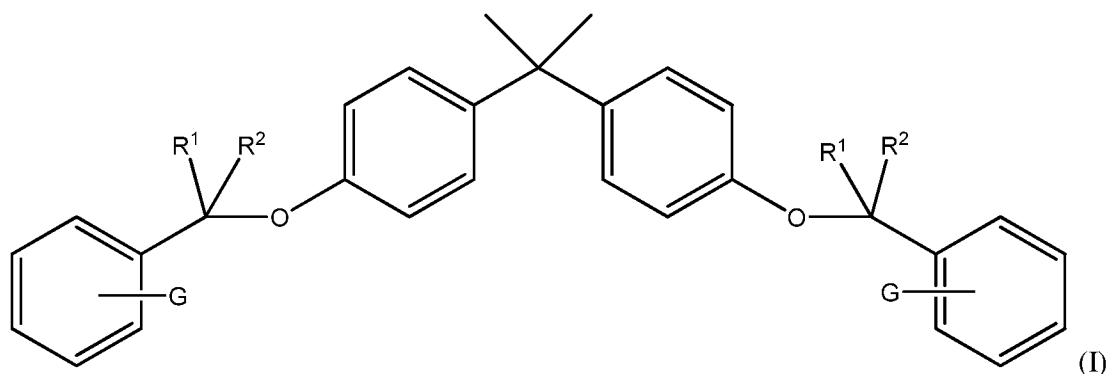
Concentration	226ppb		
n			
Rep	Area	Conc.(ppb)	%Recovery
1	41152	218.3	96.6
2	42116	221.3	97.9
3	45887	233.0	103.1
4	48805	242.1	107.1
5	48058	239.8	106.1
6	47839	239.1	105.8
Avg.	45643	232.3	102.8
Std Dev	3266	10.14	4.49
RSD	7.15	4.37	4.37

5 Note: 1. SIM: 105

2. Solvent: Dichloromethane (DCM)

CLAIMS

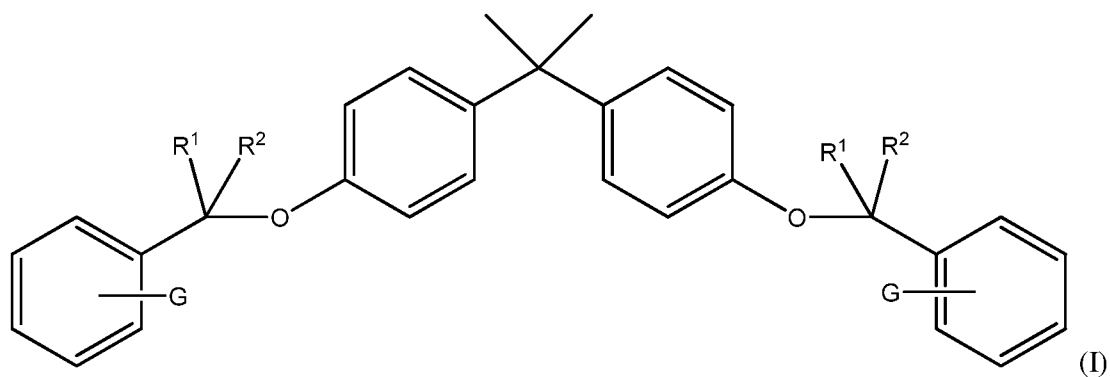
1. A compound having formula (I),



wherein R¹ and R² independently represent hydrogen or C₁-C₄ alkyl groups, and G represents hydrogen or at least one substituent selected from the group consisting of C₁-C₁₈ alkyl and C₁-C₁₈ alkoxy; provided that when R¹ and R² represent hydrogen, G does not represent hydrogen, 4-methyl, 4-methoxy, 3-methoxy, 2,6-dipropargyl, 4-vinyl, 4-ethynyl or 3-ethynyl.

2. The compound of claim 1 in which R¹ and R² independently represent hydrogen or methyl.
3. The compound of claim 2 in which G represents hydrogen or at least one substituent selected from the group consisting of C₁-C₈ alkyl and C₁-C₈ alkoxy.
4. The compound of claim 3 in which R¹ and R² represent hydrogen.
5. The compound of claim 4 in which G represents hydrogen or one or two substituents selected from the group consisting of C₁-C₆ saturated alkyl and C₁-C₆ saturated alkoxy.
6. The compound of claim 5 in which G represents one or two substituents selected from the group consisting of C₁-C₄ saturated alkyl and C₁-C₄ saturated alkoxy.
7. The compound of claim 6 in which G represents one or two substituents selected from the group consisting of methyl and ethyl.

8. A compound having formula (I),



wherein R^1 and R^2 independently represent hydrogen or C_1 - C_4 alkyl groups, and G represents at least one C_1 - C_{18} saturated alkyl substituent, provided G does not represent a single alkyl substituent in the 4-position.

9. The compound of claim 8 in which R^1 and R^2 independently represent hydrogen or methyl.

10. The compound of claim 9 in which G represents one or two C_1 - C_8 saturated alkyl substituents and R^1 and R^2 represent hydrogen.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/043137

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C39/00 C10L1/22
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)
C07C C10L

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	DOUGLAS W E ET AL: "Synthesis of acetylene-terminated monomers: 1,1'-(1-methylethylidene)bis[4-(4-ethynylphenyl)methoxy]benzene 1,3-bis[(4-ethynylphenoxy)methyl]benzene", POLYMER, ELSEVIER SCIENCE PUBLISHERS B.V, GB, vol. 35, no. 20, 1 September 1994 (1994-09-01), pages 4462-4464, XP024115735, ISSN: 0032-3861, DOI: 10.1016/0032-3861(94)90108-2 [retrieved on 1994-09-01] compound II ----- -/--	1-10



Further documents are listed in the continuation of Box C.



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

6 September 2012

Date of mailing of the international search report

14/09/2012

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/043137

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DALLA CORT ANTONELLA ET AL: "Experimental and computational study of complexes between quats and naphthalenophanes", SUPRAMOLECULAR CHEMISTRY, GORDON AND BREACH SCIENCE PUBLISHERS, US, vol. 13, no. 2, 1 January 2001 (2001-01-01), pages 313-323, XP008155673, ISSN: 1061-0278, DOI: 10.1080/10610270108027486 [retrieved on 2006-09-23] compound 6a -----	1-10
A	US 2007/184555 A1 (BANAVALI RAJIV MANOHAR [US] ET AL) 9 August 2007 (2007-08-09) cited in the application the whole document -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/043137

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		CN 101705125 A	12-05-2010
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		KR 20080072607 A	06-08-2008
		TW I345586 B	21-07-2011
		US 2007184555 A1	09-08-2007
		US 2011056121 A1	10-03-2011
