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(54) Electrochromic two-core viologen derivatives and optical articles containing them

(57) The present invention relates to a group of novel electrochromic materials. More specifically, it relates to electrochromic materials having two-core viologens and the use of these two-core viologens as a variable transmittance medium for the manufacture of an optical article, such as an ophthalmic lens.

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Description

[0001] The present invention relates to a group of novel electrochromic materials. More specifically, it relates to electrochromic materials having two-core viologens and the use of these two-core viologens as a variable transmittance medium for the manufacture of an optical article, such as an ophthalmic lens.

[0002] Electrochromism is a well-known physical phenomenon which is observed with certain classes of chemical compounds that change reversibly colour when a voltage is applied to them. The material undergoes reversible changes in optical properties by oxidation and reduction. Usually the electrochromic material may be colourless when an electric field is not applied and may be coloured when an electric field is applied. An electrochromic device, i.e. a device containing electrochromic compounds, the visible light absorbance of which depends only on the presence of an electric field, can thus have two states, i.e. a coloured state (when electrically activated) and a bleached state (in the inactive state). The optical transmission properties of the device depend on the nature of the electrochromic compounds.

[0003] There remains a need for improving an electrochromic material in order to use them as transparent media for forming high quality optical articles, in particular high quality ophthalmic lenses, while keeping electrochromic properties and having a wide range of colours.

[0004] After conducting extensive research, the present inventors provide novel electrochromic compounds exhibiting not only good electrochromic properties such as high absorption of the visible light in the coloured state, fast colouring and fading rates, long-term stability but also can be incorporated easily in a cell to form for instance an electrochromic lens.

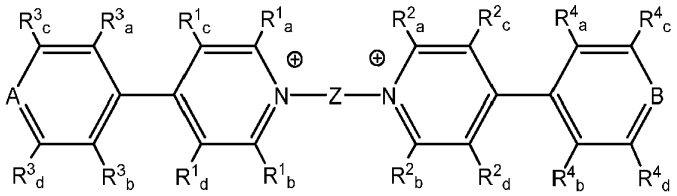
[0005] The applicants now have synthesized a group of novel electrochromic two-core viologens.

[0006] The present invention relates to electrochromic compounds of formula (I) as defined below.

[0007] The present invention also relates to an electrochromic composition comprising at least one compound of formula (I).

[0008] Finally, the present invention relates to an electrochromic device comprising said electrochromic composition, such as ophthalmic lens.

[0009] Thus, the present invention concerns electrochromic compounds represented by formula (I) :



(I)

wherein:

- Z is selected from:
  - ○ alkylene;
  - ○ cycloalkylene; and
  - ○ a bivalent group of formula -R^5-Y-R^6-, wherein
    - R^5 and R^6 are each independently selected from single bond, alkylene and cycloalkylene, and
    - Y is selected from arylene, cycloalkylene, heteroarylene, arylene-arylene or arylene-CR'R"-arylene wherein R' and R" form together with the carbon to which they are linked a carbocyclic group;

  wherein said alkylene, cycloalkylene, arylene, heteroarylene, and carbocyclic groups may be substituted by one or more substituents selected from halogen, alkyl, alkoxy, alkylthio, hydroxyalkyl, acyloxy, cycloalkyl, aryl, substituted aryl, aryloxy, heteroaryl and substituted heteroaryl;

- A and B are respectively selected from nitrogen and -N^+(R^{7a})-, and from nitrogen and - N^+(R^{7b})-, wherein R^{7a} and R^{7b} are independently selected from:

  o alkyl which may be substituted by one or more groups independently selected from halogen, alkoxy, cycloalkyl,

vinyl, allyl, aryl, substituted aryl, heteroaryl and substituted heteroaryl;
o aryl and heteroaryl which may be both substituted by one or more groups independently selected from:

- halogen, cyano, nitro, alkyl, haloalkyl, arylalkyl, cycloalkyl, cycloalkylalkyl and heterocycloalkylalkyl, alkenyl, alkynyl, allyl, vinyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, -N(aryl)$_2$, -N(aryl)CO(aryl), -CO-aryl and -CO-substituted aryl;
- -OR^8, -SR^8, -S(O)R^8, -S(O$_2$)R^8, -S(O$_2$)NR^{8}R^9, -NR^{8}R^9, -NR^{8}COR^9,-NR^{8}CO(aryl), -NR^{8}aryl, -CH$_2$OR^8, -CH$_2$SR^8, -CH$_2$R^8, -CO-R^8 and -CO$_2$R^8 wherein R^8 and R^9 are independently selected from H, alkyl, haloalkyl, arylalkyl, cycloalkyl, cycloalkylalkyl and heterocycloalkylalkyl;
- -S(O$_2$)NR^{10}R^{11} and -NR^{10}R^{11}, wherein R^{10} and R^{11} form together with the nitrogen atom to which they are linked a saturated 5 to 7 membered heterocycloalkyl which may comprise in addition to the nitrogen atom one further heteroatom selected from oxygen, nitrogen and sulfur, and which may be optionally substituted by one or two groups independently selected from halogen, -R^8, -OR^9, and -NR^{8}R^9, wherein R^8 and R^9 are as defined above;
- -V-W-R^{12} wherein:
  - V is selected from oxygen, -N(R^8)-, sulfur, -S(O)- and -S(O$_2$)-wherein R^8 is as defined above;
  - W is alkylene, which may be substituted by one or more groups independently selected from halogen and alkoxy; and
  - R^{12} is selected from -OR^8, -NR^8(alkyl) and -SR^8 wherein R^8 is as defined above; and
- -OC(O)-R^{13} wherein R^{13} is selected from alkyl, haloalkyl, alkenyl, -W-R^{12}, and aryl group which may be substituted by 1 to 4 groups selected from halogen, -R^8, -OR^8, -SR^8, -NR^{8}R^9, -NR^{10}R^{11}, -CO-R^8, -C(O)OR^8 wherein R^8, R^9, R^{10}, R^{11}, R^{12} and W are as defined above.

- R^1_a, R^1_b, R^1_c, R^1_d, R^2_a, R^2_b, R^2_c, R^2_d, R^3_a, R^3_b, R^3_c, R^3_d, R^4_a, R^4_b, R^4_c and R^4_d are each independently selected from H, alkyl, alkoxy, alkylthio, haloalkyl, haloalkoxy, haloalkythio, poly(alkylenoxy), alkoxycarbonyl, aryl, substituted aryl, heteroaryl and substituted heteroaryl, wherein the alkyl group may be substituted by one or more substituents independently selected from alkoxy, cycloalkyl, aryl, substituted aryl, heteroaryl and substituted heteroaryl;
  wherein at least one of R^1_a, R^1_b, R^1_c, R^1_d, R^2_a, R^2_b, R^2_c, R^2_d, R^3_a, R^3_b, R^3_c, R^3_d, R^4_a, R^4_b, R^4_c and R^4_d is not H;
- X- is a counterion; and
- m is 2 if A and B are nitrogen, 3 if one of A and B is nitrogen and the other is not nitrogen, and 4 if both A and B are not nitrogen.

[0010] The expression "alkylene" represents any divalent radical of a linear or branched hydrocarbon chain comprising 1 to 12 carbon atoms. Examples of C$_1$-C$_{12}$ alkylene groups include C$_1$-C$_4$ alkylene groups such as -CH$_2$-, -(CH$_2$)$_2$-, -(CH$_2$)$_3$-, -(CH$_2$)$_4$-, -CH(CH$_3$)-, -CH(CH$_3$)-CH$_2$-, -CH$_2$-CH(CH$_3$)-, -(CH$_2$)$_2$-CH(CH$_3$)-, -CH$_2$-CH(CH$_3$)-CH$_2$- or-CH(CH$_3$)-(CH$_2$)$_2$-, as well as -(CH$_2$)$_5$-, -(CH$_2$)$_6$-, -(CH$_2$)$_2$-CH(CH$_3$)-(CH$_2$)$_2$-, -(CH$_2$)$_3$-CH(CH$_3$)-CH$_2$-, -(CH$_2$)$_7$-, -(CH$_2$)$_8$-, -(CH$_2$)$_9$-, -(CH$_2$)$_{10}$-, -(CH$_2$)$_{11}$-, -(CH$_2$)$_{12}$-.

[0011] The expression "cycloalkylene" represents any divalent radical of a monocyclic or bicyclic 3 to 12 membered carbocycle. Examples of C$_3$-C$_{12}$ alkylene groups include cyclopropylene, cyclopentylene, cyclohexylene, cycloheptylene, and decahydronaphthylene.

[0012] The expression "arylene" represents any divalent radical of an aromatic hydrocarbon comprising 6 to 18 carbon atoms. Examples of C$_6$-C$_{18}$ arylene groups include phenylene, naphthylene, anthracenylene and phenanthrenylene.

[0013] The expression "carbocyclic group" represents any monocyclic or fused polycyclic hydrocarbon rings comprising 3 to 20 carbon atoms and which may comprise one or more unsaturations. Examples of C$_3$-C$_{20}$ carbocyclic groups include C$_{10}$-C$_{20}$ fused hydrocarbon rings which may comprise one or more unsaturations, such as cyclohexenylene, indene, fluorene.

[0014] The expression "halogen" includes F, Cl, Br or I. Preferred halogens are F and Cl.

[0015] The expression "alkyl" represents any monovalent radical of a linear or branched hydrocarbon chain comprising 1 to 18 carbon atoms. Examples of C$_1$-C$_{18}$ alkyl groups include C$_1$-C$_4$ alkyl groups such as methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *s*-butyl or *t*-butyl, C$_6$-C$_8$ alkyl groups such as *n*-hexyl, *n*-heptyl or *n*-octyl, as well as *n*-pentyl, 2-ethylhexyl, 3,5,5-trimethylhexyl, *n*-nonyl, *n*-decyl, *n*-undecyl, *n*-dodecyl *or n*-Octadecyl.

[0016] The expression "alkenyl" represents any monovalent radical of a linear or branched hydrocarbon chain from 2 to 18 carbon atoms and comprising one double bound. Examples of C$_2$-C$_{12}$ alkenyl groups include C$_2$-C$_4$ alkenyl groups such as ethenyl, *n*-propenyl, *i*-propenyl, *n*-butenyl or *i*-butenyl.

[0017] The expression "alkynyl" represents any monovalent radical of a linear or branched hydrocarbon chain from 2 to 12 carbon atoms and comprising one triple bound which may be either internal or terminal. Examples of C$_2$-C$_{12}$ alkynyl

groups include C_2-C_4 alkynyl groups such as ethynyl, *n*-propynyl, *n*-butynyl.

[0018] The expression "alkoxy" represents a radical of formula -OR wherein R is a C_1-C_{12} alkyl. Examples of C_1-C_{12} alkoxy groups include C_1-C_6 alkoxy groups such as $-OCH_3$,$-OCH_2CH_3$ or $O(CH_2)_5CH_3$.

[0019] The expression "cycloalkyl" represents any monovalent radical of a monocyclic or bicyclic 3 to 12 membered saturated carbocycle. Examples of C_3-C_{12} cycloalkyl groups include cyclopropyl, cyclopentyl and cyclohexyl.

[0020] The expression "heterocycloalkyl" represents any monovalent radical of a monocyclic or bicyclic 3 to 12 membered saturated ring comprising one or two heteroatoms independently selected from oxygen, nitrogen and sulfur. Examples of C_3-C_{12} heterocycloalkyl groups include for example tetrahydropyranyl or N-methylpiperidinyl.

[0021] The expression "cycloalkylalkyl" represents any (C_3-C_{12} cycloalkyl)-substituted C_1-C_{12} alkyl group. Examples of (C_3-C_{12} cycloalkyl)-C_1-C_{12} alkyl groups include (C_3-C_{12} cycloalkyl)-C_1-C_4 such as cyclohexylmethyl or cyclohexylethyl.

[0022] The expression "heterocycloalkylalkyl" represents any (C_3-C_{12} heterocycloalkyl)-substituted C_1-C_{12} alkyl group. Examples of (C_3-C_{12} heterocycloalkyl)-C_1-C_{12} alkyl groups include (C_3-C_{12} heterocycloalkyl)-C_1-C_4 such as tetrahydropyranylmethyl.

[0023] The expression "aryl" represents any monovalent radical of an aromatic hydrocarbon comprising 6 to 18 carbon atoms. Examples of C_6-C_{18} aryl groups include phenyl and naphthyl, anthacenyl, phenanthrenyl.

[0024] The expression "substituted aryl" represents any C_6-C_{18} aryl group as defined above substituted by one or more substituents selected from halogen, alkyl, alkoxy, haloalkyl, haloalkoxy, alkoxycarbonyl, alkanoyl, aroyl, formyl, nitrile, nitro, amido, alkylthio, alkylsulfinyl, alkylsulfonyl, arylthio, arylsulfinyl, arylsulfonyl, amino, alkylamino, arylamino, dialkylamino and diarylamino. Preferably, the substituents are selected from bulky or electron withdrawing groups. Examples of substituted C_6-C_{18} aryl groups include substituted phenyl groups such as p-methylphenyl, o-t-butylphenyl, p-trifluoromethoxyphenyl, o-trifluoromethoxyphenyl, m-cyanophenyl, o-*i*-propylphenyl, 2,4-dinitrophenyl, 2,6-diisopropylphenyl or 3,5-dicyanophenyl.

[0025] The expression "aryloxy" represents a radical of formula -OR wherein R is a C_6-C_{18} aryl. Examples of C_1-C_{12} aryloxy groups include phenyloxy and naphthyloxy.

[0026] The expression "heteroaryl" represents any monovalent radical of a monocyclic or bicyclic 5 to 10 membered aromatic group comprising from 1 to 3 heteroatoms independently selected from oxygen, nitrogen and sulfur. Examples of C_5-C_{10} heteroaryl groups include furyl, thienyl, pyrrolyl, pyrazoyl, imidazolyl, isoxazolyl, isothiazoyl, thiazolyl, oxazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, 1-benzofuryl, 1-benzothienyl, indolyl, benzimidazolyl, indazolyl, 1,2-benzisoxazolyl, 2,1-benzisoxazolyl 1,2-benzisothiazolyl, 2,1-benzisothiazolyl benzothiazolyl, benzoxazolyl, benzotriazolyl, pyridyl, quinolinyl, isoquinolinyl, pyridazinyl, cinnolinyl, phthalazinyl, pyrimidinyl, quinazolinyl, pyrazinyl and quinoxalinyl.

[0027] The expression "heteroarylene" represents any divalent radical of a monocyclic or bicyclic 5 to 10 membered aromatic group comprising from 1 to 3 heteroatoms independently selected from oxygen, nitrogen and sulfur. Examples of C_5-C_{10} heteroarylene groups include furylene, thienylene, pyrrolylene, pyrazoylene, imidazolylene, isoxazolylene, isothiazoylene, thiazolylene, oxazolylene, 1,2,3-triazolylene, 1,2,4-triazolylene, 1-benzofurylene, 1-benzothienylene, indolylene, benzimidazolylene, indazolylene, 1,2-benzisoxazolylene, 2,1-benzisoxazolylene, 1,2-benzisothiazolylene, 2,1-benzisothiazolylene, benzothiazolylene, benzoxazolylene, benzotriazolylene, pyridylene, quinolinylene, isoquinolinylene, pyridazinylene, cinnolinylene, phthalazinylene, pyrimidinylene, quinazolinylene, pyrazinylene and quinoxalinylene.

[0028] The expression "substituted heteroaryl" represents any C_5-C_{10} heteroaryl group as defined above substituted by one or more substituents selected from alkyl, alkoxy, alkoxycarbonyl, alkanoyl, aroyl, formyl, nitrile, nitro, amido, alkylthio, alkylsulfinyl, alkylsulfonyl, arylthio, arylsulfinyl, arylsulfonyl, amino, alkylamino, arylamino, dialkylamino and diarylamino. Preferably, the substituents are selected from bulky or electron withdrawing groups. Examples of substituted C_5-C_{10} heteroaryl groups include 4-methylthienyl, 5-methyl-2-thienyl, 6-methyl-2-pyridyl, N-methylpyrrol-2-yl and N-phenylindol-3-yl.

[0029] The expression "haloalkyl" represents any C_1-C_{12} alkyl group substituted by one or more halogen atom such as F or Cl. Examples of C_1-C_{12} haloalkyl groups include C_1-C_{12} perhaloalkyl groups, in particular C_1-C_4 perhaloalkyl groups such as $-CF_3$, as well as C_1-C_{12} (perhaloalkyl)alkyl groups, in particular (C_1-C_4 perhaloalkyl)-(C_1-C_4 alkyl) groups such as $-CH_2CF_3$.

[0030] The expression "haloalkoxy" represents a radical of formula -OR wherein R is a C_1-C_{12} haloalkyl. Examples of C_1-C_{12} haloalkoxy groups include C_1-C_{12} perhaloalkoxy groups, in particular C_1-C_4 perhaloalkoxy groups such as $-OCF_3$, as well as C_1-C_{12} (perhaloalkyl)alkoxy groups, in particular (C_1-C_4 perhaloalkyl)-(C_1-C_4 alkoxy) groups such as $-OCH_2CF_3$.

[0031] The expression "alkylthio" represents a radical of formula -SR wherein R is a C_1-C_{12} alkyl. Examples of C_1-C_{12} alkylthio groups include $-SCH_3$ and $-SCH_2CH_3$.

[0032] The expression "haloalkylthio" represents a radical of formula -SR wherein R is a C_1-C_{12} haloalkyl. Examples of C_1-C_{12} haloalkoxy groups include C_1-C_{12} perhaloalkylthio groups, in particular C_1-C_4 perhaloalkylthio groups such as $-SCF_3$, as well as C_1-C_{12} (perhaloalkyl)alkylthio groups, in particular (C_1-C_4 perhaloalkyl)-(C_1-C_4 alkylthio) groups such as $-SCH_2CF_3$.

[0033] The expression "hydroxyalkyl" represents any C_1-C_{12} alkyl group substituted by one or more hydroxyl groups. Examples of C_1-C_{12} hydroxyalkyl groups include -CH_2OH and-CH_2CH_2OH.

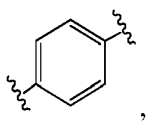
[0034] The expression "acyloxy" represents a radical of formula -OC(O)R wherein R is a C_1-C_{12} alkyl. Examples of C_1-C_{12} acyloxy groups include -$OC(O)CH_3$ and-$OC(O)CH_2CH_3$.

[0035] The expression "polyalkylenoxy" represents a radical of formula -$O(R'O)_mR$ wherein R' is a C_1-C_{12} alkylene, R is a C_1-C_{12} alkyl and m is an integer from 1 to 12. Examples of poly(C_1-C_{12} alkylenoxy) groups include OCH_2CH_2OMe.

[0036] The expression "alkoxycarbonyl" represent a radical of formula -C(O)OR wherein R is a C_1-C_{18} alkyl. Examples of C_1-C_{18} alkoxycarbonyl groups include C_1-C_4 alkoxycarbonyl groups such as -$C(O)OCH_3$ and -$C(O)OC_2H_5$.

[0037] In formula (I), Z, called "the central core", is preferably selected from C_1-C_{12} alkylene, C_3-C_7 cycloalkylene, C_3-C_{14} arylene, C_5-C_{10}heteroarylene, (C_1-C_4 alkylene)-(C_3-C_{14} arylene), (C_1-C_4 alkylene)-(C_3-C_{14} heteroarylene), (C_1-C_4 alkylene)-(C_3-C_{14} arylene)-(C_1-C_4 alkylene), (C_1-C_4 alkylene)-(C_3-C_{14} heteroarylene)-(C_1-C_4 alkylene), (C_3-C_{14} arylene)-(C_3-C_{14} arylene), (C_1-C_4 alkylene)-(C_3-C_{14} arylene)-(C_3-C_{14} arylene)-(C_1-C_4 alkylene) and (C_3-C_{14} arylene)-(CR'R")-(C_3-C_{14} arylene) wherein R' and R" form together with the carbon to which they are linked a C_3-C_{20} carbocyclic group; wherein the arylene and cycloalkylene groups may be substituted by one or more substituents selected from halogen, C_1-C_4 alkyl, C_1-C_4 alkoxy and C_3-C_7 cycloalkyl, and the alkylene groups may be substituted by one or more substituents selected from halogen, C_3-C_{14} alkyl, C_1-C_{12} alkoxy, C_2-C_{12} acyloxy, C_1-C_{12} hydroxyalkyl, C_3-C_{12} cycloalkyl, phenyl phenyloxy and substituted phenyl. In particular, substituted alkylene include -$CH_2(CR^aR^b)CH_2$- wherein R^a and R^b may be independently selected from H, C_3-C_{14} alkyl, C_3-C_{12} cycloalkyl, (cycloalkyl)methyl, aryl, substituted aryl, arylalkyl such as benzyl or phenyl(C_2-C_7 alkyl), phenyloxyethyl, substituted arylalkyl, C_1-C_{12} alkoxy, C_2-C_{12} acyloxy, C_1-C_{12} hydroxyalkyl, and C_1-C_{12} alkoxymethyl.

[0038] More preferably, Z is selected from C_1-C_{12} alkylene, aryl substituted C_1-C_{12} alkylene, phenylene, naphthylene, (C_1-C_4 alkylene)-phenylene-(C_1-C_4 alkylene), (C_1-C_4 alkylene)-naphthylene-(C_1-C_4 alkylene) such as naphthylene bis(methylene), quinoxaline-2,3-diyl, (C_1-C_4 alkylene)-quinoxaline-2,3-diyl-(C_1-C_4 alkylene) such as quinoxaline-2,3-diylbis(methylene), phenylene-phenylene, (C_1-C_4 alkylene)-phenylene-phenylene-(C_1-C_4 alkylene) and phenylene-fluorenylene-phenylene. For example, Z may be selected from-CH_2-, -$(CH_2)_2$-, -$(CH_2)_3$-, -$(CH_2)_4$-, -$(CH_2)_5$-, -CH_2-$CH(CH_3)$-CH_2-, -CH_2-$CH(CH_2Phenyl)$-CH_2-, -$(CH_2)_2$-$CH(CH_3)$-CH_2-, -$(CH_2)_3$-$CH(CH_3)$-CH_2-, -$(CH_2)_2$-$CH(CH_3)$-$(CH_2)_2$-,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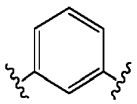
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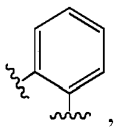
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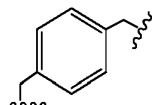
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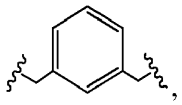
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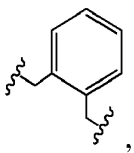
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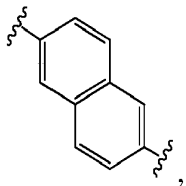
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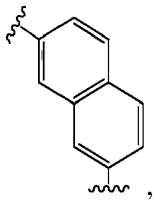
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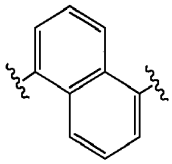
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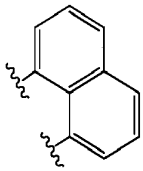
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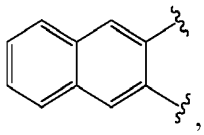
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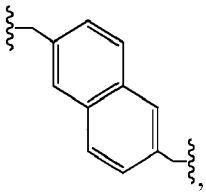
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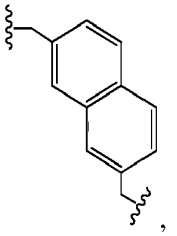
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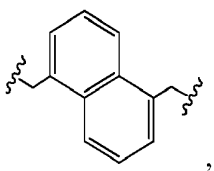
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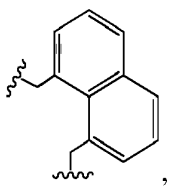
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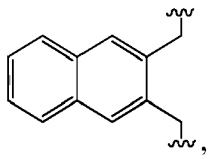
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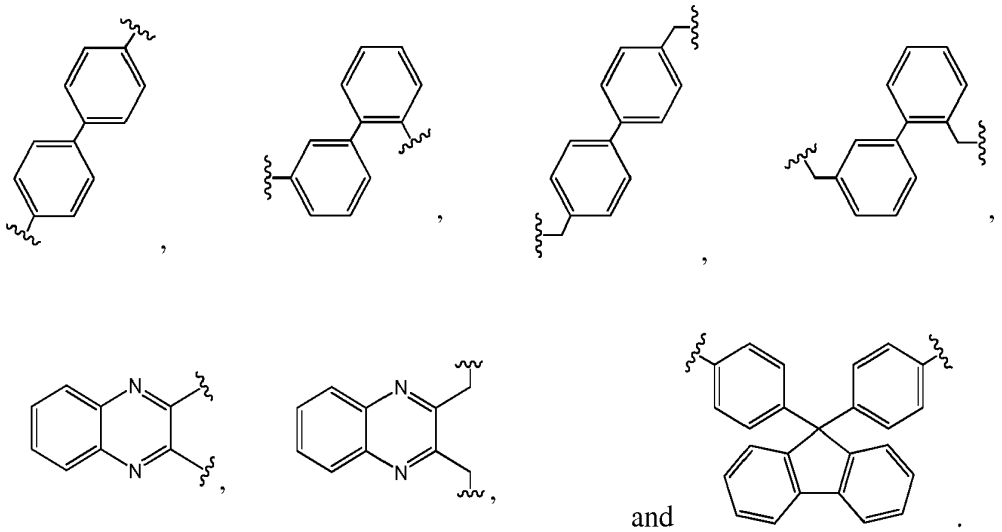
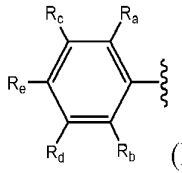


[0039] A and B are preferably respectively selected from nitrogen and -$N^+(R^{7a})$-, and from nitrogen and -$N^+(R^{7b})$-,wherein R^{7a} and R^{7b} are independently selected from C_6-C_8 alkyl, in particular *n*-hexyl, and phenyl or naphthyl, wherein phenyl and naphthyl may be both substituted by one or more substituents independently selected from halogen, cyano, nitro, hydroxy, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy, C_1-C_4 alkylthio, C_1-C_4 haloalkylthio, C_3-C_7 cycloalkyl, (C_3-C_7 cycloalkyl)C_1-C_4 alkyl.

[0040] In particular, A and B may be selected from -$N^+(C_6$-C_8 alkyl)-, preferably -$N^+(C_6H_{13})$-, more preferably -$N^+(n$-$C_6H_{13})$-, which have a good solubility in conventional solvents used in electrochromic compositions such as propylene carbonate while maintaining a fast fading rate to the bleached state. Indeed, C_1-C_5 alkyl substituted viologen compounds are more difficult to solubilise in some solvents used in electrochromic compositions like some ionic liquids. On the contrary, higher alkyl substituted two-core viologen compounds have good solubility. However, when two-core viologen compounds are substituted with long chain alkyls having more than 8 carbon atoms the fading rate tends to decrease, which prevents a fast reversibility to the bleached state.

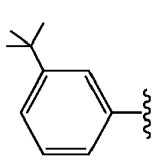
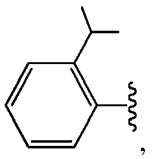
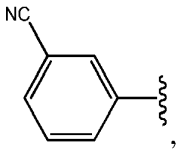
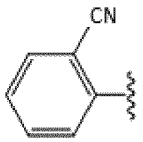
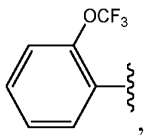
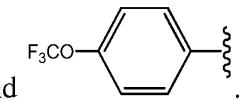
[0041] Also, the inventors have observed that the presence of aryl substituents, in particular phenyl substituents, on the viologen cores of compounds of the present invention results in the stabilization of the compounds of the invention and, consequently, in a decrease of the activation potential, which corresponds to an increase in the reduction potential, of the viologen compounds. Therefore, in a preferred embodiment, A and B may be respectively selected from nitrogen and -$N^+(R^{7a})$-, and from nitrogen and -$N^+(R^{7b})$-,wherein R^{7a} and R^{7b} are independently selected from optionally substituted phenyl groups represented by formula (II):



(II)

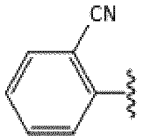
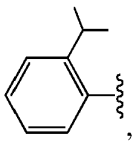
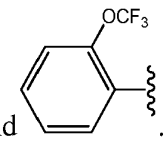
wherein R_a, R_b, R_c, R_d and R_e are each independently selected from H, halogen, cyano, nitro, hydroxyl, alkyl, benzyl, haloalkyl, alkoxy, alkylthio, haloalkoxy, acyl, aroyl, alkoxycarbonyl, cycloalkyl, allyl, aryl and heteroaryl. In a particular embodiment, at least one of R_a, R_b, R_c, R_d and R_e is not H. Preferably, at least one of R_a, R_b, R_c, R_d and R_e is selected from halogen, cyano, nitro, hydroxyl, haloalkyl, haloalkoxy, alkoxycarbonyl, aryl and heteroaryl. Indeed, the applicant found that such electron-withdrawing substituents stabilize the cation which results in a decrease of the activation potential. In a preferred embodiment, R_e is H and at least one of R_a, R_b R_c and R_d is not H.

[0042] For example, at least one of R_a, R_b, R_c, R_d and R_e may be selected from methyl, *i*-propyl, *t*-butyl, cyano, trifluoromethoxypreferably trifluoromethoxy. Thus, A and B may be repectively -$N^+(R^{7a})$- and -$N^+(R^{7b})$-,wherein R^{7a} or R^{7b} are independently selected from:

and

[0043] In a preferred embodiment, A and B are respectively -$N^+(R^{7a})$- and -$N^+(R^{7b})$-, wherein R^{7a} or R^{7b} are respectively selected from substituted phenyl groups of formula (II), wherein R_c, R_d and R_e are H and R_a and R_b are as defined above provided that at least one of R_a and R_b is not H. In particular, A and B are independently selected from -$N^+(R^{7a})$- and -$N^+(R^{7b})$-wherein R^{7a} or R^{7b} may be selected from:

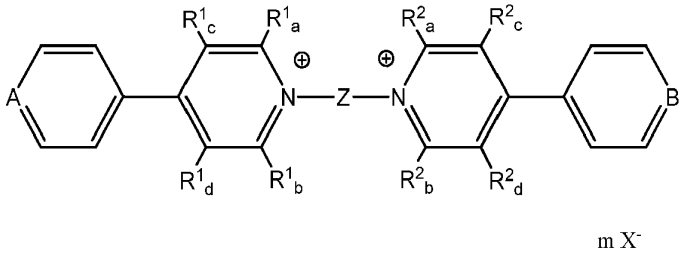
and

[0044] Indeed, the Applicant has found that the presence of a substituent in the ortho position of the phenyl group results in a hypsochromic effect compared to the meta position, which provides itself a hypsochromic effect compared to the para position. Indeed the maximum wavelength λ_{max} in the absorption spectrum for a similar compound is higher when the substituent is in the para position of the phenyl group, than in the meta position, and a fortiori than in the ortho position. Consequently, the present invention provides new electrochromic compounds that can have a wide range of colours in their coloured state, in particular in the low visible wavelength - i.e. blue couloured state -, while presenting good stability and close oxydo-reduction potential values to each other.

[0045] The counterion X^- may be any anion that maintains electric neutrality of the viologen compounds of formula (I). X- is preferably selected from halide, preferably fluoride and chloride, tetrafluoroborate, tetraphenylborate, perchlorate, hexafluorophosphate, nitrate, methanesulfonate, trifluoromethane sulfonate, toluene sulfonate, hexachloroantimonate, bis(trifluoromethanesulfonyl)imide, acetate and sulfate.

[0046] Preferably, R^1_a, R^1_b, R^1_c, R^1_d, R^2_a, R^2_b, R^2_c, R^2_d, R^3_a, R^3_b, R^3_c, R^3_d, R^4_a, R^4_b, R^4_c and R^4_d are each independently selected from hydrogen, aryl, substituted aryl, heteroaryl and substituted heteroaryl, preferably selected from optionally substituted phenyl, more preferably selected from phenyl, tolyl and cumyl.

[0047] In a first embodiment, the present invention relates to compounds of formula (I-1):



m X^-

(I-1)

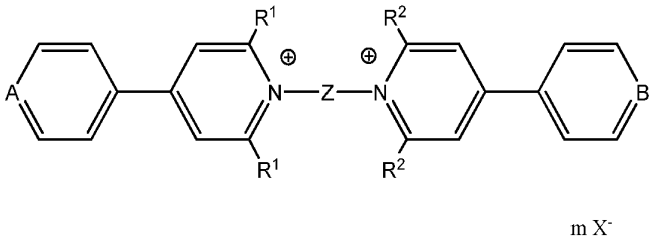
wherein Z, A, B, R^1_a, R^1_b, R^1_c, R^1_d, R^2_a, R^2_b, R^2_c, R^2_d, X^- and m are as defined above.

[0048] R^1_a, R^1_b, R^1_c, R^1_d, R^2_a, R^2_b, R^2_c and R^2_d are prefererably selected from H, aryl, substituted aryl, heteroaryl and substituted heteroaryl provided that at least one of R^1_a, R^1_b, R^1_c, R^1_d, R^2_a, R^2_b, R^2_c and R^2_d is not H.

[0049] Indeed, aryl, heteroaryl, substituted aryl and substituted heteroaryl are particularly preferred, more particularly optionally substituted phenyl such as phenyl, tolyl and cumyl, because they induce a decrease of the activation potential of the compounds of the invention. Moreover, the steric hindrance provided by the presence of such substituents on the

viologen cores of the compounds of the invention is believed to prevent π- π interactions between the aromatic viologen cores which is the cause of the stacking phenomenon on or near the electrode surface. For example, R^1_a, R^1_b, R^1_c, R^1_d, R^2_a, R^2_b, R^2_c and R^2_d may be selected from H, aryl and heteroaryl, wherein the aryl and heteroaryl may be substituted by one or more substituents selected from C_1-C_4 alkyl and C_1-C_4 haloalkyl, wherein at least one of R^1_a, R^1_b, R^1_c, R^1_d, R^2_a, R^2_b, R^2_c and R^2_d is not H.

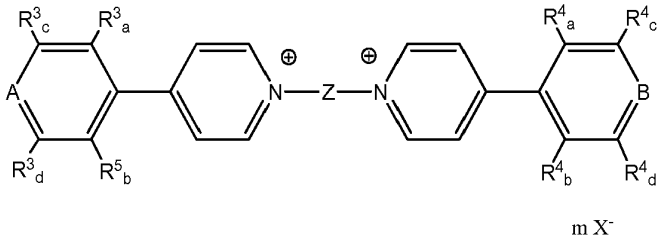
[0050] Particularly preferred compounds are compounds of formula (I-3):



(I-3)

wherein Z, A, B, X- and m are as defined above and R^1 and R^2 are each independently selected from H, alkyl, alkoxy, alkylthio, haloalkyl, haloalkoxy, haloalkythio, polyalkylenoxy, alkoxycarbonyl, aryl, substituted aryl, heteroaryl and substituted heteroaryl, wherein the alkyl group may be substituted by one or more substituents independently selected from alkoxy, cycloalkyl, aryl, substituted aryl, heteroaryl and substituted heteroaryl, provided that at least one of R^1 and R^2 is not H; preferably, none of R^1 and R^2 is H; more preferably, R^1 and R^2 are independently selected from aryl, heteroaryl, substituted aryl and substituted heteroaryl. For example, R^1 and R^2, may be independently selected from phenyl, p-methylphenyl and p-trifluoromethylphenyl. In a particular embodiment, R^1 and R^2 are identical.

[0051] In a second embodiment, the present invention relates to compounds of formula (I-4):

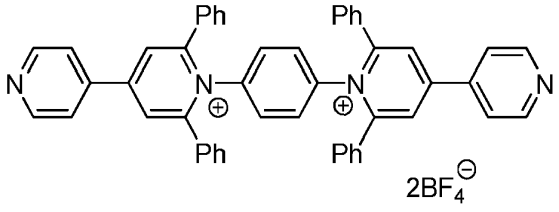


(I-4)

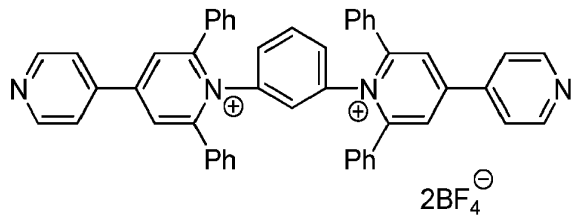
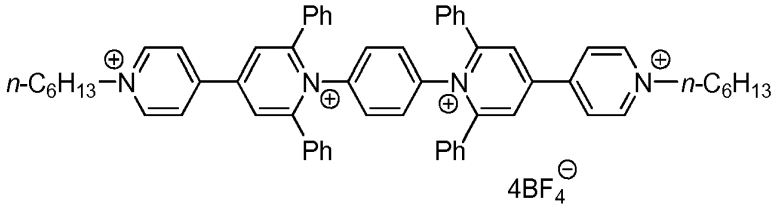
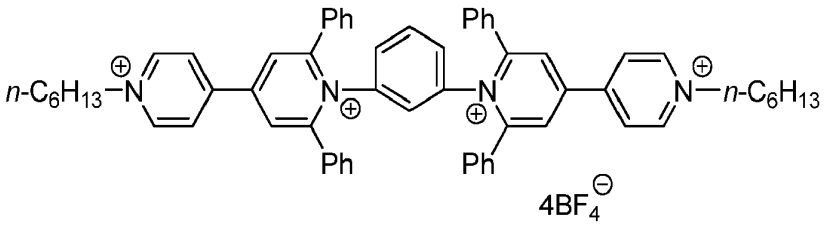
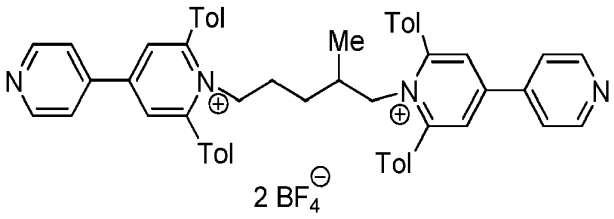
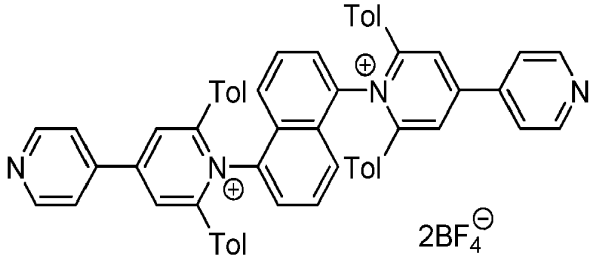
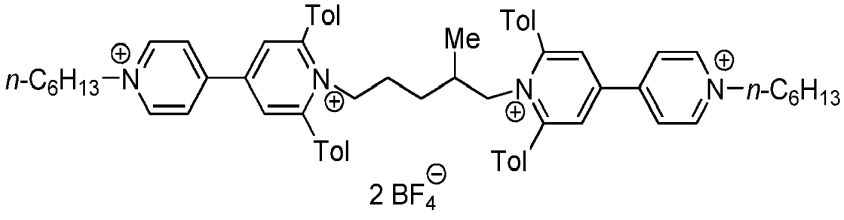
wherein Z, A, B, R^3_a, R^3_b, R^3_c, R^3_d, R^4_a, R^4_b, R^4_c, R^4_d, X^- and m are as defined above.

[0052] R^3_a, R^3_b, R^3_c, R^3_d, R^4_a, R^4_b, R^4_c and R^4_d are preferably each independently selected from H, C_1-C_4 alkyl and C_1-C_4 alkoxycarbonyl, provided that at least one of R^3_a, R^3_b, R^3_c, R^3_d, R^4_a, R^4_b, R^4_c and R^4_d is not H. For example, R^3_a, R^3_b, R^3_c, R^3_d, R^4_a, R^4_b, R^4_c and R^4_d may be independently selected from methyl and ethoxycarbonyl. In a particular embodiement, none of R^3_a, R^3_b, R^3_c, R^3_d, R^4_a, R^4_b, R^4_c and R^4_d is H.

[0053] In a particularly preferred embodiment, the compounds of the present invention are selected from the group consisting of:

Compound	Formula
1-1	

(continued)

Compound	Formula
1-2	
1-3	
1-4	
1-5	
1-6	
1-7	

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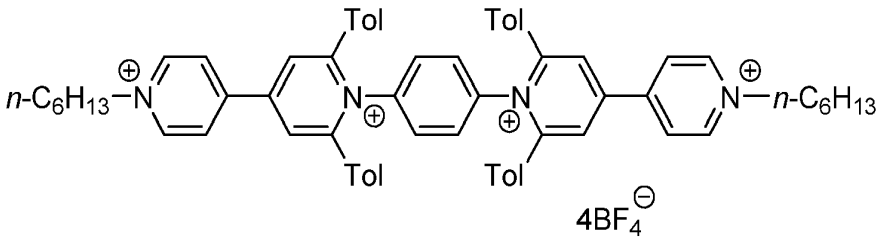
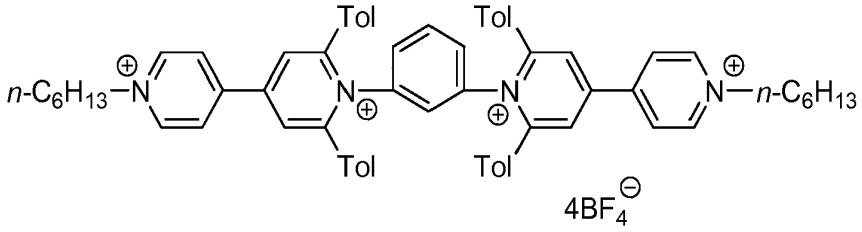
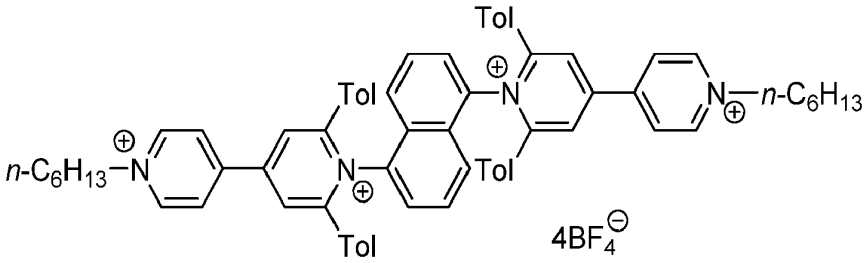
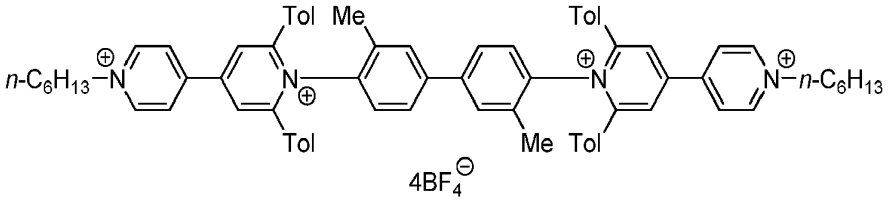
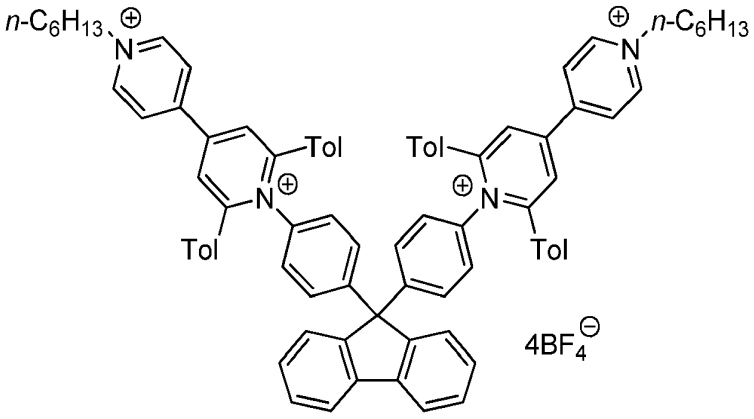
Compound	Formula
1-8	
1-9	
1-10	
1-11	
1-12	

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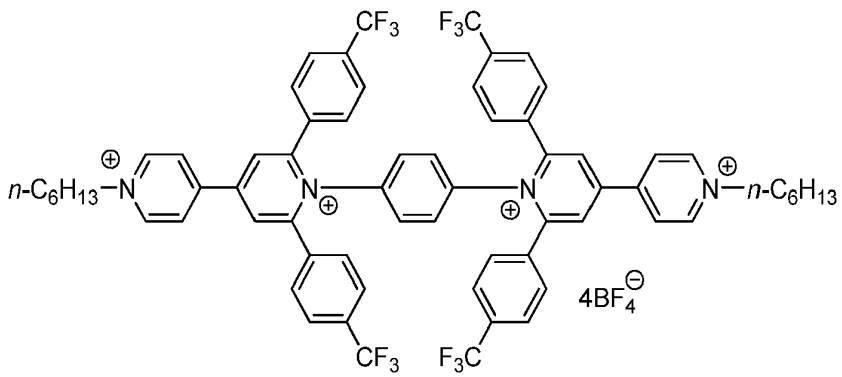
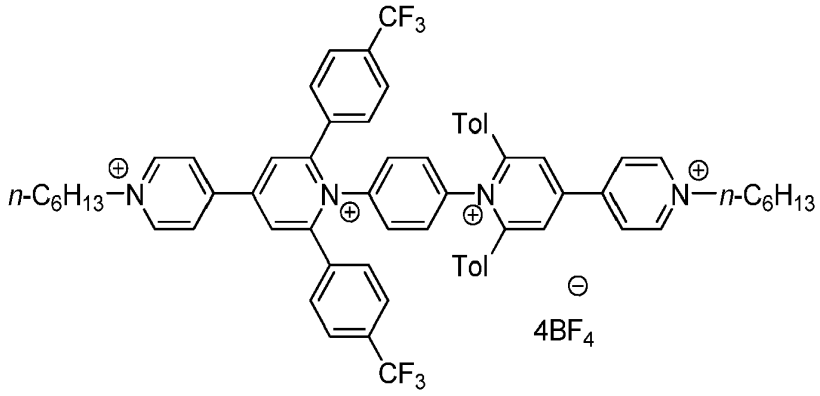
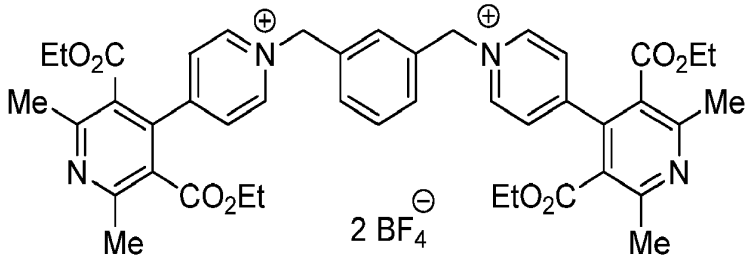
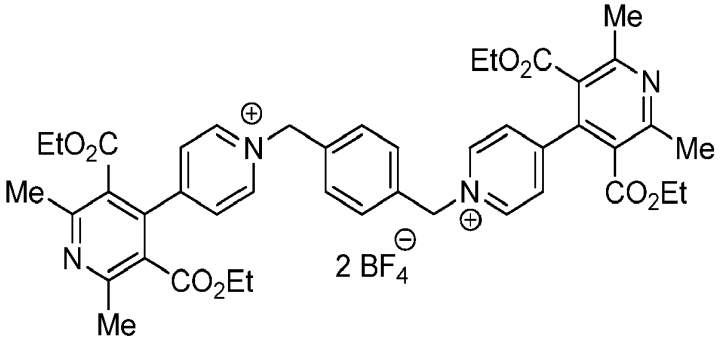
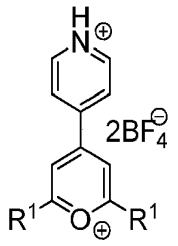
Compound	Formula
1-13	
1-14	
2-1	
2-2	

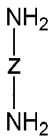
Me represents methyl; Ph represents phenyl; Tol represents 4-methylphenyl

[0054] Compounds represented by formula (I) may be prepared according to various methods well known in the art. However, the Applicant has found a particularly advantageous method for preparing compounds of formula (I-3). According to this new method, which is illustrated hereafter, a wide variety of useful alkyl, aryl and heteroaryl substituents can be readily introduced onto the C-atoms of the pyridine rings.

[0055] Such high fexiblity is not possible according to the method disclosed in US 2009/0082570 A1.() US 2009/0082570 A1 discloses a method of manufacturing a range of viologens which include a selection of arylene bridged violgens. Besides the series of bridged viologens is exemplified by symmetrically substituted arylene bridged viologens which are accessed from expensive commercially available 4,4'-bipyridine. Therefore, the present invention also relates to a method for preparing a compound of formula (I-3) comprising the step of reacting a 2,6-disubstituted-4-[(1H)-pyridinium-4-yl]pyrylium bis(tetrafluoroborate) (1) with a diamine (2):



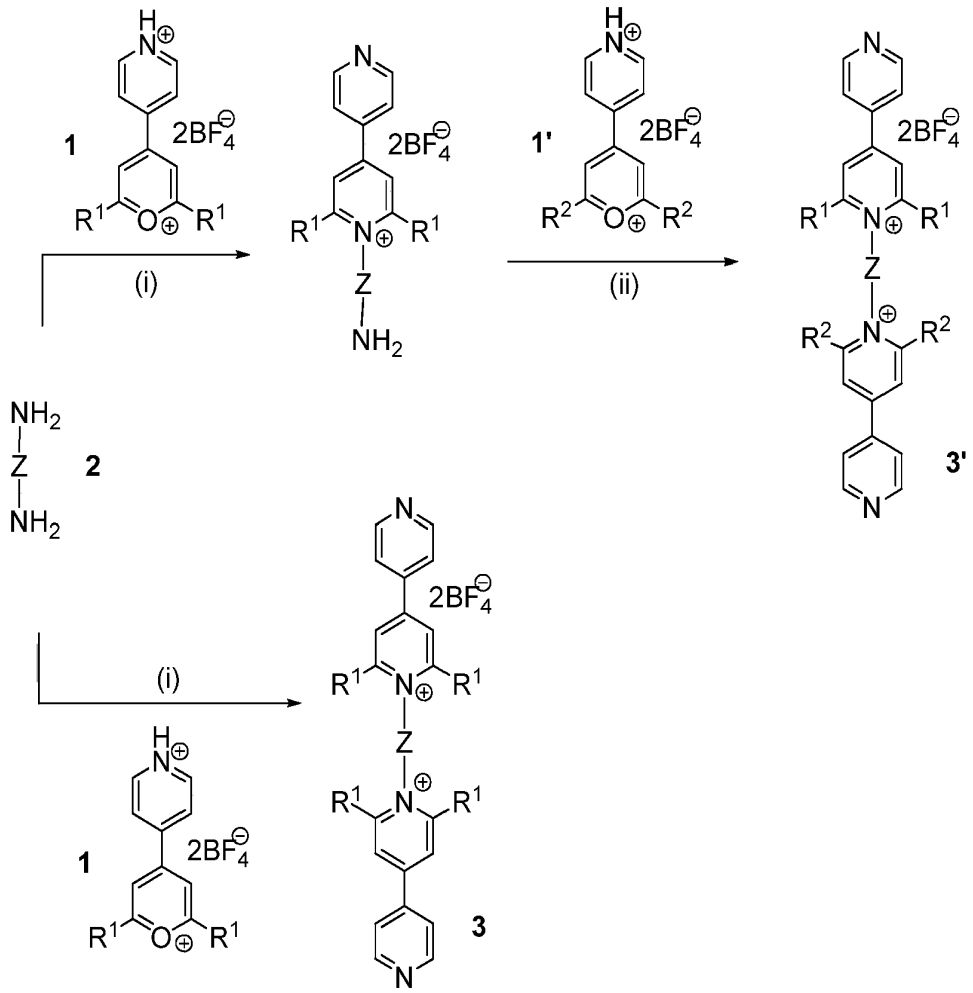
1



2

wherein Z, and R^1 are as defined above.

[0056] The use of a single 2,6-disubstituted-4-[(1H)-pyridinium-4-yl]pyrylium bis(tetrafluoroborate) (1) results in symetrically substituted two-cores viologen derivatives (3) of formula (I-3) wherein A and B are nitrogen, and R^1 and R^2 are identical. Through a control the amount of the diamine (2) and a subsequent reaction with a second 2,6-disubstituted-4-[(1H)-pyridinium-4-yl]pyrylium bis(tetrafluoroborate) (1'), unsymetrically substituted two-cores viologen derivatives (3') of formula (I-3) wherein A and B are nitrogen, and R^1 and R^2 are different can be obtained as shown on scheme A.



Scheme A

[0057] Steps (i) and (ii) disclosed in scheme A may be achieved under heat, for example from 70 to 90°C, in an alcohol and in the presence of a base.

[0058] Compounds of formula (I-3) wherein A and/or B are respectively -$N^+(R^{7a})$- and - $N^+(R^{7b})$- as defined above can be obtained from the corresponding compounds (3) or (3') using suitable reaction step well known in the art. For example, compounds of formula (I-3) wherein A and/or B are -N^+(alkyl)- can be obtained through an *N*-alkylation of the corresponding compound (3) or (3') with a suitable haloalkane.

[0059] The 2,6-disubstituted-4-[(1H)-pyridinium-4-yl]pyrylium bis(tetrafluoroborate) (1) may be prepared according to various methods well known in the art. For example, 4-(4-pyridyl)-1,5-disubstituted-1,5-diketones can be obtained by the condensation of pyridine-4-carboxaldehyde and substituted acetophenones (see for example Aryl-substituted Derivatives of 4,4'-Bipyridylium Salts: their Spectroscopic Properties and Stereochemistry, J. E. Downes, J. Chem. Soc. (C), 1967, 1491 and Pyrylogens: Synthesis, Structural, Electrochemical, and Photophysical Characterization of a New Class of Electron Transfer Sensitizers, E. L. Clennan, C. Liao, E. Ayokosok, J. Am. Chem. Soc., 2008, 130, 7552). The cyclisation of the 4-(4-pyridyl)-1,5-disubstituted 1,5-diketones can be readily accomplished by, for example, heating in glacial acetic acid containing *trans*-chalcone and boron trifluoride etherate to give the 2,5-disubstituted 4-[(1*H*)-pyridinium-4-yl]pyrylium bis(tetrafluoroborates) (1).

[0060] Further specific examples of synthesis of compounds of the invention are illustrated below.

[0061] The present invention also relates to electrochromic compositions comprising at least one compound of formula (I) as defined above as an oxydizing electrochromic compound. One or more additional oxidizing electrochromic compounds can be added to the composition of the invention so as to adapt the colour or the intensity of the coloured state of the composition. Said additional compound can be another compound of formula (I) or a different compound such as compatible dyes or pigments. For Example, the additional oxidizing electrochromic compound can be selected from alkylviologens, arylviologens, alkylarylviologens, anthraquinone and their derivatives. Preferably, the additional compound has a redox potential close to the compound of formula (I). The composition also comprises a reducing compound.

The reducing compound can be also an electrochromic compound. Example of reducing compounds include 5,10-dihydrophenazine, phenazine, phenothiazine, N,N,N',N'-tetramethyl-p-phenylenediamine, thioanthrene, tetrathiafulvalene, ferrocene and their derivatives.

[0062] The composition of the invention may comprise a fluid, mesomorphous or gel host medium in which the electrochromic compounds are preferably dissolved. The fluid or mesomorphous host medium is preferably selected from the group consisting of organic solvents, liquid crystals, polymers or liquid crystal polymers and mixtures thereof.

[0063] Suitable solvents are redox-inert solvents which cannot react with the electrochromic compounds of the composition. Examples of suitable solvents are ethylene carbonate, propylene carbonate, γ-butyrolactone, γ-valerolactone, acetronitrile, propionitrile, benzonitrile, glutaronitrile, methylglutaronitrile, dimethylformamide, N-methylpyrrolidone, sulfolane, 3-methyl sulfolane, benzene, toluene, methyl ethyl ketone, acetone, ethanol, tetrahydrofurfuryl alcohol, 2-methoxyethyl ether, xylene, cyclohexane, 3-methylcyclohexanone, ethyl acetate, ethyl phenylacetate, tetrahydrofuran, methanol, methyl propionate, ethylene glycol ethylene carbonate, ionic liquids, and mixtures thereof. Preference is given to carbonate and particularly propylene carbonate.

[0064] The liquid crystal medium that may be used in the present invention includes, without being limited to, such materials as nematic or chiral nematic media.

[0065] The polymers that may be used in the present invention includes, without being limited to polymers which are soluble with the solvent, in particular PMMA or other acrylate polymers, polyurethane, polyethylene oxide, polypropylene oxide, polyvinyl acetate, poly(N-vinyl pyrrolidone), and polyvinylidene fluoride.

[0066] Alternatively a polymeric liquid crystal medium can be used as the host material. These liquid crystal, polymer polymeric liquid crystal media are generally used in combination with an organic solvent, for example one of the organic solvents mentioned above.

[0067] The present invention also relates to an electrochromic device comprising a compound of formula (I) or a composition according to the invention. Said device may be selected from an optical article , preferably an optical lens or an optical filter, a window, preferably an aircraft window, a visor, a mirror and a display, in particular a segmented or matrix display. Preferably, the electrochromic device of the invention is an optical article, more preferably an optical lens, and even more preferably an ophthalmic lens.

[0068] Non- limiting examples of ophthalmic lens include corrective and non-corrective lenses, including single vision or multi-vision lenses, which may be either segmented or non-segmented, as well as other elements used to correct, protect, or enhance vision, including without limitation contact lenses, intra-ocular lenses, magnifying lenses and protective lenses or visors. Non-limiting examples of display elements and devices include screens and monitors. Non-limiting examples of windows include automotive, marine and aircraft windows, filters, shutters, and optical switches.

[0069] A preferred device for holding the composition of the invention in a mechanically stable can comprise a pair of opposed substrates having a gap there between for receiving the mixture of the host medium and said compound or said composition of the present invention, and a frame for holding said pair of substrates adjacent one another.

[0070] Another device of the present invention comprises an optical component provided with at least one transparent cell arrangement juxtaposed in a parallel direction to the surface thereof, as disclosed in WO 2006/013250, each cell being tightly closed and containing said fluid, mesomorphous or gel host medium and said at least one compound of the present invention. Other devices according to the invention can be a device as described in FR 2937154 or FR2950710 comprising at least one compound of the invention.

EXAMPLES

[0071] This invention will be further illustrated by the following non-limiting examples which are given for illustrative purposes only and should not restrict the scope of the appended claims.

Example 1

Synthesis of compound 1-1: 4,4'-(1,4-phenylene)-bis[(4-pyridyl)-2,6-diphenylpyridinium] bis(tetrafluoroborate)

[0072] Boron trifluoride diethyl etherate (9 equiv.) was added dropwise to a solution of the 1,5-bis(phenyl)-3-(4-pyridyl)pentan-1,5-dione (1 equiv.) and *trans*-chalcone (1.15 equiv.) in hot glacial acetic acid (9 mL). The solution was heated under reflux for 6 hours. After cooling to room temperature diethyl ether (50 mL) was added and the resulting red precipitate was collected by filtration under reduced pressure. The foregoing solid was crystallised from glacial acetic acid to afford 2,6-diphenyl-4-[(1*H*)-pyridinium-4-yl]pyrylium bis(tetrafluoroborates) as a bright orange powder (71 %) after vacuum filtration and washing with anhydrous diethyl ether.

[0073] 2,6-diphenyl-4-[(1*H*)-pyridinium-4-yl]pyrylium bis(tetrafluoroborate) (2.15 equiv.) and sodium acetate (8.5 equiv.) was added to a stirred solution of the 1,4-diaminobenzene (1.0 equiv.) in propan-2-ol (50 mL). The reaction mixture was then heated under reflux for 16 hours whereupon a pale cream/yellow precipitate had formed. Water (25

mL) was then added to the hot suspension and the reaction mixture was stirred at room temperature for 12 hours. The precipitate was collected by vacuum filtration and air dried and then dried at 20 °C under reduced pressure (1 mbar, Buchi Kugelrohr drying pistol) for 24 h to afford compound 1-1 as a yellow-beige powder (71 %), mp = >360 °C, ν_{max} 3057, 1629, 1594, 1572, 1547, 1496, 1406, 1231, 1049, 1028, 816, 757, 701, 614, 557, 508 cm^{-1}, δ_H(300 MHz, d_6-DMSO) 7.25 (16H, m, Ar-H), 7.54 (8H, m, Ar-H), 8.23 (4H, d, *J* = 6.3 Hz, N-CH=CH), 8.58 (4H, s, PhC=CH), 8.84 (4H, d, *J* = 6.3 Hz, N-CH=CH).

Example 2

Synthesis of compound 1-4: 4,4'-(1,3-phenylene)-bis[(4-pyridyl)-2,6-diphenylpyridinium] bis(tetrafluoroborate)

[0074] Compound 1-2 was obtained through an equivalent synthesis to example 1 using 1,3-diaminobenzene instead of 1,4-diaminobenzene.

Example 3

Synthesis of compound 1-4: 4,4'-(1,3-phenylene)-bis[1'-*n*-hexyl-2,6-diphenylpyridinium] tetrakis(tetrafluoroborate)

[0075] A stirred solution of compound 1-2 (1 equiv.) and 1-iodohexane (4 equiv.) in acetonitrile (30 mL), protected from daylight, was heated under reflux for ca. 16 hours. The cooled solvent was evaporated to dryness and the residue dissolved in a minimum amount of methanol (ca. 15 mL) and added dropwise to a vigorously stirred solution of $NaBF_4$ (8-10 equiv.) in water (200 mL). The resulting yellow-orange precipitate was collected by vacuum filtration and washed thoroughly with cold water and dried at 20 °C under reduced pressure (1 mbar, Buchi Kugelrohr drying pistol) for 24 h. Compound 1-4 was obtained as a pale orange-fawn powder (77 %), mp = 212 °C softens, decomp. at 320 °C, ν_{max} 3613, 3068, 2931, 2863, 1626, 1554, 1420, 1230, 1028, 849, 777, 764, 699, 519 cm^{-1}, δ_H(300 MHz, d_4-MeOH) 0.95 (6H, t, *J* = 7.2 Hz, $[(CH_2)_5CH_3]_2$), 1.40 (12H, bs, $[(CH_2)_3]_2$), 2.09 (4H, bm, $(CH_2)_2$), 4.73 (4H, t, *J* = 7.2 Hz, $(NCH_2)_2$), 7.05 (1H, app t, *J* = 8.1 Hz, NC=CH-CH), 7.15 (8H, m, Ar-H), 7.43 (8H, m, Ar-H), 7.57 (6H, m, Ar-H, NC=CH-CH), 7.74 (1H, app t, *J* = 1.8 Hz, NC-CH=CN), 8.60 (4H, s, ArC=CH), 8.69 (4H, d, *J* = 6.6 Hz, NCH=CH), 9.21 (4H, d, *J* = 6.6 Hz, NCH=CH), δ_C(75 MHz, d_4-MeOH) 14.27, 23.46, 26.88, 32.30, 32.51, 63.36, 128.76, 130.08, 130.29, 130.44, 130.55, 131.23, 132.18, 132.34, 133.75, 141.08, 146.87, 151.44, 152.43, 159.36. Found: $[M - 3BF_4^-]^{3+}$ = 316.1678; $C_{62}H_{62}B_4F_{16}N_4$ requires $[M - 3BF_4^-]^{3+}$ = 316.1675.

Example 4

Synthesis of compound 1-3: 4,4'-(1,4-phenylene)-bis[1'-*n*-hexyl-2,6-diphenylpyridinium] tetrakis(tetrafluoroborate)

[0076] Compound 1-3 was obtained through an equivalent synthesis starting from compound 1-1 instead of compound 1-2.

Example 5

Synthesis of compound 1-5: 1,1''-(2-methylpentan-1,5-diyl)bis(2,6-di(*p*-tolyl)-[4,4'-bipyridin]-1-ium) bis(tetrafluoroborate)

[0077] 2,6-di(*p*-tolyl)-4-[(1*H*)-pyridinium-4-yl]pyrylium bis(tetrafluoroborate) was obtained from 1,5-di(*p*-tolyl)-3-(4-pyridyl)pentan-1,5-dione as a bright orange powder after crystallisation from glacial acetic acid (71 %), through an equivalent synthesis to 2,6-diphenyl-4-[(1*H*)-pyridinium-4-yl]pyrylium bis(tetrafluoroborates) of example 1.

[0078] A mixture of 2,6-di-*p*-tolyl-4-[(1*H*)-pyridinium-4-yl]pyrylium bis(tetrafluoroborate) (2.10 g, 4.1 mmol), 2-methylpentan-1,5-diamine (0.21 g, 1.8 mmol) and NaOAc (1.34 g, 16.3 mmol) in isopropanol (30 mL) was heated at reflux for 16 h. After cooling, water (40 mL) was added and the resulting precipitate filtered, washed with water (2 × 20 mL) and air dried to give the compound 1-5 (1.10 g, 65 %) as a grey powder.

Example 6

Synthesis of compound 1-6: 4,4'-(1,5-naphthylene)-bis[2,6-di(*p*-tolyl)pyridinium] tetrakis(tetrafluoroborate)

[0079] 2,6-di-*p*-tolyl-4-[(1*H*)-pyridinium-4-yl]pyrylium bis(tetrafluoroborate) (2.15 equiv.) and sodium acetate (8.5 equiv.), obtained from 1,5-di-*p*-tolyl-3-(4-pyridyl)pentan-1,5-dione, was added to a stirred solution of the 1,5-diaminonaphtalene (1.0 equiv.) in propan-2-ol (50 mL). The reaction mixture was then heated under reflux for ca. 16 hours

whereupon a pale cream/yellow precipitate had formed. Water (25 mL) was then added to the hot suspension and the reaction mixture was stirred at room temperature for ca. 12 hours. The precipitate was collected by vacuum filtration, washed with aqueous ethanol and air dried to give compound 1-6.

Example 7

Synthesis of compound 1-7: 1,1''-(2-methylpentan-1,5-diyl)bis(2,6-di(*p*-tolyl)-[4,4'-bipyridin]-1-ium) tetrakis(tetrafluoroborate)

[0080] A solution of compound 1-5 obtained in example 5 (1.10 g, 1.2 mmol) and 1-iodohexane (1 g, 4.7 mmol) in MeCN (20 mL) was heated at reflux for 16 h, cooled and the volume reduced (to ~10 mL) and Et_2O (60 mL) added. The mixture was stirred for 1 h and decanted. Fresh Et_2O was added and decanted and the residue was air dried, dissolved in MeOH (5 mL) and added dropwise to a solution of $NaBF_4$ (6.6 g, 60 mml) in water (200 mL) with rapid stirring. The product was filtered, washed with water (3 × 20 mL) and air dried to give compound 1-7 (0.89 g, 56 %) as an orange powder, δ_H(400 MHz, CD_3OD) 9.07 - 9.13 (4H, m, NC<u>H</u>=CH), 8.58 (2H, d, *J* = 6.8 Hz, NCH=C<u>H</u>), 8.582 (2H, d, *J* = 6.8 Hz, NCH=C<u>H</u>), 8.37 (2H, s, NC(Tol)=CH), 8.34 (2H, s, NC(Tol)=CH), 7.60 - 7.50 (8H, m, Ar-H), 7.45 - 7.35 (8H, m, Ar-H), 4.70 - 4.10 (8H, m, NCH_2), 2.42 (6H, s, Ar-Me), 2.40 (6H, s, Ar-Me), 2.10 - 1.90 (7H, m, aliphatic-H), 1.40 - 0.70 (23H, m, aliphatic-H).

Example 8

Synthesis of compound 1-8: 4,4'-(1,4-phenylene)-bis[1'-*n*-hexyl-2,6-di(p-tolyl)pyridinium] tetrakis(tetrafluoroborate)

[0081] 4,4'-(1,4-phenylene)-bis[(4-pyridyl)-2,6-di(*p*-tolyl)-pyridinium] bis(tetrafluoroborate) was obtained through an equivalent synthesis to example 1 starting from 2,6-di(*p*-tolyl)-4-[(1*H*)-pyridinium-4-yl]pyrylium bis(tetrafluoroborate), obtained from 1,5-di(*p*-tolyl)-3-(4-pyridyl)pentan-1,5-dione.

[0082] Compound 1-8 was obtained, through an equivalent synthesis to example 3 starting from 4,4'-(1,4-phenylene)-bis[(4-pyridyl)-2,6-di(*p*-tolyl)-pyridinium] bis(tetrafluoroborate) instead of compound 1-2, as a pale orange powder (63 %), mp = 223 °C softens, decomp. at 293 °C, ν_{max} 3617, 3066, 2929, 2863, 1626, 1552, 1514, 1229, 1027, 858, 814, 520 cm^{-1}, δ_H(300 MHz, d_4-MeOH) 0.94 (6H, t, *J* = 7.2 Hz, $[(CH_2)_5C\underline{H}_3]_2$), 1.40 (12H, bs, $[(CH_2)_3]_2$), 2.09 (4H, bs, $(CH_2)_2$), 2.51 (12H, s, 4-$C\underline{H}_3C_6H_4$), 4.73 (4H, t, *J* = 7.2 Hz, $(NCH_2)_2$), 7.24 (16H, m, 4-$CH_3C_6\underline{H}_4$), 7.48 (4H, s, N-C_6H_4-N), 8.54 (4H, s, ArC=CH), 8.68 (4H, d, *J* = 6.6 Hz, NCH=C<u>H</u>), 9.20 (4H, d, *J* = 6.6 Hz, NC<u>H</u>=CH), δ_C(75 MHz, d_4-MeOH) 14.25, 21.69, 23.46, 26.88, 32.29, 32.50, 63.33, 128.66, 129.97, 130.68, 130.98, 131.07, 131.13, 141.74, 142.45, 146.87, 151.44, 151.79, 159.53. Found: $[M - 3BF_4^-]^{3+}$ = 334.8549; $C_{66}H_{70}B_4F_{16}N_4$ requires $[M - 3BF_4^-]^{3+}$ = 334.8550.

Example 9

Synthesis of compound 1-9: 4,4'-(1,3-phenylene)-bis[1'-*n*-hexyl-2,6-di(*p*-tolyl)pyridinium] tetrakis(tetrafluoroborate)

[0083] Compound 1-9 was obtained through an equivalent synthesis to example 8 using 1,3-diaminobenzene instead of 1,4-diaminobenzene.

Example 10

Synthesis of compound 1-10: 4,4'-(1,5-naphthylene)-bis[1'-*n*-hexyl-2,6-di(*p*-tolyl)pyridinium] tetrakis(tetrafluoroborate)

[0084] A stirred solution of compound 1-6 (1 equiv.), obtained in example 6, and 1-iodohexane (4 equiv.) in acetonitrile (30 mL), protected from daylight, was heated under reflux for ca. 16 hours. The cooled solvent was diluted with diethyl ether and the resulting precipitate was collected by vacuum filtration, washed with a minimum amount of diethyl ether and air dried. The foregoing precipitate was dissolved in a minimum amount of methanol (ca. 15 mL) and added dropwise to a vigorously stirred solution of $NaBF_4$ (8-10 equiv.) in water (200 mL). The resulting precipitate was collected by vacuum filtration and washed thoroughly with cold water and dried at 20 °C. Compound 1-10 was obtained as a pale orange powder (41 %), ν_{max} 3069, 2930, 2867, 1627, 1553, 1511, 1021, 822, 797, 520 cm^{-1}, δ_H(300 MHz, d_6-DMSO) 0.88 (6H, t, *J* = 7.6 Hz, $[(CH_2)_5C\underline{H}_3]_2$), 1.33 (12H, bs, $[(CH_2)_3]_2$), 2.06 (4H, bs, $(CH_2)_2$), 2.33 (12H, s, 4-$C\underline{H}_3$-C_6H_4), 4.71 (4H, t, *J* = 7.2 Hz, $(NCH_2)_2$), 7.01 (16H, m, Ar-H), 7.58 (4H, m, Ar-H), 8.05 (2H, d, *J* = 7.2 Hz, Ar-H), 8.91 (4H, s, Ar-C=CH), 9.02 (4H, d, *J* = 6.6 Hz, NCH=C<u>H</u>), 9.42 (4H, d, *J* = 6.6 Hz, NC<u>H</u>=CH), δ_C(75 MHz, d_6-DMSO) 13.8, 21.0, 21.8, 25.1, 30.5, 30.7, 61.0, 124.8, 127.0, 127.4, 128.0, 128.3, 128.5, 129.1, 129.2, 130.1, 134.9, 140.5, 145.8, 148.1, 149.8, 157.6. Found: $[M - 3BF_4^-]^{3+}$ = 351.5269; $C_{70}H_{72}BF_4N_4$ requires $[M - 3BF_4^-]^{3+}$ = 351.5279.

Example 11

Synthesis of compound 1-11: 4,4'-(2,2'-dimethyl-4,4'-biphenylene)-bis[1'-*n*-hexyl-2,6-di(4-methylphenyl)pyridiniuml tetrakis(tetrafluoroborate)

[0085] 4,4'-(2,2'-dimethyl-4,4'-biphenylene)-bis[2,6-di(4-methylphenyl)pyridinium] tetrakis(tetrafluoroborate) was obtained, through an equivalent synthesis to examples 6 using 3,3'-dimethyl-biphenyl-4,4'-diamine instead of 1,5-diaminonaphtalene.

[0086] Compound 1-11 was obtained from 4,4'-(2,2'-dimethyl-4,4'-biphenylene)-bis[2,6-di(4-methylphenyl)pyridinium] tetrakis(tetrafluoroborate), through an equivalent synthesis to example 10, as a tan powder (85 %), ν_{max} 3073, 2928, 2862, 1625, 1551, 1423, 1021, 853, 822, 519 cm^{-1}, δ_H(300 MHz, d_6-DMSO) 0.87 (6H, t, *J* = 7.6 Hz, $[(CH_2)_5C\underline{H}_3]_2$), 1.32 (12H, bs, $[(CH_2)_3]_2$), 1.91 (6H, s, (biphenyl-$CH_3)_2$), 2.01 (4H, bs, $(CH_2)_2$), 2.29 (12H, s, 4-$C\underline{H}_3$-C_6H_4), 4.71 (4H, t, *J* = 7.2 Hz, $(NCH_2)_2$), 7.22 (8H, m, Ar-H), 7.38 (8H, m, Ar-H), 7.51 (4H, m, Ar-H), 7.80 (2H, d, *J* = 8.4 Hz, Ar-H), 8.92 (4H, s, Ar-C=CH), 9.02 (4H, d, *J* = 6.9 Hz, NCH=C<u>H</u>), 9.43 (4H, d, *J* = 6.9 Hz, NC<u>H</u>=CH), δ_C(75 MHz, d_6-DMSO) 13.8, 17.2, 20.8, 21.0, 25.1, 30.5, 30.7, 61.0, 124.0, 127.0, 128.1, 128.7, 128.9, 129.2, 129.6, 130.4, 133.8, 137.9, 138.8, 140.9, 145.7, 148.3, 149.4, 157.1. Found: $[M - 3BF_4^-]^{3+}$ = 369.5432; $C_{74}H_{78}BF_4N_4$ requires $[M - 3BF_4^-]^{3+}$ = 369.5425.

Example 12

Synthesis of compound 1-12: 4,4'-(9*H*-fluorene-9,9-diyl)-bis(1,4-phenylene)-bis[1'-*n*-hexyl-2,6-di(4-methylphenyl)pyridinium] tetrakis(tetrafluoroborate)

[0087] 4,4'-(9*H*-fluorene-9,9-diyl)-bis(1,4-phenylene)-bis[2,6-di(4-methylphenyl)pyridinium] tetrakis(tetrafluoroborate) was obtained, through an equivalent synthesis to examples 6 using 9*H*-fluorene-9,9-diamine instead of 1,5-diaminonaphtalene.

[0088] Compound 1-12 was obtained from 4,4'-(9*H*-fluorene-9,9-diyl)-bis(1,4-phenylene)bis[2,6-di(4-methylphenyl)pyridinium] tetrakis(tetrafluoroborate), through an equivalent synthesis to example 10, as a pale yellow powder (96 %), δ_H(300 MHz, d_6-DMSO) 0.88 (6H, t, *J* = 7.2 Hz, $[(CH_2)_5C\underline{H}_3]_2$), 1.31 (12H, bs, $[(CH_2)_3]_2$), 1.99 (4H, bm, $(CH_2)_2$), 2.28 (12H, s, 4-$C\underline{H}_3$-C_6H_4), 4.70 (4H, t, *J* = 7.5 Hz, $(NCH_2)_2$), 6.62 (4H, d, *J* = 8.7 Hz, Ar-H), 7.08 (2H, d, *J* = 7.5 Hz, Ar-H), 7.16 (8H, m, Ar-H) 7.24 (12H, m, Ar-H), 7.33 (2H, app. t, Ar-H), 7.44 (2H, app. t, Ar-H), 7.89 (2H, d, *J* = 7.2 Hz, Ar-H), 8.88 (4H, s, Ar-C=CH), 9.02 (4H, d, *J* = 6.9 Hz, NCH=C<u>H</u>), 9.42 (4H, d, *J* = 6.9 Hz, NC<u>H</u>=CH).

Example 13

Synthesis of compound 1-13: 4,4'-(1,4-phenylene)-bis[1'-*n*-hexyl-2,6-di(4-trifluoromethylphenyl)pyridinium] tetrakis(tetrafluoroborate)

[0089] 4,4'-(1,4-phenylene)-bis[(4-pyridyl)-2,6-di(4-trifluoromethylphenyl)lpyridinium] bis(tetrafluoroborate) was obtained through an equivalent synthesis to example 1 starting from 2,6-di(4-trifluoromethylphenyl)-4-[(1*H*)-pyridinium-4-yl]pyrylium bis(tetrafluoroborate), obtained from 1,5-di(4-trifluoromethylphenyl)-3-(4-pyridyl)pentan-1,5-dione.

[0090] Compound 1-13 was obtained, through an equivalent synthesis to example 3 starting from 4,4'-(1,4-phenylene)-bis[(4-pyridyl)-2,6-di(4-trifluoromethylphenyl)lpyridinium] bis(tetrafluoroborate) instead of compound 1-2, as a pale pink powder (50 %), mp = 275.7°C decomp., ν_{max} 3072, 2935, 2867, 1632, 1619, 1558, 1322, 1111, 1031, 833, 666, 520 cm^{-1}, δ_H(300 MHz, d_4-MeOH) 0.91 (6H, bs, $[(CH_2)_5C\underline{H}_3]_2$), 1.38 (12H, bs, $[(CH_2)_3]_2$), 2.06 (4H, bs, $(CH_2)_2$), 4.70 (4H, bs, $(NCH_2)_2$), 7.61 (20H, m, 4-$CF_3C_6\underline{H}_4$, N-$C_6\underline{H}_4$-N), 8.66 (4H, bs, NCH=C<u>H</u>), 8.70 (4H, s, ArC=CH), 9.19 (4H, d, *J* = 4.5 Hz, NC<u>H</u>=CH), δ_C(75 MHz, d_6-DMSO) 11.50, 20.71, 24.14, 29.54, 29.76, 60.69, 120.48, 124.08, 124.22, 126.02, 128.25, 128.65, 129.17, 130.56, 131.00, 134.74, 138.66, 144.25, 148.21, 150.24, 154.95. Found: $[M - 4BF_4^-]^{4+}$ = 283.6116; $C_{66}H_{58}B_4F_{28}N_4$ requires $[M - 4BF_4^-]^{4+}$ = 283.6112.

Example 14

Synthesis of compound 1-14: 1-{4-1'-n-hexyl-2,6-di(4-methylphenyl)pyridinium]}-4-{4'-[1'-n-hexyl-2,6-di(4-trifluoromethylphenyl)pyridinium]}phenylene, tetrakis(tetrafluoroborate)

[0091] 2,6-Di(4-methylphenyl)-4-[(1*H*)-pyridinium-4-yl]pyrylium bis(tetrafluoroborate), prepared as outlined in Example 5, (3.00 g, 5.8 mmol) was added portionwise to a warm (80 °C) stirred solution of 1,4-diaminobenzene (3.79 g, 35.0 mmol) and sodium acetate (0.96g, 11.7 mmol) in propan-2-ol (30 mL). Upon completion of the addition of the 2,6-di(4-methylphenyl)-4-[(1*H*)-pyridinium-4-yl]pyrylium bis(tetrafluoroborate) the reaction mixture was stirred at 80 °C for 3 hours.

After cooling the precipitated solid was collected by vacuum filtration. The precipitate was then washed with propan-2-ol/water to give the 1-(4-aminophenyl)-2,6-di(4-methylphenyl)-4-(4-pyridyl)pyridinium tetrafluoroborate after drying as a pale brown powder (89 %), mp = 172 - 176 °C, ν_{max} 3488, 3392, 3034, 1621, 1597, 1513, 1402, 1312, 1235, 1094, 1050, 988, 893, 814, 539, 517 cm^{-1}, δ_H(300 MHz, d_4-MeOH) 2.35 (6H, s, $CH_3C_6H_4$), 6.40 (2H, m, H_2NC-CH), 6.89 (2H, m, H_2NC-C=CH), 7.10 (4H, m, CH_3C-CH=CH), 7.32 (4H, m, CH_3C-CH=CH), 8.09 (2H, dd, J = 4.5, 1.8 Hz, N-CH=CH), 8.49 (2H, s, ArC=CH), 8.83 (2H, dd, J = 4.5, 1.8 Hz, N-CH=CH), NH_2 signal absent in d_4-MeOH due to exchange but resonates as a broadened singlet at δ 3.87 in $CDCl_3$, δ_C(75 MHz, d_4-MeOH) 21.34, 114.63, 118.49, 123.89, 127.68, 129.74, 130.11, 130.34, 130.92, 131.96, 141.94, 144.16, 151.15, 151.68, 154.69, 159.73. Found: $[M - BF_4^-]^+ = 428.2115$; $C_{30}H_{26}BF_4N_3$ requires $[M - BF_4^-]^+ = 428.2121$.

[0092] 2,6-Di(4-trifluoromethylphenyl)-4-[(1*H*)-pyridinium-4-yl]pyrylium bis(tetrafluoroborate) (1.1 equiv.) and sodium acetate (5 equiv.) was added to a stirred solution of the foregoing 1-(4-aminophenyl)-2,6-di(4-methylphenyl)-4-(4-pyridyl)pyridinium tetrafluoroborate (1.0 equiv.) in propan-2-ol (50 mL). The reaction mixture was then heated under reflux for 15 hours whereupon a pale cream coloured precipitate had formed. Water (30 mL) was then added to the hot suspension and the reaction mixture was stirred at room temperature for 12 hours. The precipitate, 1-{4-[(4-pyridyl)-2,6-di(4-methylphenyl)pyridinium]}-4-[4'-[(4-pyridyl)-2,6-di(4-trifluoro-methylphenyl)pyridinium]}phenylene bis(tetrafluoroborate), was collected by vacuum filtration and air dried and then dried at 20 °C under reduced pressure (1 mbar, Buchi Kugelrohr drying pistol) for 24 h. A stirred solution of the foregoing dried 1-{4-[(4-pyridyl)-2,6-di(4-methylphenyl)pyridinium]}-4-[4'-[(4-pyridyl)-2,6-di(4-trifluoromethylphenyl)pyridinium]}phenylene bis(tetrafluoroborate) (1 equiv.) and 1-iodohexane (4 equiv.) in acetonitrile (35 mL), protected from daylight, was heated under reflux for 20 hours. The cooled solvent was evaporated to dryness and the residue dissolved in a minimum amount of methanol (10 mL) and added dropwise to a vigorously stirred solution of $NaBF_4$ (8 equiv.) in water (200 mL). The resulting yellow-orange precipitate was collected by vacuum filtration and washed thoroughly with cold water and dried at 20 °C under reduced pressure (1 mbar, Buchi Kugelrohr drying pistol) for 24 h to afford compound 1-14 as a pale brown powder 91 %, mp = 295 - 297 °C, δ_H(300 MHz, d_4-MeOH) 0.94 (6H, t, J = 7.2 Hz, $[(CH_2)_5CH_3]_2$), 1.42 (12H, bm, $[(CH_2)_3]_2$), 2.09 (4H, bm, $(CH_2)_2$), 2.49 (6H, s, 4-$CH_3C_6H_4$), 4.73 (4H, t, J = 7.2 Hz, $(NCH_2)_2$), 7.25 (8H, m, 4-$CH_3C_6H_4$), 7.53 (4H, s, N-C_6H_4-N), 7.60 (4H, m, F_3C-C-CH=CH), 7.69 (4H, m, F_3C-C-CH=CH), 8.64 (2H, s, Tol-C=CH), 8.69 (4H, m, NCH=CH), 8.75 (2H, s, 4-$CF_3C_6H_4$-C=CH), 9.21 (4H, m, NCH=CH), δ_C(75 MHz, d_6-DMSO) 13.77, 20.68, 21.82, 25.08, 30.51, 30.68, 61.06, 121.89, 125.51, 126.93, 128.10, 128.85, 128.95, 129.22, 129.60, 129.70, 129.81, 130.24, 130.69, 136.21, 139.06, 140.18, 140.49, 145.75, 145.91, 147.37, 147.88, 148.90, 149.38, 155.60, 157.08. Found: $[M - 2BF_4^-]^{2+} = 599.2575$; $C_{66}H_{64}B_4F_{22}N_4$ requires $[M - 2BF_4^-]^{2+} = 599.2578$.

Example 15

Synthesis of compound 2-1: 1,1"-(1,3-phenylenebis(methylene))bis(3',5'-bis(ethoxycarbonyl)-2',6'-dimethyl-[4,4'-bipyridin]-1-ium) bis-tetrafluoroborate)

[0093] *m*-Xylene dibromide (0.66 g, 2.5 mmol) and diethyl 2,6-dimethyl-4,4'-bipyridine-3,5-dicarboxylate (3.28 g, 10 mmol) were refluxed in MeCN (50 mL). After 2 days the solvent was removed under reduced pressure and residue was crystallised from DCM-hexane by slow evaporation to give the dibromide salt (2.17 g, 94 %) as a cream powder. The foregoing dibromide salt (1 g, 1.1 mmol) was dissolved in water (10 mL) and added dropwise to a solution of sodium tetrafluoroborate (1.43 g, 13 mmol) in water (10 mL) with stirring. After 0.5 h the precipitate was filtered off and dried to give compound 2-1 (0.82 g, 81 %) as tan needles, δ_H(400 MHz, d_6-DMSO) 9.32 (4H, d, J = 6.8 Hz, NCH=CH), 8.22 (4H, d, J = 6.8 Hz, NCH=CH), 7.91 (1H, s, Ar-H), 7.70 - 7.50 (3H, m, Ar-H), 5.94 (4H, s, NCH_2), 3.98 (8H, q, J = 7.2 Hz, OCH_2CH_3), 2.62 (12H, s, CH_3), 0.768 (12H, t, J = 7.2 Hz, OCH_2CH_3).

Example 16

Synthesis of compound 2-2: 1,1"-(1,4-phenylenebis(methylene))bis(3',5'-bis(ethoxycarbonyl)-2',6'-dimethyl-[4,4'-bipyridin]-1-ium) bis-tetrafluoroborate)

[0094] *p*-Xylene dibromide (0.5 g, 1.9 mmol) and diethyl 2,6-dimethyl-4,4'-bipyridine-3,5-dicarboxylate (1.86 g, 5.7 mmol) was refluxed in MeCN (50 mL). After 16 h, the mixture was cooled, filtered and washed with acetone (30 mL) and Et_2O (30 mL) and air dried to give the dibromide salt (1.6 g, 92 %) as a colourless powder. The foregoing dibromide salt (1 g, 1.1 mmol) was dissolved in MeOH-water (100 mL, 1:4) and added dropwise to sodium tetrafluoroborate (7.2 g, 65 mmol) in water (350 mL) to give, in the same manner as described for example 15, compound 2-2 (0.87 g, 96 %) as tan needles, δ_H(400 MHz, d_6-DMSO) 9.32 (4H, d, J = 6.8 Hz, NCH=CH), 8.20 (4H, d, J = 6.8 Hz, NCH=CH), 7.69 (4H, s, Ar-H), 5.92 (4H, s, NCH_2), 3.97 (8H, q, J = 7.2 Hz, OCH_2CH_3), 2.61 (12H, s, CH_3), 0.76 (12H, t, J = 7.2 Hz, OCH_2CH_3).

Example 17

Evaluation of oxydo-reduction potential and of the absorption spectrum of the compounds of the invention

[0095] The oxydo-reduction potentials of the compounds are measured by a method of cyclic voltammetry with 3 electrodes.

[0096] The 3 electrodes used are:

- 1 Platinum working electrode
- 1 Platinum auxiliary or counter electrode
- 1 Platinum reference electrode which is immersed into a solution consisting of 0.01M $AgNO_3$ + 0.1M TBAP (tetrabutylamonium perchlorate) in acetonitrile.

[0097] The potential values indicated are the first oxidative potential for the compounds, with regards to the standard hydrogen reference electrode (SHE).

[0098] The analyzed solution comprises 0.01M of the compound to be analyzed and 1M of TBAP salt.

[0099] The scan rate of the potential is fixed to 100mV/s.

[0100] The absorption spectra of the compounds are measured with a solution comprising 0.01M of the compound to be analyzed, 0.02M Phenothiazine (Phtz) or 10-Methylphenothiazine (Mephtz) and 1M of TBAP salt in propylene carbonate as solvent.

[0101] This solution is introduced into a quartz tank where at least one glass electrode coated with Indium Tin Oxide (ITO) is placed in order to colour the analyzed compound on this electrode. The absorption spectrum of the compound in the time domain is measured by a spectrophotometer.

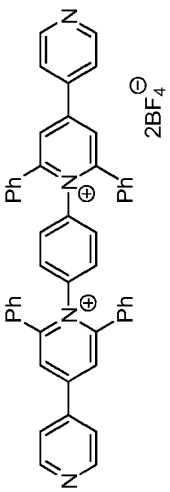
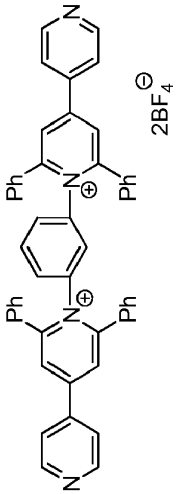
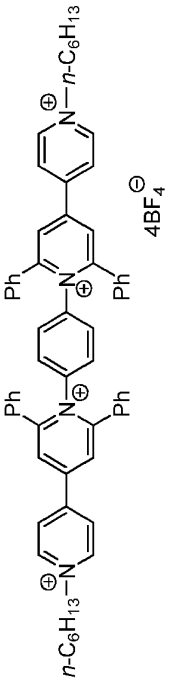
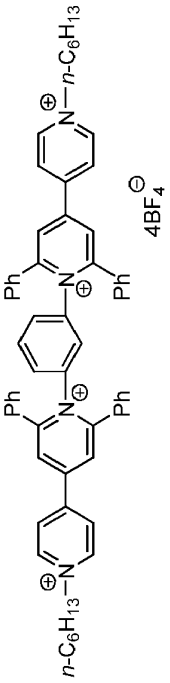
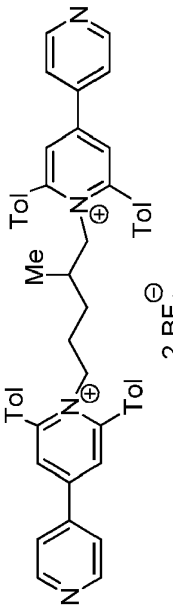
[0102] The reductive agent (phenothiazine for all compounds except compounds 1-6 and 1-7 using 10-methylphenothiazine) is colouring on another glass electrode coated with Indium Tin Oxide (ITO).

[0103] The potential applied between both electrodes, for activating the compounds, is equal to the addition, in absolute value, of E^1_{red} of the compound+ E^1_{ox} of phenothiazine (which is E^1_{ox} = 0.36V) or methylphenothiazine (which is E^1_{ox} = 0.45V).

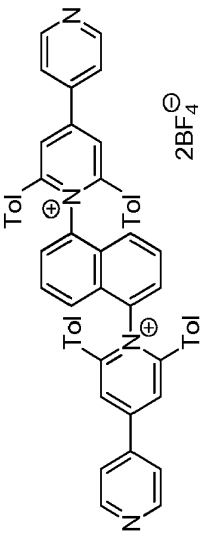
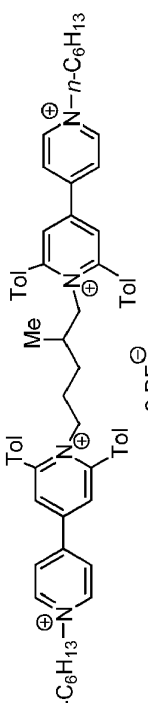
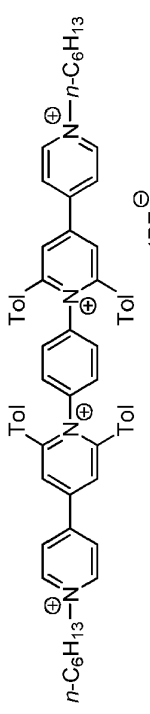
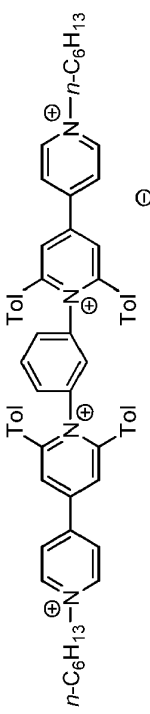
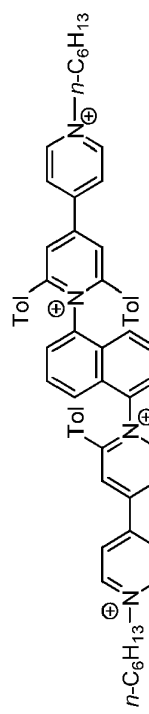
[0104] The absorption spectrum is read after 3 min of activation, in particular the λ_{max} value, which corresponds to the maximum absorption peak within the visible spectrum (between 400 and 800 nm).

[0105] The results for each of the synthesized compounds are indicated in Table 1 below. E^1_{red} corresponds to the first oxidative potential. The colour indicated in Table 1 is the visual colour perceived by emmetropic eyes under the day light. It should be noted that the λ_{max} value is just orienting the colour of the molecule, but the whole absoption spectrum has to be taken into account in order to understand the final perceived colour of one compound.

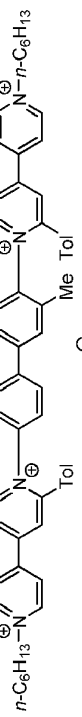
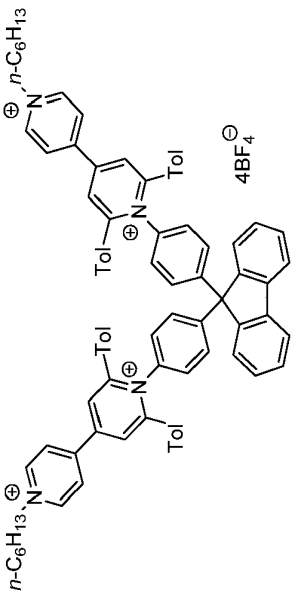
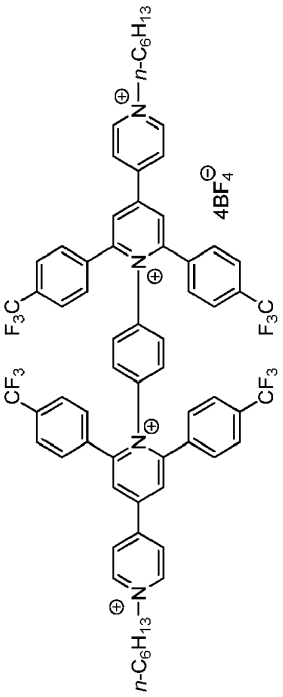
Table 1

Compound	Formula	$E1_{red}$ (V)	λ_{max} (nm)	Colour
1-1		-0.73	544	red
1-2		-0.70	420	Yellow
1-3		-0.76	629	green
1-4		-0.76	630	green
1-5		-0.79	721	green

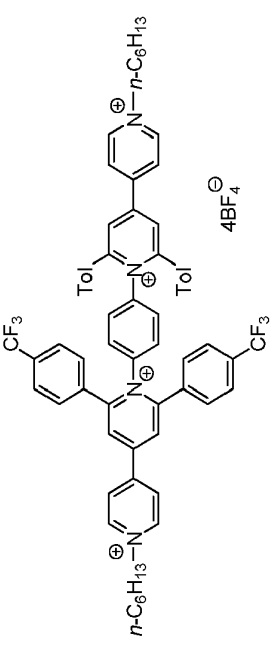
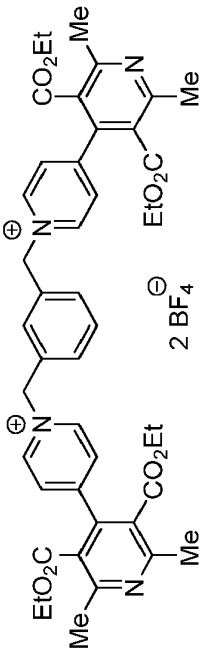
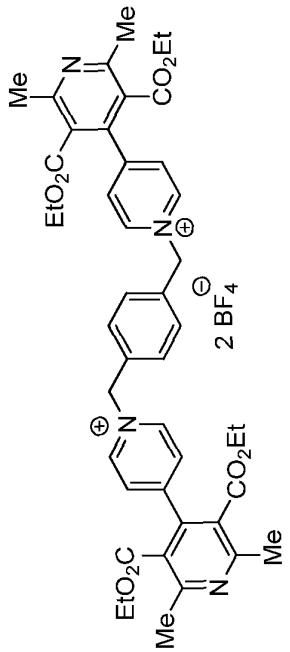
(continued)

Compound	Formula	E^1_{red} (V)	λ_{max} (nm)	Colour
1-6		-0.75	547	red
1-7		-0.8	741	green
1-8		-0.78	643	green
1-9		-0.78	628	green
1-10		-0.77	628	green

(continued)

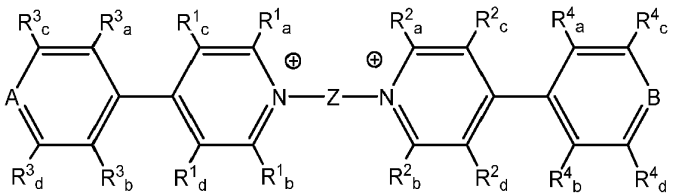
Compound	Formula	E^1_{red} (V)	λ_{max} (nm)	Colour
1-11		-0.79	643	green
1-12		-0.81	632	green
1-13		-0.65	642	green

(continued)

Compound	Formula	E^1_{red} (V)	λ_{max} (nm)	Colour
1-14		/	/	/
2-1		-1.35	/	/
2-2		-1.34	/	/

Claims

1. Compound of formula (I) :



m X^-

(I)

wherein:

- Z is selected from:
  - ○ alkylene;
  - ○ cycloalkylene; and
  - ○ a bivalent group of formula -R^5-Y-R^6-, wherein
    - • R^5 and R^6 are each independently selected from single bond, alkylene and cycloalkylene, and
    - • Y is selected from arylene, cycloalkylene, heteroarylene, arylene-arylene or arylene-CR'R"-arylene wherein R and R form together with the carbon to which they are linked a carbocyclic group;

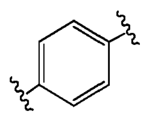
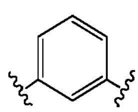
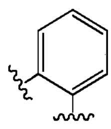
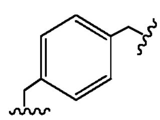
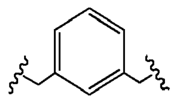
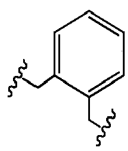
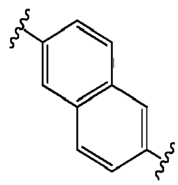
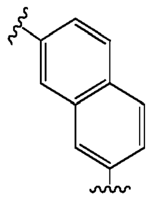
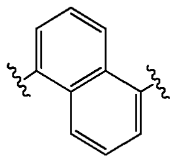
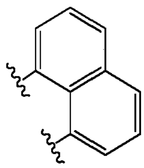
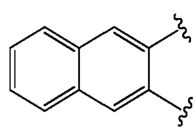
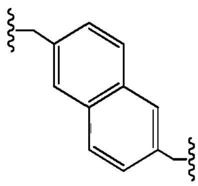
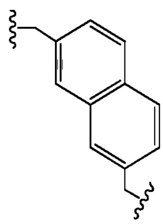
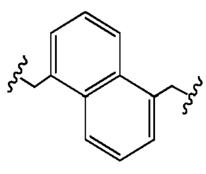
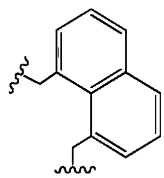
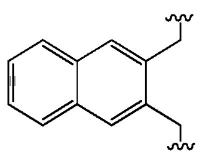
  wherein said alkylene, cycloalkylene, arylene, heteroarylene, and carbocyclic groups may be substituted by one or more substituents selected from halogen, alkyl, alkoxy, alkylthio, hydroxyalkyl, acyloxy, cycloalkyl, aryl, substituted aryl, aryloxy, heteroaryl and substituted heteroaryl;

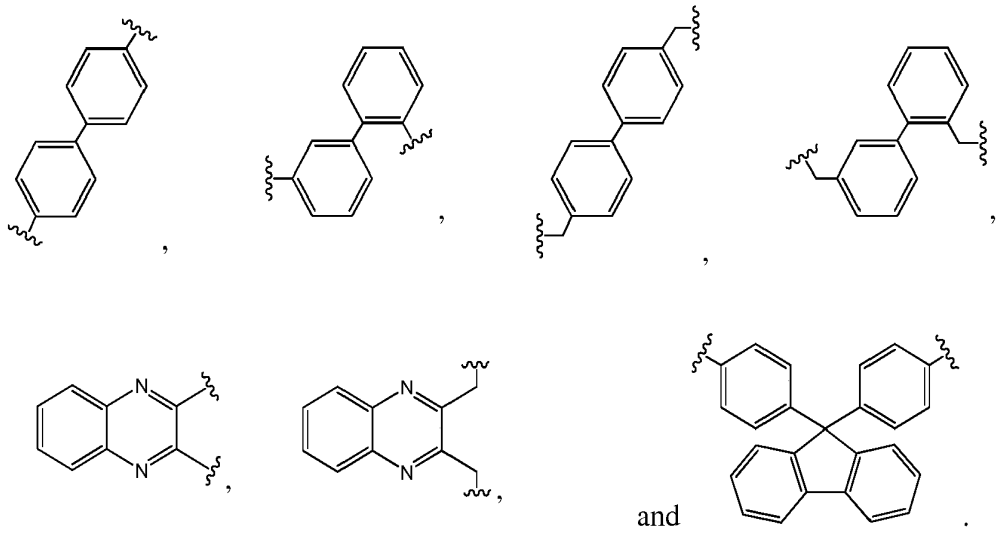
- A and B are respectively selected from nitrogen and -N^+R^{7a})-, and from nitrogen and - $N^+(R^{7b})$-, wherein R^{7a} and R^{7b} are independently selected from:
  - ○ alkyl which may be substituted by one or more groups independently selected from halogen, alkoxy, cycloalkyl, vinyl, allyl, aryl, substituted aryl, heteroaryl and substituted heteroaryl;
  - ○ aryl and heteroaryl which may be both substituted by one or more groups independently selected from:
    - • halogen, cyano, nitro, alkyl, haloalkyl, arylalkyl, cycloalkyl, cycloalkylalkyl and heterocycloalkylalkyl, alkenyl, alkynyl, allyl, vinyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, -N(aryl)$_2$, -N(aryl)CO(aryl), -CO-aryl and -CO-substituted aryl;
    - • -OR^8, -SR^8, -S(O)R^8, -S(O_2)R^8, -S(O_2)NR^8R^9, -NR^8R^9, -NR^8COR^9,-NR^8CO(aryl), -NR^8aryl, -CH_2OR^8, -CH_2SR^8, -CH_2R^8, -CO-R^8 and -CO_2R^8 wherein R^8 and R^9 are independently selected from H, alkyl, haloalkyl, arylalkyl, cycloalkyl, cycloalkylalkyl and heterocycloalkylalkyl;
    - • -S(O_2)$NR^{10}R^{11}$ and -$NR^{10}R^{11}$ wherein R^{10} and R^{11} form together with the nitrogen atom to which they are linked a saturated 5 to 7 membered heterocycloalkyl which may comprise in addition to the nitrogen atom one further heteroatom selected from oxygen, nitrogen and sulfur, and which may be optionally substituted by one or two groups independently selected from halogen, -R^8, -OR^9, and -NR^8R^9, wherein R^8 and R^9 are as defined above;
    - • -V-W-R^{12} wherein:
      - ■ V is selected from oxygen, -N(R^8)-, sulfur, -S(O)- and -S(O_2)-wherein R^8 is as defined above;
      - ■ W is alkylene, which may be substituted by one or more groups independently selected from halogen and alkoxy; and
      - ■ R^{12} is selected from -OR^8, -NR^8(alkyl) and -SR^8 wherein R^8 is as defined above; and
    - • -OC(O)-R^{13} wherein R^{13} is selected from alkyl, haloalkyl, alkenyl, -W-R^{12}, and aryl group which may

be substituted by 1 to 4 groups selected from halogen, $-R^8$, $-OR^8$, $-SR^8$, $-NR^8R^9$, $-NR^{10}R^{11}$, $-CO-R^8$, $-C(O)OR^8$ wherein R^8, R^9, R^{10}, R^{11}, R^2 and W are as defined above.

- $R^1{}_a$, $R^1{}_b$, $R^1{}_c$, $R^1{}_d$, $R^2{}_a$, $R^2{}_b$, $R^2{}_c$, $R^2{}_d$, $R^3{}_a$, $R^3{}_b$, $R^3{}_c$, $R^3{}_d$, $R^4{}_a$, $R^4{}_b$, $R^4{}_c$ and $R^4{}_d$ are each independently selected from H, alkyl, alkoxy, alkylthio, haloalkyl, haloalkoxy, haloalkythio, poly(alkylenoxy), alkoxycarbonyl, aryl, substituted aryl, heteroaryl and substituted heteroaryl, wherein the alkyl group may be substituted by one or more substituents independently selected from alkoxy, cycloalkyl, aryl, substituted aryl, heteroaryl and substituted heteroaryl;
wherein at least one of $R^1{}_a$, $R^1{}_b$, $R^1{}_c$, $R^1{}_d$, $R^2{}_a$, $R^2{}_b$, $R^2{}_c$, $R^2{}_d$,, $R^3{}_a$, $R^3{}_b$, $R^3{}_c$, $R^3{}_d$, $R^4{}_a$, $R^4{}_b$, $R^4{}_c$ and $R^4{}_d$ is not H;
- X- is a counterion; and
- m is 2 if A and B are nitrogen, 3 if one of A and B is nitrogen and the other is not nitrogen, and 4 if both A and B are not nitrogen.

2. The compound according to claim 1, wherein Z is selected from C_1-C_{12} alkylene, aryl substituted C_1-C_{12} alkylene, phenylene, naphthylene, (C_1-C_4 alkylene)-phenylene-(C_1-C_4 alkylene), (C_1-C_4 alkylene)-naphthylene-(C_1-C_4 alkylene), quinoxaline-2,3-diyl, (C_1-C_4 alkylene)-quinoxaline-2,3-diyl-(C_1-C_4 alkylene), phenylene-phenylene, (C_1-C_4 alkylene)-phenylene-phenylene-(C_1-C_4 alkylene) and phenylene-fluorenylene-phenylene, preferably Z is selected from $-CH_2-$, $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-(CH_2)_5-$, $-CH_2-CH(CH_3)-CH_2-$, $-CH_2-CH(CH_2Phenyl)-CH_2-$, $-(CH_2)_2-CH(CH_3)-CH_2-$, $-(CH_2)_3-CH(CH_3)-CH_2-$, $-(CH_2)_2-CH(CH_3)-(CH_2)_2-$,

 ,
 ,
 ,
 ,
 ,
 ,
 ,
 ,
 ,
 ,
 ,
 ,
 ,
 ,
 ,
 ,

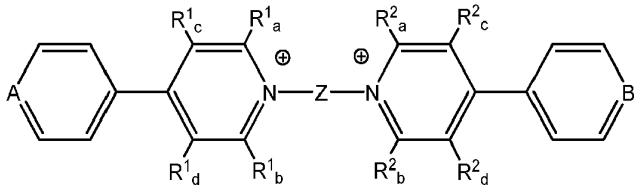


3. The compound according to claim 1 or 2, wherein A and B are respectively selected from nitrogen and -$N^+(R^{7a})$-, and from nitrogen and -$N^+(R^{7b})$-, wherein R^{7a} and R^{7b} are independently selected from C_6-C_8 alkyl, phenyl and naphthyl which may be both substituted by one or more subtituents selected from halogen, cyano, nitro, hydroxy, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy, C_1-C_4 alkylthio, C_1-C_4 haloalkylthio, C_3-C_7 cycloalkyl, (C_3-C_7 cycloalkyl)C_1-C_4 alkyl.

4. The compound according to any one of claims 1 to 3, wherein the counterion X- is selected from halide, tetrafuloroborate, tetraphenylborate, hexafluorophosphate, nitrate, methanesulfonate, trifluoromethane sulfonate, toluene sulfonate, hexachloroantimonate, bis(trifluoromethanesulfonyl)imide, perchlorate, acetate and sulfate.

5. The compound according to any one of claims 1 to 4, wherein R^1_a, R^1_b, R^1_c, R^1_d, R^2_a, R^2_b, R^2_c, R^2_d, R^3_a, R^3_b, R^3_c, R^3_d, R^4_a, R^4_b, R^4_c and R^4_d are each independently selected from hydrogen, aryl, substituted aryl, heteroaryl and substituted heteroaryl, preferably selected from optionally substituted phenyl, more preferably selected from phenyl, tolyl and cumyl.

6. The compound according to any one of claims 1 to 5, wherein said compound is represented by formula (I-1):

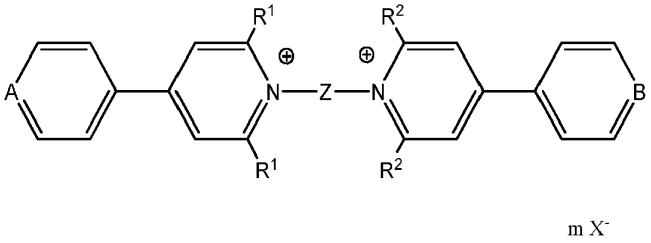


m X^-

(I-1)

wherein Z, A, B, R^1_a, R^1_b, R^1_c, R^1_d, R^2_a, R^2_b, R^2_c, R^2_d, X^- and m are as defined in claims 1 to 5.

7. The compound according to any one of claims 1 to 5, wherein said compound is represented by formula (I-3):

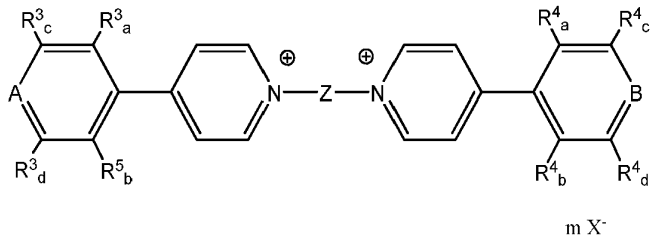


m X^-

(I-3)

wherein Z, A, B, X^- and m are as defined in claims 1 to 5, and R^1 and R^2 are each independently selected from H, alkyl, alkoxy, alkylthio, haloalkyl, haloalkoxy, haloalkythio, polyalkylenoxy, alkoxycarbonyl, aryl, substituted aryl, heteroaryl and substituted heteroaryl, wherein the alkyl group may be substituted by one or more substituents independently selected from alkoxy, cycloalkyl, aryl, substituted aryl, heteroaryl and substituted heteroaryl, provided that at least one of R^1 and R^2 is not H.

8. The compound according to any one of claims 1 to 5, wherein said compounds are represented by formula (I-4):

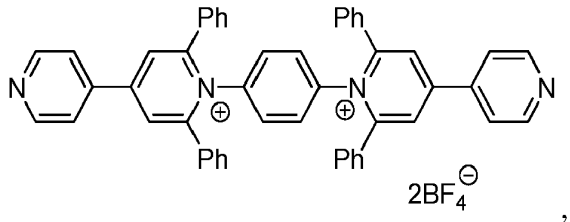


m X^-

(I-4)

wherein Z, A, B, R^3_a, R^3_b, R^3_c, R^3_d, R^4_a, R^4_b, R^4_c, R^4_d, X^- and m are as defined in claims 1 to 5.

9. The compound according to any one of claims 1 to 5, wherein said compound is selected from:



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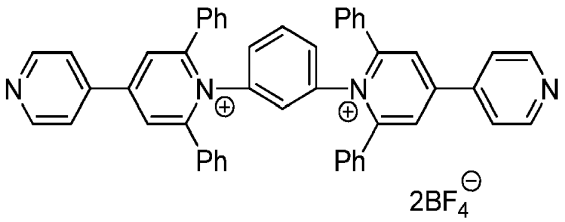

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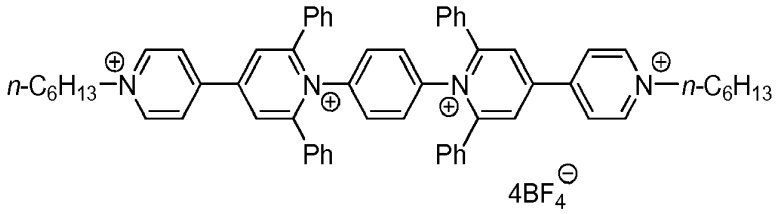

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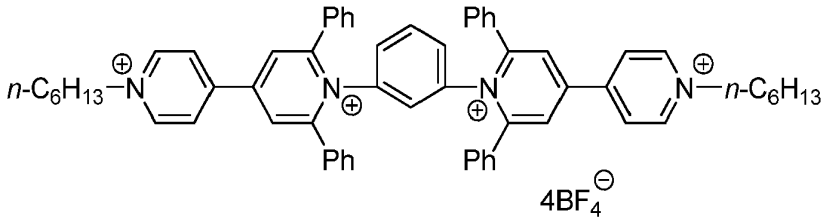

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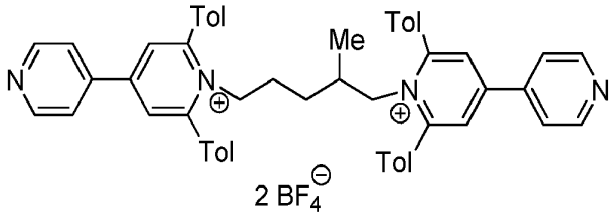

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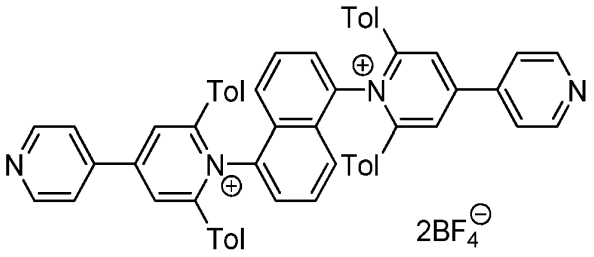

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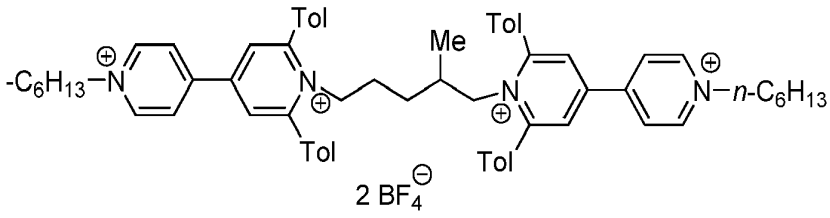

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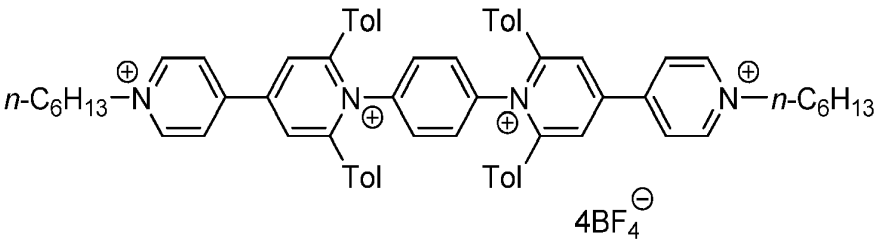

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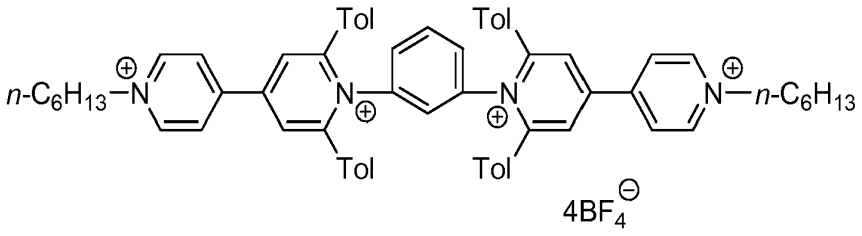
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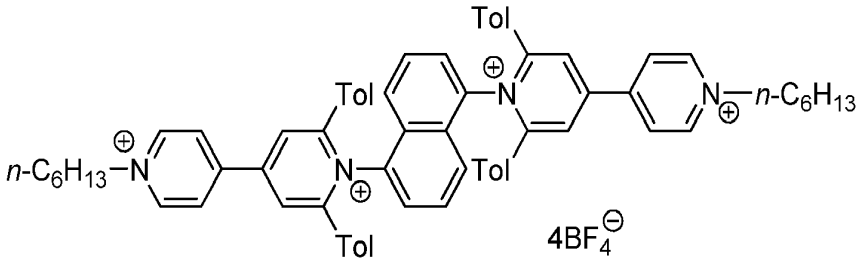
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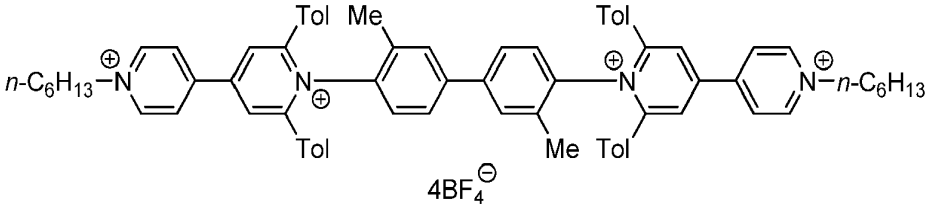
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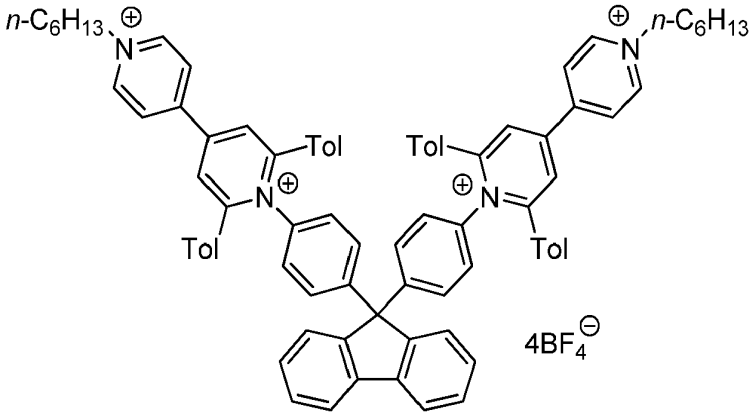
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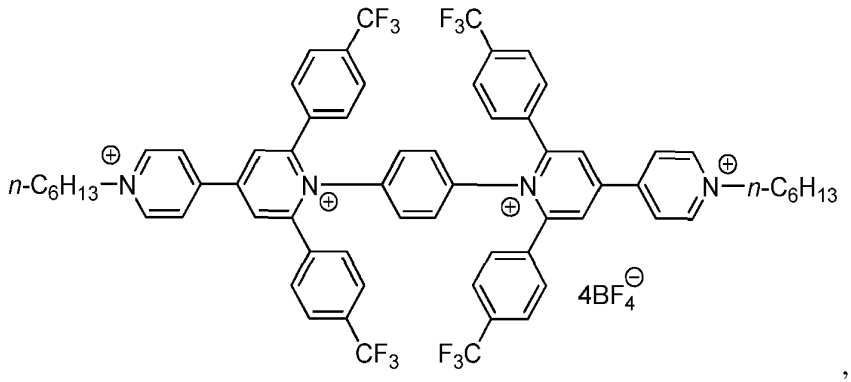

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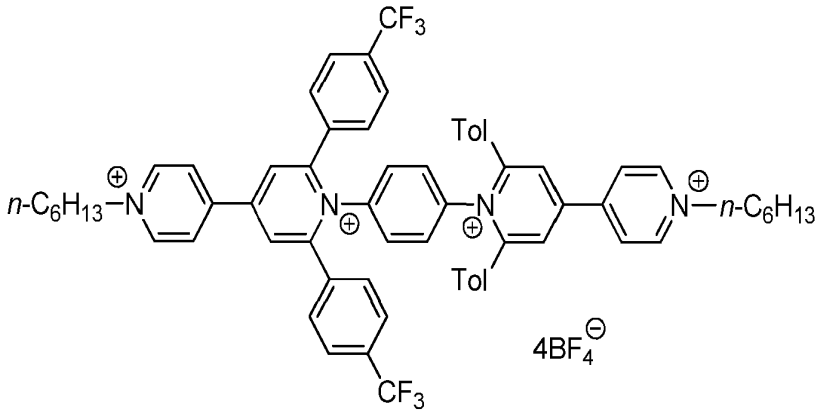

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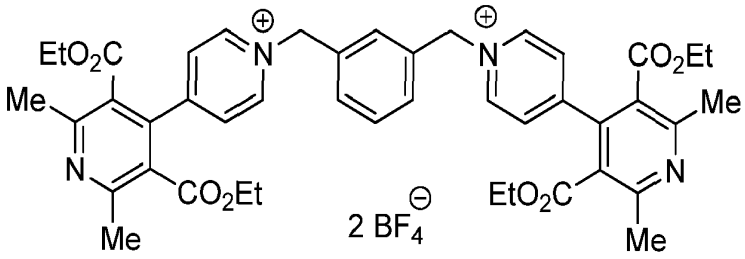

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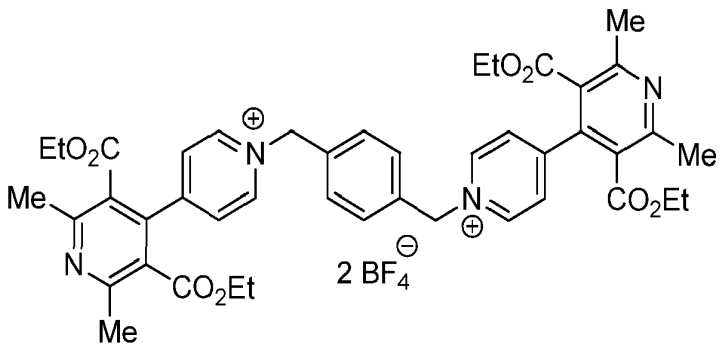

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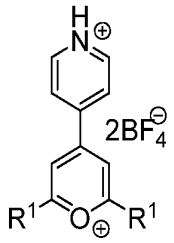
10. Method for preparing the compound (I-3) as defined in claim 7, comprising the step of reacting a 2,6-disubstituted-4-[(1H)-pyridinium-4-yl]pyrylium bis(tetrafluoroborate) (1) with a diamine (2):



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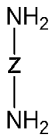

2

11. Electrochromic composition comprising at least one compound as defined in claims 1 to 9.

12. The electrochromic composition according to claim 10, wherein said composition comprises a fluid, mesomorphous or gel host medium.

13. The electrochromic composition according to claim 12, wherein the fluid or mesomorphous host medium is selected from the group consisting of organic solvents, liquid crystals, polymers, liquid crystal polymers and mixtures thereof.

14. Electrochromic device comprising a compound according to any one of claims 1 to 9, or a composition according to any one of claims 11 to 13.

15. The electrochromic device according to claim 14, wherein said device comprises a mechanism for holding said compound or said composition in a mechanically stable environment.

16. The electrochromic device according to claim 15, wherein said device comprises a pair of opposed substrates having a gap there between for receiving said compound or said composition, and a frame for holding said pair of substrates adjacent one another.

17. The electrochromic device according to claim 15, wherein said device comprises an optical component provided with at least one transparent cell arrangement juxtaposed in a parallel direction to the surface thereof, each cell being tightly closed and containing said compound or said composition.

18. The electrochromic device according to any one of claims 12 to 17, wherein said electrochromic device is selected from an optical article, preferably an optical lens or an optical filter, a window, notably an aircraft window, a visor, a mirror and a display, more preferably an optical article selected from optical lenses, and most preferably an optical article selected from ophthalmic lenses.

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EUROPEAN SEARCH REPORT

Application Number
EP 13 18 4780

DOCUMENTS CONSIDERED TO BE RELEVANT

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X A	US 4 116 535 A (PONJEE JOHANNES JACOBUS ET AL) 26 September 1978 (1978-09-26) * column 1, lines 45-56; tables A,E * * column 2, lines 16-55 * * column 5, lines 1-18 * -----	1,2,4-8, 11-18 3,9,10	
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C09K
C07D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	20 February 2014	Baldé, Kaisa

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