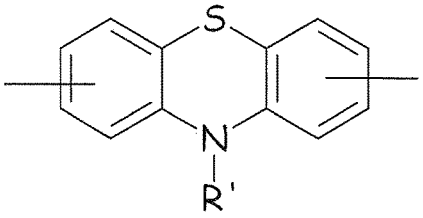
Claims

1. A rechargeable metal or metal-ion cell comprising:

   - an anode comprising at least one metal;

   - a charge-carrying electrolyte comprising a charge carrying medium and at least one metal salt;

   - an organic polymer cathode, wherein said cathode comprises at least one N-substituted polyphenothiazine polymer [polymer (P)], said polymer comprising at least one N-substituted phenothiazine recurring unit of formula:



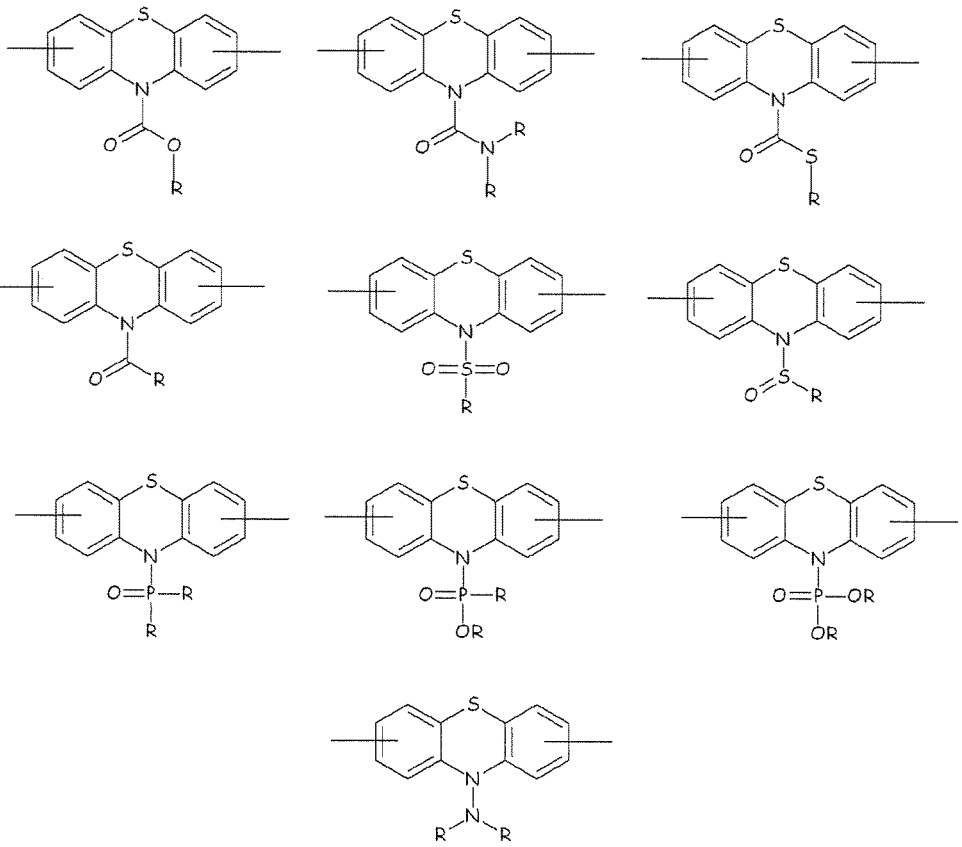
   wherein R' is an electron-withdrawing group comprising at least one heteroatom selected from O, S, P and N, and wherein

   (i) the R' group forms with the nitrogen atom of the phenothiazine ring at least one electron-withdrawing group selected from the group consisting of urethane group; urea group; thiourethane group; amide group; sulphonamide groups; sulphinamide group; hydrazine group; phosphonamide group, phosphinimide group, phosphamide group, and/or

   (ii) the N-substituted phenothiazine recurring unit additionally comprises at least one ionisable group selected from carboxylate groups, sulphonate groups, sulphonylimide groups, phosphonate groups, said ionisable group being comprised in the electron-withdrawing group R' .

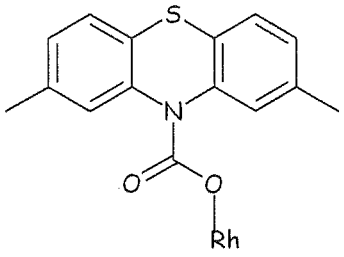
2. The cell of claim 1, wherein in the polymer (P) the R' group forms with the nitrogen atom of the phenothiazine ring at least one electron-withdrawing group selected from the group consisting of urethane group; urea group; thiourethane group; amide group; sulphonamide groups; sulphinamide group; hydrazine group; phosphonamide group, phosphinimide group, phosphamide group.

3. The cell of claim 1 or 2, wherein the N-substituted phenothiazine recurring units of the polymer (P) comply with anyone of formulae herein below:



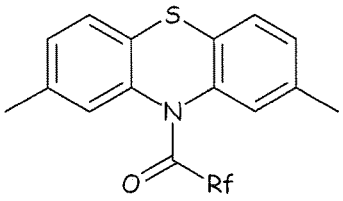
wherein each of R, equal or different from each other and at each occurrence, are selected from H or from a hydrocarbon group, possibly fluorinated, and optionally comprising one or more ionisable group.

4. The cell of claim 3, wherein each of R, equal or different from each other and at each occurrence, are a hydrocarbon group, possibly fluorinated, comprising one or more ionisable group.
5. The cell of claim 1, wherein the electron-withdrawing group R' attached to the phenothiazine has an alkyl root.
6. The cell of anyone of the preceding claims, wherein the N-substituted phenothiazine recurring unit additionally comprises at least one ionisable group selected from carboxylate groups, sulphonate groups, sulphonylimide groups, phosphonate groups, said ionisable group being comprised in the electron-withdrawing group R'.
7. The cell of claim 6, wherein the ionisable group is a sulphonate group or a sulphonylimide group.
8. The cell according to anyone of the preceding claims, wherein polymer (P) comprises recurring units selected from the group consisting of:
(I) urethane-containing phenothiazine recurring units of formula:



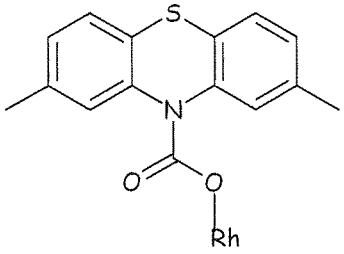
wherein Rh is a C_1-C_{24} hydrocarbon group, possibly fluorinated, optionally comprising one or more heteroatoms comprised in an additional functional group;

(II) amide-containing phenothiazine recurring units of formula:



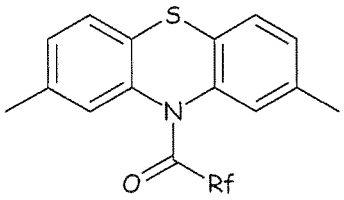
wherein Rf is a C_1-C_{24} hydrocarbon group, possibly fluorinated, optionally comprising one or more heteroatoms comprised in an additional functional group.

9. The cell according to claim 8, wherein polymer (P) comprises recurring units selected from the group consisting of urethane-containing phenothiazine recurring units of formula:



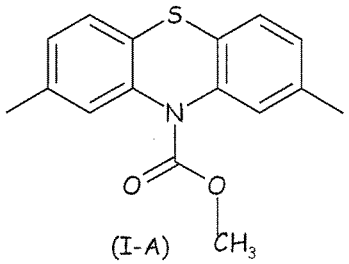
wherein Rh is a C_1-C_{24} hydrocarbon group, possibly fluorinated, comprising one or more heteroatoms comprised in an additional functional group.

10. The cell according to claim 8, wherein polymer (P) comprises recurring units selected from the group consisting of amide-containing phenothiazine recurring units of formula:

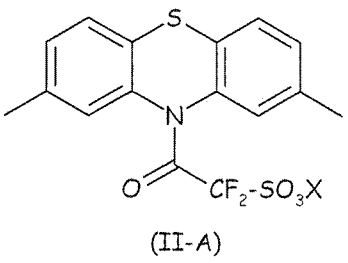


wherein Rf is a C_1-C_{24} fluorinated hydrocarbon group comprising one or more heteroatoms comprised in an additional functional group.

11. The cell according to claim 8, wherein polymer (P) comprises recurring units of formula (I-A) and/or (II-A) herein below:



(I-A)



(II-A)

X in formula (II-A) being a metal.

12. The cell according to anyone of the preceding claims, wherein the metal ion cell is an alkaline or alkaline-earth secondary battery, wherein the anode comprises a negative electrode material selected from the group consisting of:
    - alkaline or alkaline-earth metal;
    - graphitic carbons able to intercalate alkaline or alkaline-earth metal;
    - alkaline or alkaline-earth metal alloy compositions;
    - alkaline or alkaline-earth metal titanates.
13. The cell according to claim 12, wherein the alkaline or alkaline-earth secondary battery is a Lithium-ion cell wherein the anode comprises a negative electrode material selected from the group consisting of:
    - graphitic carbons able to intercalate lithium;
    - lithium metal;
    - lithium alloy compositions;
    - lithium titanates;
    - lithium-silicon alloys;
    - lithium-germanium alloys.
14. The cell according to anyone of the preceding claims, wherein said charge carrying medium is selected from the group consisting of ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl-methyl carbonate, butylene carbonate, vinylene carbonate, fluoroethylene carbonate, fluoropropylene carbonate, gamma-butyrolactone, methyl difluoroacetate, ethyl

difluoroacetate, dimethoxyethane, diglyme (bis(2-methoxyethyl) ether), non-protonic ionic liquids, poly(oxyethylene)s and combinations thereof.

15. The cell according to anyone of the preceding claims, wherein said cell is a Lithium-ion cell wherein said metal salt is a lithium salt selected from the group consisting of $LiPF_6$, $LiBF_4$, $LiClO_4$, lithium bis(oxalato)borate ("LiBOB"), $LiN(CF_3SO_2)_2$, $LiN(C_2F_5SO_2)_2$, $M[N(CF_3SO_2)(R_FSO_2)]_n$ with R_F being C_2F_5, C_4F_9, $CF_3OCF_2CF_2$, $LiAsF_6$, $LiC(CF_3SO_2)_3$ and combinations thereof.

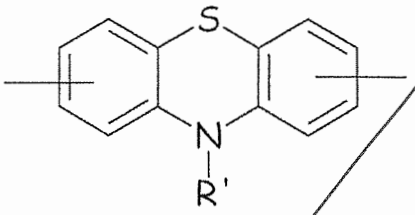
Claims

1. A rechargeable metal or metal-ion cell comprising:

   - an anode comprising at least one metal;

   - a charge-carrying electrolyte comprising a charge carrying medium and at least one metal salt;

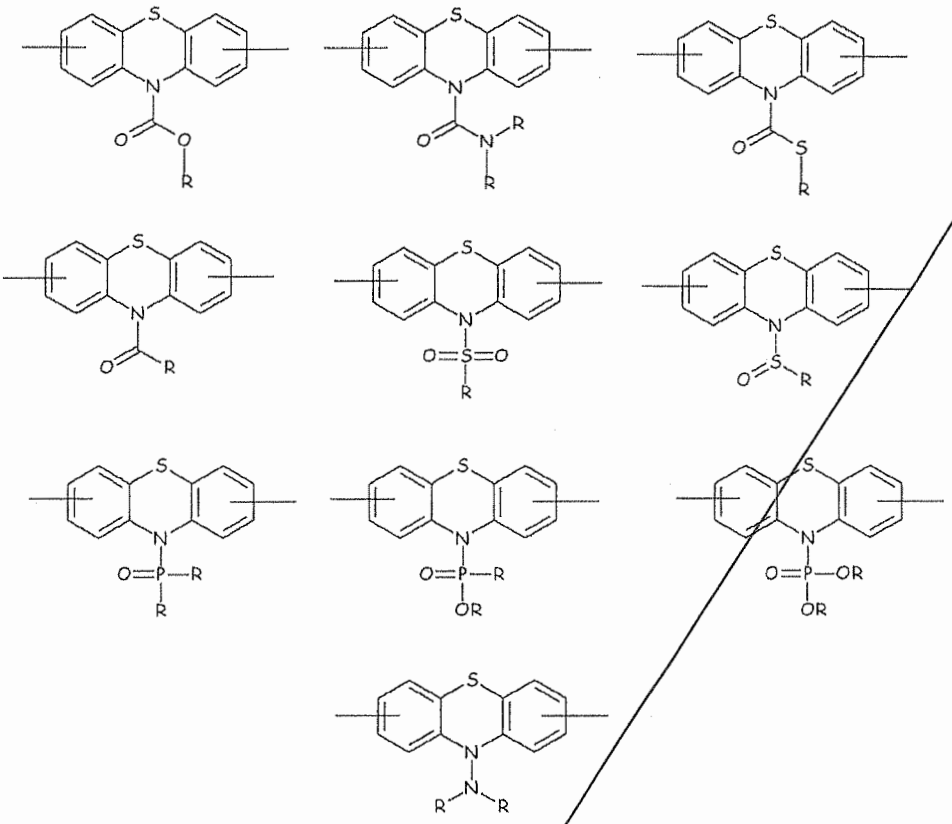
   - an organic polymer cathode, wherein said cathode comprises at least one N-substituted polyphenothiazine polymer [polymer (P)], said polymer comprising at least one N-substituted phenothiazine recurring unit of formula:



   wherein R' is an electron-withdrawing group comprising at least one heteroatom selected from O, S, P and N.

2. The cell of claim 1, wherein in the polymer (P) the R' group forms with the nitrogen atom of the phenothiazine ring at least one electron-withdrawing group selected from the group consisting of urethane group; urea group; thiourethane group; amide group; sulphonamide groups; sulphinamide group; hydrazine group; phosphonamide group, phosphinimide group, phosphamide group.

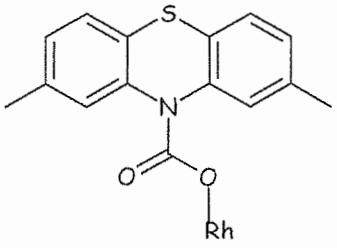
3. The cell of claim 1 or 2, wherein the N-substituted phenothiazine recurring units of the polymer (P) comply with anyone of formulae herein below:



wherein each of R, equal or different from each other and at each occurrence are selected from H or from a hydrocarbon group, possibly fluorinated, and optionally comprising one or more ionisable group.

4. The cell of anyone of the preceding claims, wherein the N-substituted phenothiazine recurring unit additionally comprises at least one ionisable group selected from carboxylate groups, sulphonate groups, sulphonylimide groups, phosphonate groups, with sulphonate and sulphonylimide groups being preferred.

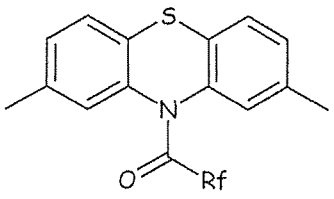
5. The cell according to anyone of the preceding claims, wherein polymer (P) comprises recurring units selected from the group consisting of:
(I) urethane-containing phenothiazine recurring units of formula:



wherein Rh is a C_1-C_{24} hydrocarbon group, possibly fluorinated, optionally comprising one or more heteroatoms comprised in an additional functional

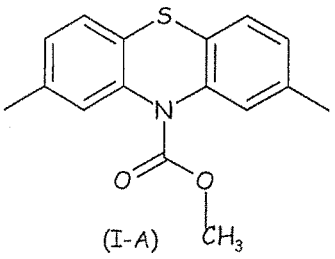
group;

(II) amide-containing phenothiazine recurring units of formula:

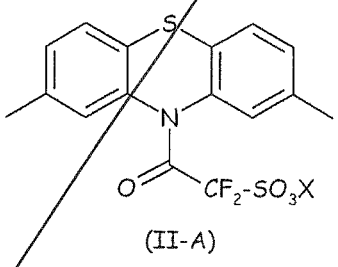


wherein Rf is a C_1-C_{24} hydrocarbon group, preferably fluorinated optionally comprising one or more heteroatoms comprised in an additional functional group.

6. The cell according to claim 5, wherein polymer (P) comprises recurring units of formula (I-A) and/or (II-A) herein below:



(I-A)



(II-A)

X in formula (II-A) being a metal, preferably an alkaline metal, more preferably Li.

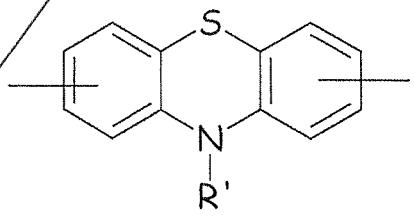
7. The cell according to anyone of the preceding claims, wherein the metal ion cell is an alkaline or alkaline-earth secondary battery, wherein the anode comprise a negative electrodes material selected from the group consisting of:
- alkaline or alkaline-earth metal;
- graphitic carbons able to intercalate alkaline or alkaline-earth metal, typically existing in forms such as powders, flakes, fibers or spheres hosting at least one alkaline or alkaline-earth metal;
- alkaline or alkaline-earth metal alloy compositions, including silicon-based alloys, germanium-based alloys;
- alkaline or alkaline-earth metal titanates, advantageously suitable for intercalating alkaline or alkaline-earth metal with no induced strain

8. The cell according to claim 7, wherein the alkaline or alkaline-earth secondary battery is a Lithium-ion cell wherein the anode comprises a negative electrodes material selected from the group consisting of:
- graphitic carbons able to intercalate lithium, typically existing in forms such as

powders, flakes, fibers or spheres hosting lithium;

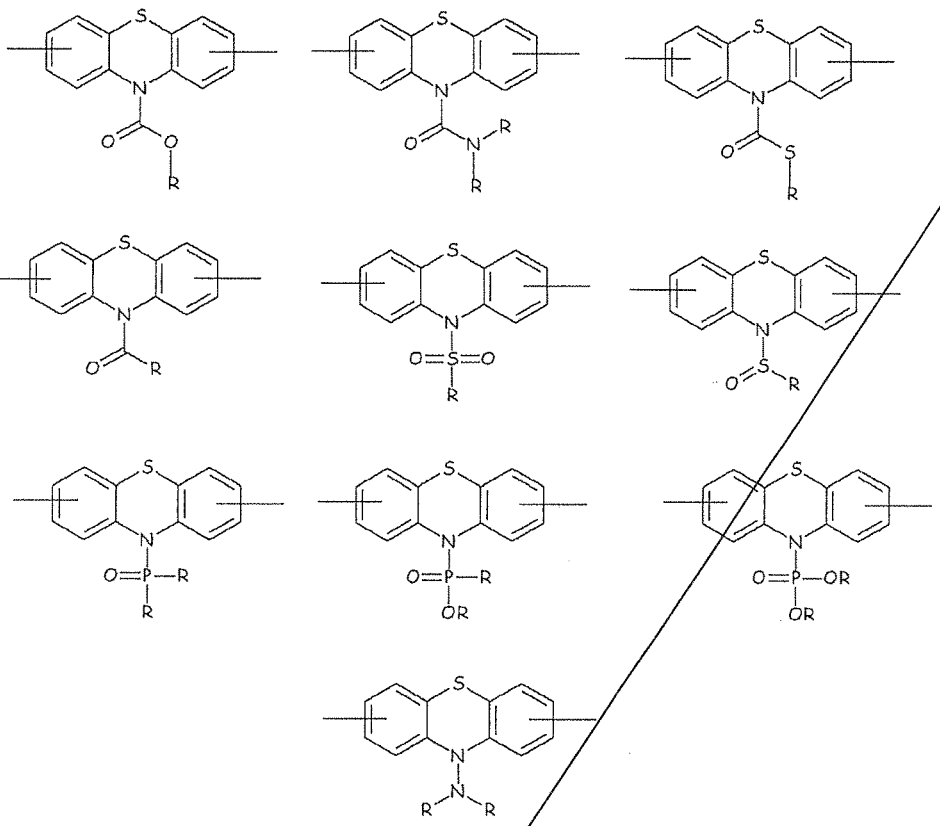
- lithium metal;
- lithium alloy compositions;
- lithium titanates, generally represented by formula $Li_4Ti_5O_{12}$;
- lithium-silicon alloys, generally known as lithium silicides with high Li/Si ratios, in particular lithium silicides of formula $Li_{4.4}Si$;
- lithium-germanium alloys, including crystalline phases of formula $Li_{4.4}Ge$.

9. The cell according to anyone of the preceding claims, wherein said charge carrying medium is selected from the group consisting of ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl-methyl carbonate, butylene carbonate, vinylene carbonate, fluoroethylene carbonate, fluoropropylene carbonate, gamma-butyrolactone, methyl difluoroacetate, ethyl difluoroacetate, dimethoxyethane, diglyme (bis(2-methoxyethyl) ether), non-protonic ionic liquids, poly(oxyethylene)s and combinations thereof.
10. The cell according to anyone of the preceding claims, wherein said cell is a Lithium-ion cell wherein said metal salt is a lithium salt selected from the group consisting of $LiPF_6$, $LiBF_4$, $LiClO_4$, lithium bis(oxalato)borate ("LiBOB"), $LiN(CF_3SO_2)_2$, $LiN(C_2F_5SO_2)_2$, $M[N(CF_3SO_2)(R_FSO_2)]_n$ with R_F being C_2F_5, C_4F_9, $CF_3OCF_2CF_2$, $LiAsF_6$, $LiC(CF_3SO_2)_3$ and combinations thereof.
11. A N-substituted polyphenothiazine polymer [polymer (P)], comprising at least one N-substituted phenothiazine recurring unit of formula:



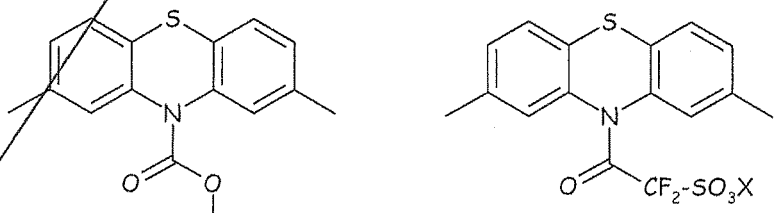
wherein R' is an electron-withdrawing group comprising at least one heteroatom selected from O, S, P and N.

12. The N-substituted polyphenothiazine polymer of claim 11, wherein the N-substituted phenothiazine recurring unit complies with anyone of formulae herein below:



wherein each of R, equal or different from each other and at each occurrence are selected from H or from a hydrocarbon group, possibly fluorinated, and optionally comprising one or more ionisable group.

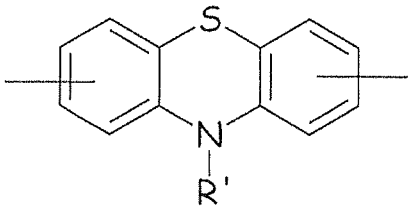
13. The N-substituted polyphenothiazine polymer of claim 11 or 12, wherein the N-substituted phenothiazine recurring unit additionally comprises at least one ionisable group selected from carboxylate groups, sulphonate groups, sulphonylimide groups, phosphonate groups, with sulphonate and sulphonylimide groups being preferred.
14. The N-substituted polyphenothiazine polymer of claim 11 to 13, said polymer (P) comprising recurring units of formula (I-A) and/or (II-A) herein below:



(I-A) (II-A)

X in formula (II-A) being a metal, preferably an alkaline metal, more preferably Li.

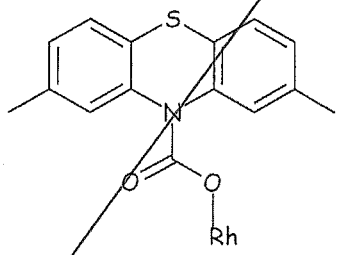
15. A monomer compound comprising at least one N-substituted phenothiazine moiety of formula:



wherein R' is an electron-withdrawing group comprising at least one heteroatom selected from O, S, P and N, wherein said moiety additionally comprises at least one ionisable group selected from carboxylate groups, sulphonate groups, sulphonylimide groups, phosphonate groups, with sulphonate and sulphonylimide groups being preferred.

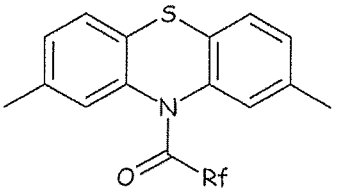
16. A monomer compound comprising at least one N-substituted phenothiazine moiety selected from the group consisting of:

(I) urethane-containing phenothiazine recurring units of formula:



wherein Rh is a C_1-C_{24} hydrocarbon group, possibly fluorinated, optionally comprising one or more heteroatoms comprised in an additional functional group;

(II) amide-containing phenothiazine recurring units of formula:



wherein Rf is a C_1-C_{24} fluorinated hydrocarbon group, optionally comprising one or more heteroatoms comprised in an additional functional group.

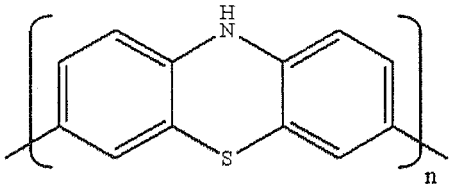
[00113]

Table 1

Compound	$E^{1/2}_1$ 1st system (V vs SHE)	ΔE (mV)	$E^{1/2}_2$ 2nd system (V vs SHE)	ΔE (mV)	$\Delta E^{1/2}$ (mV)
I	0.982	103	1.376	160	0.394
II	0.973	135	1.627	137	0.654
III	1.089	100	1.700	101	0.611
IV	0.932	106	1.603	123	0.671
V	1.052	93	1.664	133	0.612
VI	0.930	117	1.597	103	0.667
VII	1.062	95	1.677	106	0.615
VIII	0.926	108	1.595	103	0.669
IX	1.050	82	1.667	95	0.617
X	1.545	137	1.776	137	0.231
XI	1.608	68	1.814	61	0.206
XII	0.980	110	1.375	160	0.395
XIII	1.038	105	1.690	162	0.652

[00114] III) Polymerization of phenothiazine monomers

III)-1) Polymerization of compound XII by microwave assisted Suzuki coupling to yield Poly(I) - of comparison:



The **Poly(I)** was synthesized following procedures described in A. Tsami, X.H. Yang, T. Farrell, D. Neher, E. Holder / *Journal of Polymer Science Part A: Polymer Chemistry 46*, **2008**, 7794-7808 ; M. Melucci, G. Barbarella, G. Sotgiu / *The Journal of Organic Chemistry 67*, **2002**, 8877-8884 ; A. Britze, J. Jacob, V. Choudhary, V. Moellmann, G. Grundmeier, H. Luftmann, D. Kuckling / *Polymer 51*, **2010**, 5294-5303.

To 5 mL of freshly distilled dimethylacetamide, 143 mg of compound **XII** (0.4 mmol), one molar equivalent of bispinacolatodiboron (104 mg ; 0.4