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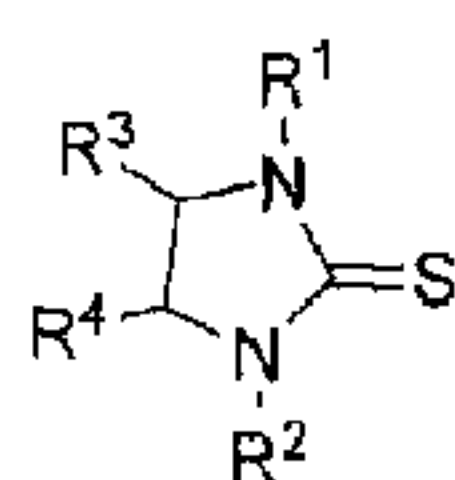
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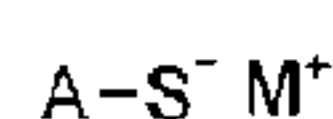
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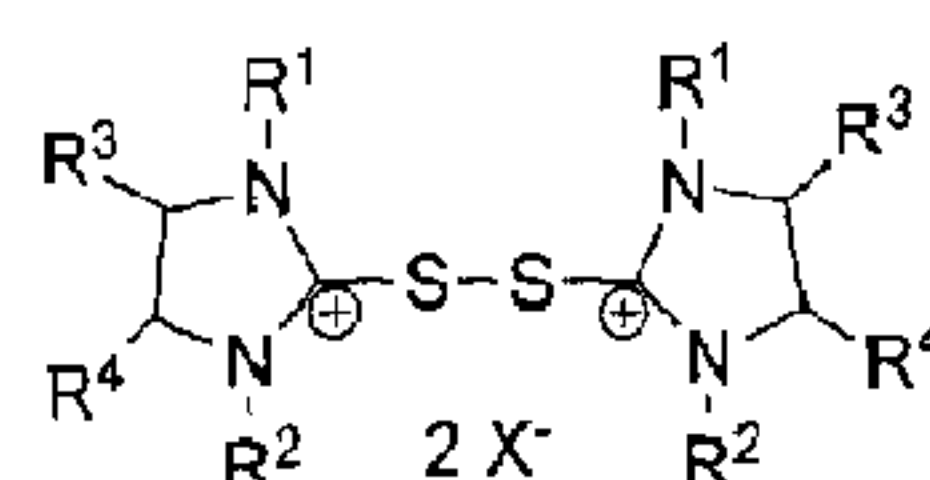
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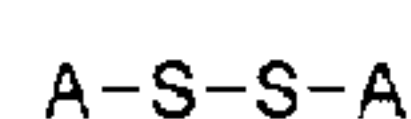
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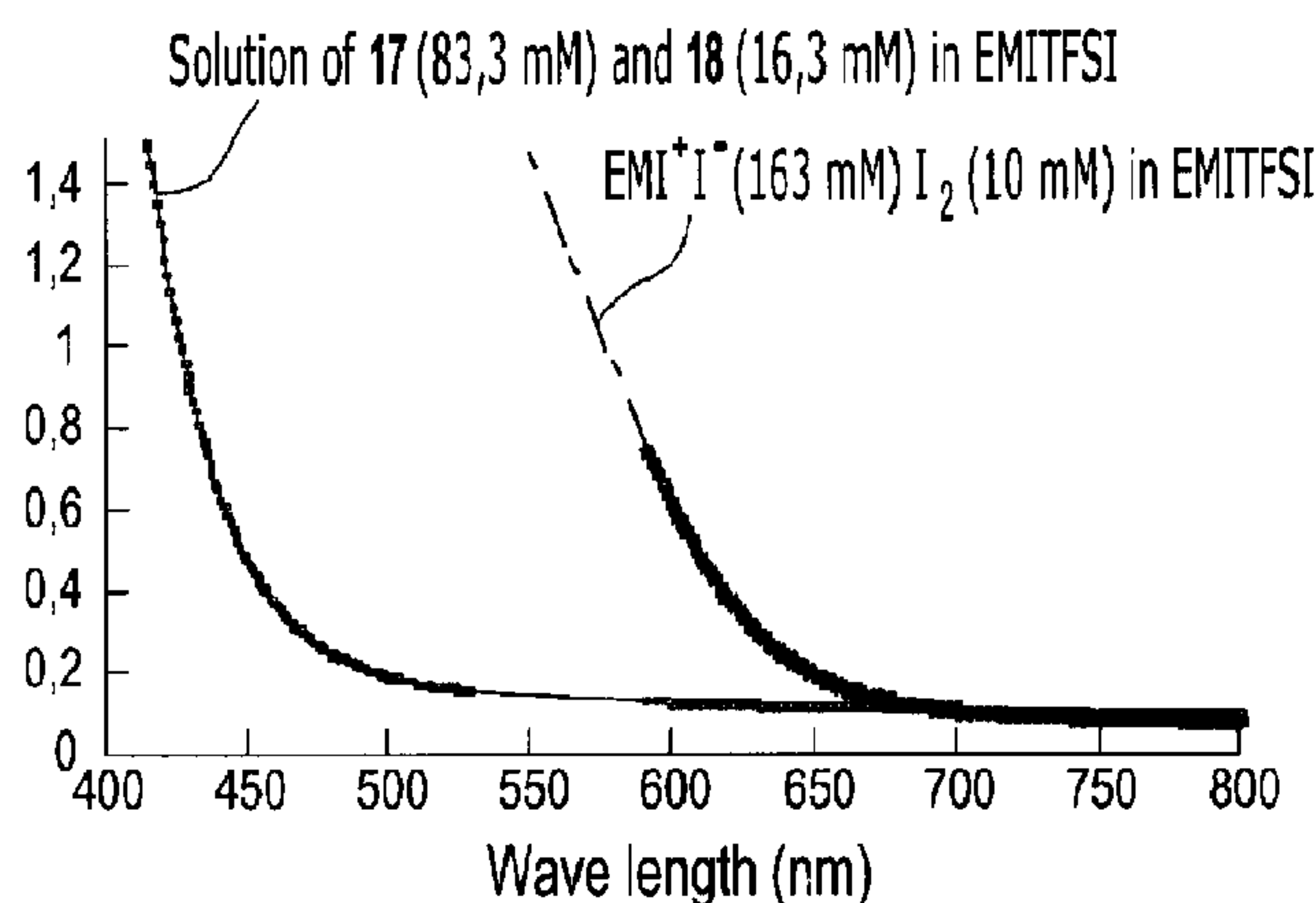
(III)



(II)



(IV)



(57) Abrégé/Abstract:

There is provided a composition comprising a first compound chosen from compounds of formulas (I) and (III) and a second compound chosen from compounds of formulas (II) and (IV): Various chemical entities can be used for R¹ to R⁴, A, M, and Z. This composition can be particularly useful as a redox couple.

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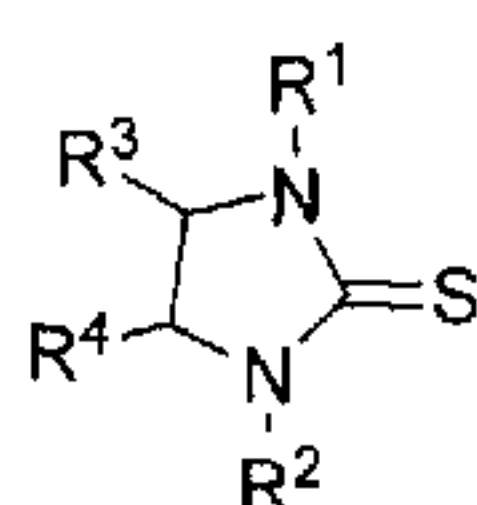
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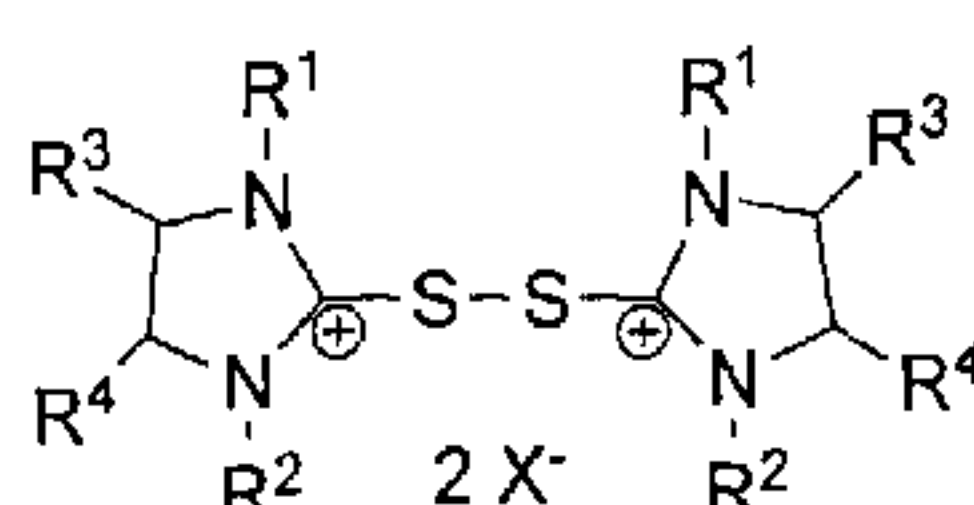
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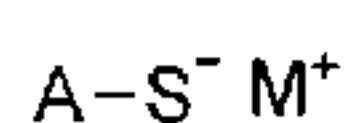
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(I)



(II)

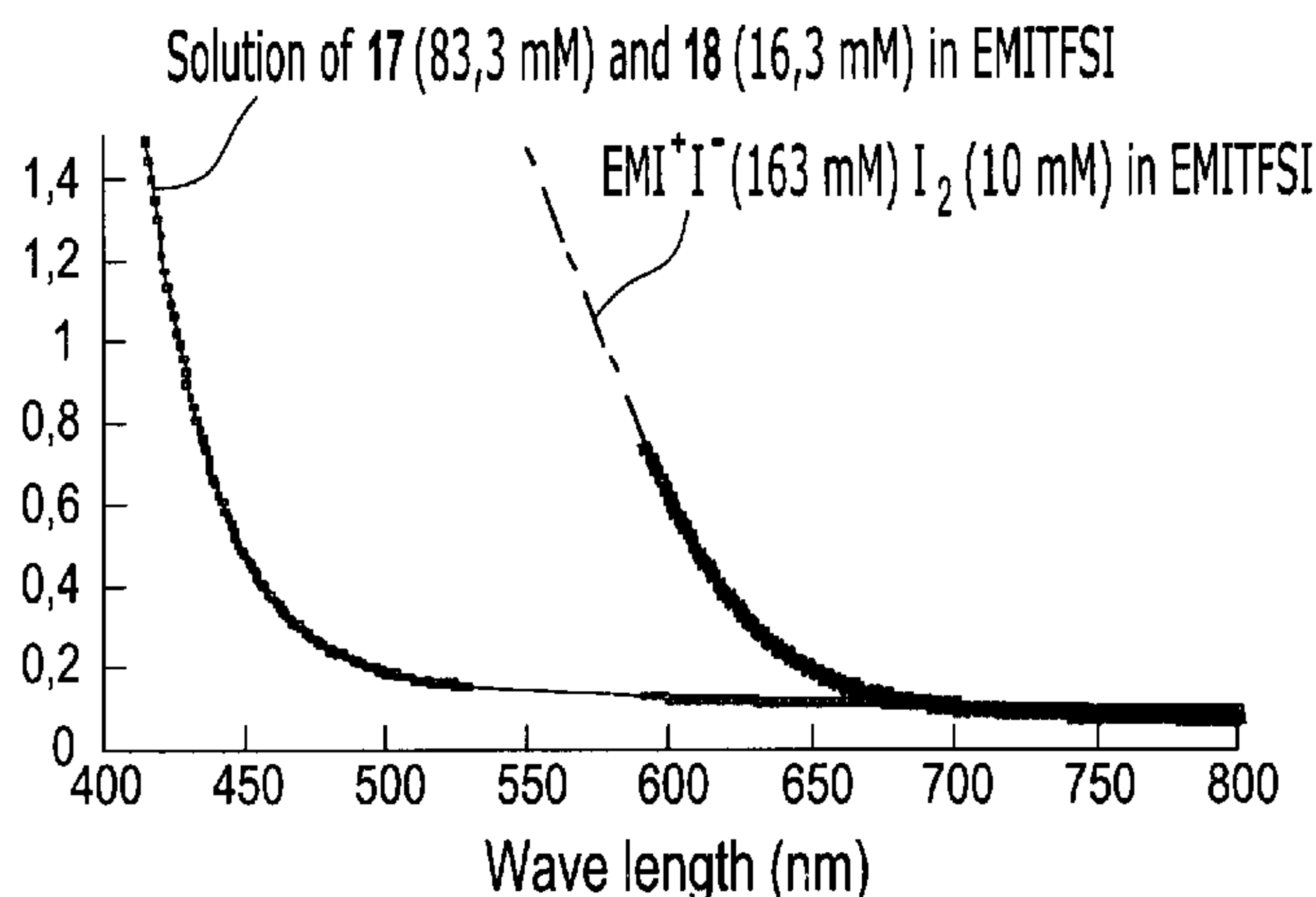


(III)



(IV)

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REDOX COUPLES, COMPOSITIONS AND USES THEREOF

TECHNICAL FIELD

The present document relates to improvements in the field of electrochemistry. In particular, this document relates to compositions that can be used as redox couples.

BACKGROUND OF THE INVENTION

Sun is a free and unlimited renewable source of energy. It can be converted directly to electricity by using *p-n* heterojunction solar cells (like silicon-based devices), electrochemical photovoltaic cells (EPC's) or dye-sensitized solar cells (DSSC's). EPC's are systems based on a junction between a semiconductor (*p*-type or *n*-type) and an electrolyte containing one redox couple; an auxiliary electrode completes the device. Owing to the built-in potential developed at the semiconductor/electrolyte interface, the photogenerated electrons and holes are separated and used to undergo oxidation and reduction reactions at the electrodes, respectively with the reduced and oxidized species of the redox couple. On the other hand, DSSC's are systems based on a junction between dye-chemisorbed nanocrystalline TiO₂ particles, deposited on a conductive glass substrate, and a non-aqueous electrolyte containing the I⁻/I₃⁻ redox couple; a platinum-coated conductive glass electrode completes the device. In such systems, the light absorption (by the dye molecules) and charge-carrier transport (in the conduction band of the semiconductor to the charge collector) processes are separated. Homogeneous oxidation of I⁻ species serves to regenerate the photoexcited dye molecules whereas the heterogeneous reduction of I₃⁻ species takes place at the platinum-coated electrode.

There is extensive prior art on EPC's and DSSC's. However, one main issue still to resolve is to find a redox couple that is electrochemically stable, non-corrosive, with a high degree of reversibility and a high electropositive (in

conjunction with *n*-type semiconductors) or electronegative (in conjunction with *p*-type semiconductors) potential, and colorless (substantially optically clear) when used in concentrations allowing high electrolyte ionic conductivities.

I^-/I_3^- is the most investigated redox couple for DSSC's. Cations may be alkali metals or organic cations containing quaternary ammonium groups such as dialkylimidazolium (Papageorgiou *et al.*, *J. Electrochem. Soc.* **143**, 3099(1996) Stathatos *et al.*, *Chem. Mater.*, **15**, 1825 (2003)). The main limitations of this system are (i) the fact that it absorbs a significant part of the visible light of the solar spectrum when used in the concentration range giving reasonably good ionic conductivities (which leads to a decrease in the energy conversion efficiency); (ii) its low redox potential (which limits the device photovoltage); (iii) its reactivity towards metals such as silver copper, etc. (which causes a difficulty about the use of these metals as a current collector); and (iv) the high volatility of the electrolyte when usual organic solvents are employed (which causes an irreversible instability of the device).

Nusbaumer *et al.* in *Chem. Eur. J.*, **9**, 3756 (2003) studied alternative redox couples for DSSC's based on much more expensive cobalt complexes. Although the fact that these systems are less colored and possess more positive potential than the I^-/I_3^- redox couple, the oxidized species (Co^{III}) may be reduced at the conductive glass acting as a substrate for the TiO_2 particles, in which case the energy conversion efficiency is decreased. Moreover, regeneration of the dye molecules by the reduced species (Co^{II}) (absolutely necessary to the operation of the device) may become more difficult due to association of the oxidized species (Co^{III}) with the sensitizer. Another serious disadvantage of this Co^{III}/Co^{II} system is the bigger molecular size that causes a limitation of photocurrent under high illumination intensity (100 mW/cm^2).

In EPC's, various redox couples dissolved in water were studied, such as $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$, I^-/I_3^- , Fe^{2+}/Fe^{3+} , S^{2-}/S_n^{2-} , Se^{2-}/Se_n^{2-} and V^{2+}/V^{3+} , and devices exhibiting a good energy conversion efficiency were generally unstable under sustained white light illumination due to photocorrosion of the

semiconductor electrode. The use of non-aqueous electrolytic media (liquid, gel or polymer) could eliminate the photocorrosion process, but in these cases the number of redox couples is very limited. For examples, the I^-/I_3^- (Skotheim and Inganäs, *J. Electrochem. Soc.*, 132, 2116 (1985)) and S^{2-}/S_n^{2-} (Vijh and Marsan, *Bull. Electrochem.*, 5, 456 (1989)) redox couples were dissolved in polyethylene oxide (PEO) and modified PEO, respectively, and investigated in EPC's. In addition to the coloration and potential problems occurring with the I^-/I_3^- couple, as mentioned above, the device stability has not been demonstrated. Regarding the S^{2-}/S_n^{2-} redox couple, the same problems were observed but in this case the stability under white light illumination has been reported.

A cesium thiolate (CsT)/disulfide (T_2) redox couple, where T^- stands for 5-mercapto-1-methyltetrazolate ion and T_2 for the corresponding disulfide, was dissolved in modified PEO and studied in an EPC (Philiass and Marsan, *Electrochim. Acta*, 44, 2915 (1999)). Its more positive potential than that of the S^{2-}/S_n^{2-} redox couple, its better dissociation in organic media including polymers (giving much more conductive electrolytes) and its much less intense coloration are responsible for the significant increase of the device energy conversion efficiency. Despite this improvement, the T^-/T_2 redox couple is quite electrochemically irreversible, with a difference between the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials, symbolized as ΔE_p , of 1.70 V at a platinum electrode (scanning speed of 100 mV/s), even when put in a more conductive gel electrolyte comprising 50 mM of T^- and 5 mM of T_2 dissolved in 80% DMF / DMSO (60/40) and incorporated in 20% poly(vinylidene fluoride), PVdF. Furthermore, its solubility is not very good in organic media.

Thus, based on prior art relative to redox couples for EPC's and DSSC'S, there are no redox couples permitting to maximize the device energy conversion efficiency.

Therefore, new redox couples having improved properties with respect to the redox couples of the prior art would be highly desired. Moreover, redox

couples permitting to avoid the drawbacks of the prior art are also highly desired.

SUMMARY OF THE INVENTION

It is therefore an object to provide a redox couple which would overcome the above-mentioned drawbacks.

It is another object to provide a redox couple which has a good solubility.

It is another object to provide a redox couple which is substantially colorless or substantially optically clear at concentrations permitting a good conductivity.

It is another object to provide a redox couple which has a low vapor pressure.

It is another object to provide a redox couple which has a high thermal stability.

It is another object to provide a redox couple which is highly electropositive as example for application in DSSC'S or EPC's using *n*-type semiconductors.

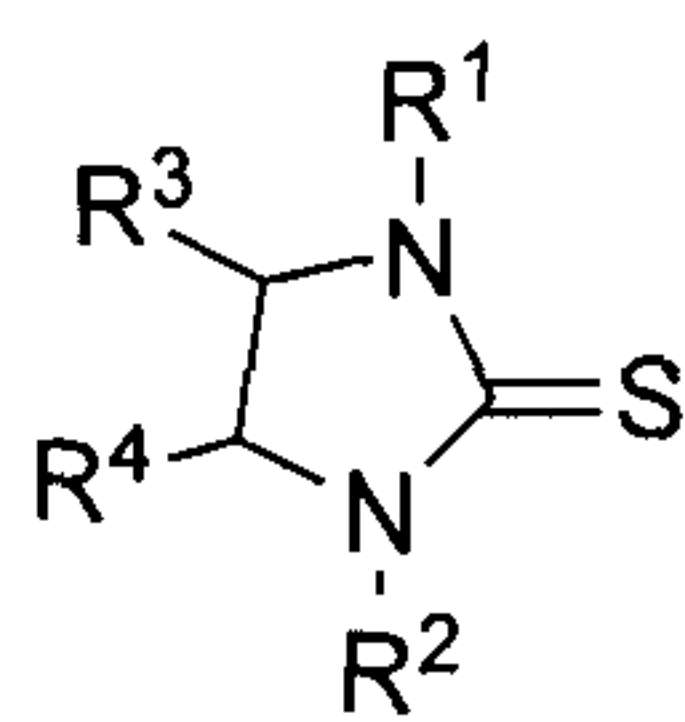
It is another object to provide a redox couple which is highly electronegative as example for application in EPC's using *p*-type semiconductors.

It is another object to provide a redox couple which will not corrode other components when used in a device.

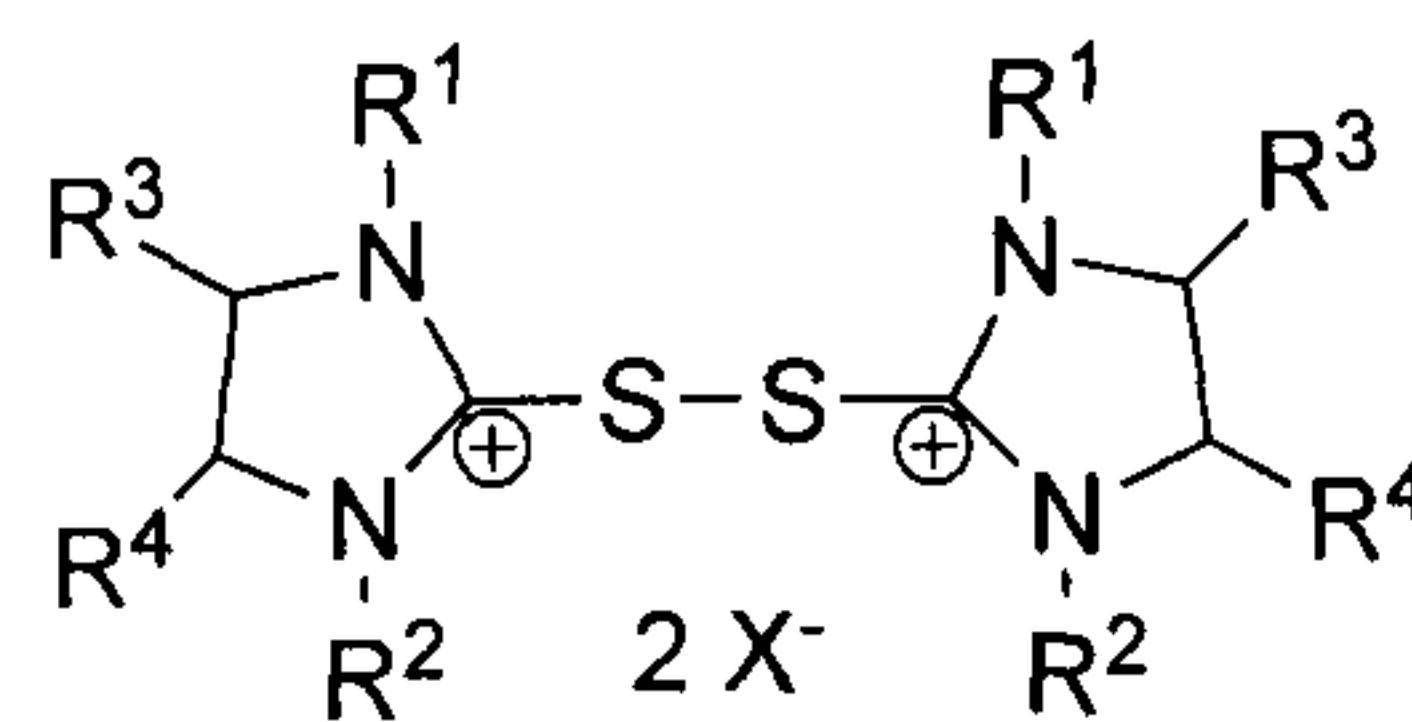
It is another object to provide a redox couple which has a small ΔE_p .

It is another object to provide a redox couple which has a high degree of reversibility.

In accordance with one aspect, there is provided a composition comprising a first compound chosen from compounds of formulas (I) and (III) and a second compound chosen from compounds of formulas (II) and (IV):



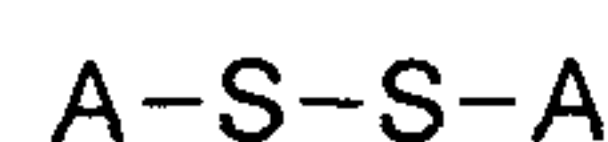
(I)



(II)



(III)



(IV)

wherein

R^1 and R^2 are the same or different and are chosen from a hydrogen atom, C_1 - C_{30} alkyl which is linear or branched and optionally halogenated, C_3 - C_{12} cycloalkyl, C_1 - C_{12} heterocyclyl, C_2 - C_8 alkenyl, C_2 - C_8 alkynyl, C_6 - C_{12} aryl, C_6 - C_{30} aralkyl, C_6 - C_{30} alkylaryl, and C_1 - C_{12} heteroaryl, C_6 - C_{30} alkylheteroaryl, and C_6 - C_{30} alkylheterocyclyl, or R^1 and/or R^2 is part of a polymer chain or network

R^3 and R^4 are the same or different and are chosen from a hydrogen atom, C_1 - C_{30} alkyl which is linear or branched and optionally halogenated, C_3 - C_{12} cycloalkyl, C_1 - C_{12} heterocyclyl, C_2 - C_8 alkenyl, C_2 - C_8 alkynyl, C_6 - C_{12} aryl, C_6 - C_{30} aralkyl, C_6 - C_{30} alkylaryl, and C_1 - C_{12} heteroaryl, C_6 - C_{30} alkylheteroaryl, and C_6 - C_{30} alkylheterocyclyl, F, Cl, Br, I, CF_3 , CN, SO_3H , C_nF_{2n+1} , $HC_nF_{2n+1}-$, CF_3O- , $C_nF_{2n+1}O-$, $HC_nF_{2n+1}O-$, CF_3S- , $C_nF_{2n+1}S-$, $HC_nF_{2n+1}S-$, $ClC_nF_{2n+1}-$, $ClC_nF_{2n+1}O-$, $ClC_nF_{2n+1}S-$, $BrC_nF_{2n+1}-$, $BrC_nF_{2n+1}O-$, $BrC_nF_{2n+1}S-$, $IC_nF_{2n+1}-$, $IC_nF_{2n+1}O-$, $IC_nF_{2n+1}S-$, $CH_2=CHC_nF_{2n+1}-$, $CH_2=CHC_nF_{2n+1}O-$, $CH_2=CHC_nF_{2n+1}S-$, $R^2OC_nF_{2n+1}-$, $R^2OC_nF_{2n+1}O-$, $R^2OC_nF_{2n+1}S-$, CF_3CH_2- , CF_3CH_2O- , $(CF_3)_2CH-$, $(CF_3)_2CHO-$, CHF_2- , CHF_2O- , CHF_2S- , $CClF_2-$, $CClF_2O-$, $CClF_2S-$, CCl_2F- , CCl_2FO- , $CClF_2S-$, CCl_3- , CCl_3O- , C_6F_5- , $CF_3C_6F_4-$, C_6F_5O- , $CF_3C_6F_4O-$, 3,5- $(CF_3)_2C_6H_2-$,

C_6Cl_5- , C_6Cl_5O- , FSO_2CF_2- , $ClSO_2(CF_2)_n-$, $^-SO_3(CF_2)_n-$, $^-CO_2(CF_2)_n-$,
 $FSO_2N^{(-)}SO_2(CF_2)_n-$, $CF_3SO_2N^{(-)}SO_2(CF_2)_n-$, $C_nF_{2n+1}SO_2N^{(-)}SO_2(CF_2)_n-$,
 $R^2SO_2N^{(-)}SO_2(CF_2)_n-$, $FSO_2(CF_2)_n-$, $ClSO_2(CF_2)_n-$,
 $C_nF_{2n+1}SO_2N^{(-)}(CF_2)_n-$, and $R^2SO_2N^{(-)}(CF_2)_n-$

or R^3 and/or R^4 is part of a polymer chain or network, or
absent

X^- is $(FSO_2)_2N^-$, $(CF_3SO_2)_2N^-$, $(C_2F_5SO_2)_2N^-$, $(CF_3SO_2)_3C^-$,
 $CF_3SO_3^-$, CF_3COO^- , AsF_6^- , CH_3COO^- , $(CN)_2N^-$, $(CN)_3C^-$, NO_3^- , $2.3HF$, Cl^- , Br^- , I^- ,
 PF_6^- , BF_4^- , ClO_4^- , SCN^- ;

M is H , an organic cation or an inorganic cation;

A is a C_1 - C_{12} heteroaryl, a C_1 - C_{12} heterocyclyl, C_6 - C_{12}
 aryl, C_6 - C_{30} aralkyl, or C_6 - C_{30} alkylaryl

wherein the alkyl, cycloalkyl, heterocyclyl, alkenyl, alkynyl, aryl,
 aralkyl, alkylaryl, heteroaryl, alkylheteroaryl, and alkylheterocyclyl optionally
 includes a heteroatom in the form of $-O-$, $=N-$, $-S-$, $=P-$, $=(P=O)-$, $-SO-$, $-$
 SO_2- ;

wherein the alkyl, cycloalkyl, heterocyclyl, alkenyl, alkynyl, aryl,
 aralkyl, alkylaryl, heteroaryl, alkylheteroaryl, and alkylheterocyclyl being
 unsubstituted or substituted with 1 to 3 substituents chosen from R^3 , R^4 , F , Cl ,
 Br , I , OH , a C_1 - C_6 alkoxy, a C_1 - C_6 hydroxy alkyl, NO_2 , CN , CF_3 , SO_3H , C_nF_{2n+1} ,
 C_1 - C_{12} alkyl which is linear or branched, C_6 - C_{12} aryl, C_nH_{2n+1} , $Ph_2P(O)-$, Ph_2P- ,
 $Me_2P(O)-$, Me_2P , $Ph_2P(S)$, $Me_2P(S)$, $Ph_3P=N-$, $Me_3P=N-$, $C_6H_5C_pH_{2p}-$,
 $C_pH_{2p+1}C_6H_4-$, $C_pH_{2p+1}C_6H_4C_nH_{2n}-$, $CH_2=CHC_pH_{2p}-$, $CH_2=CHC_6H_5-$,
 $CH_2=CHC_6H_4C_pH_{2p+1}-$, and $CH_2=CHC_pH_{2p}C_6H_4-$;

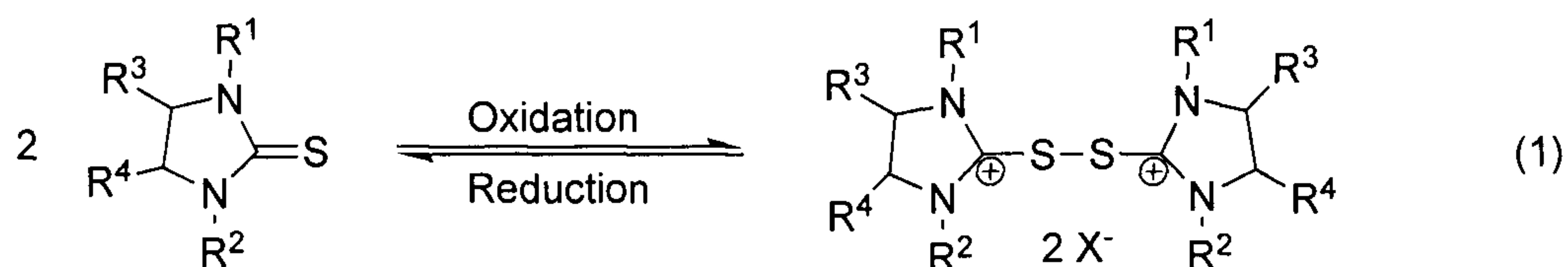
n is an integer having a value from 1 to 48;

m is an integer having a value from 2 to 12; and

p is an integer having a value from 1 to 48.

It was found that such compositions are quite useful as redox couples.

In accordance with another aspect, there is provided a redox couple according to scheme 1 or scheme 2:



wherein R^1 , R^2 , R^3 , R^4 , X^- , M and A are as previously defined.

It was found that the redox couples previously presented can have a very good degree of reversibility since they can have a relatively small ΔE_p . Moreover, it has been found that these redox couples have a high thermal stability, and a good solubility in various solvents. It also has been found that these redox couples are substantially colorless (or substantially optically clear) at concentrations permitting a good conductivity. Such characteristics make them particularly interesting in various applications like solar cells or photovoltaic cells. It also has been found that these redox couples do not have tendency to corrode other components when used in devices such as solar cells or photovoltaic cells.

The expression "redox couple" as used herein refers to a couple comprising an oxidized member and a reduced member.

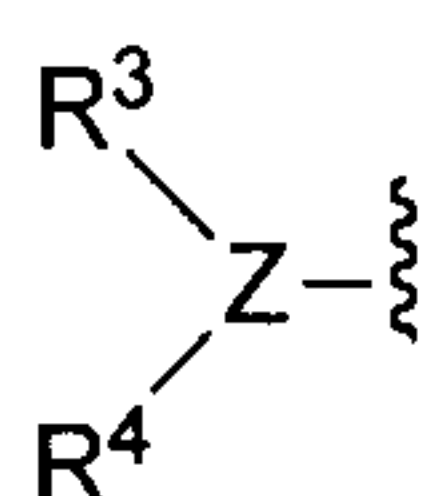
The term "aryl" as used herein refers to a cyclic or polycyclic aromatic ring. According to one example, the aryl group can be phenyl or naphthyl.

The term "heteroaryl" as used herein refers to an aromatic cyclic or fused polycyclic ring system having at least one heteroatom chosen from N, O, and

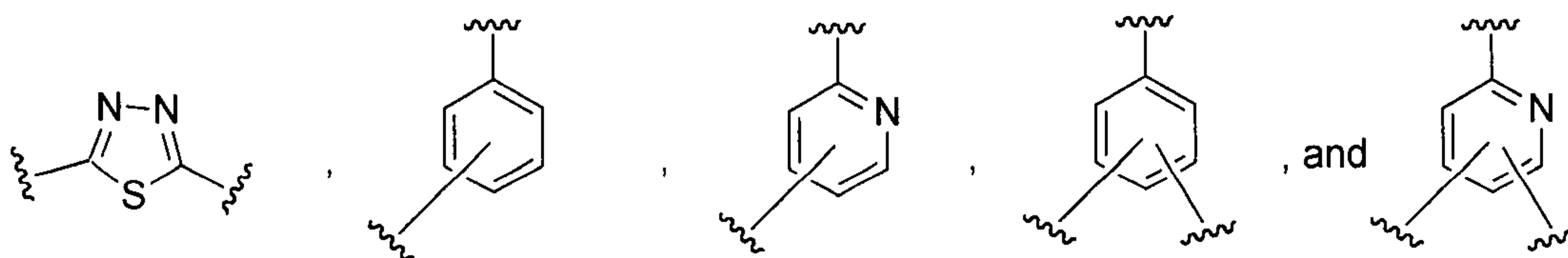
S. Examples include heteroaryl groups such as furyl, thienyl, pyridyl, quinoliny, isoquinoliny, indolyl, isoindolyl, triazolyl, pyrrolyl, tetrazolyl, imidazolyl, pyrazolyl, oxazolyl, thiazolyl, benzofuranyl, benzothiophenyl, carbazolyl, benzoxazolyl, pyrimidinyl, benzimidazolyl, quinoxaliny, benzothiazolyl, naphthyridinyl, isoxazolyl, isothiazolyl, purinyl, quinazoliny, and so on.

The term "heterocyclyl" includes non-aromatic rings or ring systems that contain at least one ring having at least one hetero atom (such as nitrogen, oxygen or sulfur). For example, such a term can include all of the fully saturated and partially unsaturated derivatives of the above mentioned heteroaryl groups. Examples of heterocyclic groups include pyrrolidinyl, tetrahydrofuranyl, morpholinyl, thiomorpholinyl, piperidinyl, piperazinyl, thiazolidinyl, isothiazolidinyl, and imidazolidinyl.

In the compositions and redox couples previously presented, A can be of formula



wherein Z is chosen from

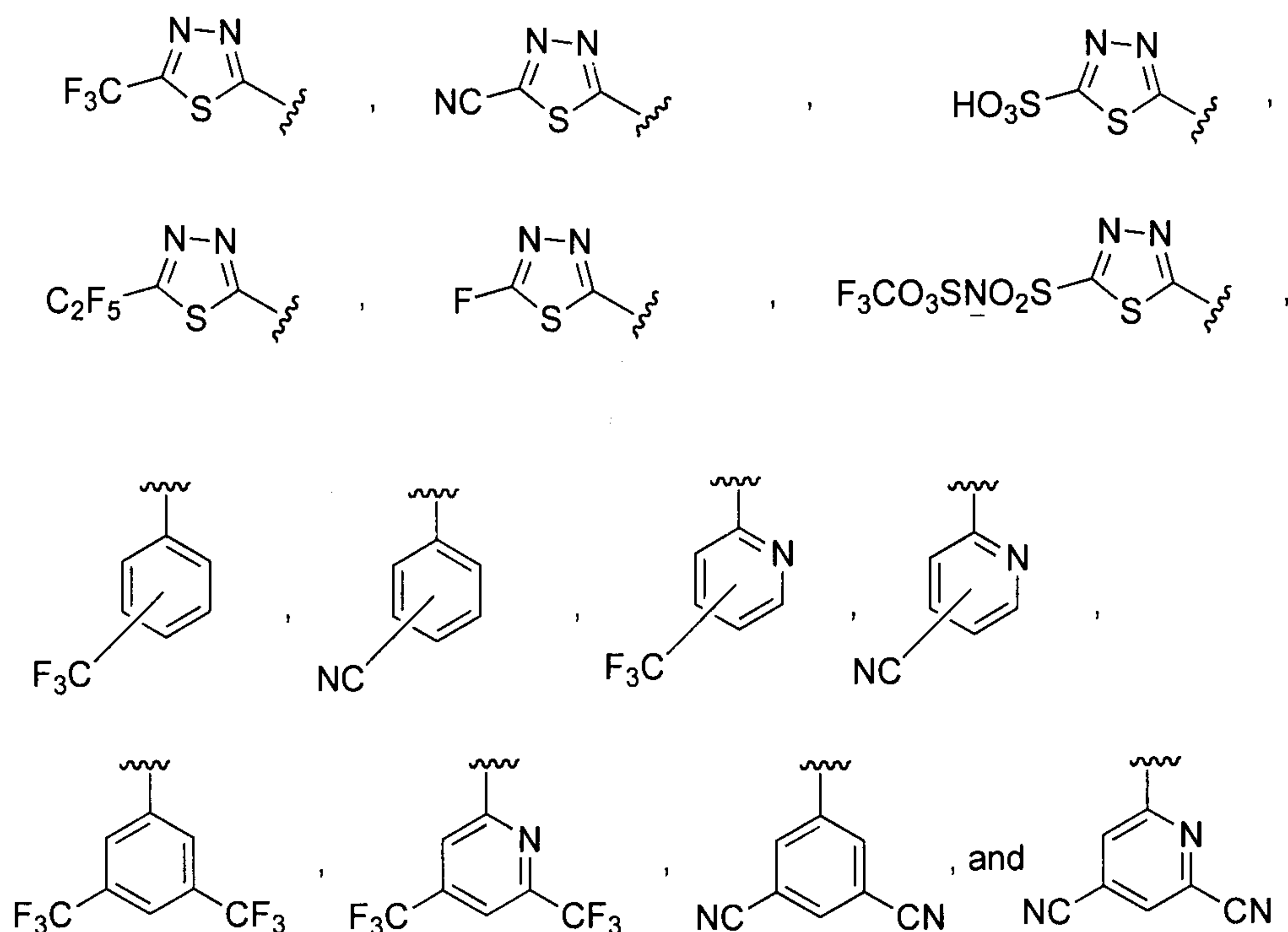


wherein R_3 and R_4 are as previously defined.

A can also be chosen from thiadiazoles, pyridines, and phenylenes. The thiadiazoles, pyridines, and phenylenes can be unsubstituted or substituted with with 1 to 3 substituents chosen from F, Cl, Br, I, OH, a C_1 - C_6 alkoxy, a C_1 - C_6 hydroxy alkyl, NO_2 , CN, CF_3 , SO_3^- , $\text{C}_n\text{F}_{2n+1}$, C_1 - C_{12} alkyl which is linear or branched, C_6 - C_{12} aryl, $\text{C}_n\text{H}_{2n+1}$, $\text{Ph}_2\text{P}(\text{O})^-$, Ph_2P^- , $\text{Me}_2\text{P}(\text{O})^-$, Me_2P , $\text{Ph}_2\text{P}(\text{S})$,

Me₂P(S), Ph₃P=N-, Me₃P=N-, C₆H₅C_pH_{2p}-, C_pH_{2p+1}C₆H₄-, C_pH_{2p+1}C₆H₄C_nH_{2n}-,
 , CH₂=CHC_pH_{2p}-, CH₂=CHC₆H₅-, CH₂=CHC₆H₄C_pH_{2p+1}-, and
 CH₂=CHC_pH_{2p}C₆H₄-.

A can also be chosen from

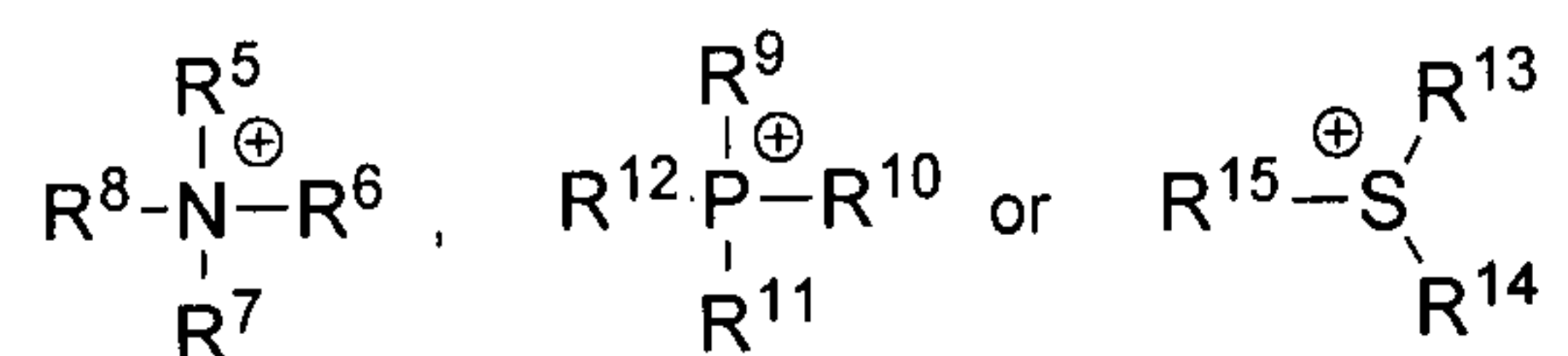


In the compositions and redox couples, X⁻ can be (CF₃SO₂)₂N⁻, (C₂F₅SO₂)₂N⁻, (CF₃SO₂)₃C⁻, CF₃SO₃⁻, (CN)₂N⁻, PF₆⁻, BF₄⁻ or ClO₄⁻. For example, X⁻ is (CF₃SO₂)₂N⁻.

M can be chosen from a positively charged C₁-C₁₂ heteroaryl or a C₁-C₁₂ heterocyclyl, wherein said heteroaryl or said heterocyclyl is unsubstituted or substituted with 1 to 3 substituents chosen from F, Cl, Br, I, OH, a C₁-C₆ alkoxy, a C₁-C₆ hydroxy alkyl, NO₂, CN, CF₃, SO₃⁻, C_nF_{2n+1}, C₁-C₁₂ alkyl which is linear or branched, C₆-C₁₂ aryl, C_nH_{2n+1}, Ph₂P(O)-, Ph₂P-, Me₂P(O)-, Me₂P, Ph₂P(S), Me₂P(S), Ph₃P=N-, Me₃P=N-, C₆H₅C_pH_{2p}-, C_pH_{2p+1}C₆H₄-,

$C_pH_{2p+1}C_6H_4C_nH_{2n}-$, $CH_2=CHC_pH_{2p}-$, $CH_2=CHC_6H_5-$, $CH_2=CHC_6H_4C_pH_{2p+1}-$, and $CH_2=CHC_pH_{2p}C_6H_4-$.

M can also be an inorganic cation such as Li^+ , K^+ , Na^+ , and Cs^+ . M can also be an organic cation of formula



wherein

R^5 , R^6 , R^7 and R^8 are same or different and each independently represent a C_1 - C_{20} alkyl which is linear or branched, C_3 - C_{12} cycloalkyl, C_1 - C_{12} heterocyclyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{12} aryl, C_6 - C_{20} aralkyl, C_6 - C_{20} alkylaryl, and C_1 - C_{12} heteroaryl;

R^9 , R^{10} , R^{11} and R^{12} are same or different and each independently represent a C_1 - C_{20} alkyl which is linear or branched, C_3 - C_{12} cycloalkyl, C_1 - C_{12} heterocyclyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{12} aryl, C_6 - C_{20} aralkyl, C_6 - C_{20} alkylaryl, and C_1 - C_{12} heteroaryl; and

R^{13} , R^{14} and R^{15} are same or different and each independently represent a C_1 - C_{20} alkyl which is linear or branched, C_3 - C_{12} cycloalkyl, C_1 - C_{12} heterocyclyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{12} aryl, C_6 - C_{20} aralkyl, C_6 - C_{20} alkylaryl, and C_1 - C_{12} heteroaryl,

wherein the alkyl, cycloalkyl, heterocyclyl, alkenyl, alkynyl, aryl, aralkyl, alkylaryl, heteroaryl, alkylheteroaryl, and alkylheterocyclyl being unsubstituted or substituted with 1 to 3 substituents chosen from F, Cl, Br, I, OH, a C_1 - C_6 alkoxy, a C_1 - C_6 hydroxy alkyl, NO_2 , CN, CF_3 , SO_3^- , C_nF_{2n+1} , C_1 - C_{12} alkyl which is linear or branched, C_6 - C_{12} aryl, C_nH_{2n+1} , $C_6H_5C_pH_{2p}-$, $C_pH_{2p+1}C_6H_4-$, $C_pH_{2p+1}C_6H_4C_nH_{2n}-$, $CH_2=CHC_pH_{2p}-$, $CH_2=CHC_6H_5-$, $CH_2=CHC_6H_4C_pH_{2p+1}-$, and $CH_2=CHC_pH_{2p}C_6H_4-$.

M can also be chosen from N-substituted imidazoliums. The substituents can each independently be a C₁-C₁₂ alkyl or a C₁-C₆ alkyl which is linear (for example 1,3-methylethylimidazolium) or branched or tetralkylammoniums, wherein each of the alkyl groups is independently C₁-C₁₂ alkyl which is linear or branched (for example tetrabutylammonium).

The compositions can further comprise a solvent chosen from nitriles (such as CH₃CN), CH₂Cl₂, alcohols (such as ethanol, isopropanol), DMSO, amides (such as DMF), hexane, heptane, toluene, linear carbonates (such as dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate), cyclic esters (such as ethylene carbonate, propylene carbonate), urea (tetramethylurea), ionic liquids such as dialkylimidazolium, trialkylsulfonium, and quaternary amine (such as C₁-C₂₀ tetraalkylammonium) and quaternary phosphonium (such as C₁-C₂₀ tetraalkylphosphonium or C₆-C₁₂ tetraarylphosphonium) salts associated with stable anion such as (FSO₂)₂N⁻, (CF₃SO₂)₂N⁻, (C₂F₅SO₂)₂N⁻, (CF₃SO₂)₃C⁻, CF₃SO₃⁻, CF₃COO⁻, AsF₆⁻, CH₃COO⁻, (CN)₂N⁻, (CN)₃C⁻, NO₃⁻, 2.3HF, Cl⁻, Br⁻, I⁻, PF₆⁻, BF₄⁻, ClO₄⁻, SCN⁻, and mixtures thereof. For example, the solvent is nitriles (such as CH₃CN), amides (such as DMF), linear carbonates (such as dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate), cyclic esters (such as ethylene carbonate, propylene carbonate), ionic liquids such as dialkylimidazolium, trialkylsulfonium, and quaternary amine (such as C₁-C₂₀ tetraalkylammonium) and quaternary phosphonium (such as C₁-C₂₀ tetraalkylphosphonium or C₆-C₁₂ tetraarylphosphonium) salts associated with stable anion such as (FSO₂)₂N⁻, (CF₃SO₂)₂N⁻, (C₂F₅SO₂)₂N⁻, (CF₃SO₂)₃C⁻, CF₃SO₃⁻, CF₃COO⁻, AsF₆⁻, CH₃COO⁻, (CN)₂N⁻, (CN)₃C⁻, NO₃⁻, 2.3HF, Cl⁻, Br⁻, I⁻, PF₆⁻, BF₄⁻, ClO₄⁻, SCN⁻ and mixtures thereof.

In the compositions, the first compound can be, for example, present in the composition in a molar ratio of about 0.1 to about 99.9 % and the second compound can be present in a molar ratio of about 99.9 to about 0.1 %. According to another example, the first compound can be present in the

composition in a molar ratio of about 5.0 to about 95.0 % and the second compound is present in a molar ratio of about 95.0 to about 5.0 %.

The compositions can be in the form of an uncolored and / or translucent solution. The compositions can also be substantially optically clear.

The compositions can comprise a compound of formula (I) and a compound of formula (II) or they can comprise a compound of formula (III) and a compound of formula (IV).

In accordance with another aspect, there is provided a photovoltaic cell comprising an anode, a cathode, and a composition as previously defined in the present document.

In accordance with another aspect, there is provided a photovoltaic cell comprising an anode, a cathode, a composition as defined in the present document, and a solvent, a polymer, a molten salt, an ionic liquid, a gel or any combination thereof.

In accordance with another aspect, there is provided a photovoltaic cell comprising an anode, a cathode, and a redox couple as defined in the present document.

In accordance with another aspect, there is provided a photovoltaic cell comprising an anode, a cathode, a redox couple as defined in the present document, and a solvent, a polymer, a molten salt, an ionic liquid, a gel or any combination thereof.

The redox couples of the present document can be used in a solar cell, a fuel cell, a battery, a sensor or a display.

BRIEF DESCRIPTION OF FIGURES

Further features and advantages will become more readily apparent from the following description of specific embodiments as illustrated by way of examples in the appended figures wherein:

Fig. 1 shows a cyclic voltammogram of a composition according to one embodiment, wherein the oxidized member (compound **5**) and the reduced member (compound **3**) of the composition are present at the beginning of the experiment in a 1:1 ratio.

Fig. 2 shows another cyclic voltammogram of the composition tested in the voltammogram of Fig. 1, wherein the ratio reduced member (compound **3**) / oxidized member (compound **5**) is about 2 : 1 at the beginning of the experiment;

Fig. 3 shows another cyclic voltammogram of the composition tested in the voltammogram of Fig. 1, wherein the ratio reduced member (compound **3**) / oxidized member (compound **5**) is about 1 : 2 at the beginning of the experiment;

Fig. 4 shows cyclic voltammograms comparing the composition at various proportions of the reduced and oxidized members, which are the proportions analyzed in Figs. 1 to 3;

Fig. 5 shows other cyclic voltammograms comparing two different working electrodes with the composition used in the same proportion as in the voltammogram of Fig. 3;

Fig. 6 shows a cyclic voltammogram of a composition according to another embodiment, wherein the ratio reduced member (compound **7**) / oxidized member (compound **8**) is about 3 : 1 at the beginning of the experiment;

Fig. 7 shows a cyclic voltammogram of a composition according to another embodiment, wherein the ratio reduced member (compound **9**) / oxidized member (compound **10**) is about 3 : 1 at the beginning of the experiment;

Fig. 8 shows a cyclic voltammogram of a composition according to another embodiment, wherein the ratio reduced member (compound **11**) / oxidized member (compound **12**) is about 2 : 1 at the beginning of the experiment;

Fig. 9 shows a cyclic voltammogram of a composition according to another embodiment, wherein the ratio reduced member (compound **13**) / oxidized member (compound **14**) is about 1 : 3 at the beginning of the experiment;

Fig. 10 shows a cyclic voltammogram of a composition according to another embodiment, wherein the ratio reduced member (compound **17**) / oxidized member (compound **18**) is about 5 : 1 at the beginning of the experiment;

Fig. 11 is a comparison between the visible spectrum of a solution comprising compounds **17** and **18** in ethyl-1-methyl-3-imidazolium-bis-fluoro-sulfonylimide (EMITFSI) and the visible spectrum of $\text{EMI}^+\text{I}^- / \text{I}_2$ in EMITFSI; and

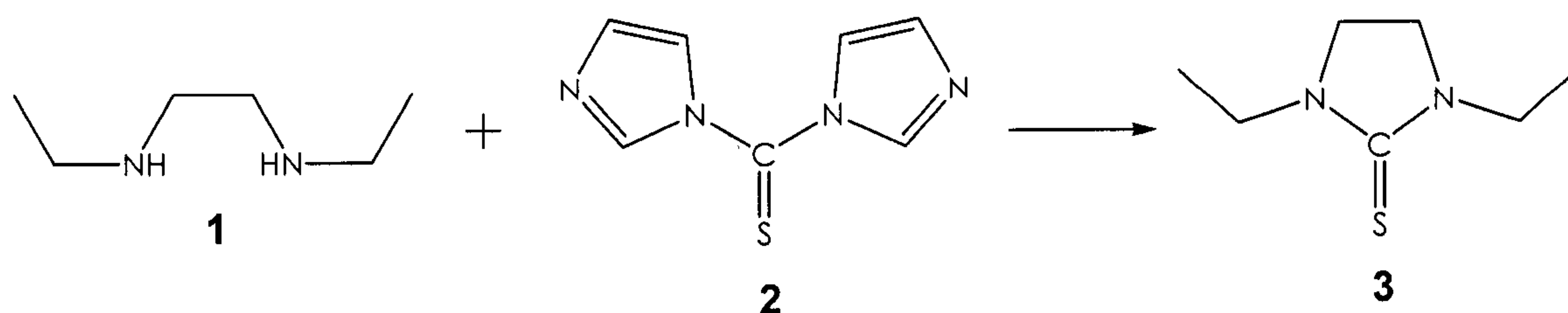
Fig. 12 shows cyclic voltammograms of the solution comprising compounds **17** and **18** in EMITFSI, wherein stability tests at a temperature of 70 ° C have been carried out.

DETAILED DESCRIPTION OF VARIOUS EMBODIMENTS

The following examples are given in a non-limitative manner.

For example, the compositions and redox couples of the present document can be made by the following general procedure.

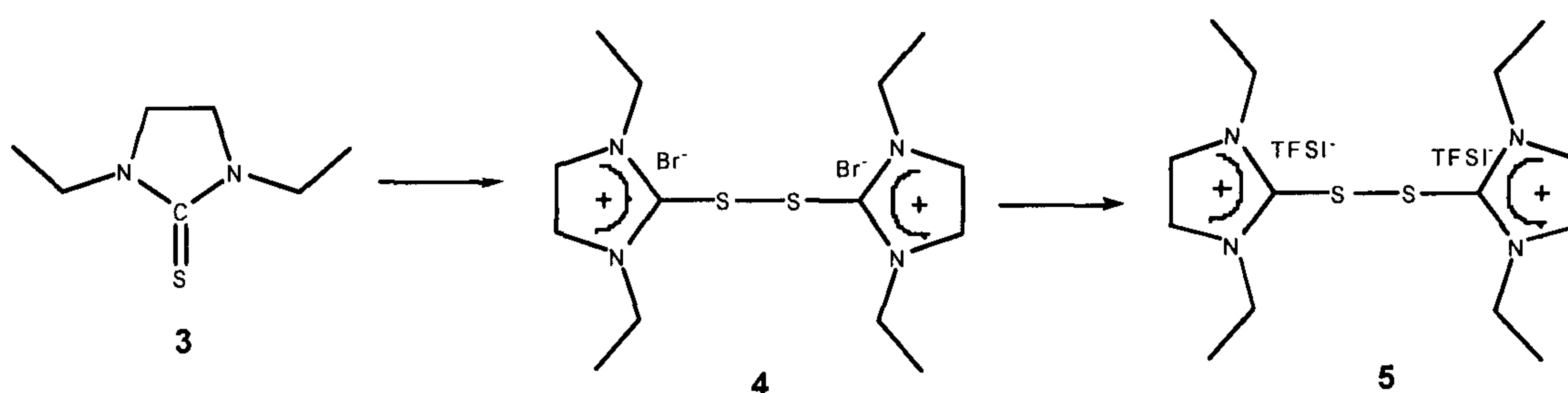
Synthesis of compound 3 (1,3-diethyl-imidazolidine-2-thione)



In a 100 mL two-neck flask 30 mL of tetrahydrofuran (THF), 1.6 mL (11.2 mmol; 1 eq) of **1** were introduced. Then, 2 g (11.1 mmol; 1 eq) of **2** were added. The resulting solution was stirred for 12 hours. The reaction was performed in a glove box. The reaction mixture was then concentrated with a rotative evaporator and an orange paste is obtained. Thereafter,

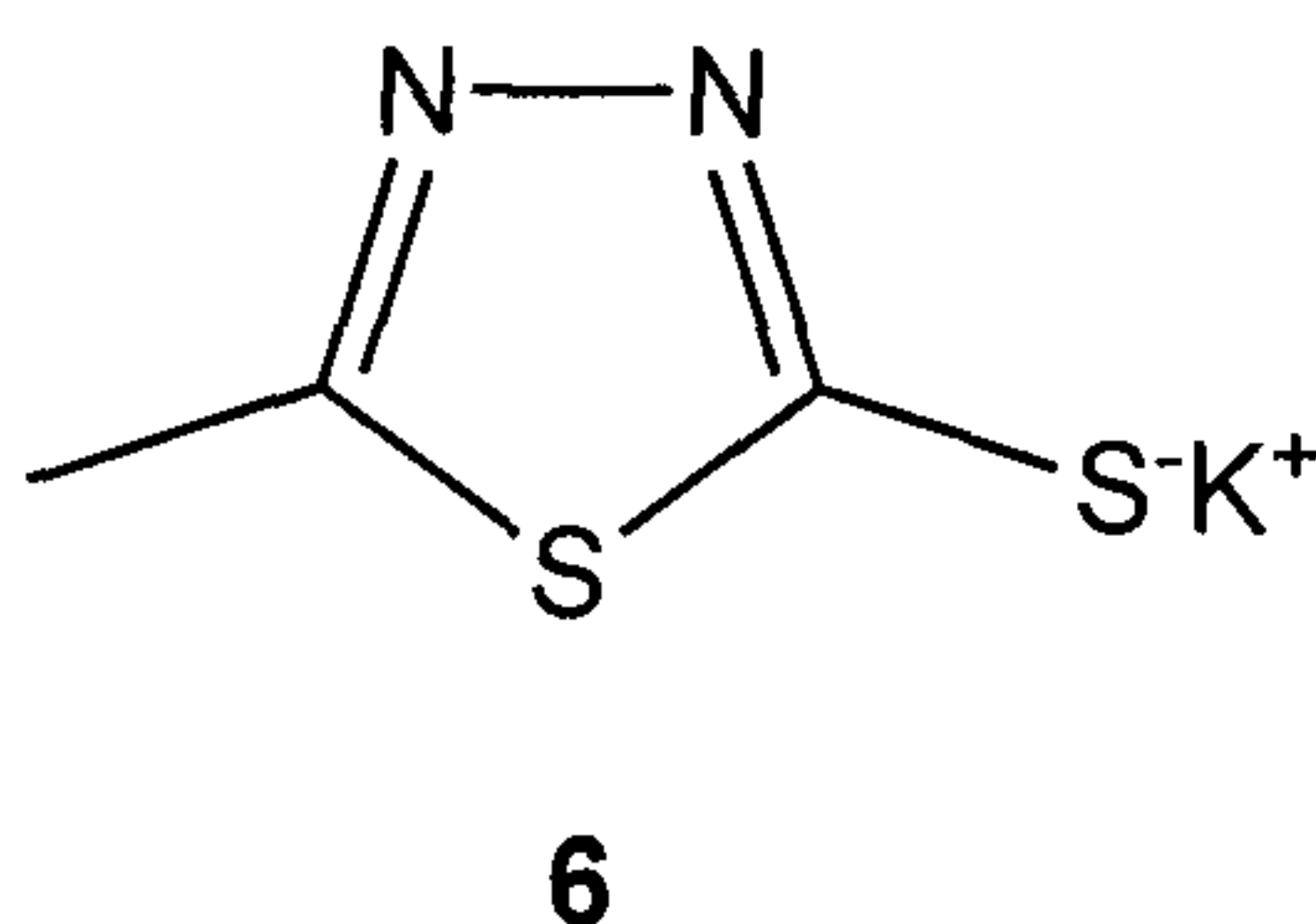
approximately 30 mL of Et₂O were added to it. **3** then precipitated and the impurities were solubilized in Et₂O. A filtration on paper was carried out and **3** was thus recovered. **3** was concentrated using a rotative evaporator. Again, an orange paste was obtained and approximately 30 mL of Et₂O were added to this mixture. **3** precipitated. This step was repeated until no more precipitate was obtained when Et₂O is added.

Synthesis of compound 5 (1,3-diethyl-imidazolidine-2-thione disulfide)



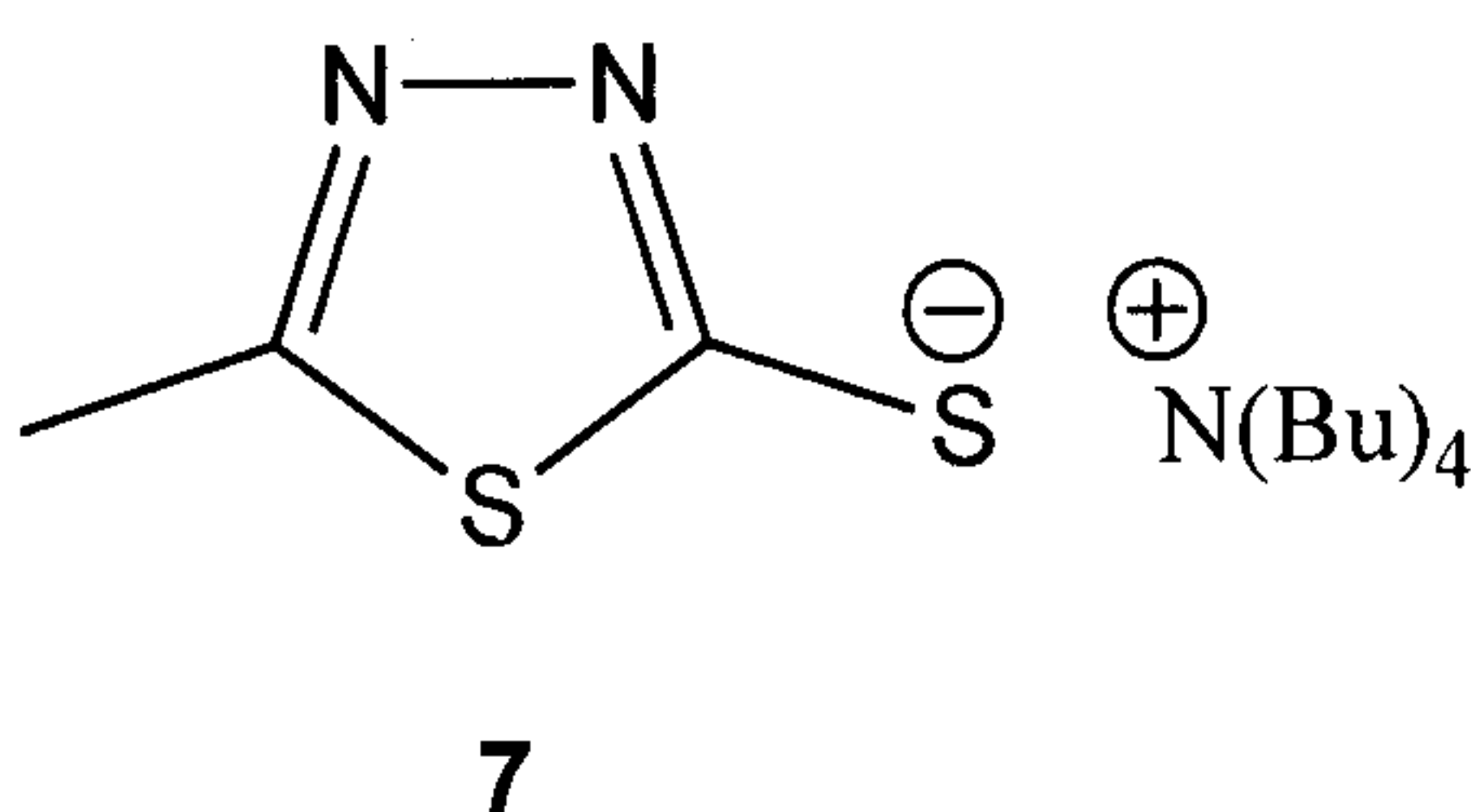
In a 125 mL reactional flask, 1 g (6.32 mmol; 1 eq) of compound **3** was introduced with 30 mL of water. 0.2 mL of Br₂ (0.50 g; 3.16 mmol; ½ eq) were then added dropwise. It is also possible to add an excess of Br₂. The solution was stirred for 1 hour at room temperature. In a separate 50 mL two-neck flask filled with 20 mL of water, 1.81g (6.32 mmol; 1 eq) of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were dissolved. This mixture was then added to the previous one. A yellowish oil (**5**) was formed. Compound **5** was extracted with 50 mL of Et₂O. The organic layer was separated and dried with anhydrous MgSO₄. The organic layer was then concentrated using a rotative evaporator. A yellowish oil **5** was obtained.

Synthesis of compound 6 (potassium salt of 5-methyl-2-mercapto-1,3,4-thiadiazole)

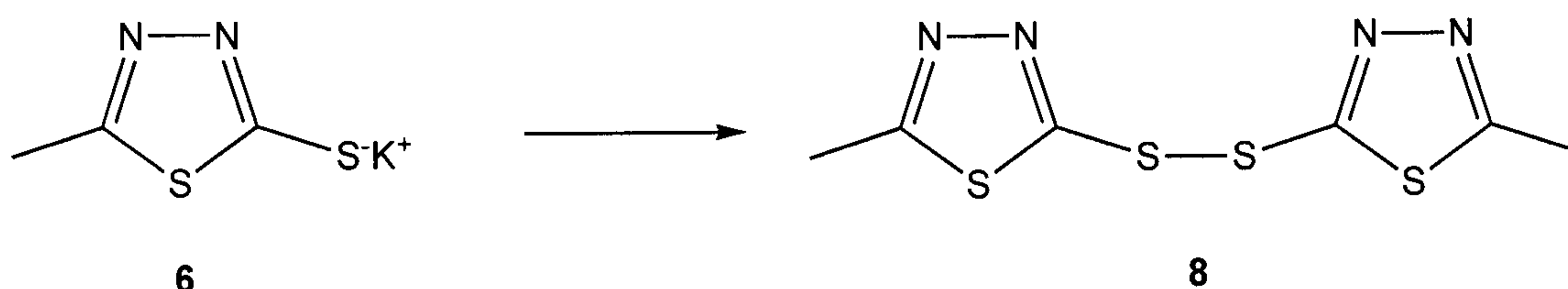


Commercially available 5-methyl-2-mercapto-1,3,4-thiadiazole from ALDRICH™ (1 eq) was neutralized with potassium carbonate K_2CO_3 (0.5 eq) in methanol (concentrations : 0.5 M). The resulting solution was stirred in an ultrasonic bath until complete dissolution of K_2CO_3 (almost 2 h 30 min). The mixture was then filtrated with a Büchner funnel fitted with a filter Whatman no. 40 ("Ashless"). The filtrate was concentrated with a rotative evaporator and a slightly yellow solid was obtained and dried under high vacuum in a desiccator for 12 h. At last, the slightly yellow solid **6** was rinsed with CH_2Cl_2 and dried under vacuum (yield $\approx 70\%$). Compound **6** ($C_3H_3KN_2S_2$) has a molecular weight of 170.29 g/mol.

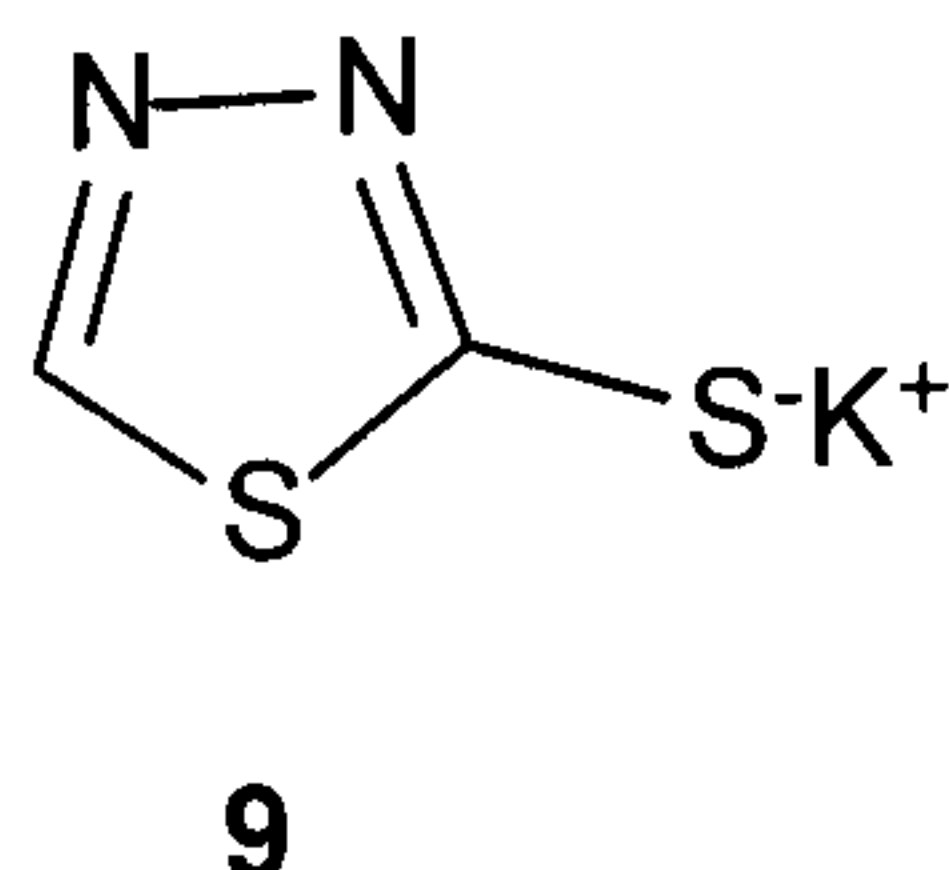
Synthesis of compound 7 (tetrabutylammonium (TBA) salt of the 5-methyl-2-mercapto-1,3,4-thiadiazole)



In a first reaction flask, acetone and compound **6** (1 eq) were introduced (concentration : 1 M). In a second reaction flask acetone and commercially available tetrabutylammonium perchlorate from ALFA AESAR™ were introduced (concentration : 1 M). After complete dissolution of the compounds in each flask, the solution of tetrabutylammonium perchlorate was added to the solution of **7**. The resulting mixture was stirred in an ultrasonic bath for 1 hour and a white solid ($KClO_4$) starts to precipitate. Then, the mixture was introduced in a freezer for one night in order to complete the crystallisation of $KClO_4$. After filtration of the reaction medium with a Büchner funnel fitted with a filter paper Whatman no. 40 (Ashless), the filtrate was concentrated with a rotative evaporator and a slightly yellow solid **7** was obtained, then dried under high vacuum in a desiccator for 12 hours. The yield was quantitative. Compound **7**, $C_{19}H_{39}N_3S_2$ has a molecular weight of 373.66 g/mol.

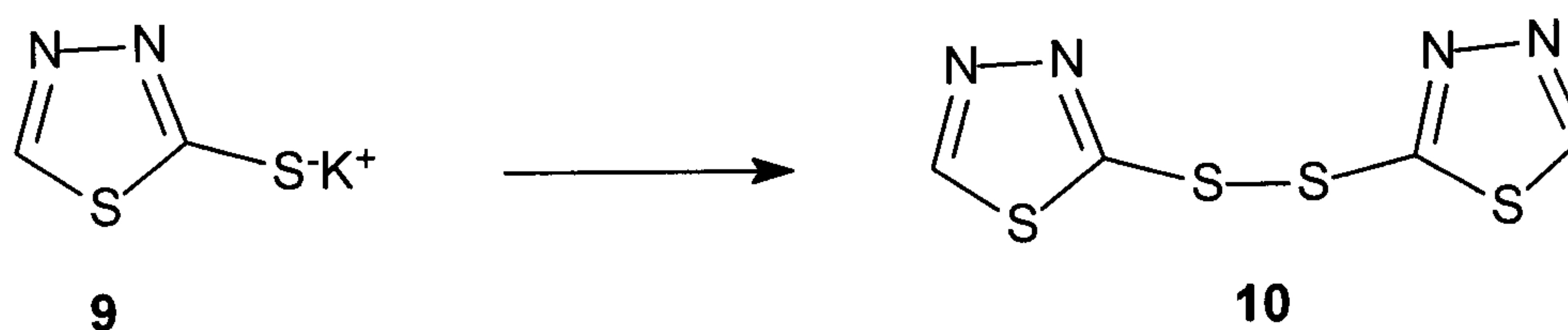
Synthesis of compound 8

Compound **6** (200 mg ; 0.89 mmol, 1 eq) was charged into 50 mL flask filled with 20 mL H₂O. After complete dissolution, I₂ (50.3 mg ; 0.44 mmol ; 0.5 eq) was added to the solution. Immediately a white suspension appeared. The solution was stirred until I₂ was completely dissolved, then the white solid was filtrated under vacuum with a Büchner funnel fitted with a Whatman filter (no. 40 : Ashless). The solid was washed with H₂O (100 mL) and dried under vacuum for 24 h to give 97.34 mg (yield of 30 %) of product **8**.

Synthesis of compound 9 (potassium salt of 2-mercapto-1,3,4-thiadiazole)

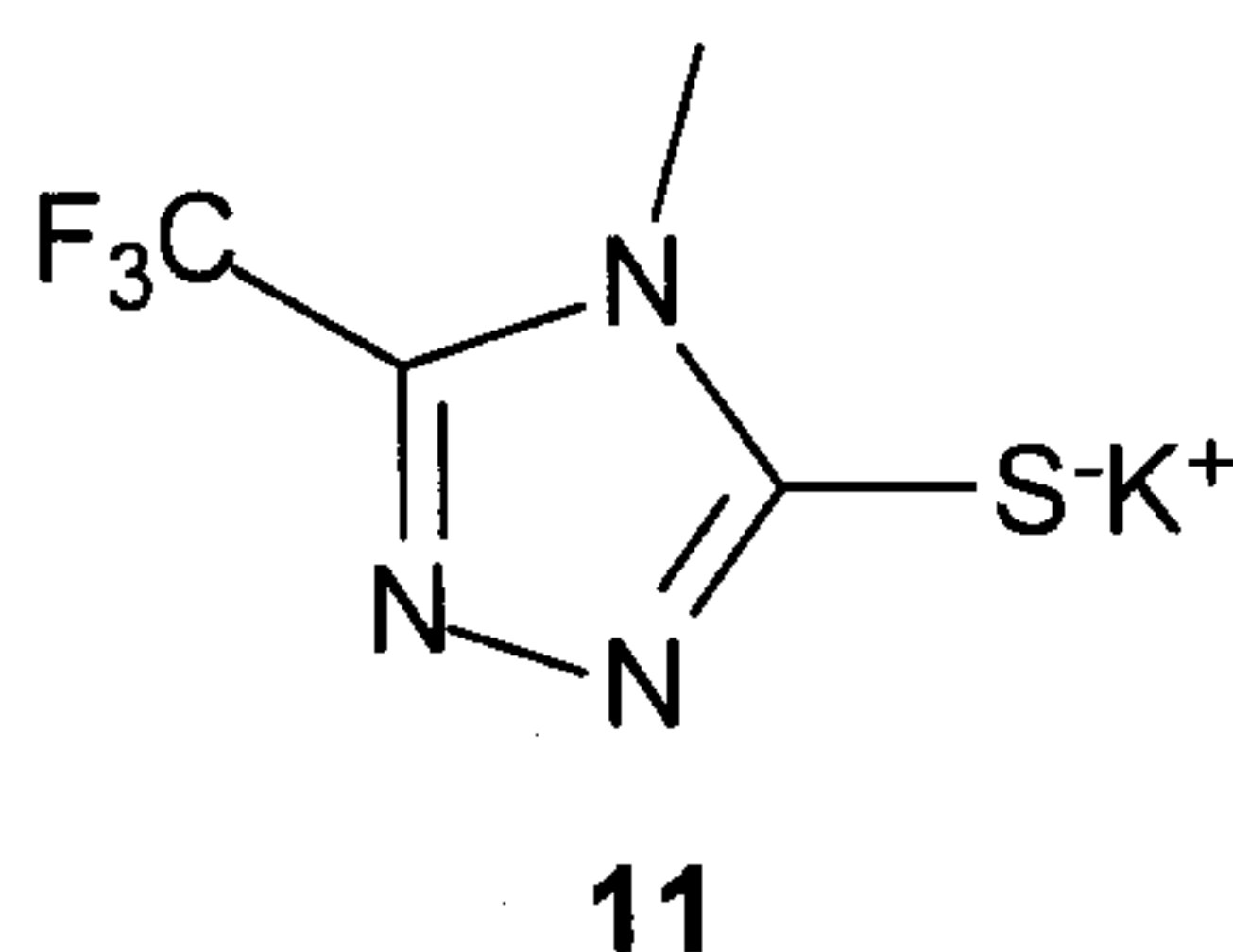
2-mercapto-1,3,4-thiadiazole (1.18 g, 10 mM, 1 eq) was neutralized with potassium carbonate K₂CO₃ (0.5 eq) in methanol (concentrations : 0.5 M). The resulting solution was stirred in an ultrasonic bath until complete dissolution of K₂CO₃ (almost 2 h 30 min). The mixture was then filtrated with a Büchner funnel fitted with a filter Whatman no. 40 ("Ashless"). The filtrate was concentrated with a rotative evaporator and a slightly yellow solid was obtained and dried for 12 h at 60 °C. At last, the slightly yellow solid **6** was washed with 50 mL CH₂Cl₂ and dried under vacuum over night at 60°C (yield ≈ 80 %).

Synthesis of compound 10

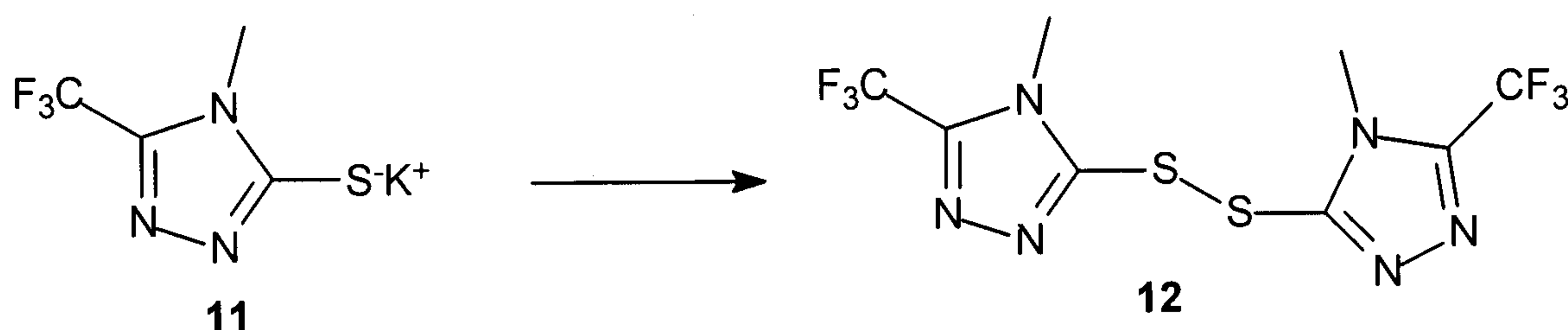


Compound **9** (500 mg ; 0.32 mmol, 1 eq) was charged into 50 mL flask filled with 20 mL distilled H₂O. After complete dissolution, I₂ (56.3 mg ; 0.44 mmol ; 0.5 eq) was added to the solution. Immediately, a white suspension appeared. The solution was stirred until I₂ was completely dissolved, then the white precipitate was filtrated under vacuum with a Büchner funnel fitted with a Whatman filter (no. 40 : Ashless). The solid was washed with H₂O (100 mL) and dried under vacuum for 24 h at 60°C to give 29.9 mg (yield of 40 %) of product **10**.

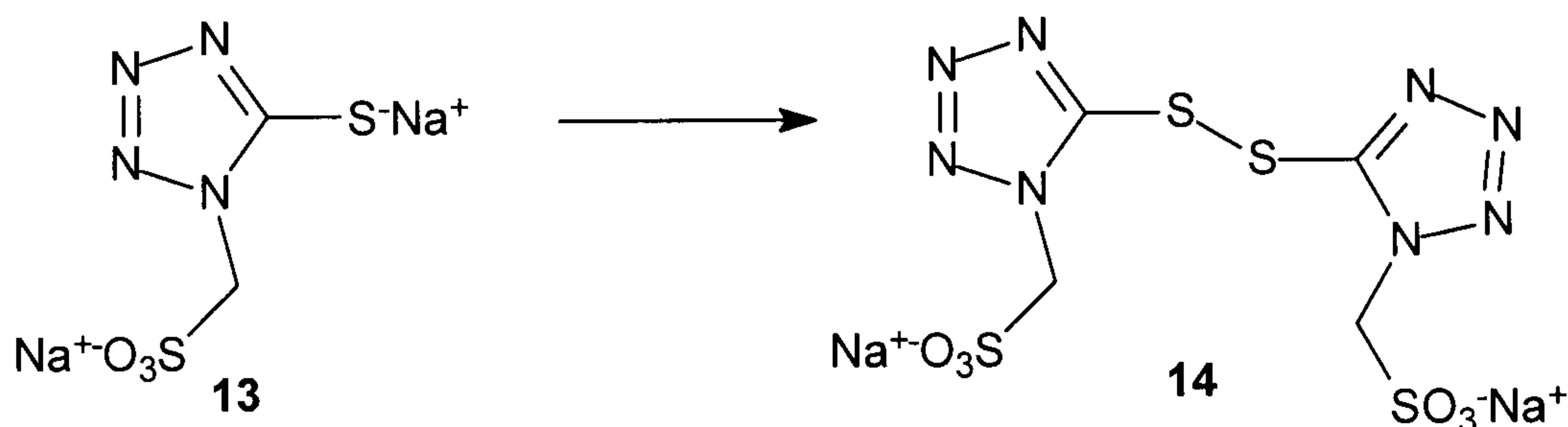
Synthesis of compound 11 (4-Methyl-5-trifluoromethyl-4H-1,2,4-triazolin-3(2H)-thione potassium salt)



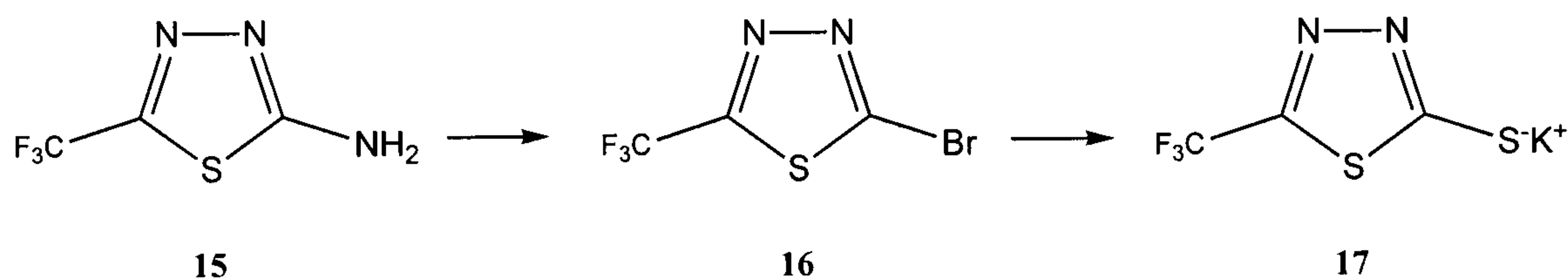
4-Methyl-5-trifluoromethyl-4H-1,2,4-triazolin-3(2H)-thione (1.82 g, 10 mM, 1 eq) was neutralized with potassium carbonate K_2CO_3 (0.5 eq) in methanol (concentration : 0.5 M). The resulting solution was stirred in an ultrasonic bath until complete dissolution of K_2CO_3 (almost 2 h 30 min). The mixture was then filtrated with a Büchner funnel fitted with a filter Whatman no. 40 ("Ashless"). The filtrate was concentrated with a rotative evaporator and a white solid was obtained and dried under vacuum for 12 h at 60°C. The white solid **11** was rinsed with 100 mL CH_2Cl_2 and dried under vacuum (yield $\approx$ 75 %). Compound **11** ($C_4H_3F_3KN_3S$) has a molecular weight of 220.96 g/mol.

Synthesis of compound 12

Compound **11** (500 mg ; 0.23 mmol, 1 eq) was charged into 50 mL flask filled with 20 mL distilled H₂O. After complete dissolution, I₂ (14.1 mg ; 0.12 mmol ; 0.5 eq) was added to the solution. Immediately, a white suspension appeared. The solution was stirred until I₂ was completely dissolved, then the white solid was filtrated out under vacuum with a Büchner funnel fitted with a Whatman filter (no. 40 : Ashless). The solid was washed with H₂O (100 mL) and dried under vacuum for 24 h at 60°C to give 25.1 mg (yield of 30 %) of compound **12**.

Synthesis of compound 14

5-Mercapto-1*H*-tetrazole-1-methanesulfonic acid disodium salt **13** (500 mg ; 0.21 mM, 1 eq) was charged into 50 mL flask filled with 30 mL DMSO. The well-stirred mixture was heated at 65°C for 2 hours and then concentrated. The white solid was washed with acetone (100 mL), purified by recrystallization in a mixture of methanol and ethanol, and then, dried under vacuum for 24 h at 60°C to give 73.9 mg (yield of 80 %) of compound **14**.

Synthesis of compound 17

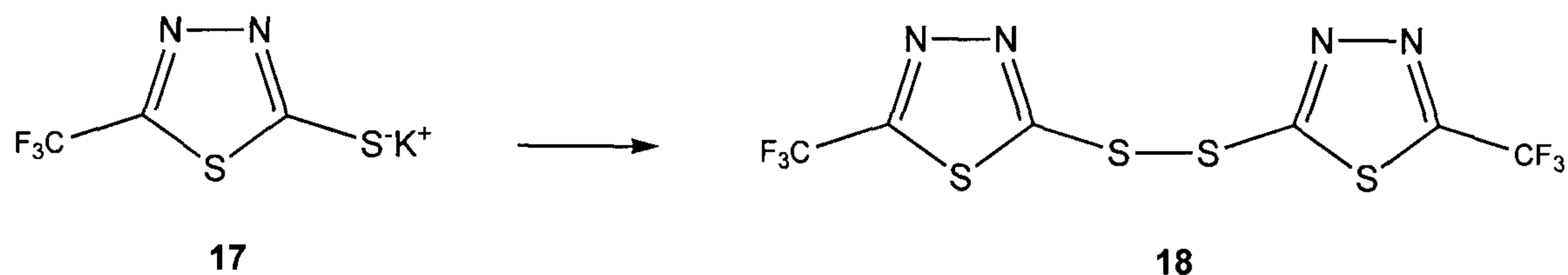
Compound **15** (10.0026 g ; 59.1 mmol ; 1 eq) was introduced in a 250 mL reaction flask. This flask was put in an ice bath and a solution of HBr (48 % in H₂O; 46.0 mL) as well as water (12.0 mL) were added. After the complete dissolution (5 min) of compound **15**, a solution of NaNO₂ (8.3214 g ; 120.0 mmol ; 2 eq) in H₂O (16 mL) was added dropwise over a period of 45 minutes (gas emission and brown coloration were observed). The resulting solution was stirred for 2 hours at room temperature. Then, the reaction mixture was extracted twice with 40 mL of Et₂O. The organic layers were separated, washed with a portion of 60 mL of water and dried over anhydrous MgSO₄. After concentration of the solution with a rotative evaporator, a brown oil (compound **16**) was obtained.

Compound **16** was then added dropwise over a period of 40 minutes to a 150 mL reaction flask containing Li₂S (8.1432 g ; 177.3 mmol). The reaction mixture was stirred for 2 h and then concentrated. The residue was cooled to - 20°C and a solution of HCl (3 M ; 50 mL) was added dropwise over a period of 20 minutes in order to destroy the excess of Li₂S. The crude product was then extracted twice with 40 mL of Et₂O. The organic layers were washed with portions of 80 mL of saturated solutions of Na₂S₂O₃ and NaCl, H₂O and dried over anhydrous MgSO₄. After concentration with a rotative evaporator,

a solid was obtained. The sublimation of this solid under vacuum (heat temperature of 70°C) allowed to provide translucent crystals.

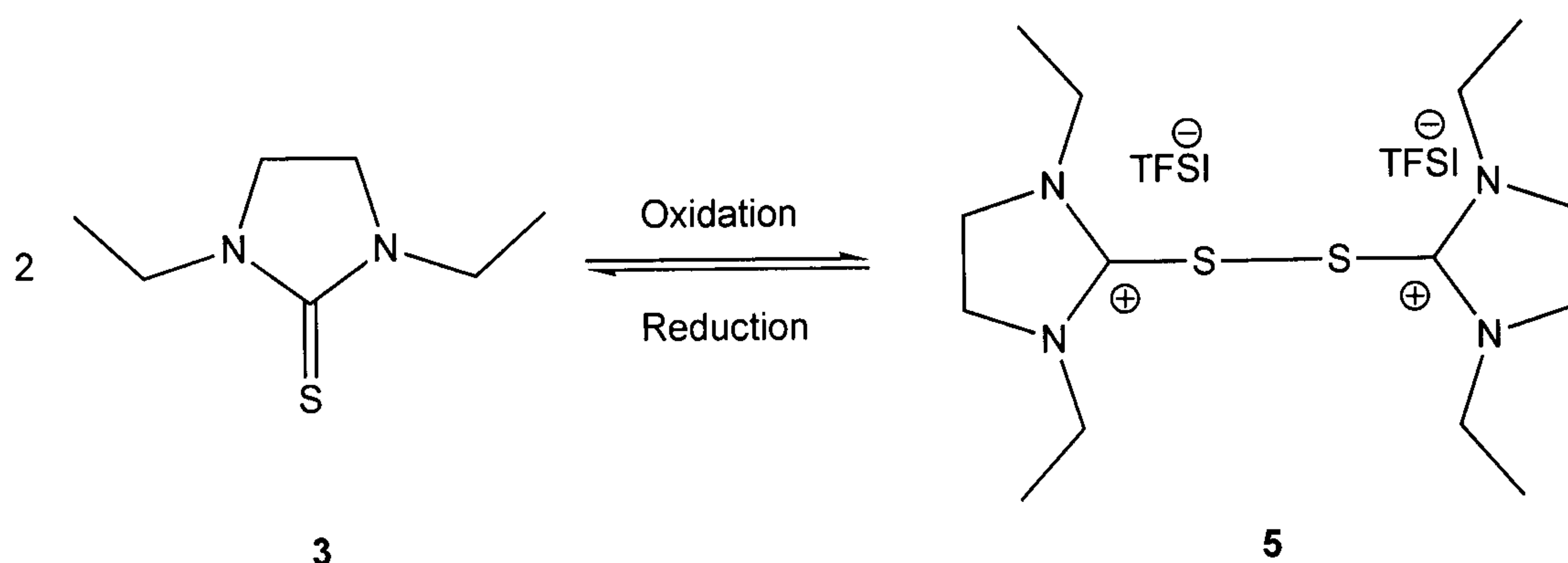
The crystalline product (7.0531 g ; 37.9 mmol ; 1 eq) was then neutralized with potassium carbonate K_2CO_3 (2.6597 g ; 19.3 mmol ; 0.5 eq) in methanol (40 mL). The resulting solution was stirred for 2 hours and 30 minutes and filtrated. The filtrate was concentrated with a rotative evaporator and dried under vacuum in a dessicator for 12 h. A white solid (compound **17**) (4.7214 g yield of 55.7 % for this step and 35.7 % for the entire procedure) was obtained.

Synthesis of compound 18



Compound **17** (200 mg ; 0.89 mmol, 1 eq) was introduced in a 50 mL reaction flask filled with H_2O (20 mL) so as to obtain a solution. I_2 (50.3 mg ; 0.44 mmole ; 0.5 eq) was added to this solution. Immediately after the addition of iodine, a white solid in suspension was appeared. The solution was stirred until I_2 was dissolved and the white solid was filtrated under vacuum with a Büchner funnel fitted with a WhatmanTM filter (no. 40 : Ashless). The solid was rinsed with H_2O (100 mL) and dried under vacuum in a dessicator for 24 h to give 292.3 mg (yield of 90 %) of product **18**.

Some experiments have been made with the redox couple **3** / **5**, which is as follows:



Various cyclic voltammetry experiments were carried out using the redox couple **3** / **5**.

In Fig. 1, there is shown a cyclic voltammogram of a solution comprising compound **3** (1,3-diethyl-imidazolidine-2-thione) (0.25 M) and compound **5** (disulfide form) (0.25 M) in EMITFSI at 22 °C. A platinum electrode ($A = 0.0249 \text{ cm}^2$) was used as working electrode and referenced to an Ag wire. Scan rate was 100 mV/s.

In Fig. 2, there is shown a cyclic voltammogram of a solution comprising compound **3** (1,3-diethyl-imidazolidine-2-thione) (0.25 M) and compound **5** (disulfide form) (0.13 M) in EMITFSI at 22 °C. A platinum electrode ($A = 0.0249 \text{ cm}^2$) was used as working electrode and referenced to an Ag wire. Scan rate was 100 mV/s.

In Fig. 3, there is shown a cyclic voltammogram of a solution comprising compound **3** (1,3-diethyl-imidazolidine-2-thione) (0.13 M) and compound **5** (disulfide form) (0.25 M) in EMITFSI at 22 °C. A platinum electrode ($A = 0.0249 \text{ cm}^2$) was used as working electrode and referenced to an Ag wire. Scan rate was 100 mV/s.

In Fig. 4, there is shown cyclic voltammograms of three solutions comprising compounds **3** and **5** at different ratios (compound **3** : compound **5**) (1:1; 2:1; 1:2), in EMITFSI at 22 °C. A platinum electrode ($A = 0.0249 \text{ cm}^2$) was used as working electrode and referenced to an Ag wire. Scan rate was 100 mV/s.

In Fig. 5, there is shown cyclic voltammograms of a solution comprising compound **3** (1,3-diethyl-imidazolidine-2-thione) (0.25 M) and compound **5** (disulfide form) (0.5 M) in EMITFSI at 22 °C. A platinum electrode ($A = 0.0249 \text{ cm}^2$) or an ITO-CoS electrode (surface area of 0.1 cm^2) was used as working electrode and referenced to an Ag wire. Scan rate was 50 mV/s. The ITO-CoS electrode is described in US 20050089681.

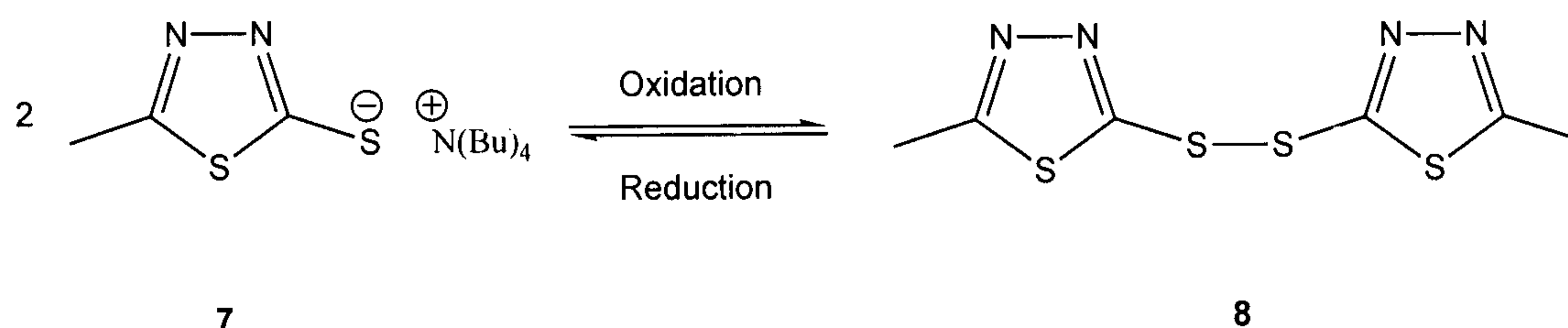
The tests carried out show that 1,3-diethyl-imidazolidine-2-thione and its disulfide is a good redox couple which has the potential to replace the redox couple used in Grätzel solar cells (DSSCs using I^-/I_3^-). The good results obtained in conductivity (electrical properties) and in cyclic voltammetry (electrochemical properties) prove it. Moreover, it was observed that such a composition is substantially colorless or substantially optically clear. It should be noted that the Red:Ox ratio has more influence on the current density ($J_{1:1} > J_{1:2} > J_{2:1}$) than on ΔE_p values. The greater current densities were obtained for the 1:1 ratio. It is interesting to point out that the ITO-CoS electrode (see Fig. 5) improves the electrochemical reversibility, shifts the potentials towards a more positive area, enhances both the anodic and cathodic current densities, and increases the reversibility (ΔE_p is decreased). Therefore, this electrode would act as an excellent catalyst to reduce the oxidized species in a photovoltaic device using an *n*-type semiconductor as the (photo)anode.

Table 1 gives the conductivity ($\times 10^{-3} \text{ S/cm}$) of three solutions of 1,3-diethyl-imidazolidine-2-thione and its disulfide form in EMITFSI in different ratios (1:1 [0.1 M:0.1 M]; 2:1 [0.2 M:0.1 M]; 1:2 [0.1 M:0.2 M]). Four temperatures were studied (20, 40, 60 and 80 °C). The results show that the conductivity is higher than or equal to $6.0 \times 10^{-3} \text{ S/cm}$ at 20 °C, which represents an excellent value for a (photo)electrochemical device. As expected, conductivity values are enhanced when the temperature is increased, which could be attributed to the significant decrease of viscosity of EMITFSI at higher temperatures.

Table 1

	Conductivity ($\times 10^{-3}$ S/cm)			
	20 °C	40 °C	60 °C	80 °C
Ratio 1:1	6.29	11.61	18.96	27.17
Ratio 2:1	6.76	12.58	20.33	29.15
Ratio 1:2	6.00	11.14	18.29	26.43

Some experiments have also been made with the redox couple **7** / **8**, which is as follows:



In Fig. 6, there is shown a cyclic voltammogram [I (mA. cm^{-2}) vs E (V vs Ag)] of a solution comprising compound **7** (tetrabutylammonium salt of 5-methyl-2-mercapto-1,3,4-thiadiazole) (75 mM) and compound **8** (25 mM) in EMITFSI at 22 °C. A platinum electrode (surface area of 0.025 cm^2) was used as working electrode and referenced to an Ag wire. The initial scan direction was oxidizing and the scan rate used was 50 mV. s^{-1} . The results demonstrate that the redox couple is less reversible than the one formed with compounds **3** and **5** (see Fig. 4), and that the anodic and cathodic current densities are lower. Corrosion tests were also carried out on the redox couple **7** / **8**, and it was shown that over a period of 4 months, this redox couple did not corrode silver.

In Fig. 7, there is shown a cyclic voltammogram of a solution comprising compound **9** (0.75 M) and compound **10** (disulfide form) (0.25 M) in EMITFSI at 22 °C. A platinum electrode ($A = 0.0249 \text{ cm}^2$) was used as working electrode and referenced to an Ag wire. Scan rate was 50 mV/s . The results

show that the redox couple **9** / **10** is more reversible than the redox couple **7** / **8** (see Fig. 6).

In Fig. 8, there is shown a cyclic voltammogram of a solution comprising compound **11** (0.66 M) and compound **12** (disulfide form) (0.34 M) in DMF-DMSO : 60-40 containing TBAP (0.2 M), at 22 °C. A platinum electrode ($A = 0.0249 \text{ cm}^2$) was used as working electrode and referenced to an Ag wire. Scan rate was 50 mV/s. The results show that the redox couple **11** / **12** is much less reversible than the redox couple **9** / **10** (see Fig. 7), probably due to the use of a less conducting electrolytic medium (an ionic liquid is not utilized as the solvent of the redox couple **11** / **12**).

In Fig. 9, there is shown a cyclic voltammogram of a solution comprising compound **13** (0.25 M) and compound **14** (disulfide form) (0.75 M) in DMF-DMSO : 60-40 containing TBAP (0.2 M), at 22 °C. A platinum electrode ($A = 0.0249 \text{ cm}^2$) was used as working electrode and referenced to an Ag wire. Scan rate was 50 mV/s. It can be noted interestingly that the redox couple **13** / **14** leads to enhanced current densities.

In Fig. 10, there is shown a cyclic voltammogram [I (A) vs E (V vs Ag)] of a solution comprising compound **17** (83.3 mM) and compound **18** (disulfide form) (16.3 mM) in EMITFSI at 22 °C. A platinum electrode ($A = 0.0249 \text{ cm}^2$) was used as working electrode and referenced to an Ag wire. Scan rate was 50 mV/s. The results demonstrate that the presence of the ionic liquid EMITFSI in the solution favors a better electrochemical reversibility, when compared to the redox couples **11** / **12** (see Fig. 8) and **13** / **14** (see Fig. 9).

In Fig. 11, there is shown a comparison between the UV-visible spectrum of a solution comprising compounds **17** (83.3 mM) and **18** (16.3 mM) in EMITFSI and a UV-visible spectrum of EMI^+I^- (163 mM) / I_2 (10 mM) in EMITFSI (redox couple used in Grätzel solar cells). As it can be seen from Fig. 11, the solution comprising compounds **17** and **18** in EMITFSI absorbs only partially in the visible area of the spectrum (more significantly at wavelengths lower than 500 nm), which contrasts with the solution of EMI^+I^- / I_2 in EMITFSI since the latter

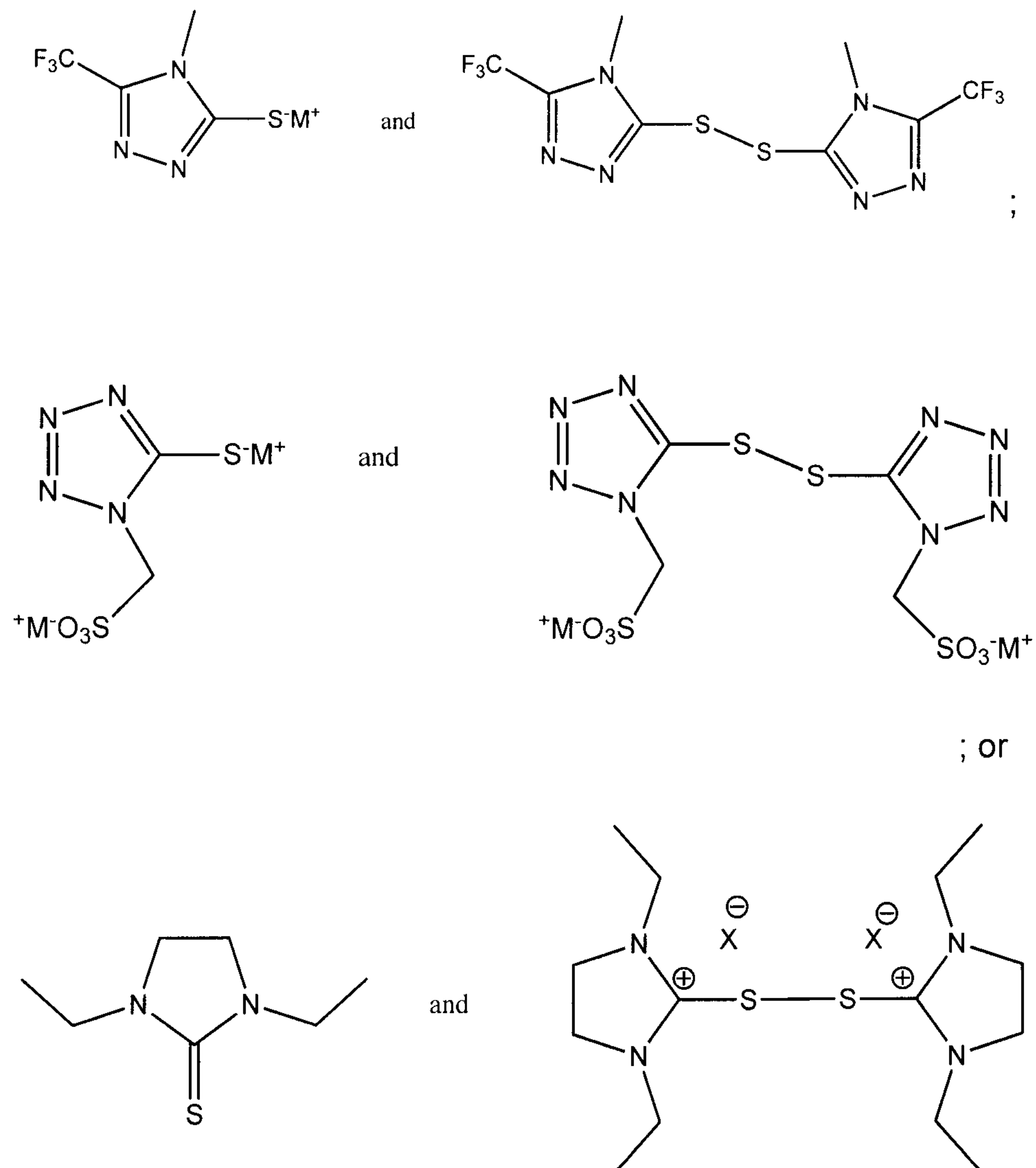
considerably absorbs in the visible area of the spectrum at wavelengths lower than 650 nm. Fig. 11 thus demonstrates that the composition comprising compounds **17** and **18** is substantially colorless or substantially optically clear.

In Fig. 12, there is shown a stability test that was performed on the solution comprising compounds **17** and **18** in EMITFSI (the solution tested in Figs. 10 and 11) The test was carried out at a temperature of 70 ° C and 1000 cycles were performed as shown on the cyclic voltammogram of Fig. 12. It can thus be said that the redox couple **17** / **18** has a high electrochemical and thermal stability. An ITO-CoS electrode (surface area of 0.25 cm²) was used as working electrode and referenced to an Ag wire.

While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modifications and this application is intended to cover any variations, uses, or adaptations of the invention following, in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice within the art to which the invention pertains and as may be applied to the essential features herein before set forth, and as follows in the scope of the appended claims.

WHAT IS CLAIMED IS:

1. A composition comprising:

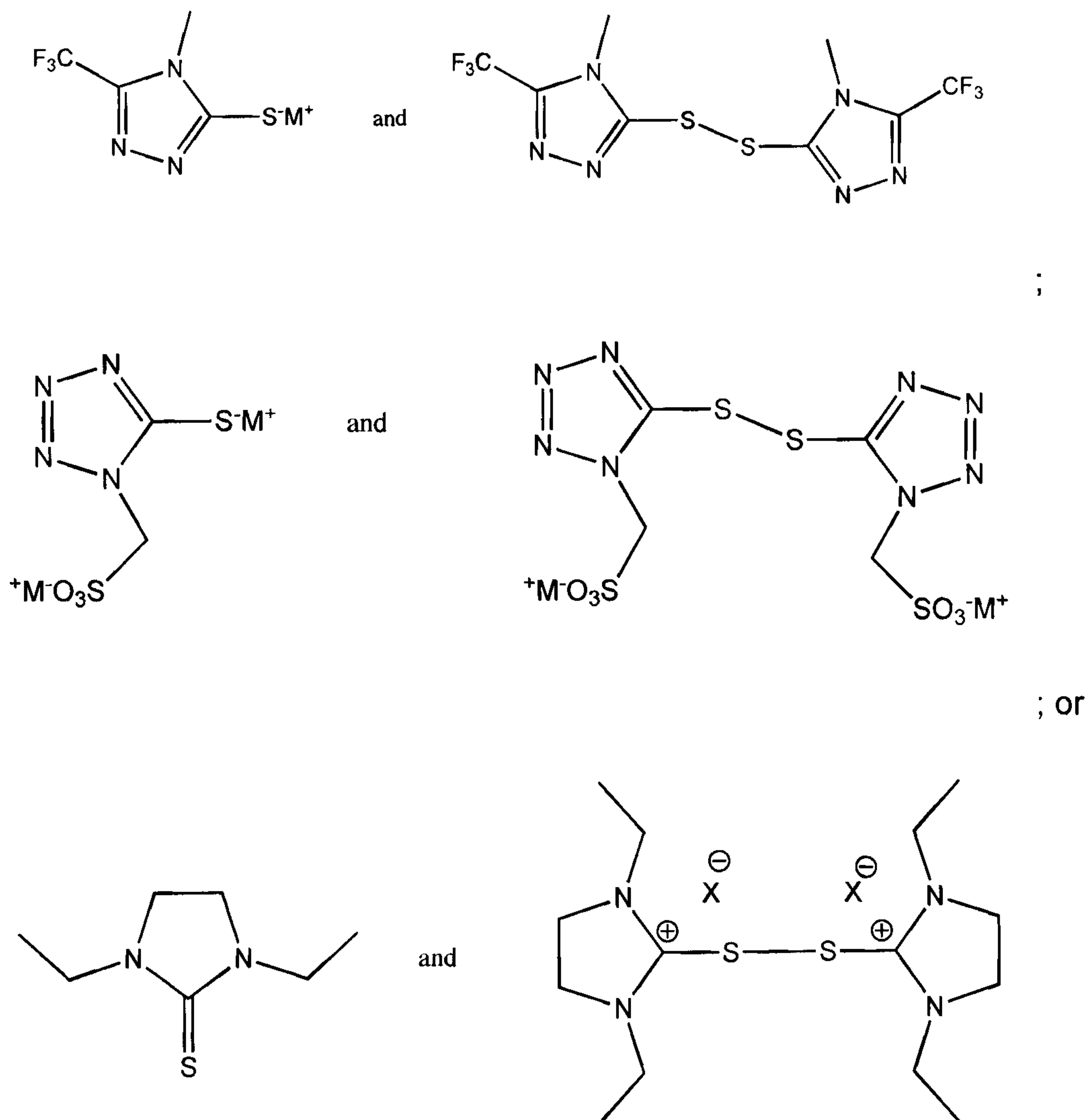


wherein

X⁻ is (FSO₂)₂N⁻, (CF₃SO₂)₂N⁻, (C₂F₅SO₂)₂N⁻, (CF₃SO₂)₃C⁻, CF₃SO₃⁻, CF₃COO⁻, AsF₆⁻, CH₃COO⁻, (CN)₂N⁻, (CN)₃C⁻, NO₃⁻, 2.3HF, Cl⁻, Br⁻, I⁻, PF₆⁻, BF₄⁻, ClO₄⁻ or SCN⁻; and

M⁺ is H⁺, an inorganic cation, or an organic cation.

2. A composition comprising:



wherein

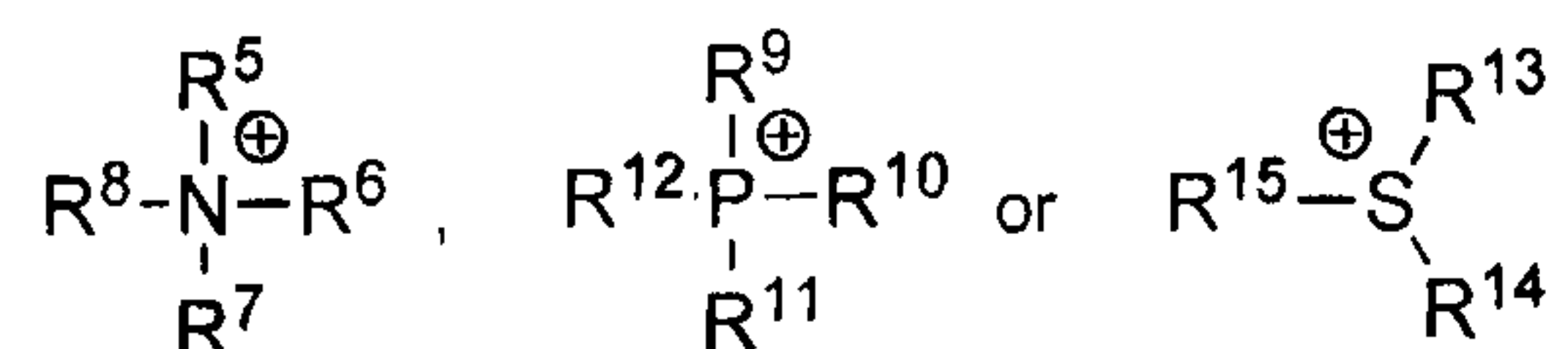
X^- is $(\text{FSO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_3\text{C}^-$, CF_3SO_3^- , CF_3COO^- , AsF_6^- , CH_3COO^- , $(\text{CN})_2\text{N}^-$, $(\text{CN})_3\text{C}^-$, NO_3^- , 2.3HF , Cl^- , Br^- , I^- , PF_6^- , BF_4^- , ClO_4^- or SCN^- ; and

M^+ is H^+ , an inorganic cation, or an organic cation,

for use as a redox couple.

3. The composition of claim 1 or 2, wherein X^- is $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_3\text{C}^-$, CF_3SO_3^- , $(\text{CN})_2\text{N}^-$, PF_6^- , BF_4^- or ClO_4^- .

4. The composition of claim 3, wherein X^- is $(CF_3SO_2)_2N^-$.
5. The composition of claim 1 or 2, wherein M^+ is an organic cation chosen from a positively charged C_1 - C_{12} heteroaryl or a C_1 - C_{12} heterocyclyl, wherein said heteroaryl or said heterocyclyl is unsubstituted or substituted with 1 to 3 substituents chosen from F, Cl, Br, I, OH, a C_1 - C_6 alkoxy, a C_1 - C_6 hydroxy alkyl, NO_2 , CN, CF_3 , SO_3^- , C_nF_{2n+1} , C_1 - C_{12} alkyl which is linear or branched, C_6 - C_{12} aryl, C_nH_{2n+1} , $Ph_2P(O)-$, Ph_2P- , $Me_2P(O)-$, Me_2P , $Ph_2P(S)$, $Me_2P(S)$, $Ph_3P=N-$, $Me_3P=N-$, $C_6H_5C_pH_{2p}-$, $C_pH_{2p+1}C_6H_4-$, $C_pH_{2p+1}C_6H_4C_nH_{2n}-$, $CH_2=CHC_pH_{2p}-$, $CH_2=CHC_6H_5-$, $CH_2=CHC_6H_4C_pH_{2p+1}-$, and $CH_2=CHC_pH_{2p}C_6H_4-$; n is an integer having a value from 1 to 48 and p is an integer having a value from 1 to 48.
6. The composition of claim 1 or 2, wherein M^+ is an organic cation is of formula



wherein

R^5 , R^6 , R^7 and R^8 are same or different and each independently represent a C_1 - C_{20} alkyl which is linear or branched, C_3 - C_{12} cycloalkyl, C_1 - C_{12} heterocyclyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{12} aryl, C_6 - C_{20} aralkyl, C_6 - C_{20} alkylaryl, and C_1 - C_{12} heteroaryl;

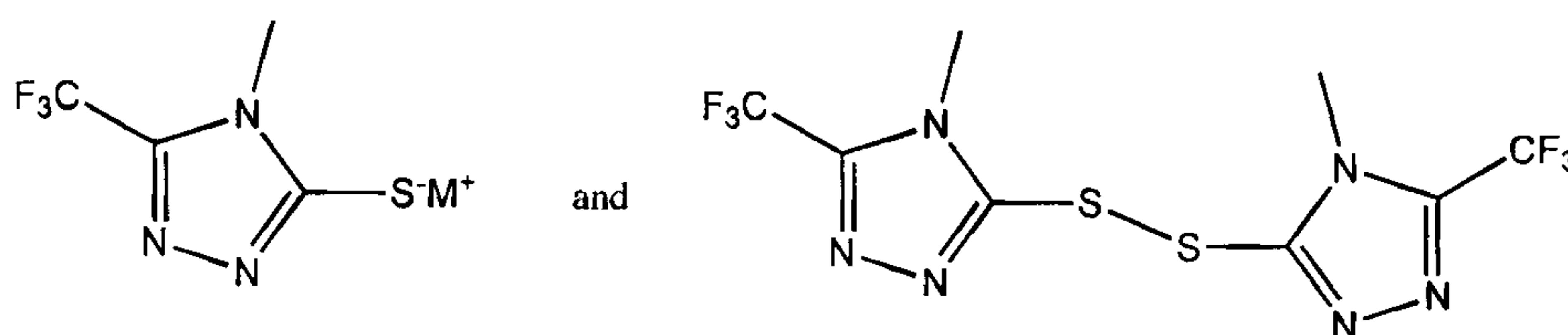
R^9 , R^{10} , R^{11} and R^{12} are same or different and each independently represent a C_1 - C_{20} alkyl which is linear or branched, C_3 - C_{12} cycloalkyl, C_1 - C_{12} heterocyclyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{12} aryl, C_6 - C_{20} aralkyl, C_6 - C_{20} alkylaryl, and C_1 - C_{12} heteroaryl; and

R^{13} , R^{14} and R^{15} are same or different and each independently represent a C_1 - C_{20} alkyl which is linear or branched, C_3 -

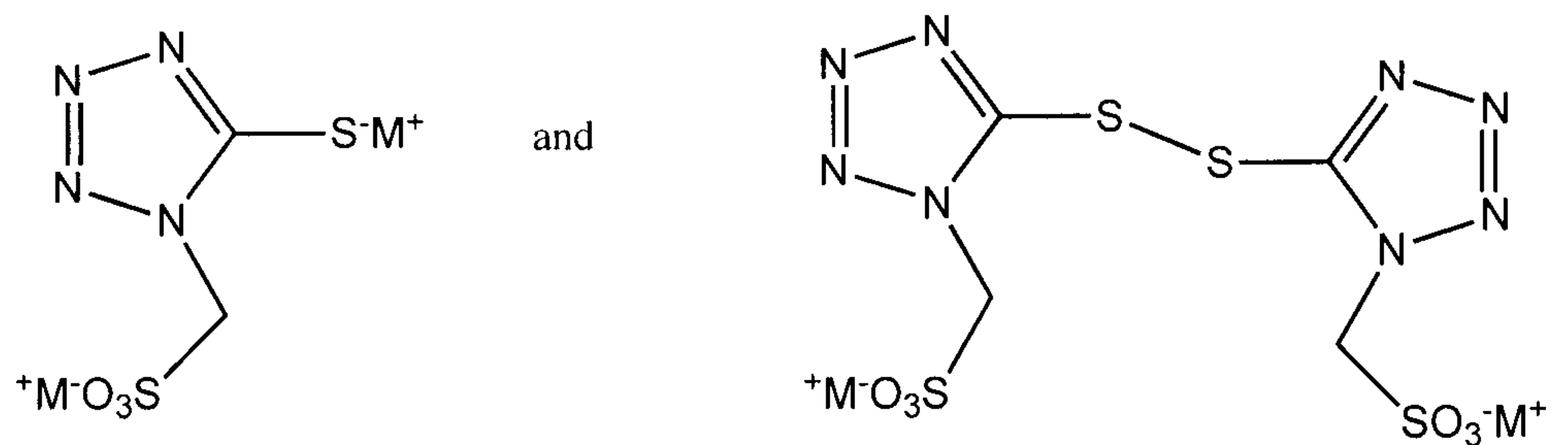
C₁₂ cycloalkyl, C₁-C₁₂ heterocyclyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₁₂ aryl, C₆-C₂₀ aralkyl, C₆-C₂₀ alkylaryl, and C₁-C₁₂ heteroaryl,

wherein said alkyl, cycloalkyl, heterocyclyl, alkenyl, alkynyl, aryl, aralkyl, alkylaryl, heteroaryl, alkylheteroaryl, and alkylheterocyclyl being unsubstituted or substituted with 1 to 3 substituents chosen from F, Cl, Br, I, OH, a C₁-C₆ alkoxy, a C₁-C₆ hydroxy alkyl, NO₂, CN, CF₃, SO₃⁻, C_nF_{2n+1}, C₁-C₁₂ alkyl which is linear or branched, C₆-C₁₂ aryl, C_nH_{2n+1}, C₆H₅C_pH_{2p}-, C_pH_{2p+1}C₆H₄-, C_pH_{2p+1}C₆H₄C_nH_{2n}-, CH₂=CHC_pH_{2p}-, CH₂=CHC₆H₅-, CH₂=CHC₆H₄C_pH_{2p+1}-, and CH₂=CHC_pH_{2p}C₆H₄-, n is an integer having a value from 1 to 48 and p is an integer having a value from 1 to 48.

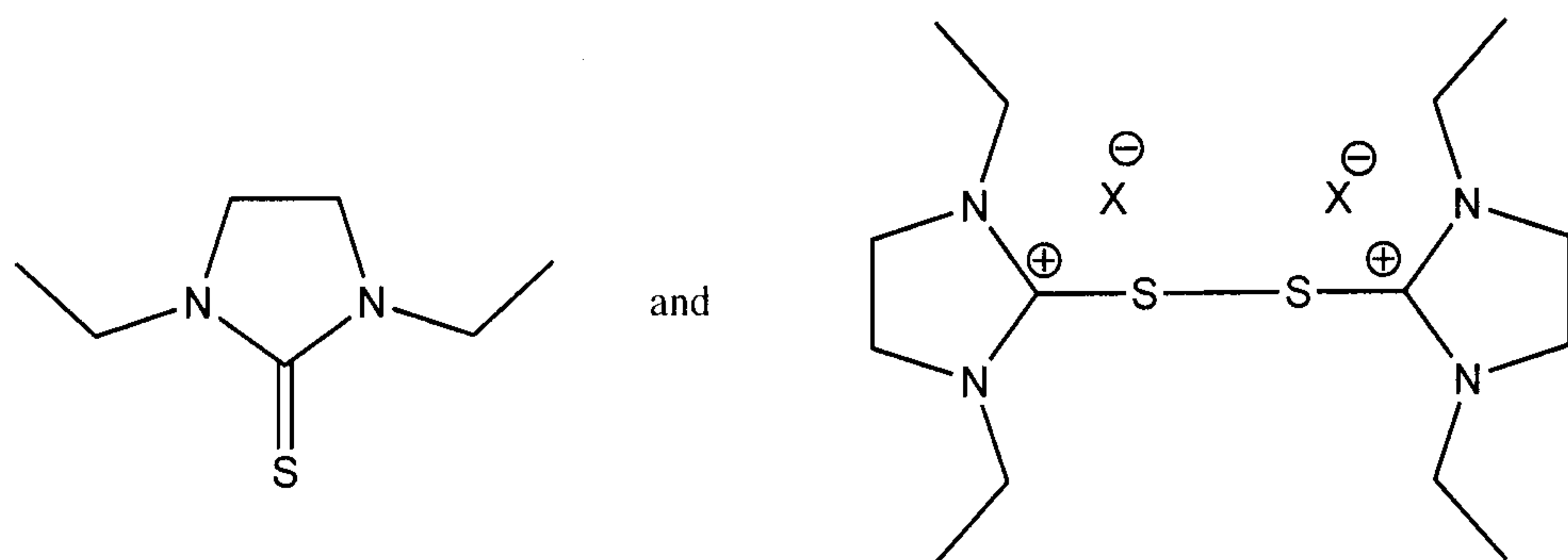
7. The composition of claim 1 or 2, wherein M⁺ is an organic cation chosen from N-substituted imidazoliums, said substituent being a C₁-C₁₂ alkyl which is linear or branched.
8. The composition of claim 1 or 2, wherein M⁺ is an organic cation chosen from tetralkylammoniums, wherein each of said alkyl groups is independently C₁-C₁₂ alkyl which is linear or branched.
9. The composition of claim 1 or 2, wherein M⁺ is chosen from Li⁺, Na⁺ and K⁺, and Cs⁺.
10. The composition of any of claims 1, 2 and 5 to 9, wherein said composition comprises :



11. The composition of any of claims 1, 2 and 5 to 9, wherein said composition comprises :

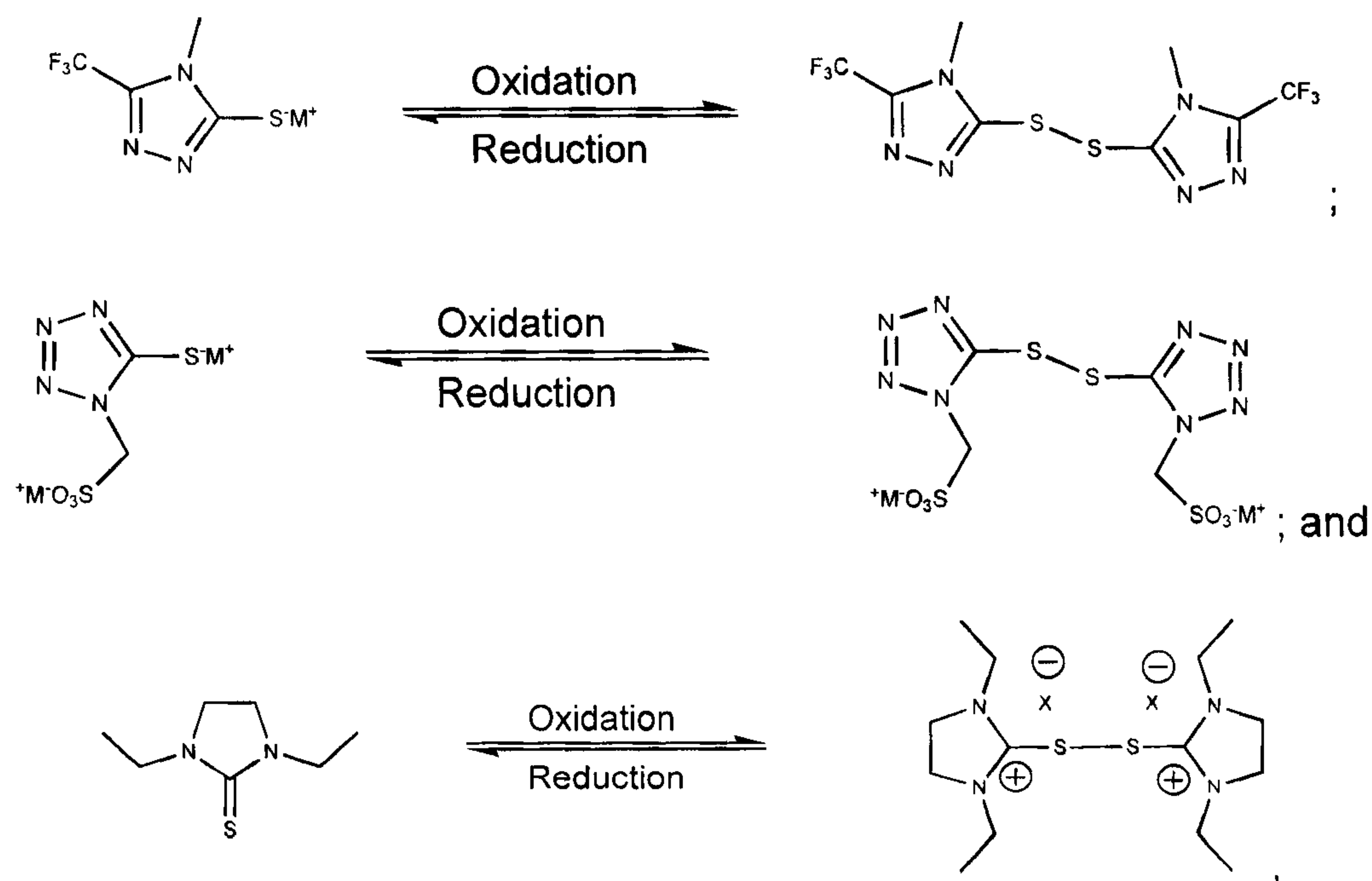


12. The composition of any one of claims 1 to 4, wherein said composition comprises :



13. The composition of any one of claims 1 to 12, wherein said composition further comprises a solvent chosen from nitriles, CH_2Cl_2 , alcohols, DMSO, amides, hexane, heptane, toluene, linear carbonates, cyclic esters, ureas, ionic liquids, and quaternary amines and quaternary phosphonium salts associated with a stable anion chosen from $(\text{FSO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_3\text{C}^-$, CF_3SO_3^- , CF_3COO^- , AsF_6^- , CH_3COO^- , $(\text{CN})_2\text{N}^-$, $(\text{CN})_3\text{C}^-$, NO_3^- , 2.3HF, Cl^- , Br^- , I^- , PF_6^- , BF_4^- , ClO_4^- , and SCN^- , and mixtures thereof.
14. The composition of any one of claims 1 to 12, wherein said composition further comprises a solvent chosen from CH_3CN , DMF, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, ethylene carbonate, propylene carbonate, dialkylimidazolium, trialkylsulfonium, and $\text{C}_1\text{-C}_{20}$ tetraalkylammonium, $\text{C}_1\text{-C}_{20}$ tetraalkylphosphonium or $\text{C}_6\text{-C}_{12}$ tetraarylphosphonium salts associated with a stable anion chosen from $(\text{FSO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_3\text{C}^-$, CF_3SO_3^- , CF_3COO^- , AsF_6^- , CH_3COO^- , $(\text{CN})_2\text{N}^-$, $(\text{CN})_3\text{C}^-$, NO_3^- , 2.3HF, Cl^- , Br^- , I^- , PF_6^- , BF_4^- , ClO_4^- , and SCN^- and mixtures thereof.

15. The composition of any one of claims 1 to 14, wherein said composition is in the form of an uncolored solution, a translucent solution, or a substantially optically clear solution.
16. A photovoltaic cell comprising an anode, a cathode, and a composition as defined in any one of claims 1 to 15.
17. A photovoltaic cell comprising an anode, a cathode, a composition as defined in any one of claims 1 to 15, and a solvent, a polymer, a molten salt, an ionic liquid, a gel or any combination thereof.
18. Use of a composition as defined in any one of claims 1 to 15, in a solar cell, a fuel cell, a battery, a sensor or a display.
19. A redox couple chosen from:

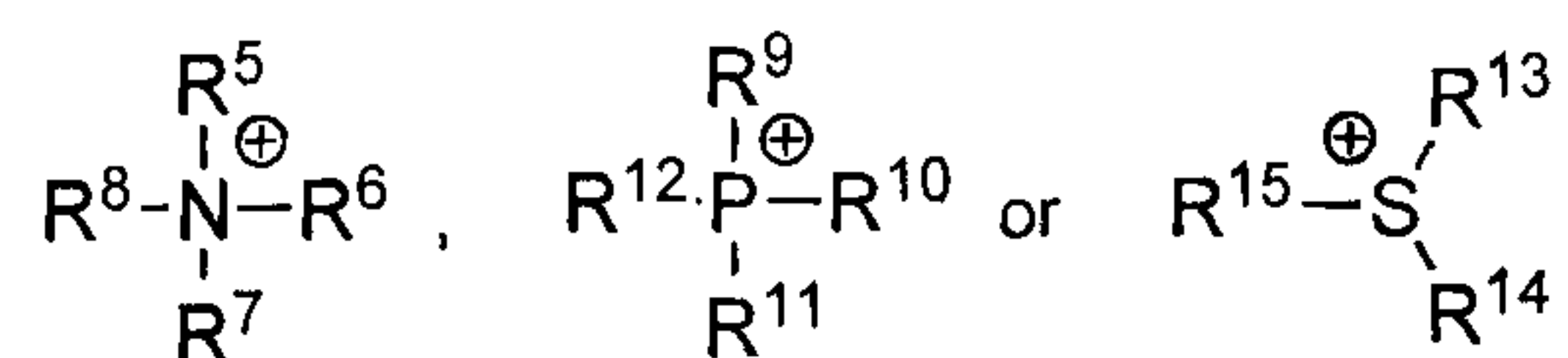


wherein

X^- is $(\text{FSO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_3\text{C}^-$, CF_3SO_3^- , CF_3COO^- , AsF_6^- , CH_3COO^- , $(\text{CN})_2\text{N}^-$, $(\text{CN})_3\text{C}^-$, NO_3^- , 2.3HF , Cl^- , Br^- , I^- , PF_6^- , BF_4^- , ClO_4^- or SCN^- ; and

M^+ is H^+ , an inorganic cation, or an organic cation.

20. The redox couple of claim 19, wherein X^- is $(CF_3SO_2)_2N^-$, $(C_2F_5SO_2)_2N^-$, $(CF_3SO_2)_3C^-$, $CF_3SO_3^-$, $(CN)_2N^-$, PF_6^- , BF_4^- or ClO_4^- .
21. The redox couple of claim 19, wherein X^- is $(CF_3SO_2)_2N^-$.
22. The redox couple of claim 19, wherein M^+ is an organic cation chosen from a positively charged C_1 - C_{12} heteroaryl or a C_1 - C_{12} heterocyclyl, wherein said heteroaryl or said heterocyclyl is unsubstituted or substituted with 1 to 3 substituents chosen from F, Cl, Br, I, OH, a C_1 - C_6 alkoxy, a C_1 - C_6 hydroxy alkyl, NO_2 , CN, CF_3 , SO_3^- , C_nF_{2n+1} , C_1 - C_{12} alkyl which is linear or branched, C_6 - C_{12} aryl, C_nH_{2n+1} , $Ph_2P(O)-$, Ph_2P- , $Me_2P(O)-$, Me_2P , $Ph_2P(S)$, $Me_2P(S)$, $Ph_3P=N-$, $Me_3P=N-$, $C_6H_5C_pH_{2p}-$, $C_pH_{2p+1}C_6H_4-$, $C_pH_{2p+1}C_6H_4C_nH_{2n}-$, $CH_2=CHC_pH_{2p}-$, $CH_2=CHC_6H_5-$, $CH_2=CHC_6H_4C_pH_{2p+1}-$, and $CH_2=CHC_pH_{2p}C_6H_4-$, n is an integer having a value from 1 to 48 and p is an integer having a value from 1 to 48.
23. The redox couple of claim 19, wherein M^+ is an organic cation is of formula



wherein

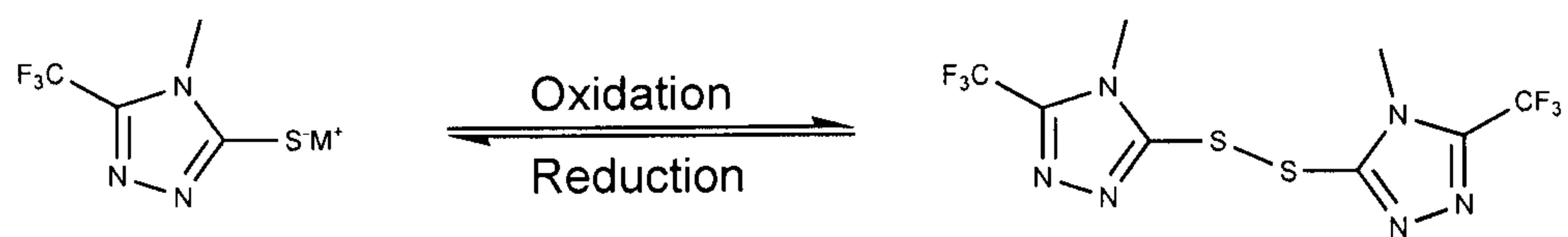
R^5 , R^6 , R^7 and R^8 are same or different and each independently represent a C_1 - C_{20} alkyl which is linear or branched, C_3 - C_{12} cycloalkyl, C_1 - C_{12} heterocyclyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{12} aryl, C_6 - C_{20} aralkyl, C_6 - C_{20} alkylaryl, and C_1 - C_{12} heteroaryl;

R^9 , R^{10} , R^{11} and R^{12} are same or different and each independently represent a C_1 - C_{20} alkyl which is linear or branched, C_3 - C_{12} cycloalkyl, C_1 - C_{12} heterocyclyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{12} aryl, C_6 - C_{20} aralkyl, C_6 - C_{20} alkylaryl, and C_1 - C_{12} heteroaryl; and

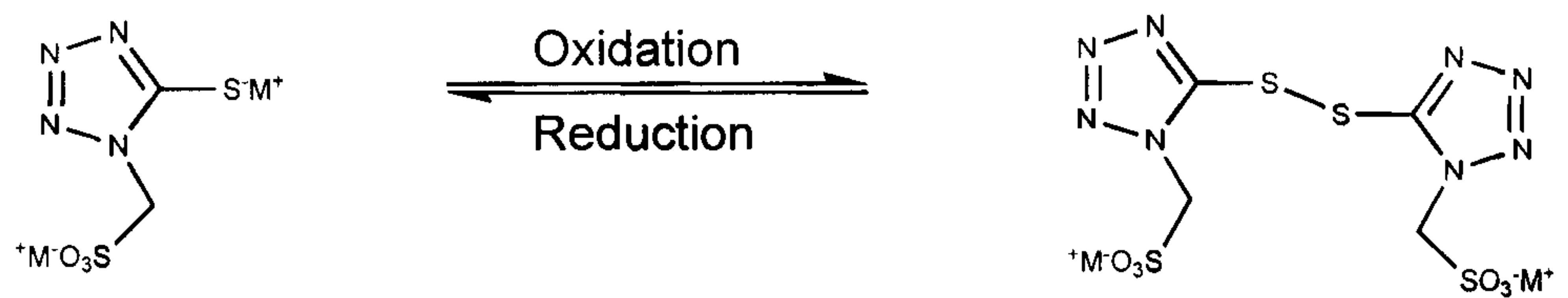
R^{13} , R^{14} , and R^{15} are same or different and each independently represent a C_1 - C_{20} alkyl which is linear or branched, C_3 - C_{12} cycloalkyl, C_1 - C_{12} heterocyclyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{12} aryl, C_6 - C_{20} aralkyl, C_6 - C_{20} alkylaryl, and C_1 - C_{12} heteroaryl,

wherein said alkyl, cycloalkyl, heterocyclyl, alkenyl, alkynyl, aryl, aralkyl, alkylaryl, heteroaryl, alkylheteroaryl, and alkylheterocyclyl being unsubstituted or substituted with 1 to 3 substituents chosen from F, Cl, Br, I, OH, a C_1 - C_6 alkoxy, a C_1 - C_6 hydroxy alkyl, NO_2 , CN, CF_3 , SO_3^- , C_nF_{2n+1} , C_1 - C_{12} alkyl which is linear or branched, C_6 - C_{12} aryl, C_nH_{2n+1} , $C_6H_5C_pH_{2p}-$, $C_pH_{2p+1}C_6H_4-$, $C_pH_{2p+1}C_6H_4C_nH_{2n}-$, $CH_2=CHC_pH_{2p}-$, $CH_2=CHC_6H_5-$, $CH_2=CHC_6H_4C_pH_{2p+1}-$, and $CH_2=CHC_pH_{2p}C_6H_4-$, n is an integer having a value from 1 to 48 and p is an integer having a value from 1 to 48.

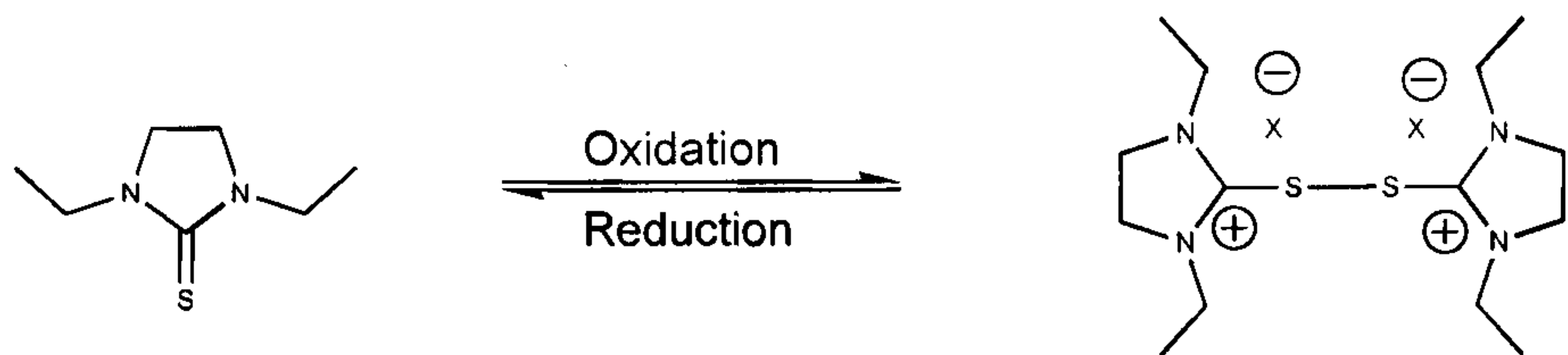
24. The redox couple of claim 19, wherein M^+ is an organic cation chosen from N-substituted imidazoliums, said substituent being a C_1 - C_{12} alkyl which is linear or branched.
25. The redox couple of claim 19, wherein M^+ is an organic cation chosen from tetralkylammoniums, wherein each of said alkyl groups is independently C_1 - C_{12} alkyl which is linear or branched.
26. The redox couple of claim 19, wherein M^+ is chosen from Li^+ , Na^+ and K^+ , and Cs^+ .
27. The redox couple of any one of claims 19 and 22 to 26, wherein said redox couple is as follows:



28. The redox couple of any one of claims 19 and 22 to 26, wherein said redox couple is as follows:

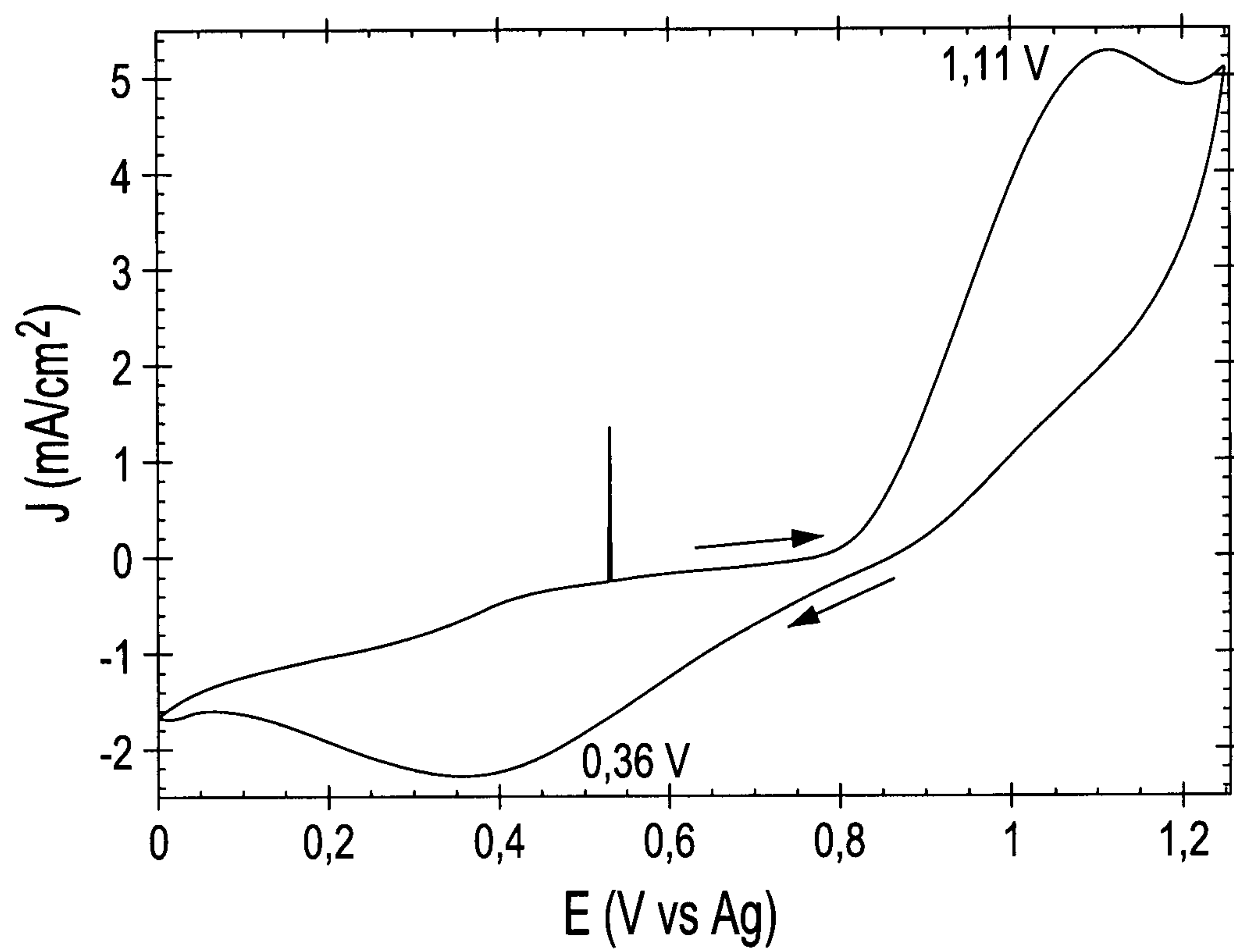
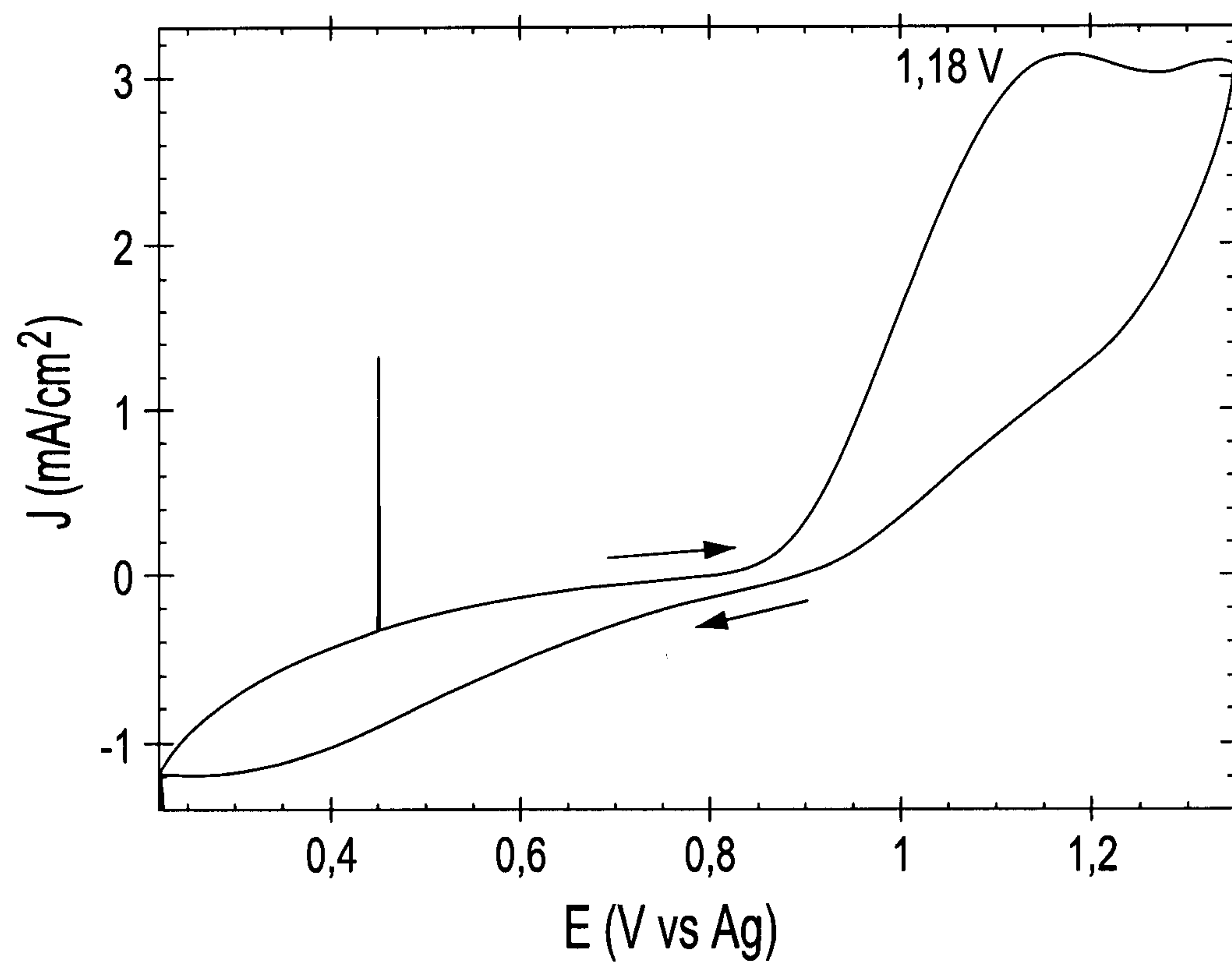


29. The redox couple of any one of claims 19 to 21, wherein said redox couple is as follows:

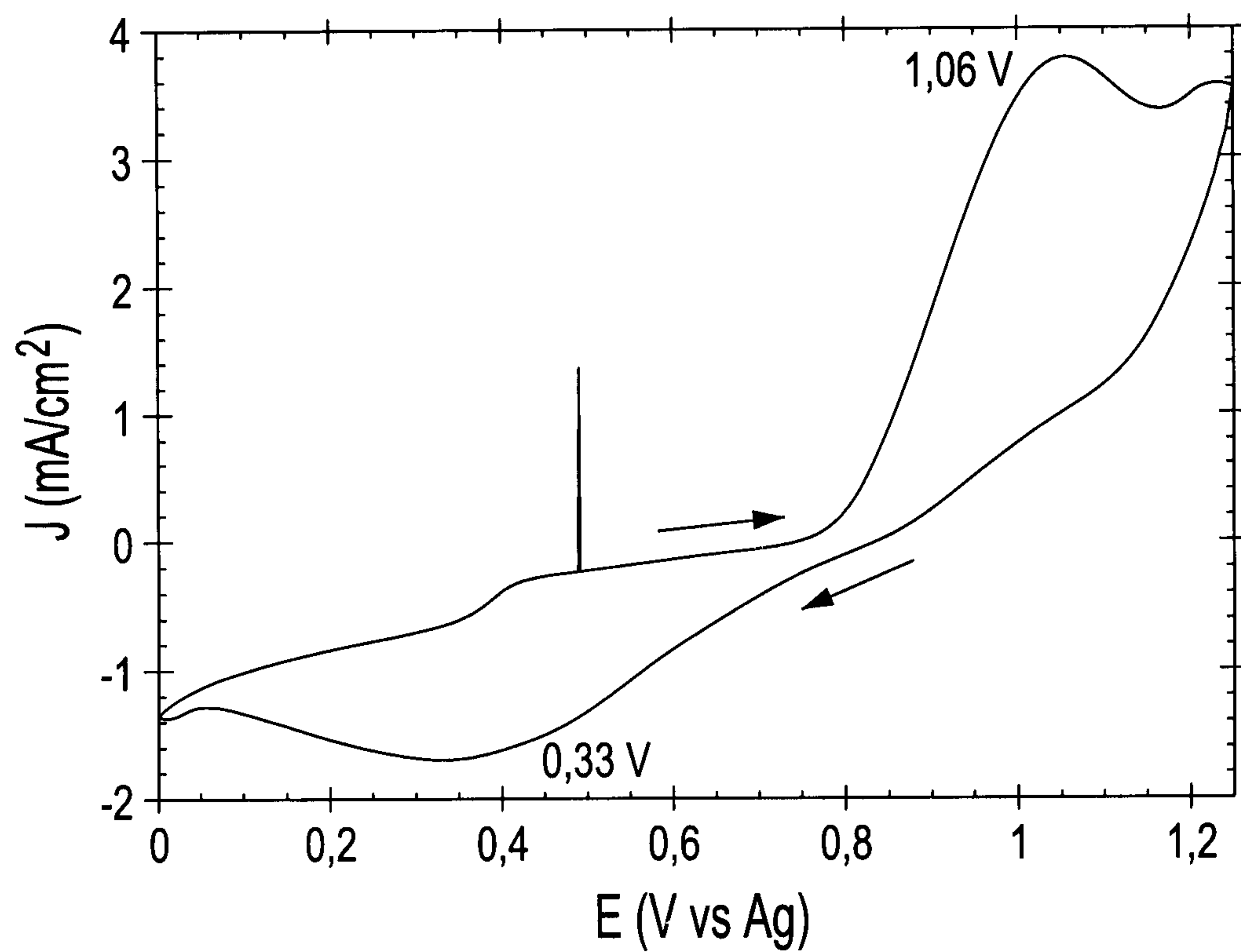
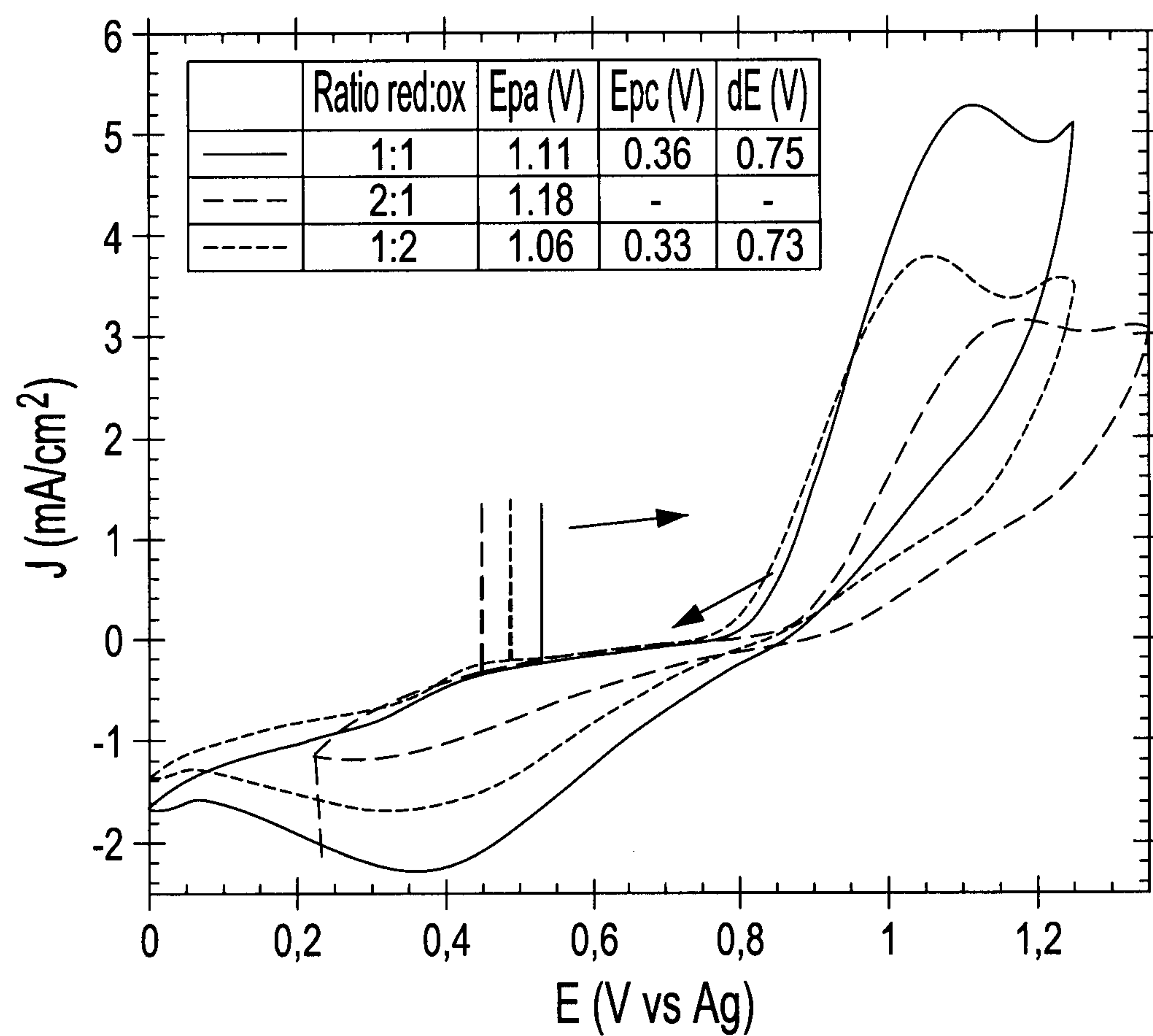


30. A photovoltaic cell comprising an anode, a cathode, and a redox couple as defined in any one of claims 19 to 29.
31. A photovoltaic cell comprising an anode, a cathode, a redox couple as defined in any one of claims 19 to 29, and a solvent, a polymer, a molten salt, an ionic liquid, a gel or any combination thereof.
32. Use of a redox couple as defined in any one of claims 19 to 29, in a solar cell, a fuel cell, a battery, a sensor or a display.

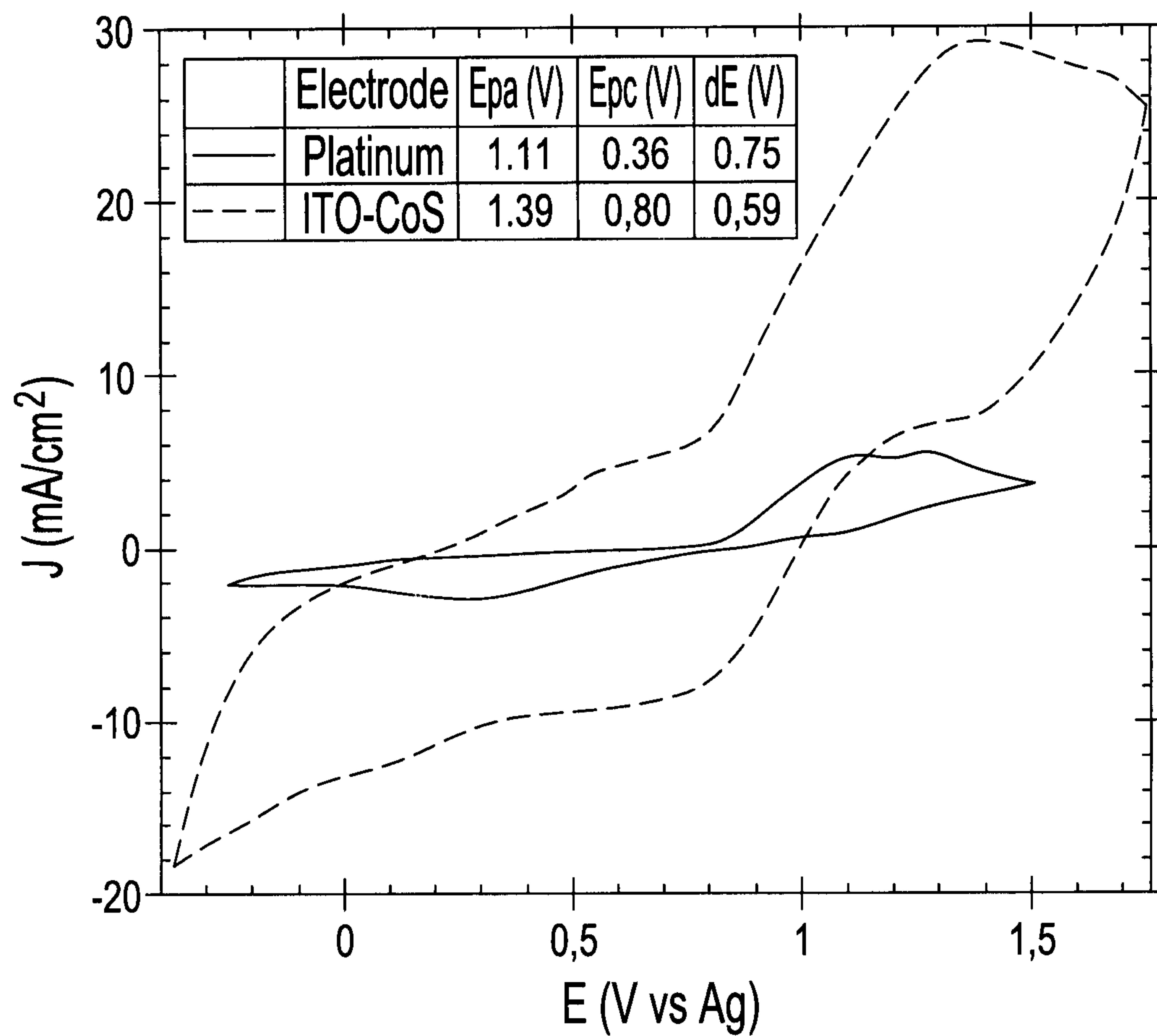
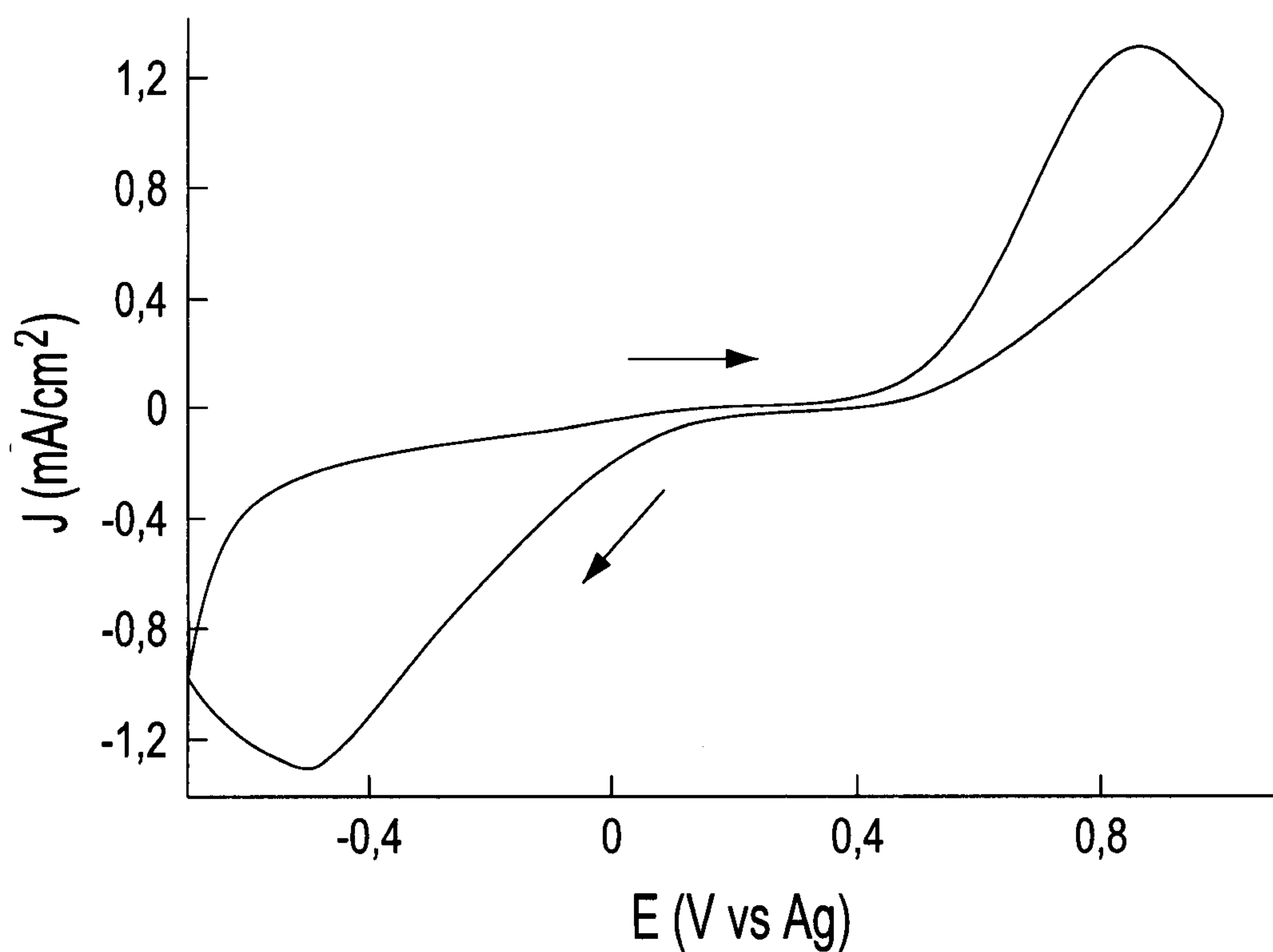
1 / 6

Fig. 1Fig. 2

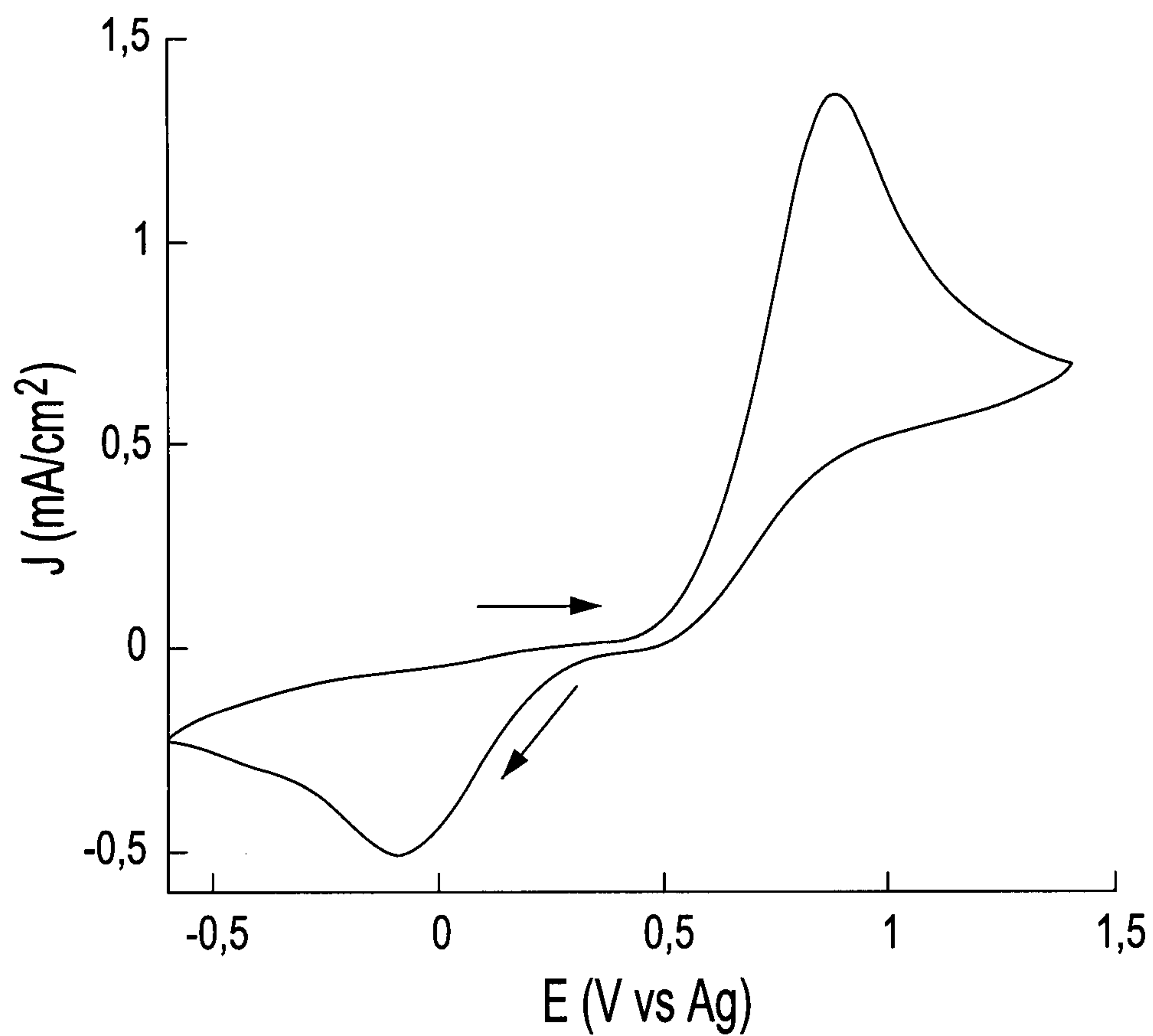
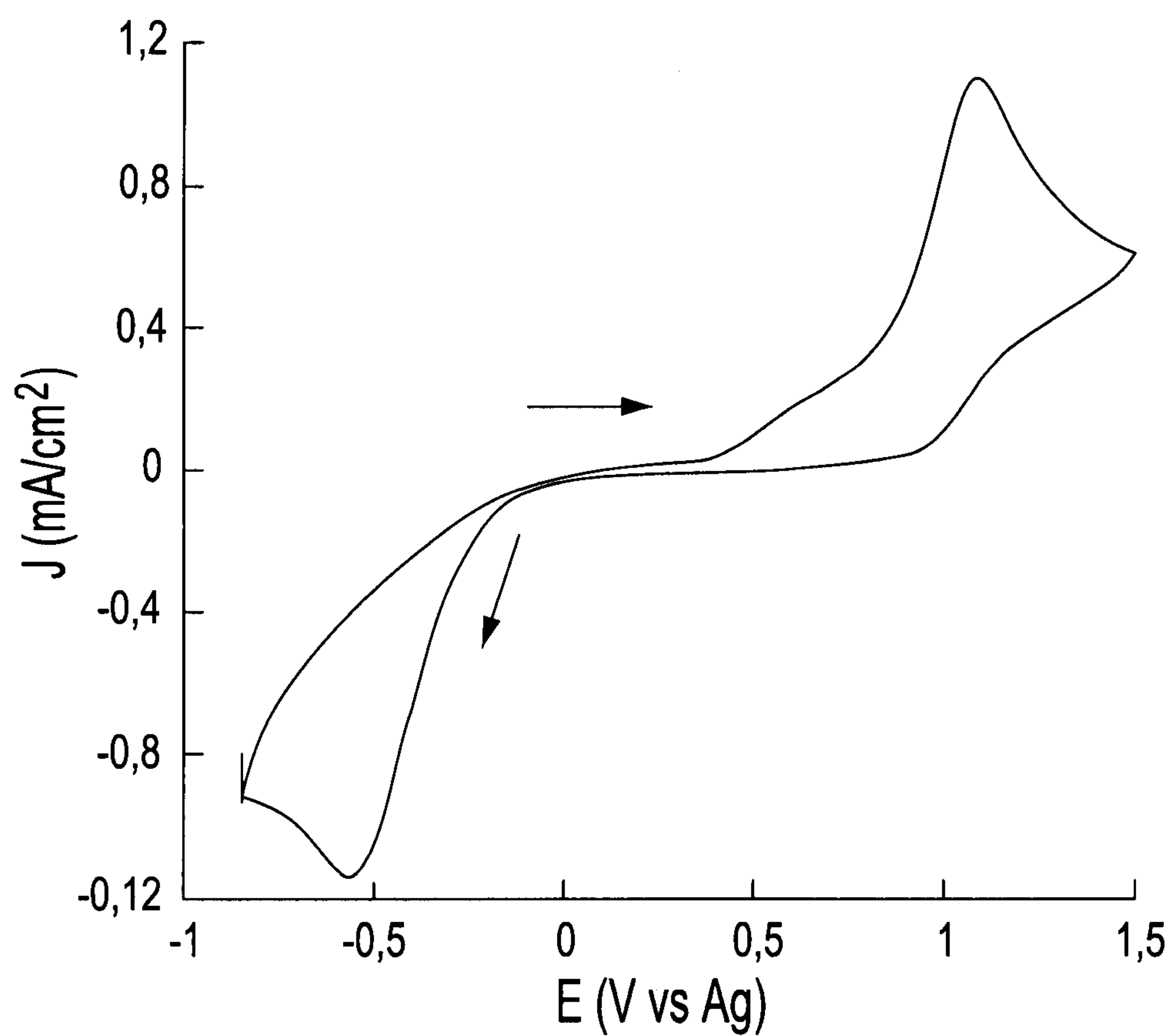
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FIG. 3FIG. 4

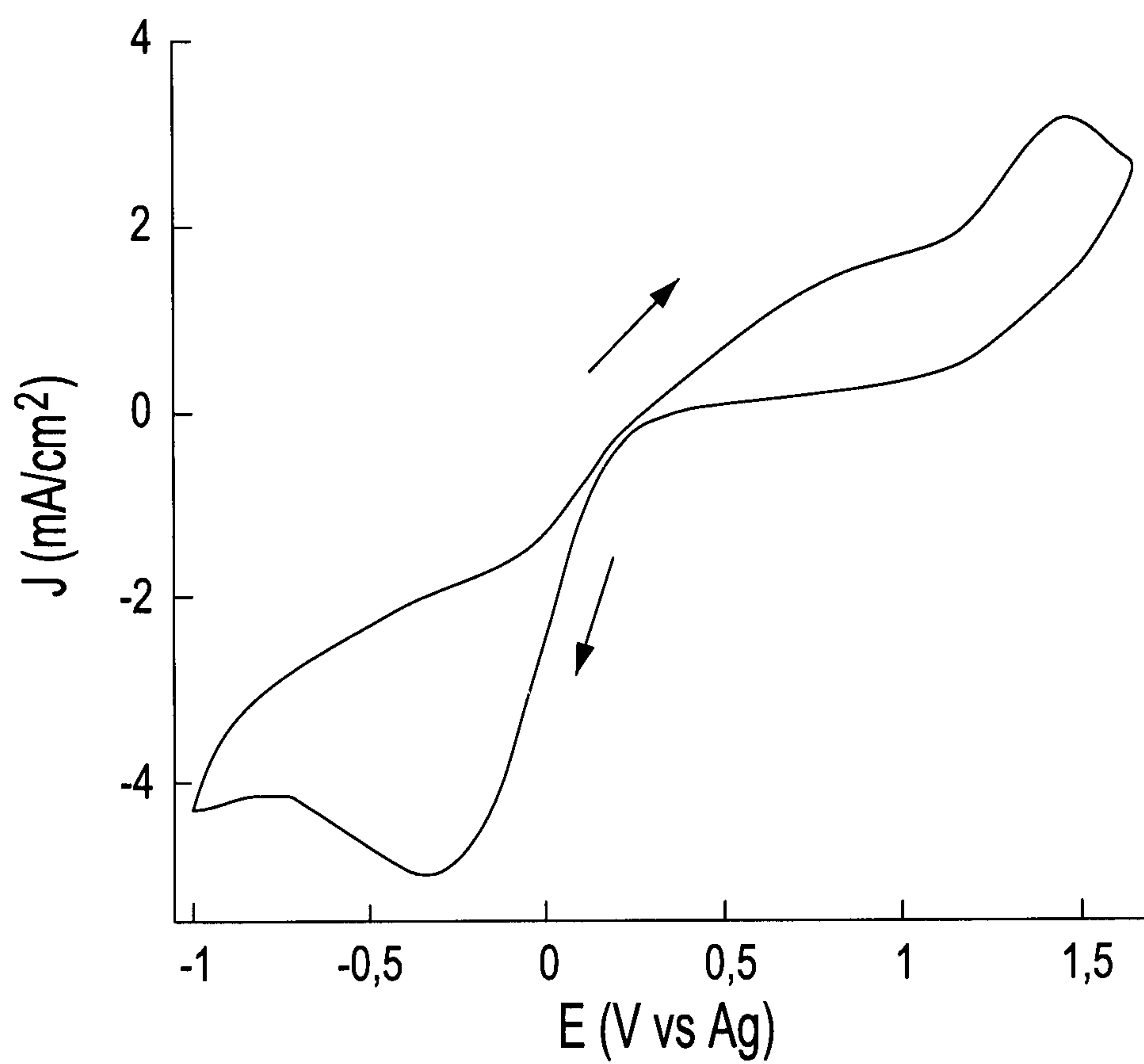
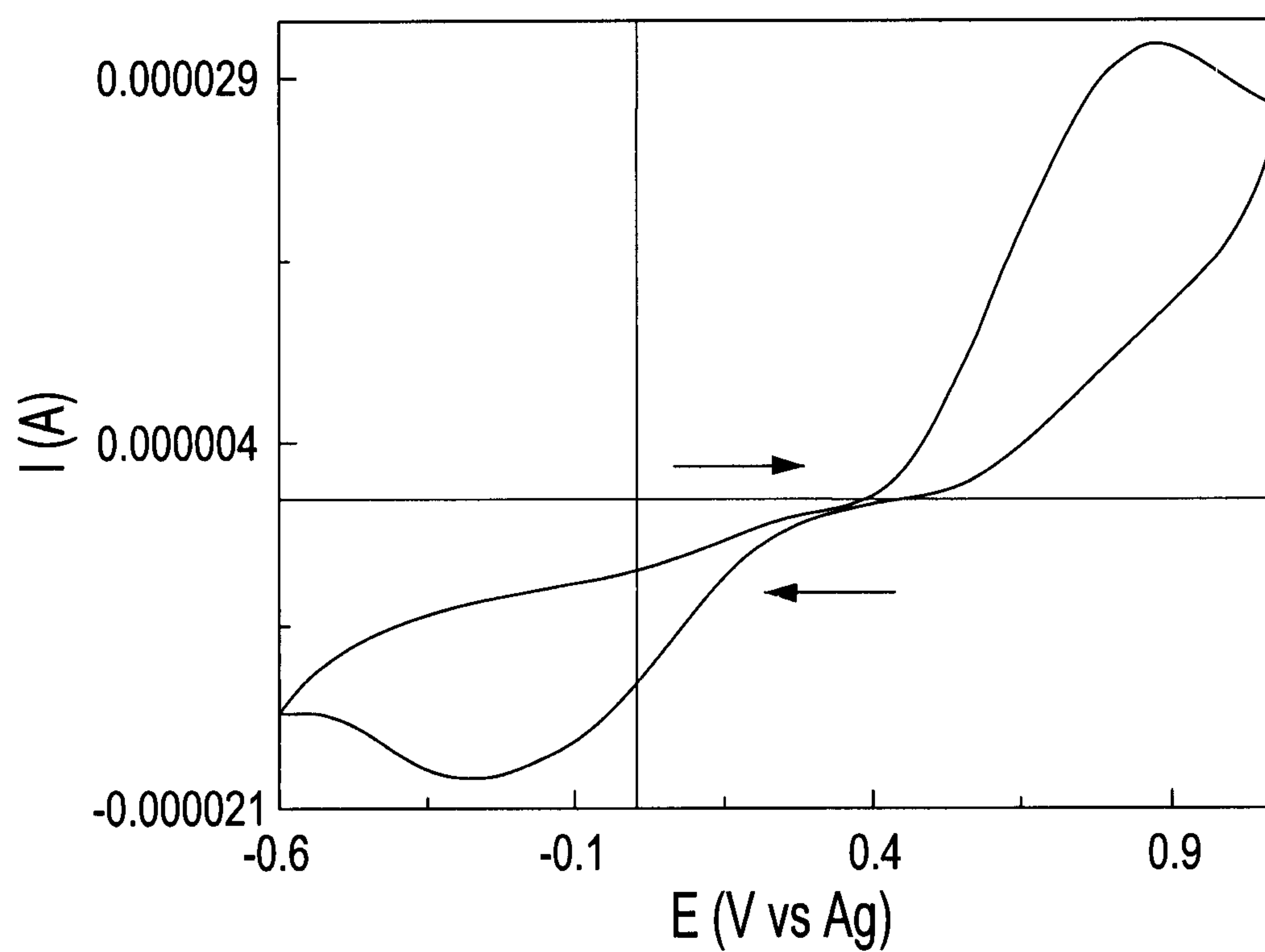
3 / 6

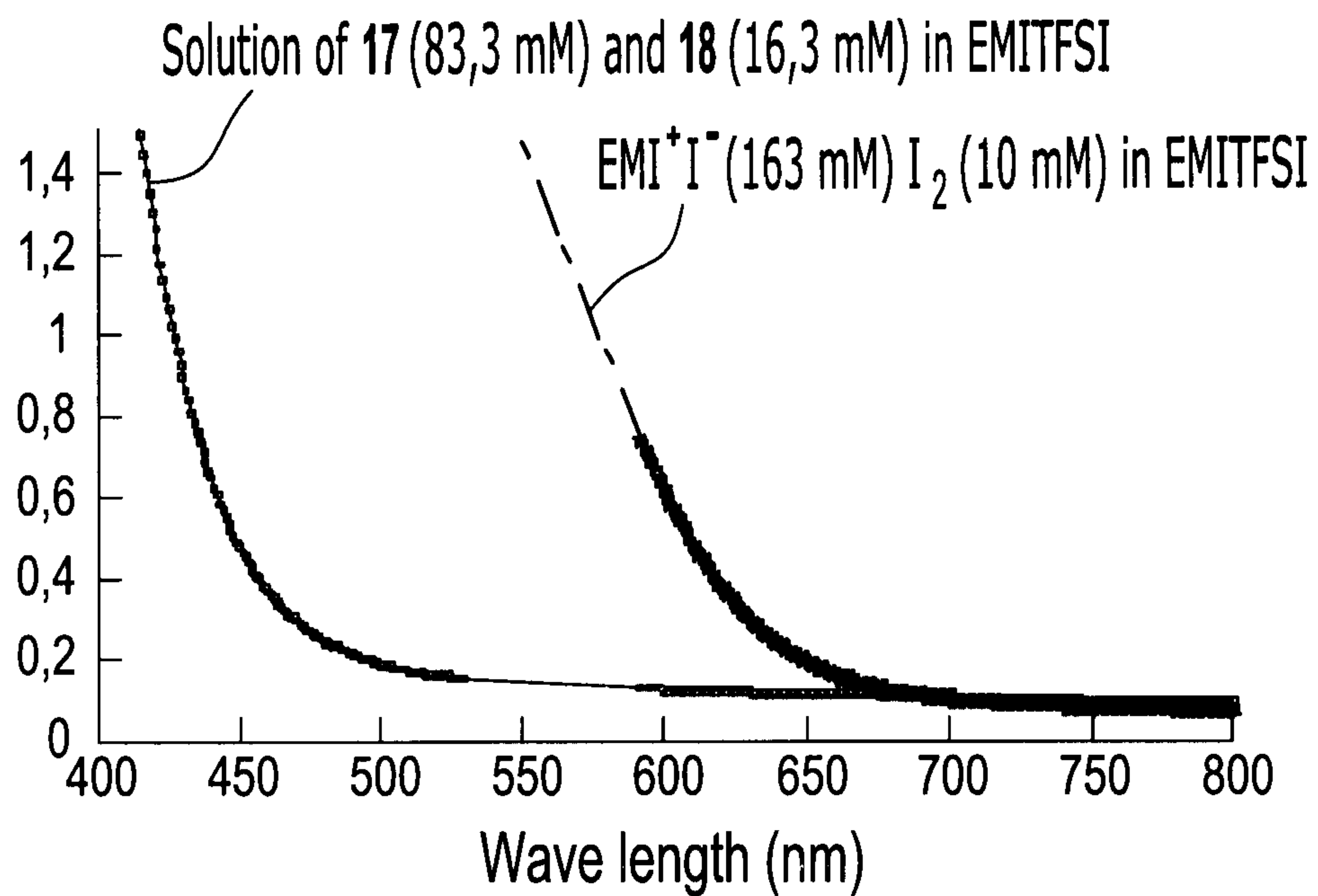
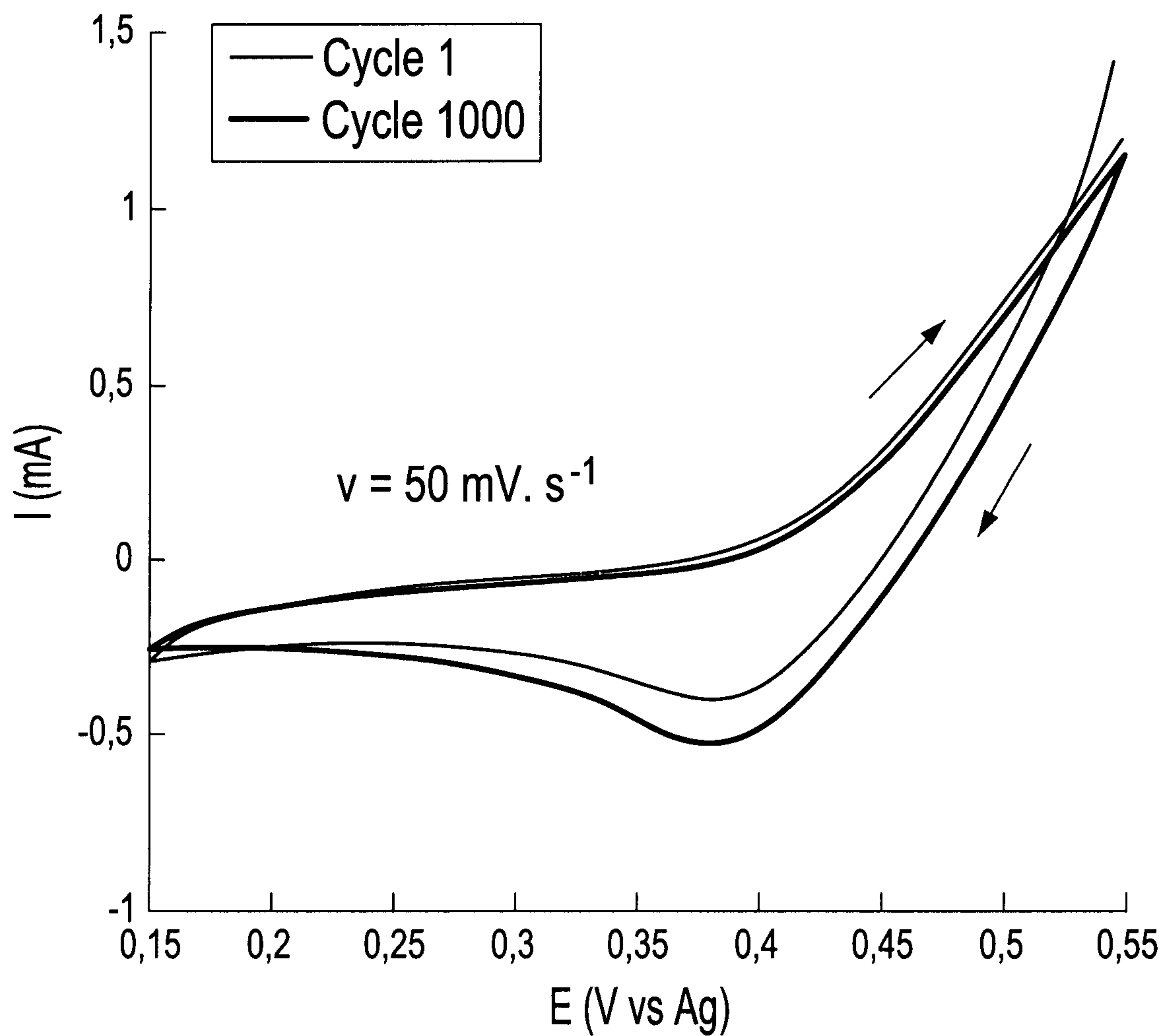
Fig. 5Fig. 6

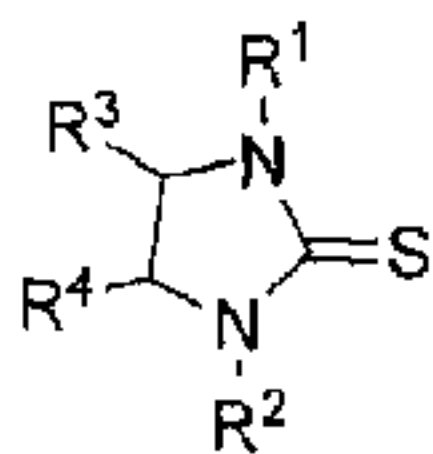
4 / 6

Figure 7Figure 8

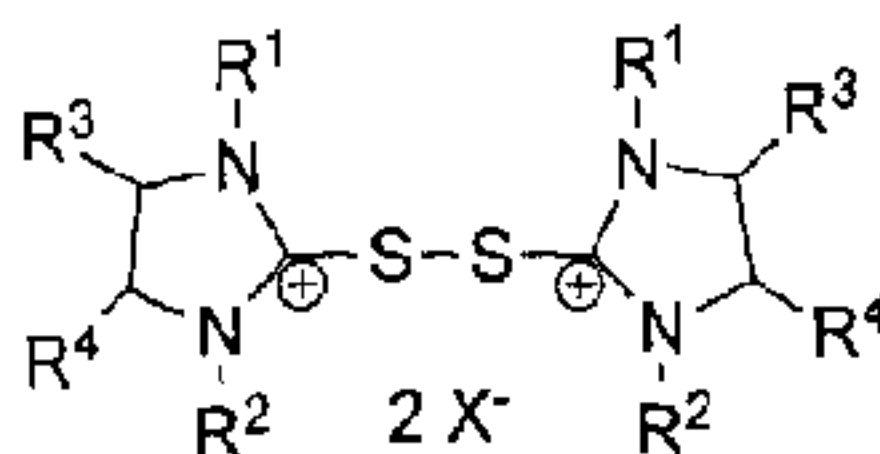
5 / 6

Fig. 9Fig. 10

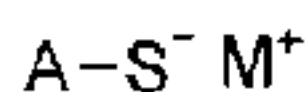
Fig. 11Fig. 12



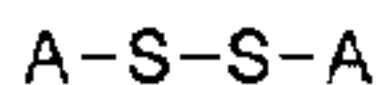
(I)



(II)



(III)



(IV)

Solution of **17** (83,3 mM) and **18** (16,3 mM) in EMITFSI

