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(54) **A METHOD FOR PRODUCING AN IONIC LIQUID**

(57) The present invention relates to a method for the electrochemical production of an aprotic ionic liquid of a cation and a halide based anion X^- wherein a reaction mixture containing a solvent, a supporting electrolyte, an anion source and a reactant which responds to formula

$$R'_m\text{-}Y^1\text{-}(CR)_n\text{-}Y^2\text{-}R''_p \qquad (1)$$

wherein
- Y^1 and Y^2 may be the same or different and are selected from the group of N, P and S
- m and p may be the same or different and may be 2 or 3,
- all R' may be the same or different, all R" may be the same or different, R' may be the same as or different from R" and may, independently of each other be H, a straight chain or a branched saturated alkyl group, a cyclic alkyl group or an aromatic hydrocarbon moiety
- At least one R next to Y^1 is CH_2
- And n is at least 1, preferably at least 2, more preferably maximum 10, most preferably n is 1, 2 or 3,

wherein Y is N, P or S
is subjected to an anodic electrochemical potential to cause oxidative electrolysis of the reactant, wherein the supporting electrolyte simultaneously functions as anion source and comprises a salt of the halide ion X^-, selected from the group of fluoride, chloride, bromide or iodide.

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Description

[0001] The present invention relates to a method for the electrochemical production of an aprotic ionic liquid of a cation and a halide based anion X^-, according to the preamble of the first claim.

[0002] Ionic liquids are generally composed of a bulky, asymmetric organic cation and an anion, often of inorganic nature (1). Usually, ionic liquids (ILs) are organic salts with a melting point of below 100 °C, most of them being liquid at ambient temperature. In recent decades, ionic liquids have aroused broad research and industrial interest because of their outstanding physicochemical properties, such as their extremely low vapor pressure, their high thermal stability and good solvation ability, which make them suitable candidates for a wide range of applications (2). Moreover, properties of ionic liquids such as melting point, viscosity, density, and hydrophobicity can be modified by changing the structure of the cation, the anion, or both. This makes it possible to design ionic liquids that suit requirements imposed by a particular process in which their use is envisaged (3). The use of ionic liquids has been explored in many fields of chemistry, for example, their use as solvents or catalysts in synthesis processes (4), in extraction processes (5), as media for CO_2 capture (6), as stationary phase in gas chromatography (7) or as supporting electrolyte in electrochemistry (8).

[0003] At present, the synthesis of ionic liquids typically comprises a first step wherein the desired cation is formed, followed by an anion exchange, if necessary. The following classical synthesis routes may be distinguished in general:

1) an acid-base reaction between an inorganic or organic acid and an organic base to form a protic ionic liquid, which contains a hydrogen atom directly attached to a heteroatom of the cation, and
2) an alkylation of a precursor for example an amine, a phosphine, a heterocyclic compound, which results in an aprotic ionic liquid. In an aprotic ionic liquid, no hydrogen atom is directly attached to the heteroatom of the cation. The alkylation method is usually carried out at high temperatures (e.g. 80 °C) and yields halide-based ionic liquids and involves an anion exchange. These ionic liquids may easily be converted into other ionic liquids with different anions such as tetrafluoroborate (BF_4^-) or hexafluorophosphate (PF_6^-) (10).

[0004] Ionic liquids have also been synthesized using non-conventional and greener methods, e.g. methods using microwaves or ultrasound irradiation (11, 12). Microwave-assisted synthesis of ionic liquids has provided a higher energy efficiency than conventional heating, however consecutive microwave irradiation, may render heat control rather difficult because of the nonvolatile nature of Ionic liquids (13). Ultrasound reactions also provide a few advantages, the main one being the use of non-hazardous acoustic radiation as an energy source. Yet, the main disadvantage is the non-homogeneous distribution of energy which hinders the industrial feasibility of the method as reactors need to be modified for upscaling (14).

[0005] A few studies report the use of electrosynthesis for the synthesis of organic salts with characteristics of ionic liquids. Ohmori *et al.* reported the anodic oxidation of triphenylphosphine in acetonitrile in the presence of various primary amines, yielding to the formation of monoalkylaminotriphenylphosphonium salts (16). Nikitin *et al.* described the electrosynthesis of diphosphonium salts through anodic electrolysis of trialkyl- and triaryl-phosphines in anhydrous acetonitrile, using sodium perchlorate as supporting electrolyte (17). Recently, Gallardo and Vilà reported the electrosynthesis of substituted imidazolinium and tetrahydropyrimidinium salts by electro-oxidation of dialkyldiamines in dimethylformamide (DMF), using lithium perchlorate as supporting electrolyte (18). In these ionic liquid electrosynthesis studies, use is made of perchlorate salts both as supporting electrolyte and as anion source. This represents an important disadvantage in the synthesis of ionic liquids, because perchlorate salts can form explosive compounds in the presence or organic solvents. For example, the mixture $LiClO_4$-DMF has an explosive force that is approximately 50% of that of trinitrotoluene, aka TNT (19), thus creating important risks for upscaling. Moreover, once formed, perchlorate ionic liquids are not compliant for conversion into other ionic liquids with different anions, and perchlorates salts have been found to be toxicologically hazardous for humans, e.g. inhibiting thyroid function (20).

[0006] There is thus a need to find an electrochemical method for producing ionic liquids, which makes use of other anions instead of perchlorates, which do not show the safety issues associated with the use of perchlorates.

[0007] The present invention therefore seeks to provide a method for producing ionic liquids, which is not compromised by the safety issues of the prior art electrochemical production methods.

[0008] This is achieved according to the present invention with a method, which shows the technical features of the characterizing portion of the first claim.

[0009] Thereto in the method of the present invention for the electrochemical production of an aprotic ionic liquid of a cation and a halide based anion X-, wherein a reaction mixture containing a solvent, a supporting electrolyte and a reactant which responds to formula

$$R'_m\text{-}Y^1\text{-}(CR)_n\text{-}Y^2\text{-}R''_p \qquad (1)$$

wherein

- Y^1 and Y^2 may be the same or different and are selected from the group of N, P and S
- m and p may be the same or different and may be 2 or 3,
- all R' may be the same or different, all R" may be the same or different, R' may be the same as or different from R" and may, independently of each other be H, a straight chain or a branched saturated alkyl group, a cyclic alkyl group or an aromatic hydrocarbon moiety
- At least one R next to Y^1 is CH_2
- And n is at least 1, preferably at least 2, more preferably maximum 10, most preferably n is 1, 2 or 3,

is subjected to an anodic electrochemical potential to cause oxidative electrolysis of the reactant, wherein the supporting electrolyte simultaneously functions as anion source and comprises a salt of the halide ion X^-, selected from the group of fluoride, chloride, bromide or iodide.

[0010] The method of this invention has been found suitable for producing ionic liquids from a compound or a reactant selected from the group of compounds represented by the formula (1) above. These reactants proved to be extremely suitable precursors for the intended ionic liquid reaction products as the risk that they give rise to the formation of unwanted side products is minimal. The reaction product is an ionic liquid which comprises the halide based anion and a cation which is obtained by electrochemical oxidation of the compound of formula (1) above.

[0011] In the present invention, a halide salt, in particular a chloride salt is used as anion source as an alternative to the perchlorates known from prior art synthesis methods for ionic liquids. Thereby, the halide salt acts both as anion source in the electrochemical reaction for the anion of the envisaged ionic liquid reaction end product, and as supporting electrolyte in the electrochemical process.

[0012] Despite their wide use in classical organic synthesis, chlorides have been so far overlooked for the electrosynthesis of ionic liquids, the main reason being that they are regarded as more electrochemically active than the organic cation precursors under the typical ionic liquid electrochemical synthesis conditions, and therefore prone to yield a negative impact on the overall ionic liquid synthesis selectivity and efficiency or to even impede the desired reaction. The inventors have observed that although the halide ion, in particular the chloride anion, is not electrochemically inert at the electrochemical potential at which the reactant is oxidized, the risk to oxidation of the halide anion may nevertheless be reduced to a minimum. The inventors have thus surprisingly found that the reactant is capable of counteracting or even inhibiting oxidation of the halide anion, in particular the chloride anion.

[0013] The inventors have further observed that any oxidation of the halide anion that might occur has a negligible or even no effect on the electrochemical conversion of the reactant. In other words, it has been found that any oxidation of the halide anion that might possibly occur does not seem to hamper the electrochemical conversion of the reactant.

[0014] The use of a salt of a halide presents the advantage that the formation of explosive compounds in the presence or organic solvents, as is the case with prior art methods using perchlorate salts, can be avoided.

[0015] Halide ionic liquids, in particular chloride based ionic liquids present the additional advantage that they are compliant for conversion into other ionic liquids wherein the halide anion, in particular the chloride anion, may be exchanged for another anion, thereby showing a higher versatility in electrosynthesis of ionic liquids. Besides that, the toxicity of halide ionic liquids, in particular the toxicity of chloride based ionic liquids to humans is substantially lower or even negligible in comparison to ionic liquids derived from perchlorates. In this sense, halide salts, in particular chloride salts arise as an extremely suitable alternative to perchlorates.

[0016] The skilled person will be capable of selecting the nature of the halide salt taking into account its electrochemical stability window, so that its electrochemical stability window falls within the electrochemical potential at which the method of this invention is carried out.

[0017] Electrosynthesis has proven to be an environmentally-friendly method for diverse organic syntheses (non-ionic liquid cases mostly), because the electrons active in the electrochemical synthesis process permit to dispense with the use of hazardous redox agents. Moreover, the electrons active in the electrochemical synthesis process can be obtained from renewable energy sources. Additionally, high efficiency and selectivity can be achieved by controlling the current or the potential of the reaction, which is typically carried out at room temperature and atmospheric pressure.

[0018] In general, the reaction mixture may contain the halide salt in a slight molar excess with respect to the reactant. With a slight excess is meant a molar excess of maximum 10%, preferably maximum 7.5 %, more preferably maximum 5%. In a preferred embodiment, the reactant is present in the reaction mixture in a high concentration. With a high concentration is meant that the reaction mixture contains the halide salt in a high concentration, i.e. in a concentration which is such that the molar ratio of the concentration of the reactant with respect to the halide salt varies between 0.9 and 1.5, preferably between 0.9 and stoichiometric. This is surprising as electrochemical reactions are usually carried out in a reaction medium wherein the molar ratio of the supporting electrolyte to the electroactive species varies around a value of 10. When the molar ratio of the concentration of the reactant with respect to the halide salt is smaller than 0.9, the risk increases to oxidation of the halide.

[0019] The inventors have surprisingly found that carrying out the process of this invention within these concentration ranges permits minimizing the risk to the formation of an X_2 or an X_3^- species, which is unwanted. In particular, at these concentrations Cl^- oxidation may be inhibited and the oxidation of the reactant takes precedence over CL- oxidation. Without wanting to be bound by this theory, the inventors assume that the halide ion X^-, in particular the Cl^- anion, is oxidized in a process that involves a two-electron transfer from which chlorine (Cl_2) and a trichloride anion (Cl_3^-) may be generated. These processes may be described by the following reactions:

$$2Cl^- + 2e^- \rightarrow Cl_2$$

$$Cl_2 + Cl^- \leftrightarrow Cl_3^-$$

[0020] Within the scope of this invention the halide salt is a salt selected from the group of $M^{2+}X_2$, $M^{3+}X_3$ or a halide salt of an organic aprotic cation, wherein M^{2+} and M^{3+} are respectively divalent and trivalent metal cations, wherein the halide X is preferably chloride. M^{2+} and M^{3+} respectively represent divalent and trivalent metal cations, for example Fe^{3+} or Ni^{2+} or Co^{2+}. According to another preferred embodiment, the halogen salt is an organic ammonium halide, preferably an organic ammonium chloride, preferably an alkylammonium chloride. Examples of suitable ammonium chlorides include trimethylammonium chlorides (Me_3RNCl), wherein the additional alkyl group R on the N is a C1-C18 alkyl groups, tetraalkylammonium chlorides (R_4NCl) which may be symmetric, in particular ammonium chlorides containing C_1-C_{12} alkyl groups, tetramethylammonium chloride, tetraethylammonium chloride, tetrabutylammonium chloride, choline chloride, benzalkonium chloride. It shall however be clear to the skilled person that many other ammonium halides, in particular many other ammonium chlorides exist, which may be suitably be used in the method of the present invention.

[0021] Suitable reactants for use with the present invention include di-amines which respond to the formula:

$$R^1R^2\text{-}N\text{-}(CR)_n\text{-}N\text{-}R^3R^4 \qquad (2)$$

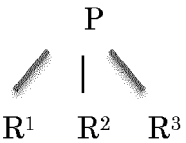
wherein

- R, R^1, R^2,R^3, R^4, may be the same or different and may, independently of each other be H, a straight chain or a branched saturated alkyl group, a cyclic alkyl group or an aromatic hydrocarbon moiety. Preferably however, R, R, R^1, R^3, R^4, will contain between 1-20 carbon atoms, more preferably between 1 and 12 carbon atoms
- At least one R next to the N is CH_2
- And n is at least 1, preferably at least 2. In a preferred embodiment, n is maximum 10, preferably maximum 5, more preferably n is 2 or 3 as this results in the formation of stable 5 or 6 membered rings.

[0022] In a preferred embodiment one or more of R, R^1, R^2,R^3, R^4, may be substituted with one or more substituents selected from the group of a -OH, - OR, -COOH, -COOR moiety.

[0023] Examples of di-amines suitable for use with the present invention include di-amines selected from the group of an N,N'-dialkylethylenediamine and an N,N'-dialkylpropanediamine, preferably a 1,3-dialkylethylenediamine and a 1,3-dialkylpropanediamine. More preferably the reactant is selected from the group of N, N'-diethylethylenediamine, N,N'-dipropylethylenediamine, N,N'-di-tert-butylethylenediamine and N,N'-dimethylpropanediamine, N,N'-di-ethylpropanediamine, N.N'-dipropylpropanediamine , N,N'-di-tert-butylethylenediamine or derivatives of the afore-mentioned compounds. It shall however be clear to the skilled person that many other N-substituted diamines or N, N' di-substituted diamines exist and that many other diamines may be used in the present invention. Whereas symmetric di-substituted N, N'-diamines will usually give rise to symmetric substituted ionic reaction products, asymmetric di-substituted N, N'-diamines will usually give rise to asymmetric substituted ionic reaction products. Mono substituted N-alkylethylenediamine and N-alkylpropanediamine and their derivates will usually give asymetric substituted ionic reaction products.

[0024] Suitable reactants for use with the present invention also include phosphines which respond to the formula (3):



Wherein R^1, R^2,R^3, may be the same or different and may, independently of each other be H, a straight chain or a branched saturated alkyl group, a cyclic alkyl group or an aromatic hydrocarbon moiety.

[0025] Preferably a trialkylphosphine is used, which may be symmetric, i.e. with R^1, R^2,R^3, being the same, or asymmetric with one or more of R^1, R^2,R^3, being different from the others. Preferably R^1, R^2, R^3 will contain between 1-20

carbon atoms, more preferably between 1 and 12 carbon atoms

[0026] In a preferred embodiment one or more of R^1, R^2,R^3, may be substituted with one or more substituents selected from the group of a -OH, -OR, -COOH, -COOR moiety.

[0027] The phosphine reactants described above may be converted into phosphonium based ionic liquids.

[0028] Table 1 and 2 below provides some examples of reactants and the reaction products that may be produced therefrom using the method of this invention. It shall be clear to the skilled person that the use of other reactants will give rise to the formation of other reaction products.

Table 1. General structure of the compounds that could be synthesized using the proposed method.

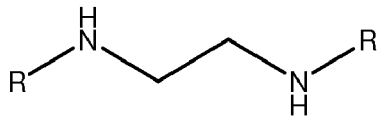
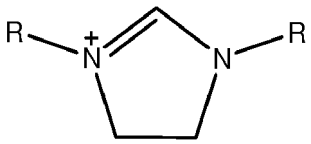
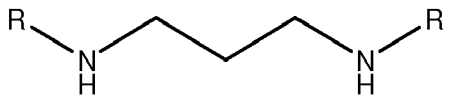
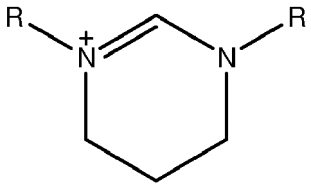
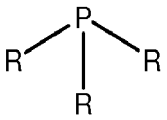
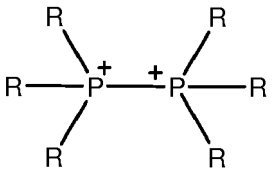
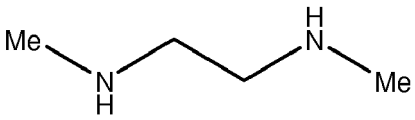
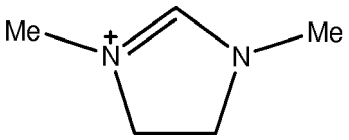
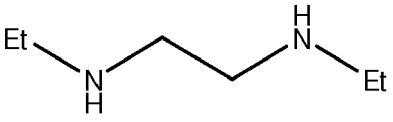
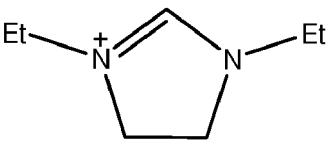
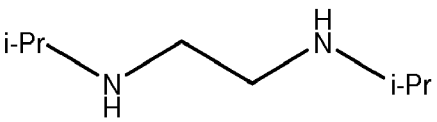
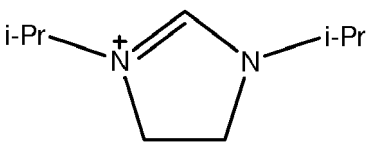
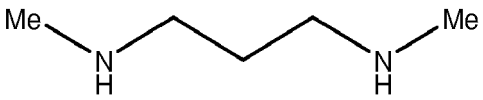
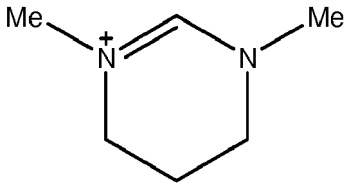
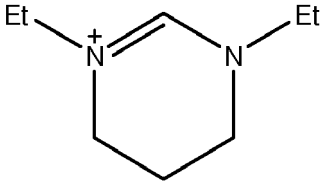
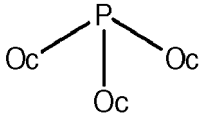
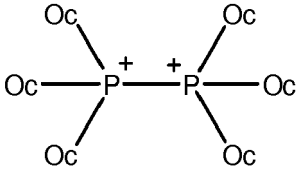
Starting Material	Product
 N,N'-Dialkylethylenediamines	 1,3-Dialkylimidazolinium salts
 N,N'-Dialkylpropanediamines	 1,3-Dialkyl-1,4,5,6-tetrahydropyrimidin-3-ium salts
 Trialkylphosphines	 Hexaalkyldiphosphonium salts
*Where R might be any alkyl radical	

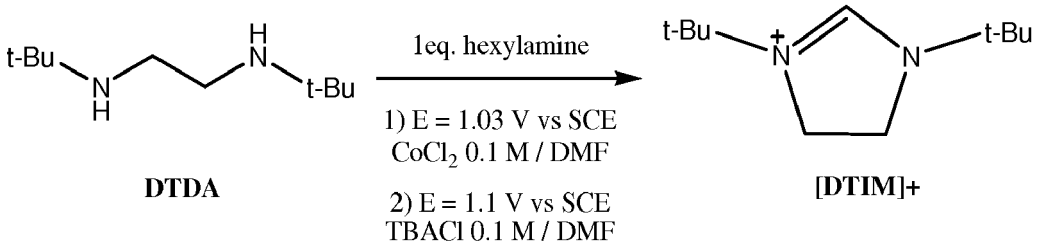
Table 2. Examples of reactants and reaction products that can be produced therefrom using the method of this invention

Starting Material	Product
	
	
	

(continued)

Starting Material	Product
	
	
	

[0029] In table 2 above, Me indicates a methyl group, Et indicates an ethyl group, i-Pr indicates iso-propyl, Oc indicates an octyl group. Schem 1 below shows the general electrochemical conversion scheme of DTDA into 1,3-di-tert-butylimidazolinium ([DTIM]$^+$)



DTDA **[DTIM]+**

Scheme 1. General diagram for the electrosynthesis of 1,3-di-tert-butylimidazolinium ([DTIM]$^+$) starting from N,N'-di-tert-butylethylenediamine (DTDA), in the presence of chlorides (i.e. $CoCl_2$ or TBAC).

[0030] In order to achieve full conversion of the reactant, the reactant is subjected to a charge which is at least

$$Q_{theor} = \frac{n\mathrm{F}VC}{M}$$

[0031] Herein where n is the number of electrons involved in the process, F is Faraday's constant (96485 C mol^{-1}), V is the volume of the working solution (L), C is the concentration of electroactive species in the solution (g L^{-1}), and *M* is the molecular mass of the electroactive species (g mol^{-1}). In the above, n is known to the skilled person, for example where the reactant is a di-amine, n will usually be at least 3, where the reactant is a phosphine, n will usually be 2.

[0032] In a preferred embodiment, the reaction mixture may further contain a proton scavenger or the reaction mixture is subjected to proton scavenging. Protons released in the course of the oxidation of the reactant may lead to the formation of non-electroactive protonated species and risk to reduce the yield of the desired end product. The presence of a weak Bronsted base, capable of acting as a proton acceptor or a proton scavenger, permits to minimize the risk to the occurrence of this step. Within the scope of this invention, a weak Bronsted base is understood to refer to a compound having a pKb which is below the pKb of the reactant. In a preferred embodiment a weak Bronsted base is understood to refer to a compound having a pKb of at least 2.5. In general the pKb will not be more than 4, preferably not more 3.5. The concentration of the proton scavenger in the reaction mixture is not critical to the invention. However if a maximum yield and selectivity towards the desired end product is envisaged, the proton scavenger will be present in an equimolar

concentration to the reactant or a concentration which is maximum 10 % below or maximum 10 % higher than an equimolar amount.

[0033] Within the scope of the present invention a wide variety of compounds capable of acting as a proton scavenger may be used, as long as it does not react at the electrochemical potential at which the process of this invention is carried out, and as long as it shows a sufficient solubility in the reaction mixture. Preferably however use is made of an organic amine or a mixture of two or more organic amines, in particular a monoamine or a mixture of two or more thereof, more preferably an aliphatic amine, a cyclic amine and an aromatic amine, more in particular an alkyl amine, which may be represented by the formula

$$R\text{-}NH_2 \qquad (4)$$

Wherein R is H or a C_1-C_{10} alkyl group, preferably a C_4-C_8 alkyl group. Herein R may be branched, but preferably is a R straight chain alkyl group. Usually R will not contain further substituents, but this is not imperative.

[0034] Examples of suitable proton scavengers include tert-butylamine, triethylamine, pyridine. n-hexylamine has been found to be particularly suitable for use with the present invention as it is oxidized at an electrochemical potential which is sufficiently higher than the electrochemical potential at which the reactant is oxidized. In general, the skilled person will take care to employ a proton scavenger which is electrochemically stable at the electrochemical potential at which the reaction is carried out. In particular, the skilled person will take care to select a proton scavenger which is oxidized at an electrochemical potential sufficiently above the electrochemical potential at which the reactant is oxidized. From figure S1, it can be observed that the electrochemical potential at which hexylamine is oxidized is 1.35 V vs SCE (Fig. S1 has been extracted from electronic supplementary information (ESI)).

[0035] As an alternative or in addition to the above, proton scavenging may also be achieved by cathodic deprotonation.

[0036] The amount of proton scavenger contained in the reaction mixture may vary within some ranges. However, in order to achieve optimal results, the amount of proton scavenger is at least equimolar to the amount of reactant and halogen salt contained in the reaction mixture.

[0037] In order to minimize the risk to the formation of undesired byproducts, in particular the formation of an adduct of the reaction product or an intermediate with water, the reaction mixture is substantially water-free, which means that it contains less than 100.00 ppm of water. Minimizing the water content may be achieved by subjecting the halide salt to drying in advance of supplying it to the reaction mixture. Minimizing the water content may further involve subjecting one or more of the other components of the reaction mixture, including the reactant, the proton scavenger and the solvent to drying before supplying them to the reaction mixture.

[0038] It may further be preferred to carry out the method of this invention in an inert atmosphere, i.e. in He, Ar, Ne or under N_2 gas atmosphere, to minimize the risk that oxygen would interfere in the anodic oxidation. In general the skilled person will take care that the oxygen concentration in the reaction mixture is less than 1000 ppm, preferably less than 100 ppm.

[0039] The process of the present invention is generally carried out in a liquid phase, which contains the reactants in a solution in an aprotic solvent, preferably an organic aprotic solvent. In general the solvent will be chosen such that the reactant and other compounds that interact in the method of this invention, show a sufficient solubility in or miscibility with the solvent. To minimize the risk to the formation of unwanted side products, the aprotic solvent is preferably selected such that it does not react at or within the electrochemical potential window used to carry out the method of this invention. Many suitable solvents are known to the skilled person, and include a.o. dimethylformamide (DMF), dimethylsulfoxide (DMSO), acetonitrile, etc.

[0040] The reaction mixture of the present invention contains a supporting electrolyte. Besides the salt of the halide X-, the supporting electrolyte may contain other compounds. These compounds shall however be selected such that they do not adversely affect the yield and selectivity of the present invention.

[0041] In the method of this invention the risk to the formation of by-products due to undesired conversion, for example oxidation, of other compounds than the reactant, may be minimized by selecting an appropriate temperature window for carrying out the method. Therefore, the method of this invention is preferably carried out at a constant temperature between10 °C and 75 °C, preferably between 10 °C and 60 °C, more preferably between 15 °C and 60°C or between 15 °C and 50°C, most preferably between 15 °C and 45 °C. Within this ranges in particular the risk of unwanted oxidation of the proton scavenger may be reduced to a minimum, and volatility of the solvent and/or reactants used does not play a major role.

[0042] In a preferred embodiment the method of this invention is carried out at an electrochemical potential of between 0.5-1.25 V, preferably between 0.74 and 1.1 V.

[0043] The present invention is further illustrated in the figures, description of the figures and examples below.

Fig. 1 shows a diagrammatical view of the electrochemical setup for: a) Cyclic voltammetry experiments, b) Electrolysis reactions. 1. Pt counter electrode, 2. Glassy carbon electrode, 3. Saturated calomel electrode, 4. Purge

tube, 5. Bridge tube, 6. Graphite tissue counter electrode, 7. Graphite tissue working electrode.

Fig. 2 shows a CV of DTDA 4 mM (-) and DTDA 4mM + HexA 4 mM (-), in DMF and $TBAPF_6$ 0.1 M as supporting electrolyte, on a glassy carbon electrode (GCE) (o = 3.0 mm) at 100 mV s^{-1}. Forward sweep →.

Fig. 3 shows a CV of 0.1 M $CoCl_2$ (-) and 93 mM DTDA + 93 mM HexA in 0.1 M $CoCl_2$ (-) in DMF, on a glassy carbon electrode GCE (ø = 3.0 mm) at 100 mV s^{-1}. Inset figure: CV of 93 mM DTDA + 93 mM HexA in 0.1 M $CoCl_2$ at 10 mV s^{-1}. Forward sweep →; backward sweep ←.

Fig. 4 shows a CVs of 0.1 M TBAC (-) and 93 mM DTDA + 93 mM HexA + 0.1 M TBAC (-) in DMF, on a glassy carbon electrode (GCE) (ø = 3.0 mm) at 100 mV s^{-1}. Forward sweep →.

Fig. 5 shows MS spectra of the freshly electrolyzed solutions of the electrolysis of DTDA after consumption of Q_{theor}. a) Reaction carried out in $CoCl_2$. b) Reaction carried out in TBAC.

Fig. S1 shows a CV of HexA in DMF and $TBAPF_6$ 0.1 M.

Fig. S2 shows the electrochemical window of $CoCl_2$ in DMF.

Fig. S3 shows the electrochemical window of TBAC in DMF.

Fig. S4 shows the CV of $TBAPF_6$ 0.1 M in DMF.

Fig. S5 shows the CV of DTDA 93 mM in DMF and $TBAPF_6$ 0.1 M.

Fig. S6 shows the MS spectra of the electrolysis of DTDA in $CoCl_2$ at 25°C.

Fig. S7 shows the MS spectra of the electrolysis of DTDA in TBAC at 25 °C.

Fig. S9 shows the MS spectra of the electrolysis of DTDA in $CoCl_2$ at 45 °C.

Fig. S10 shows the. MS spectra of the electrolysus of HexA in $CoCl_2$.

Fig. S11-14 show the graph of current vs. time of the electrolyses carried out.

Chemicals

[0044] The following chemicals were used, purchased from the indicated supplier : N,N'-di-tert-butylethylenediamine (DTDA) (Alfa Aesar, 98%), n-hexylamine (HexA) (Alfa Aesar, 99%), cobalt (II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) (Alfa Aesar, 98%), tetrabutylammonium chloride (TBAC) (Sigma-Aldrich, ≥97%), tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (Sigma-Aldrich, ≥99%) and anhydrous dimethylformamide (DMF) (Sigma-Aldrich, 99.8%) were used as purchased without further purification.

Electrochemical instrumentation and setup

[0045] Cyclic voltammetry (CV) and bulk potentiostatic electrolysis were performed using a multi-potentiostat (VSP Bio-Logic). A three-electrode borosilicate glass conical cell (80 mL, Bio-Logic), which allows temperature control and gas purging, was employed. For CV experiments, a glassy carbon disk (GCE) (d = 3 mm, A = 0.071 cm^2, Bio-Logic) was used as working electrode (WE); the counter electrode (CE) was a platinum wire (d = 0.5 mm, l = 20 mm, A = 0.32 cm^2, Bio-Logic) and a saturated calomel electrode (SCE) (Bio-Logic) with a ceramic junction was used as reference electrode, which was separated from the solution by a bridge tube containing a solution with supporting electrolyte. All potentials reported in this article are with respect to this reference electrode, unless otherwise specified. For the bulk potentionstatic electrolysis experiments, two graphite tissue pieces (40 mm x 10 mm x 50 μm, PaxiTech) were used as WE and CE, respectively. In the electrolyses, the CE was not protected from the working solution. A diagram of the electrochemical setup here used is shown in Fig. 1.

Analytical instrumentation

[0046] The products of the electrolysis reactions were evaluated using a high resolution mass spectrometer (Q Exactive Thermo Scientific) with positive electrospray ionization (HRMS-pESI) method with a resolution setting of 70000. Freshly electrolyzed samples were diluted, with methanol prior to direct infusion to the mass spectrometer.

Cyclic voltammetry analysis.

[0047] The electrochemical behavior of DTDA in the presence of the chlorides salts in DMF was characterized using cyclic voltammetry. Given that during in the oxidation of DTDA protons are released into the medium, cyclic voltammetry experiments were also carried out in the presence of the mild base HexA, which was used as a proton scavenger. Through the cyclic voltammetry analysis, the working potentials for the electrolyses were fixed. As a point of reference, the cyclic voltammetry of DTDA 4 mM, with or without an equimolar amount of HexA, using $TBAPF_6$ 0.1 M as supporting electrolyte was performed in DMF. The electrochemical behavior of either $CoCl_2$ or TBAC 0.1 M was also carried out in DMF in the absence and in the presence of the amines. For the case when $CoCl_2$ was analyzed, forward sweeps (from 0.0 to 1.4 V vs SCE) and backward sweeps (from 0.0 to -1.2 V vs SCE) were carried out. In the case for TBAC only

forward sweeps (from 0.0 to 1.6 V vs SCE) were performed. All the experiments were carried out at 25 °C and at 100 V s^{-1} unless otherwise stated.

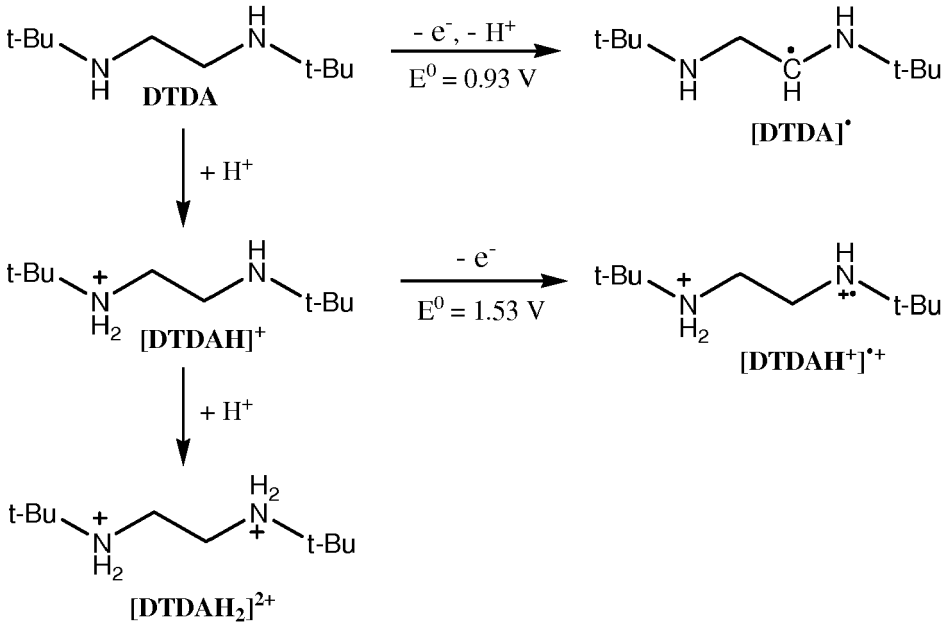
Examples : Oxidative electrolysis of N,N'-di-tert-butylethylenediamine

[0048] Oxidative electrolysis experiments were carried out following a modified method from the previously reported by Gallardo and Vila. Oxidative electrolysis experiments were carried in nitrogen gas atmosphere and at 25 °C, controlled potential electrolyses were performed in a DTDA 93 mM solution in DMF, containing HexA in an equimolar amount to DTDA and $CoCl_2$ or TBAC 0.1 M as supporting electrolyte and chloride source. The working electrode polarization potential was previously determined by CV analysis.

Electrochemical behavior of DTDA in the presence of the chloride salts in DMF

[0049] CVs of DTDA in DMF were carried out. Firstly, TBAPFs was employed as supporting electrolyte, with the purpose to serve as point of reference for the behavior observed with $CoCl_2$ and TBAC. The CV of 4 mM DTDA in DMF and 0.1 M $TBAPF_6$, at 100 mV s^{-1}, shows two irreversible oxidation peaks at 0.93 V and 1.53 V vs SCE (Fig. 2), respectively, which agrees with previously reported behavior (18). The peak at 0.93 V vs SCE is related to the monoelectronic oxidation of one of the secondary amino groups of DTDA followed by a deprotonation reaction, which occurs on the C_a-H bond next to the amino group (Scheme 2) leading to the formation of the radical species $[DTDA]^{\cdot}$. The proton released can react with a neutral molecule of DTDA, yielding a monoprotonated species ($[DTDAH]^+$) which is oxidized at 1.53 V vs SCE in a monoelectronic process to form the radical cation $[DTDAH^+]^{\cdot+}$.

[0050] As the protons released in the oxidation process may lead to the formation of a non-electroactive diprotonated species of DTDA ($[DTDAH_2]^{2+}$) (Scheme 2), the mild base, hexylamine (HexA), was added to the solution to act as a proton scavenger and avoid this step. In the presence of an equimolar amount of HexA, the CV of DTDA shows an increase in the current magnitude for the first peak and a slight displacement of the potential to 1.05 V vs SCE, while the second peak stays almost invariable (Fig. 2). As per the data reported by Gallardo and Vilá (18), this behavior was expected since the formation of $[DTDAH]^+$ is minimized in the presence of HexA. Moreover, HexA undergoes an oxidation process at 1.35 V vs SCE per se (Fig. S1, in electronic supplementary information (ESI)), which makes possible its use in the electrolysis experiments.



Scheme **2.** Reaction mechanism of the electrooxidation of N,N'-di-tert-butylethylenediamine (DTDA) and the formation of the species $[DTDAH]^+$, $[DTDAH_2]^{2+}$, $[DTDA]^{\cdot}$ and $[DTDAH^+]^{\cdot+}$. Modified from Gallardo and Vila, 2010 (18).

[0051] The electrochemical behavior of the chloride salts in the absence of amines was also carried out in DMF. Fig. 3 shows the CV of 0.1 M $CoCl_2$ in DMF at 100 mV s^{-1}. The forward sweep (from 0.0 to 1.4 V vs SCE) displays an oxidation wave from 0.95 V to 1.4 V vs SCE, whereas in the corresponding reversal sweep, a reduction peak, approximately at 0.7 V vs SCE, is observed. Also, in the backward sweep (from 0.0 to -1.2 V vs SCE), a reduction wave is observed from -1.0 V to -1.2 V vs SCE, as well as an oxidation peak in the corresponding reversal sweep about 0.0 V

vs SCE. The electrochemical behavior of $CoCl_2$, when dissolved in DMF, might be governed by its ionization equilibrium in this solvent which results in the formation of a $[Co(DMF)_6]^{2+}\cdot 2[CoCl_3(DMF)]^-$ complex electrolyte (21); thus, the reduction wave in the backward sweep and the oxidation peak in its reversal sweep may be associated to the redox processes of Co^{2+} in the $[Co(DMF)_6]^{2+}$ complex (22, 23), as follows:

$$[Co(DMF)_6]^{2+} + 2e^- \rightarrow Co^0 + 6DMF \quad (1)$$

$$Co^0 + 6DMF - 2e^- \rightarrow [Co(DMF)_6]^{2+} \quad (2)$$

[0052] Similarly, the electrochemical behavior in the forward sweep, and its corresponding reversal sweep, can be attributed to the redox process of chloride ions in the $[CoCl_3(DMF)]^-$ complex (23).

[0053] On the other hand, the CV of 0.1 M TBAC in DMF at 100 mV s^{-1} (Fig. 4) shows an oxidation current wave from 0.8 V to 1.5 V vs SCE in the forward sweep (from 0.0 to 1.6 V vs SCE) and a reduction peak at 0.4 V vs SCE in the reversal sweep. This behavior is attributed to the oxidation of the Cl- anion (24). The Cl- anion is oxidized in a process that involves a two-electron transfer from which two species may be generated, chlorine (Cl_2) and the trichloride anion (Cl_3^-) (24, 25). The reduction peak in the reversal sweep is in good agreement with the reduction of the Cl_2 formed (24). These processes are described by the following reactions:

$$2Cl^- + 2e^- \rightarrow Cl_2 \quad (3)$$

$$Cl_2 + Cl^- \leftrightarrow Cl_3^- \quad (4)$$

[0054] A different behavior was observed when DTDA and HexA were present in high concentrations (93 mM) in the solution. The CV of 93 mM DTDA in the presence of 93 mM HexA and 0.1 M $CoCl_2$ in DMF at 100 mV s^{-1} (Fig. 3) shows an oxidation wave from 0.65 V to 1.4 V vs SCE, in the forward sweep and a reduction wave from -0.25 V to -1.2 V in the backward sweep. As it can be seen in Fig. 3, the CV shape of the latter solution is completely different than when $CoCl_2$ is alone, this is because ethylenediamine derivatives can form an octahedral complex with $CoCl_2$ (26) and the CV features are consistent with the electrochemical behavior of the redox reaction of Co^{2+}/Co^{3+} in this type of complexes (27). However, when the CV is carried out at 10 mV s^{-1}(inset in Fig. 3), an oxidation peak at about 1.03 V vs SCE is noted, which could be attributed to the oxidation of DTDA. On the other hand, in the CV of DTDA 93 mM in presence of HexA 93 mM and TBAC 0.1 M in DMF, at 100 mV s^{-1} (Fig. 4), it can be observed that the oxidation current wave on the forward cycle starts at a less positive potential (0.6 V vs SCE) and its current value is higher, compared to the CV of TBAC alone, while the reduction peak in the reversal sweep disappears completely. This behavior suggests that the oxidation of Cl- is inhibited at high concentrations of DTDA, and the oxidation of the latter takes place.

Electrosynthesis of $[DTIM]^+$ through the electrolysis of DTDA using $CoCl_2$ or TBAC as supporting electrolytes in DMF

[0055] The chloride salts here evaluated are not electrochemically inert at the potentials where DTDA is oxidized (about 1.0 V vs SCE, Fig. 2) as the electrochemical window of $CoCl_2$ 0.1 M in DMF is from -1.0 V to 1.0 V vs SCE, whereas the anodic limit potential of the electrochemical window of TBAC 0.1 M in DMF is at 0.8 V vs SCE, in comparison with $TBAPF_6$ whose anodic limit potential is settled at 1.6 V (see Figs. S2-S4 in ESI). However, our evidence suggests that when DTDA is present at high concentrations (93 mM) its oxidation predominantly takes place, as the peaks associated to oxidation of the chlorides anions in $CoCl_2$ or TBAC disappear when DTDA is added (Figs. 2 and 3), thus, the possibility to use $CoCl_2$ or TBAC in the electrolysis of DTDA becomes feasible. To corroborate this, electrolysis of DTDA at controlled potentials in the presence of $CoCl_2$ or TBAC were carried out. The chosen potential was 1.03 V vs SCE for the electrolysis using $CoCl_2$ as supporting electrolyte which corresponds to the oxidation peak of DTDA 93 mM in the presence of HexA 93 mM and $CoCl_2$ in DMF at 10 mV s^{-1} (inset in Fig. 3). The working potential for the experiments with TBAC was set at 1.1 V vs SCE. As no discernible oxidation peak was found in the CV of DTDA using TBAC as supporting electrolyte, the potential chosen was determined by the potential of the oxidation peak of DTDA 93 mM in DMF and $TBAPF_6$ 0.1 M as supporting electrolyte (Fig. S5, ESI).

[0056] The theoretical charge (Q_{theor}) necessary for a complete conversion of DTDA was calculated using the following equation:

$$Q_{theor} = \frac{nFVC}{M} \quad (6)$$

where n is the number of electrons involved in the process, presumably at least 3 according to a previously reported mechanism. F is Faraday's constant (96485 C mol^{-1}), V is the volume of the working solution (L), C is the concentration of electroactive species in the solution (g L^{-1}), and M is the molecular mass of the electroactive species (g mol^{-1}).

[0057] To evaluate that the oxidation of DTDA took place at the working potentials and that the $[DTIM]^+$ cation was formed, samples of the electrolysis experiments were taken before the Q_{theor} was reached (at 36 C and 145 C, respectively, for the experiments with $CoCl_2$ and TBAC). These samples were analyzed by means of HRMS-pESI. In both cases, the MS spectra showed the presence of the peak associated to $[DTIM]^+$ (*m*/*z* 183), to DTDA (*m*/*z* 173), and other minor peaks, which confirmed that the targeted reactions were taking place; therefore, the reactions were continued until the reaction reached the Q_{theor}. These spectra can be found in the Fig. S6 and Fig. S7 of ESI.

[0058] By the end of electrolysis, the MS spectra of freshly electrolyzed samples from the reaction in presence of $CoCl_2$ (Fig. 5a) displayed the presence of a peak associated to DTDA (*m*/*z* 173) together with $[DTIM]^+$ (*m*/*z* 183), as well as two other important byproducts (*m*/*z* 157 and 213). Performing the reaction at temperatures (below or above 25 °C) did not improve the selectivity of the reaction nor the full conversion of DTDA to $[DTIM]^+$. The MS spectra of the reactions carried out at 15 °C and 45 °C can be found, respectively, in Fig. S8 and Fig. S9 of ESI. An electrolysis experiment containing only HexA in the presence of $CoCl_2$ at the same conditions allowed to identify the byproducts (*m*/*z* 157 and 213) as products of the oxidation of HexA (Fig. S10 in ESI). These results indicate that when $CoCl_2$ is used as supporting electrolyte, parallel reactions to the oxidation of DTDA occur and therefore the complete conversion of the latter is not achieved even when the total Q_{theor} is consumed.

[0059] In contrast, when the electrolysis of DTDA is performed in the presence of TBAC, the MS spectrum (Fig. 5b) of a freshly electrolyzed sample, shows that the presence of DTDA is almost negligible, and the peak for $[DTIM]^+$ has the highest relative abundance; although some byproducts from the oxidation of HexA are still present in far less relative abundance, DTDA is completely oxidized. These results indicate that the reaction in TBAC is more selective than in $CoCl_2$, possibly because DTDA is not forming complexes in the solution; besides, the oxidation of Cl- does not seem to hamper the electrolysis of DTDA. It is also important to note that in some cases the formation of a water adduct of $[DTIM]^+$ cation (*m*/*z* 201) was evidenced in the MS spectra (Fig. 5b and Fig. S8 in ESI) indicating that the presence of water in the system may lead to the formation of another undesired byproduct. Graphs of "current vs time" of the electrolysis of all cases here described can be found in the ESI (Figs. S11-S14).

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[0060]

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Claims

1. A method for the electrochemical production of an aprotic ionic liquid of a cation and a halide based anion X-, wherein a reaction mixture containing a solvent, a supporting electrolyte, an anion source and a reactant which responds to formula

$$R'_m\text{-}Y^1\text{-}(CR)_n\text{-}Y^2\text{-}R''_p \qquad (1)$$

wherein

- Y^1 and Y^2 may be the same or different and are selected from the group of N, P and S
- m and p may be the same or different and may be 2 or 3,
- all R' may be the same or different, all R" may be the same or different, R' may be the same as or different from R" and may, independently of each other be H, a straight chain or a branched saturated alkyl group, a cyclic alkyl group or an aromatic hydrocarbon moiety
- At least one R next to Y^1 is CH_2
- And n is at least 1, preferably at least 2, more preferably maximum 10, most preferably n is 1, 2 or 3,

wherein Y is N, P or S
is subjected to an anodic electrochemical potential to cause oxidative electrolysis of the reactant, wherein the supporting electrolyte simultaneously functions as anion source and comprises a salt of the halide ion X^-, selected from the group of fluoride, chloride, bromide or iodide.

2. A method as claimed in claim 1 wherein the halide salt is a salt selected from the group of $M^{2+}X_2$, $M^{3+}X_3$ or a halide salt of an organic protic cation, wherein M^{2+} and M^{3+} are respectively divalent and trivalent metal cations, wherein the halide X is preferably chloride.

3. A method as claimed in claim 2, wherein the halide salt is $FeCl_3$, $NiCl_2$, $CoCl_2$ or an organic ammonium chloride, preferably an alkylammonium chloride, more preferably organic ammonium chloride, preferably an alkylammonium chloride, more preferably tetramethylammonium chloride, tetraethylammonium chloride, tetrabutylammonium chloride, choline chloride or benzalkonium chloride.

4. A method as claimed in any of the previous claims, wherein the reactant is selected from the group of a diamine, a phosphine and a dithiol.

5. A method as claimed in any of the previous claims, wherein the reactant is a di-amine which responds to the formula :

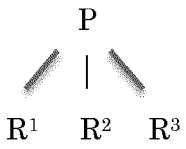
$$R^1R^3\text{-}N\text{-}(CR^2)_n\text{-}N\text{-}R^4R^5 \qquad (2)$$

wherein

- R^1, R^2,R^3, R^4, R^5 may be the same or different and may, independently of each other be H, a straight chain or a branched saturated alkyl group, a cyclic alkyl group or an aromatic hydrocarbon moiety
- At least one R^2 next to the N is CH_2
- And n is at least 1, preferably at least 2, more preferably maximum 10, most preferably n is 1, 2 or 3.

6. A method as claimed in claim 4, wherein the reactant is a di-amine selected from the group of an N,N'-dialkylethylenediamine and an N,N'-dialkylpropanediamine, preferably a 1,3-dialkylethylenediamine and a 1,3-dialkylpropanediamine, more preferably the reactant is selected from the group of N, N'-ethylethylenediamine, N,N'-dipropylethylenediamine, N,N'-di-tert-butylethylenediamine and N,N'-dimethylpropanediamine, N,N'-di-ethylpropanediamine, N.N'-dipropylpropanediamine (or derivatives of the afore-mentioned compounds.

7. A method as claimed in claim 4, wherein the phosphine is a compound which respond to the formula :



(3)

Wherein R^1, R^2,R^3, may be the same or different and may, independently of each other be H, a straight chain or a branched saturated alkyl group, a cyclic alkyl group or an aromatic hydrocarbon moiety.

8. A method as claimed in any of the previous claims, wherein , a molar ratio of the concentration of the reactant with respect to the halide salt varies between 0.9 and 1.5, preferably between 0.9 and stoichiometric.

9. A method as claimed in any of the previous claims, wherein the reaction mixture further contains a proton scavenger, preferably a weak Bronsted base having a pKb which is lower than a pKb of the reactant, more preferably a weak Bronsted base having a pKb of at least 2.5 and not more than 4, preferably not more 3.5.

10. A method as claimed in claim 9, wherein the proton scavenger is selected from the group of aliphatic amines, cyclic amines and aromatic amines, preferably hexylamine or wherein proton scavenging is achieved by cathodic deprotonation.

11. A method as claimed in claim 9 or 10, wherein the amount of proton scavenger supplied to the reaction mixture is at least equimolar to the amount of reactant and halogen salt contained in the reaction mixture.

12. A method as claimed in any of the previous claims, wherein the reaction mixture contains less than 100.00 ppm of water.

13. A method as claimed in any of the previous claims, wherein the electrochemical reaction is carried out in inert atmosphere, preferably in a nitrogen gas atmosphere.

14. A method as claimed in any of the previous claims, wherein the method mixture contains an aprotic organic solvent, preferably selected from the group of dimethylformamide, dimethylsulfoxide (DMSO), acetonitrile,

15. A method as carried out in any of the previous claims, wherein the electrochemical reaction is carried out at a constant temperature between10 °C and 75 °C, preferably between 10 °C and 60 °C, more preferably between 15 °C and 60°C or between 15 °C and 50°C, most preferably between 15 °C and 45 °C.

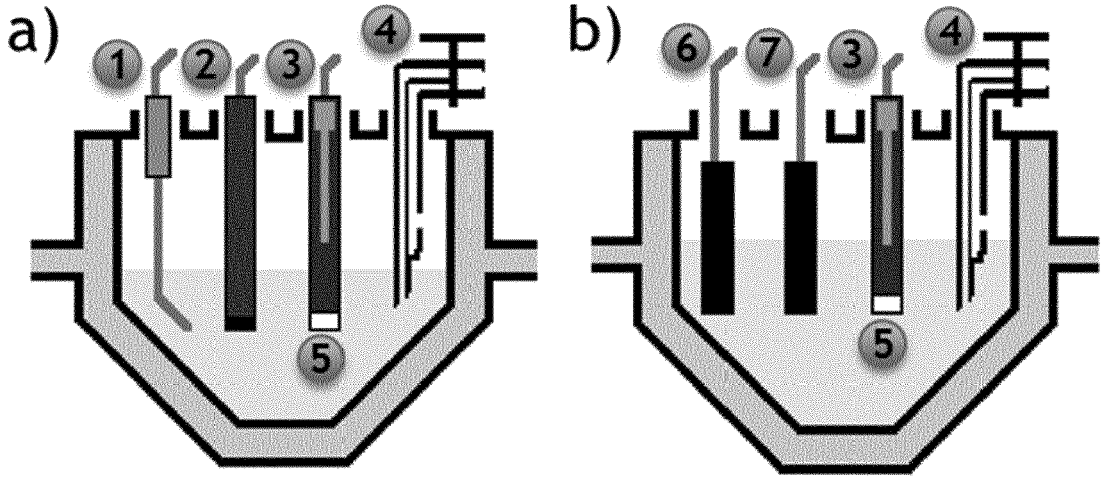


Fig. 1. Diagram of the electrochemical setup for: a) Cyclic voltammetry experiments, b) Electrolysis reactions. 1. Pt counter electrode, 2. Glassy carbon electrode, 3. Saturated calomel electrode, 4. Purge tube, 5. Bridge tube, 6. Graphite tissue counter electrode, 7. Graphite tissue working electrode.

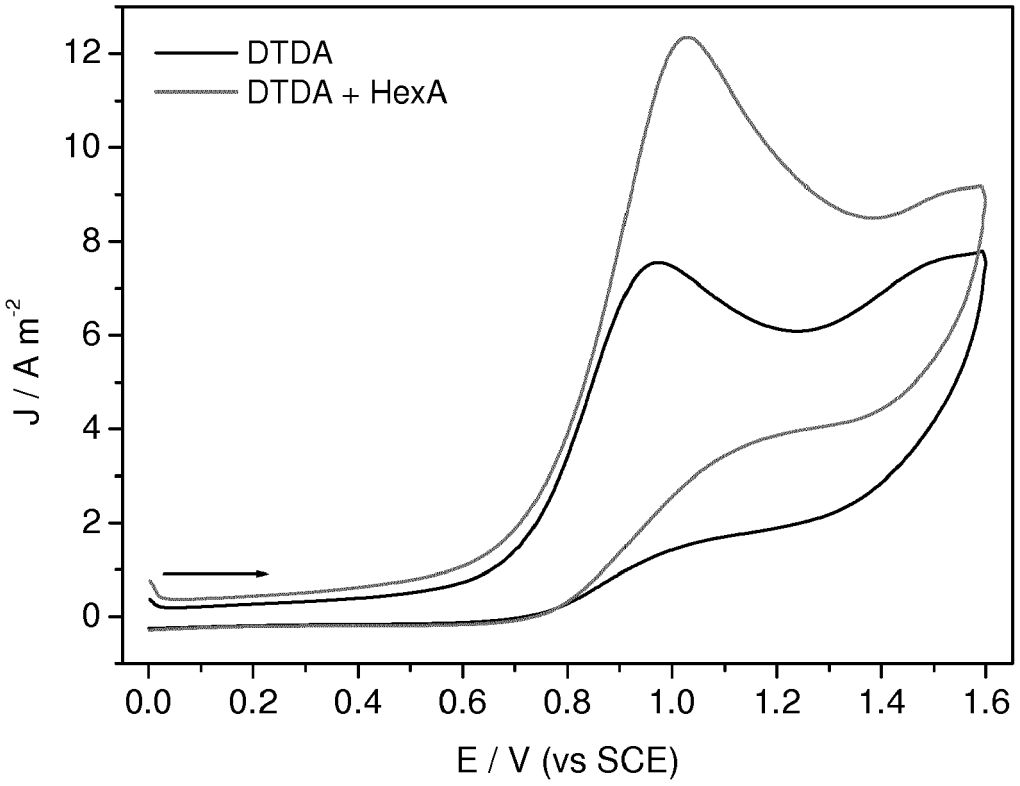


Fig. 2. CV of DTDA 4 mM (—) and DTDA 4mM + HexA 4 mM (—), in DMF and $TBAPF_6$ 0.1 M as supporting electrolyte, on a glassy carbon electrode (GCE) (ø = 3.0 mm) at 100 mV s^{-1}. Forward sweep →.

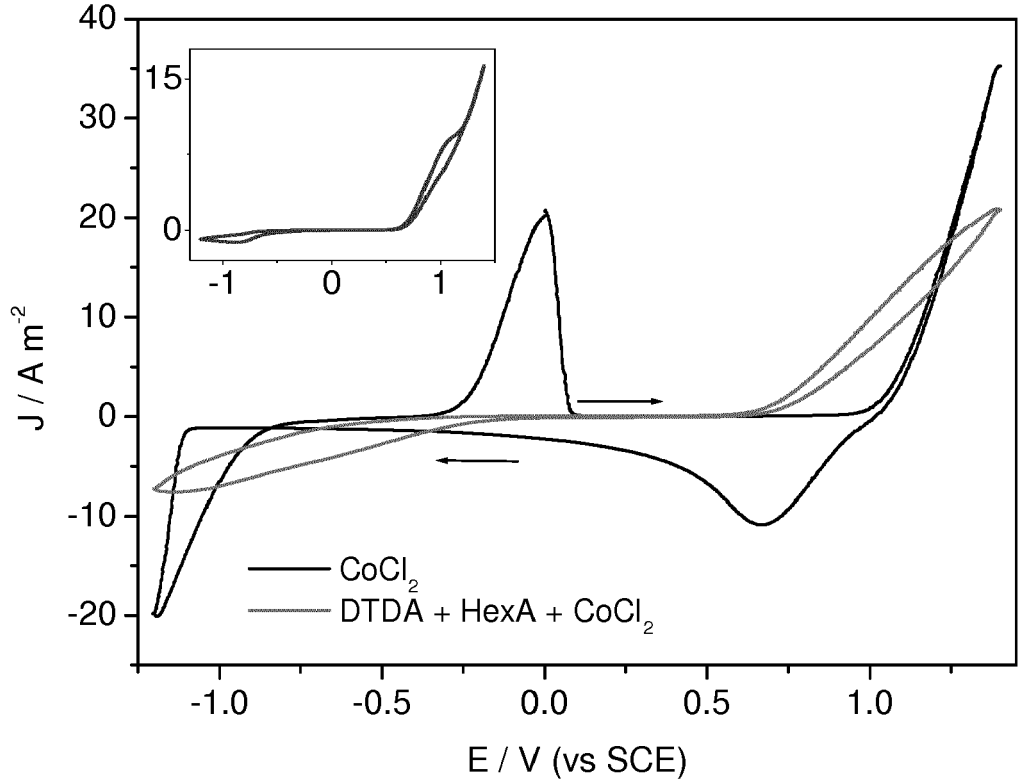


Fig. 3. CV of 0.1 M $CoCl_2$ (—) and 93 mM DTDA + 93 mM HexA in 0.1 M $CoCl_2$ (—) in DMF, on a glassy carbon electrode GCE (ø = 3.0 mm) at 100 mV s^{-1}. Inset figure: CV of 93 mM DTDA + 93 mM HexA in 0.1 M $CoCl_2$ at 10 mV s^{-1}. Forward sweep →; backward sweep ←.

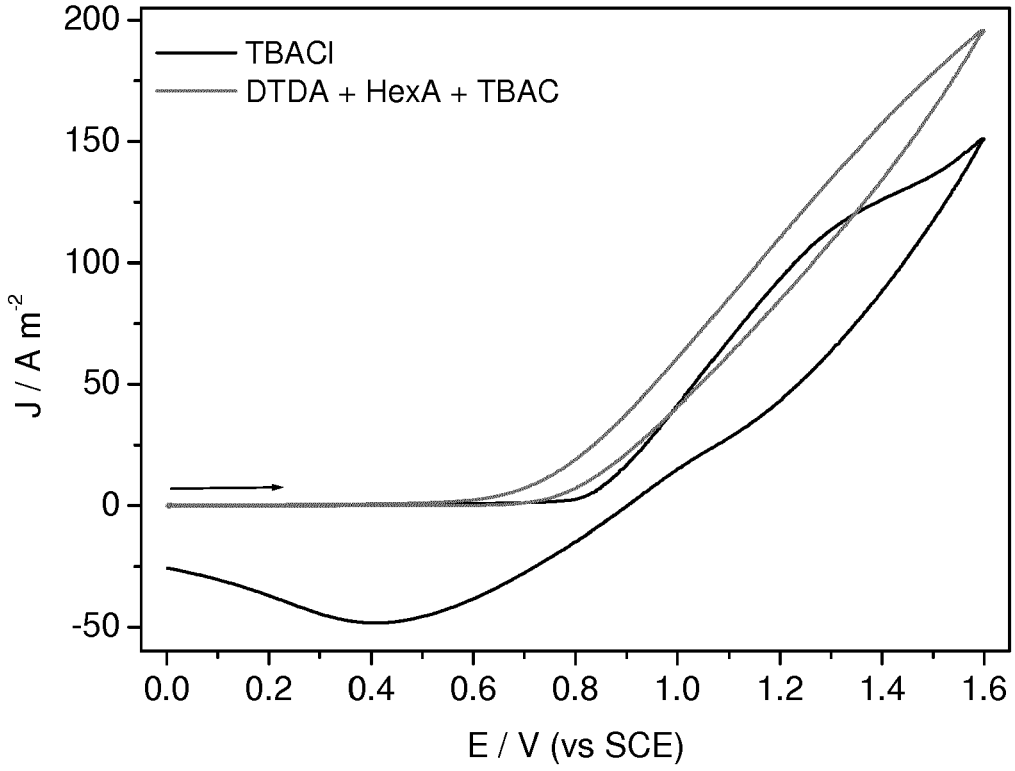


Fig. 4. CVs of 0.1 M TBAC (—) and 93 mM DTDA + 93 mM HexA + 0.1 M TBAC (—) in DMF, on a glassy carbon electrode (GCE) (ø = 3.0 mm) at 100 mV s^{-1}. Forward sweep →.

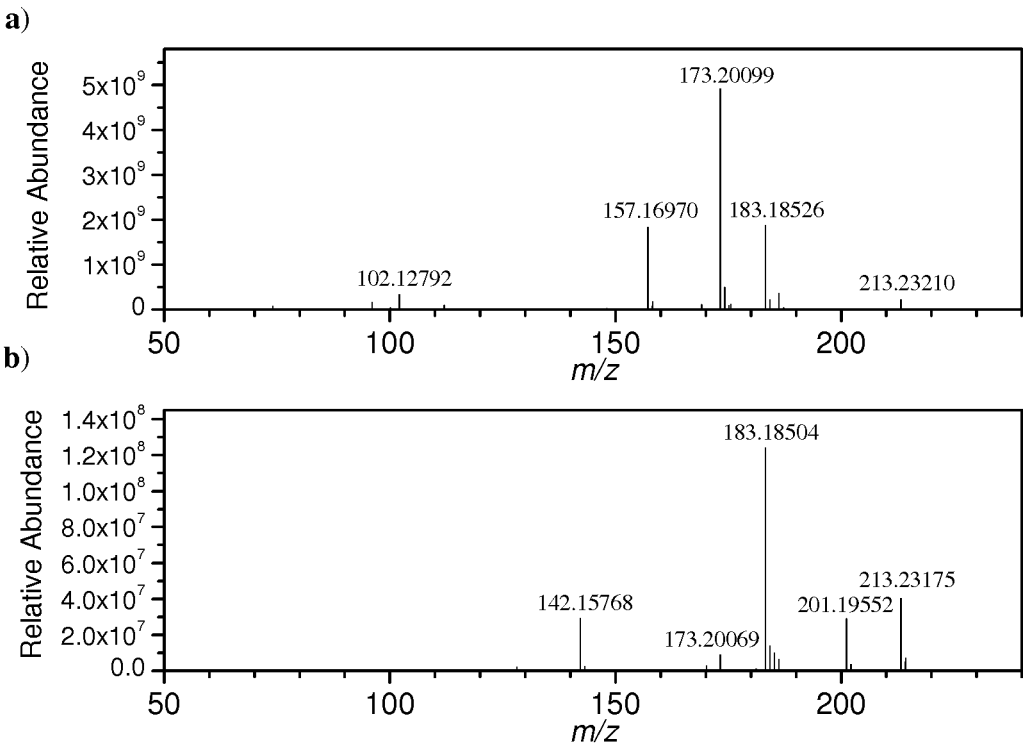


Fig. 5. MS spectra of the freshly electrolyzed solutions of the electrolysis of DTDA after consumption of Q_{theor}. a) Reaction carried out in $CoCl_2$. b) Reaction carried out in TBAC.

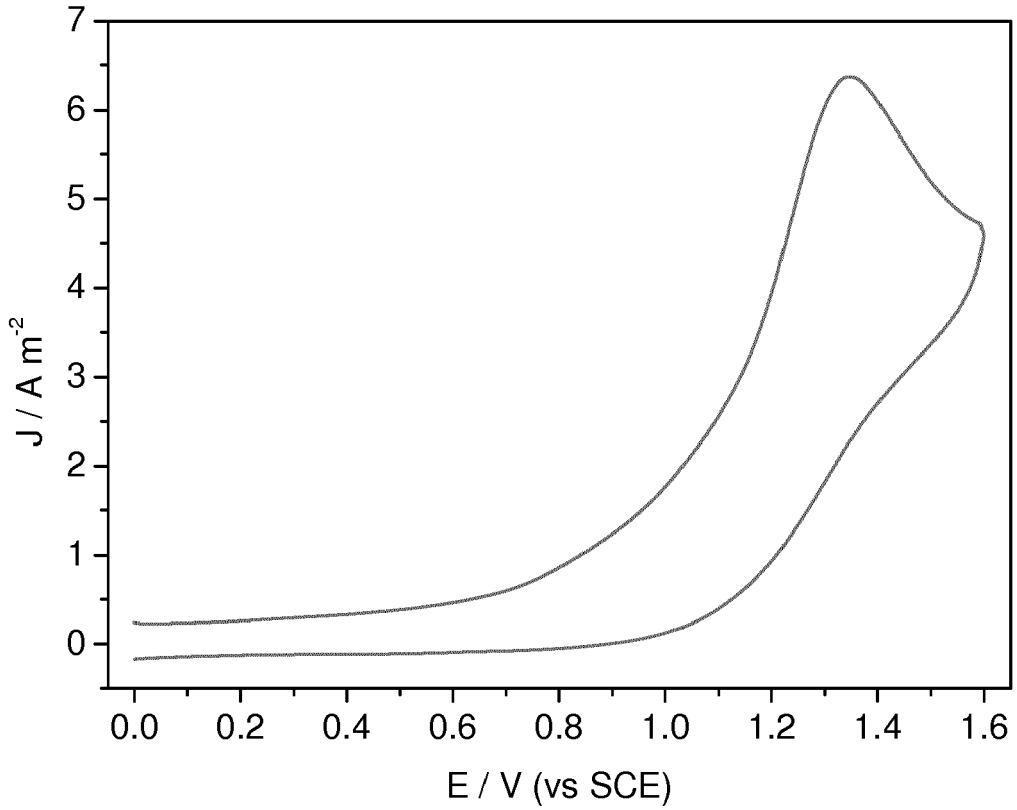


Fig. S1. CV of HexA 4 mM in DMF and $TBAPF_6$ 0.1 M as supporting electrolyte, on a glassy carbon electrode (GCE) (ø = 3.0 mm) at 100 mV s^{-1}.

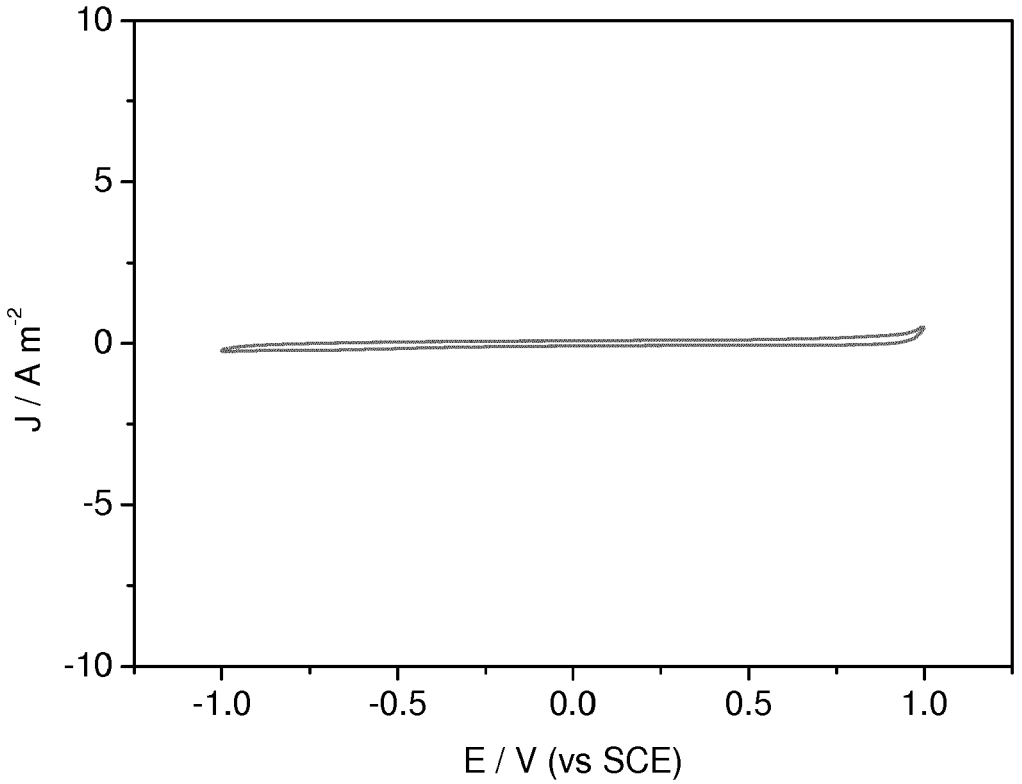


Fig. S2. CV showing the electrochemical window of $CoCl_2$ 0.1 M in DMF, on a glassy carbon electrode (GCE) (ø = 3.0 mm) at 100 mV s^{-1}. From –1.0 V to 1.0 V vs SCE.

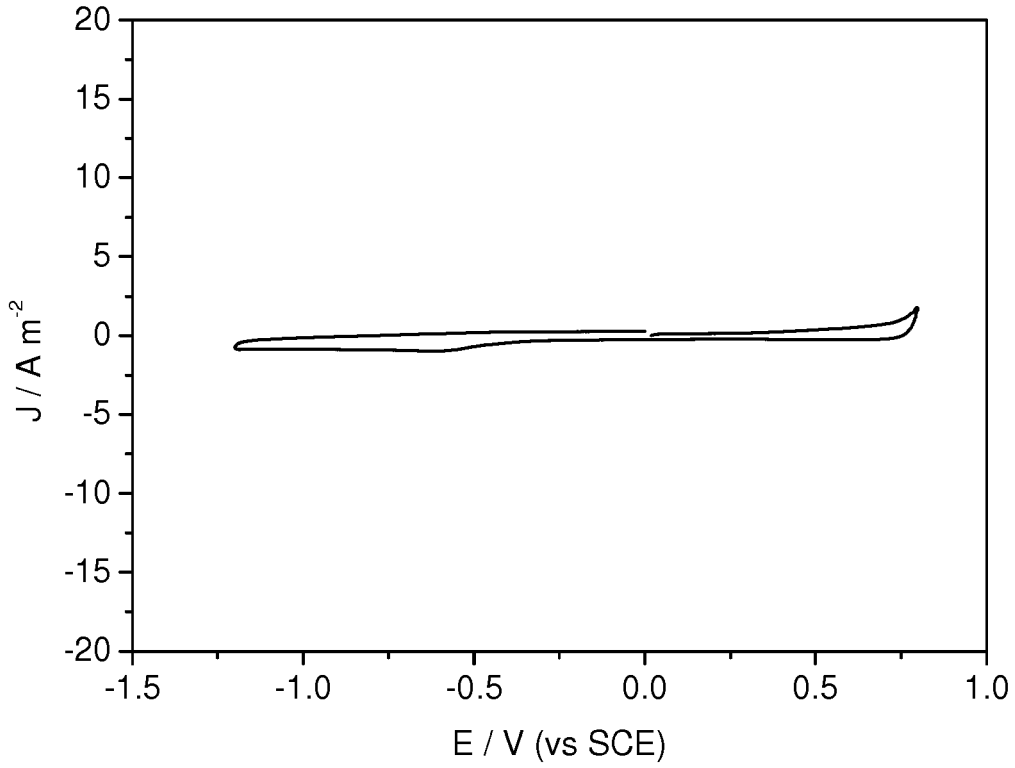


Fig. S3. CV showing the electrochemical window of TBAC 0.1 M in DMF, on a glassy carbon electrode (GCE) (ø = 3.0 mm) at 100 mV s^{-1}. From –1.2 V to 0.8 V vs SCE (Note: potentials below 1.2 V were not explored as it was not the purpose of the research).

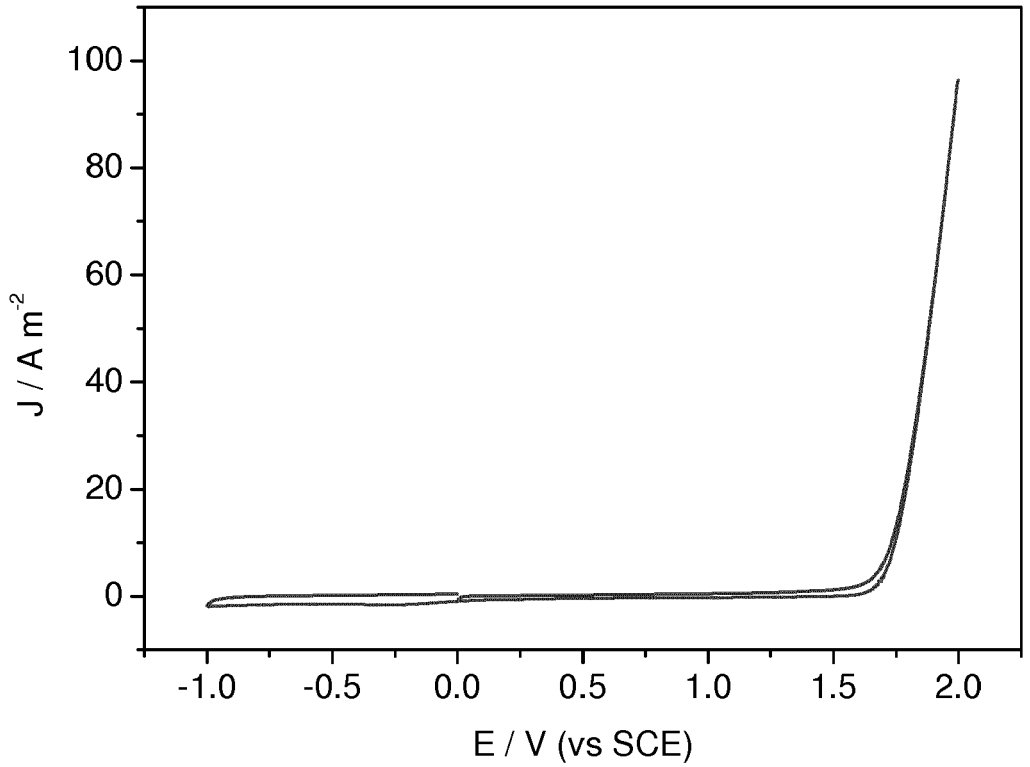


Fig. S4. CV of $TBAPF_6$ 0.1 M in DMF, on a glassy carbon electrode (GCE) (ø = 3.0 mm) at 100 mV s^{-1}. From –1.2 V to 2.0 V vs SCE.

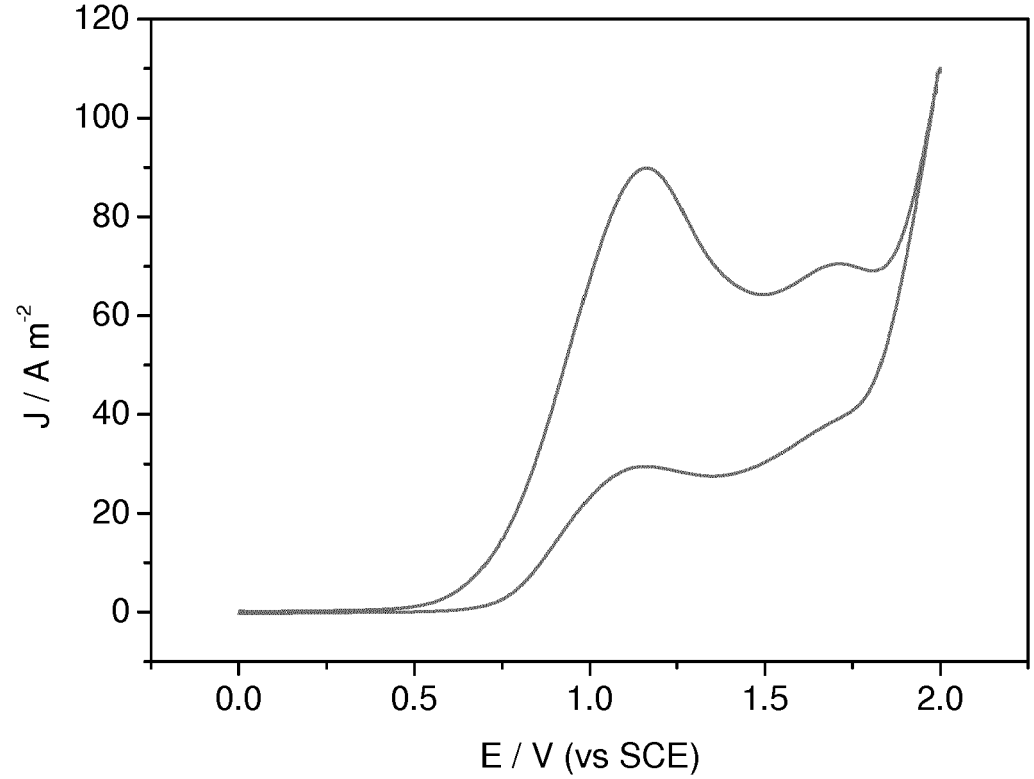


Fig. S5. CV of DTDA 93 mM in DMF and $TBAPF_6$ 0.1 M as supporting electrolyte, on a glassy carbon electrode (GCE) (ø = 3.0 mm) at 100 mV s^{-1}.

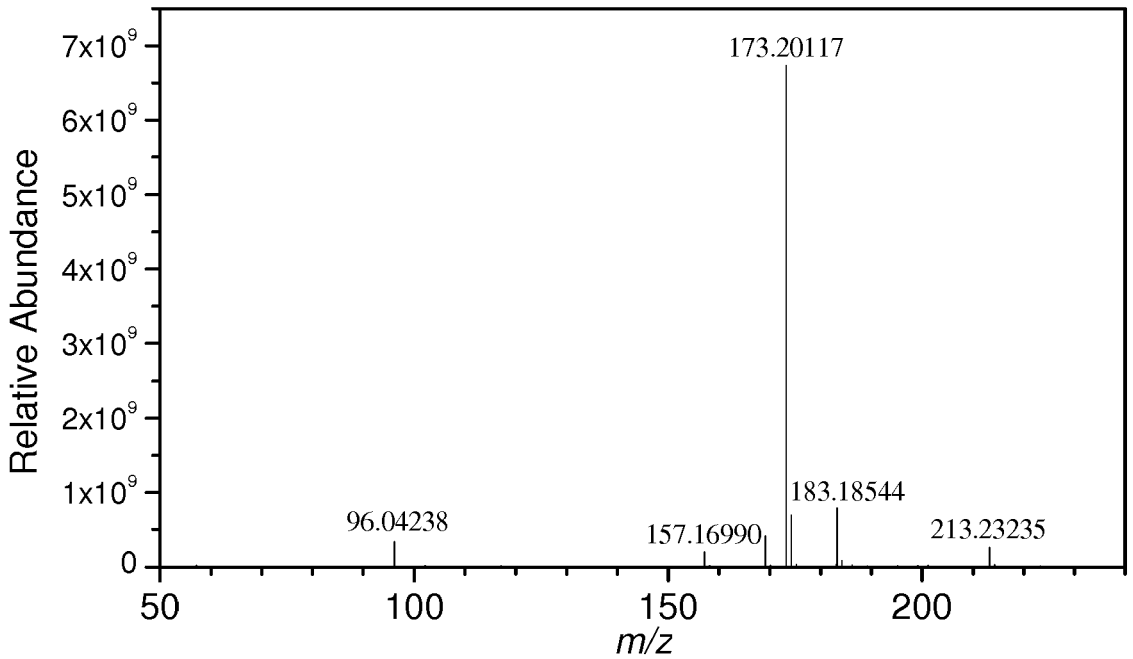


Fig. S6. MS spectra of the electrolysis of DTDA in the presence of $CoCl_2$ 0.1 M in DMF at 25 °C after 36 C were consumed.

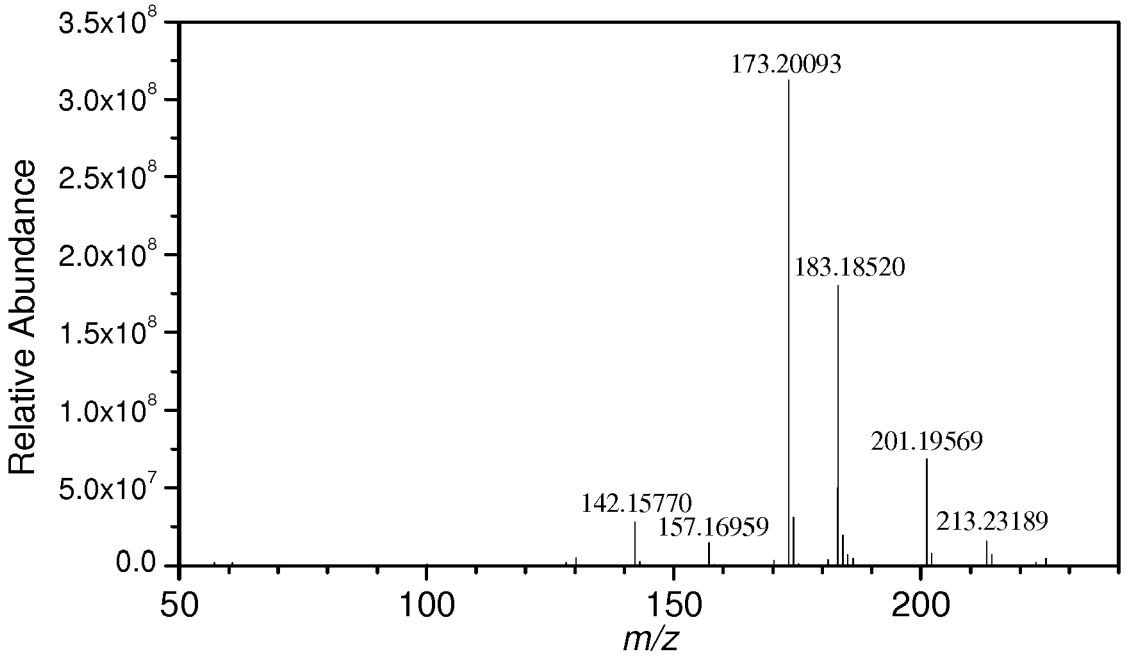


Fig. S7. MS spectra of the electrolysis of DTDA in the presence of TBAC 0.1 M in DMF at 25 °C after 146 C were consumed.

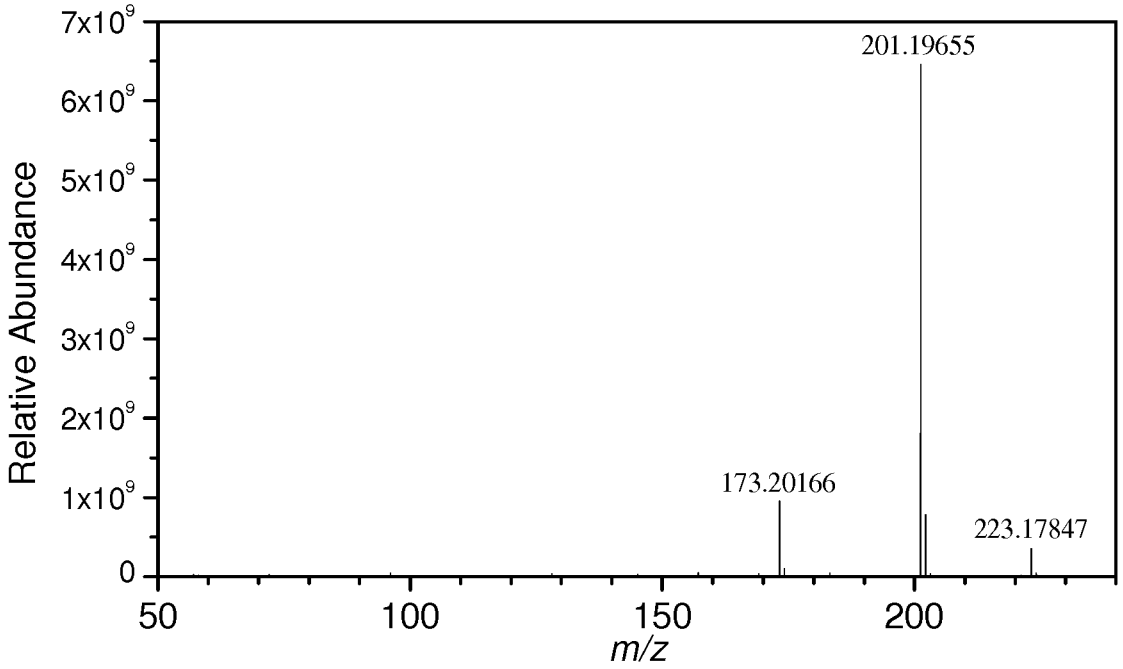


Fig. S8. MS spectra of the electrolysis of DTDA in the presence of $CoCl_2$ 0.1 M in DMF at 15 °C.

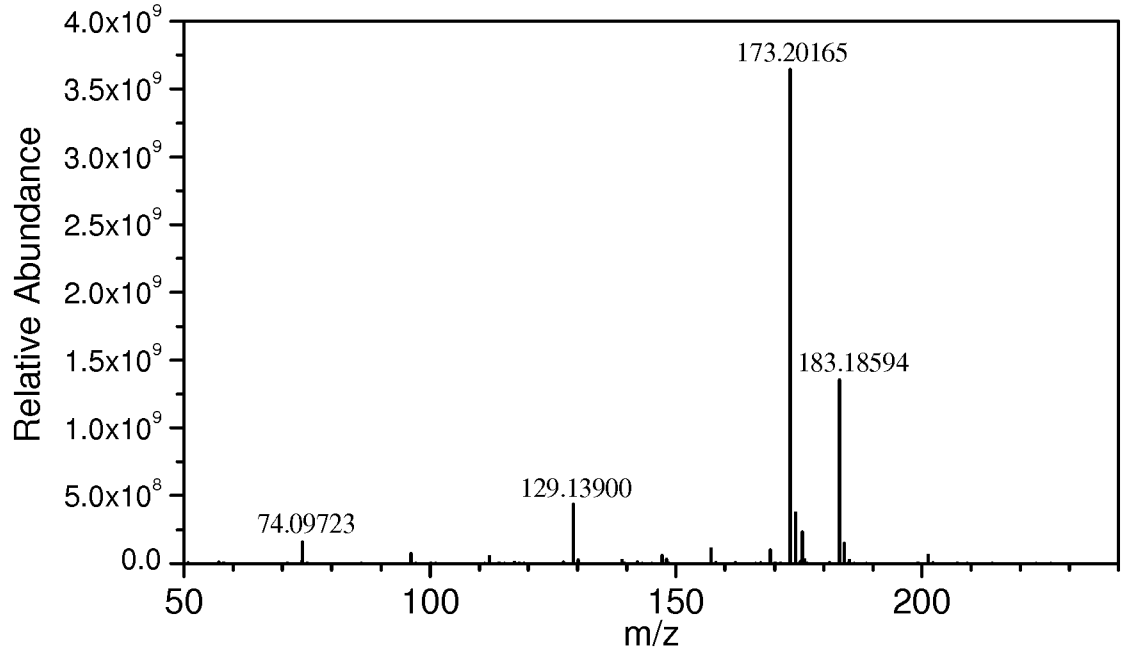


Fig. S9. MS spectra of the electrolysis of DTDA in the presence of $CoCl_2$ 0.1 M in DMF at 45 °C.

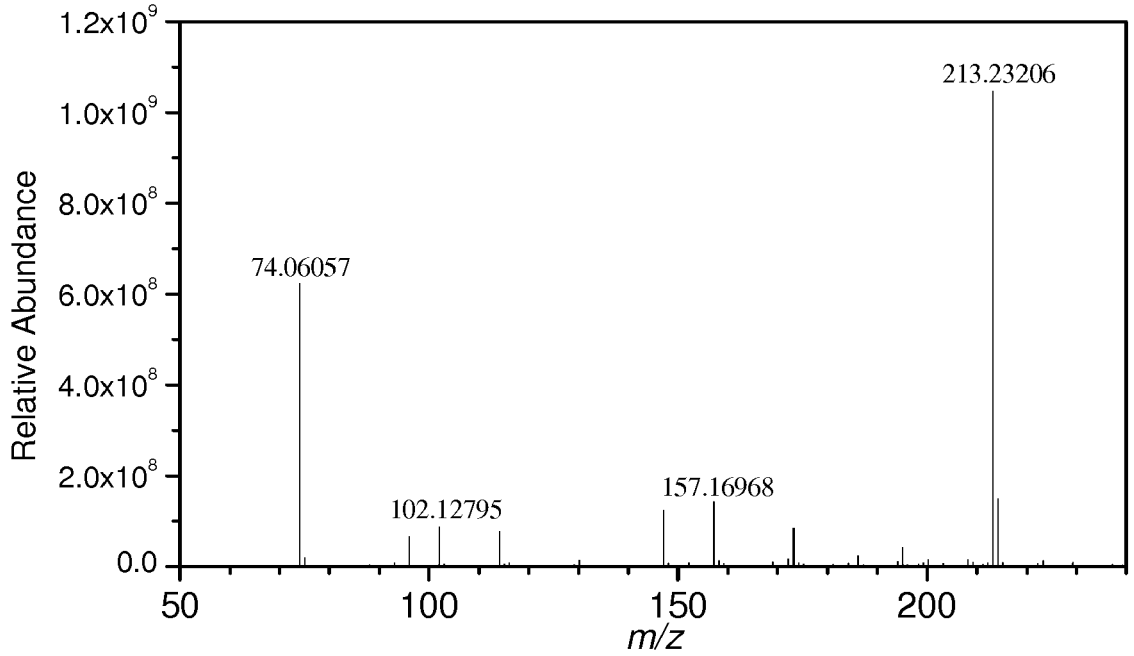


Fig. S10. MS spectra of the electrolysis of HexA in the presence of $CoCl_2$ 0.1 M in DMF at 25 °C.

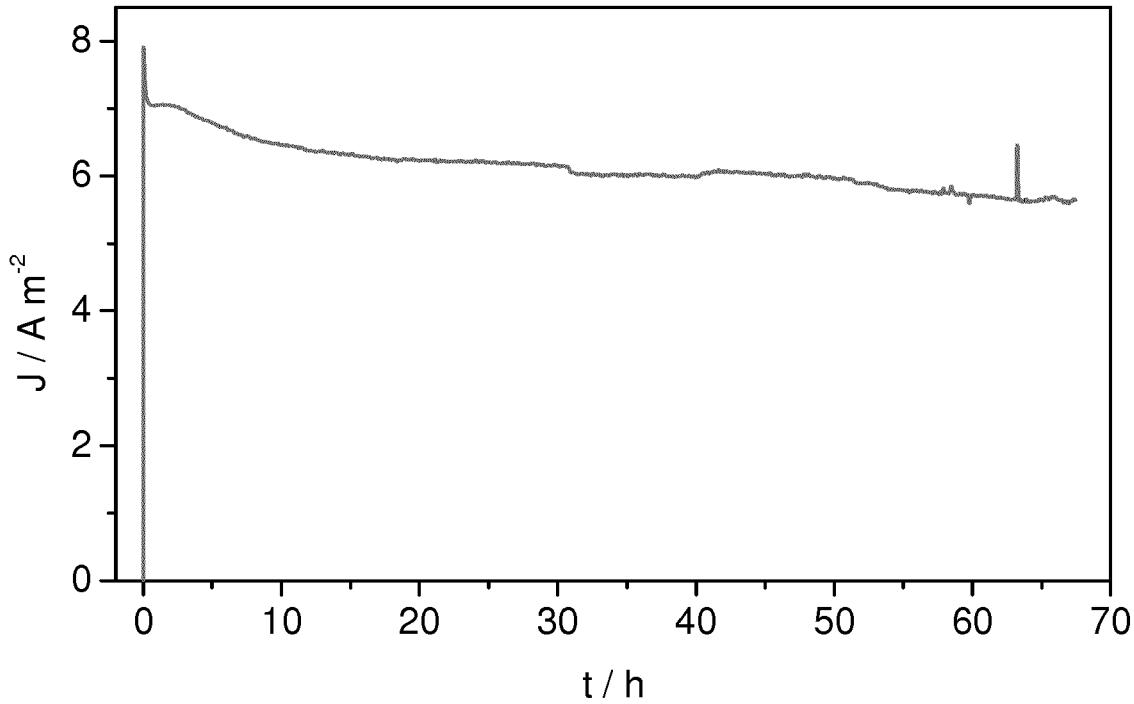


Fig. S11. Graph of current vs time of the electrolysis of DTDA in the presence of $CoCl_2$ 0.1 M in DMF at 25 °C and 1.03 V vs SCE.

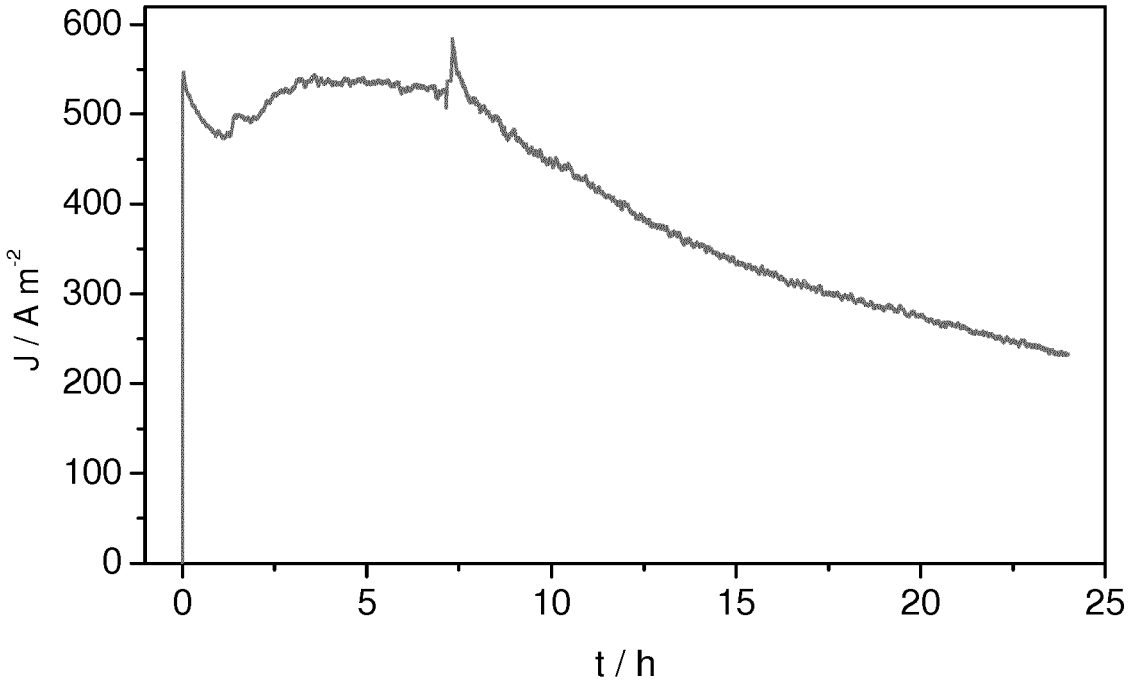


Fig. S12. Graph of current vs time of the electrolysis of DTDA in the presence of TBAC 0.1 M in DMF at 25 °C and 1.1 V vs SCE.

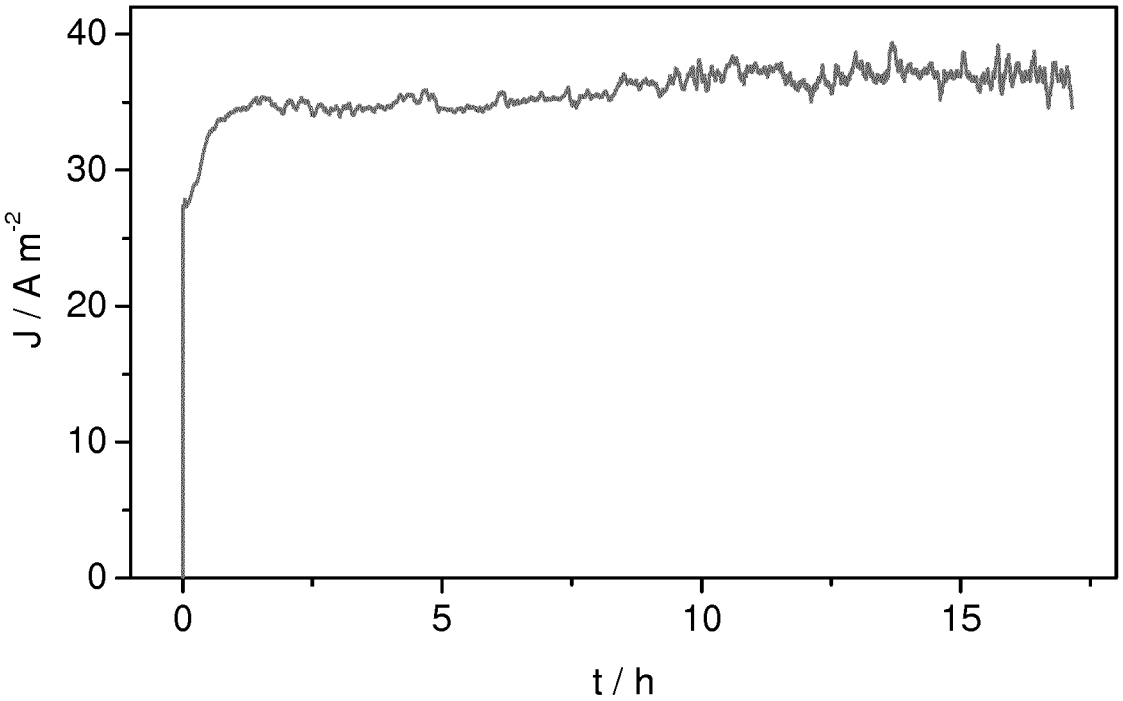


Fig. S13. Graph of current vs time of the electrolysis of DTDA in the presence of $CoCl_2$ 0.1 M in DMF at 15 °C and 1.03 V vs SCE.

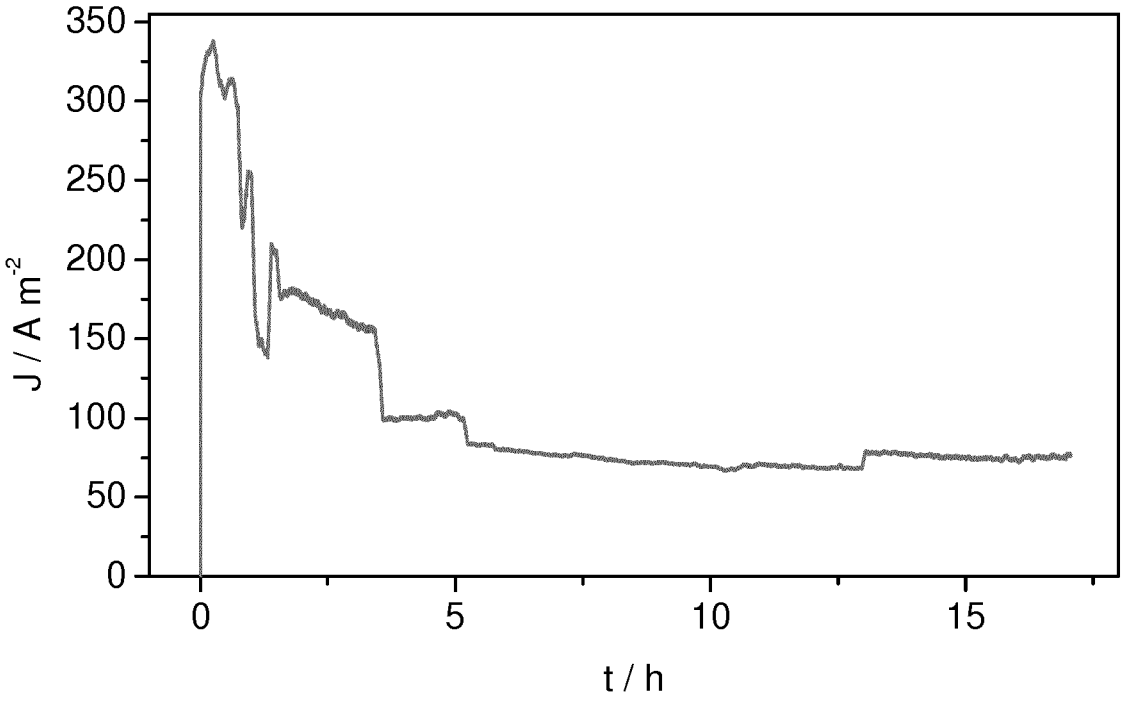


Fig. S14. Graph of current vs time of the electrolysis of DTDA in the presence of $CoCl_2$ 0.1 M in DMF at 45 °C and 1.03 V vs SCE.

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EUROPEAN SEARCH REPORT

Application Number
EP 17 17 6456

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y,D	ILUMINADA GALLARDO ET AL: "One-Pot Electrosynthesis of Substituted Imidazolinium and Tetrahydropyrimidinium Salts from Secondary Alkyldiamines: An Electrochemical Route toward Ionic Liquids", THE JOURNAL OF ORGANIC CHEMISTRY, vol. 75, no. 3, 5 February 2010 (2010-02-05), pages 680-689, XP055050539, ISSN: 0022-3263, DOI: 10.1021/jo9017606 * the whole document *	1-6,8-15	INV. C25B3/02
Y,D	NIKITIN E V ET AL: "Electrochemical synthesis of diphosphonium salts, their reactivity and role in organic electrosynthesis", ELECTROCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS, BARKING, GB, vol. 42, no. 13, 1 January 1997 (1997-01-01), pages 2217-2224, XP004061817, ISSN: 0013-4686, DOI: 10.1016/S0013-4686(97)85502-8 * the whole document *	1-4,7-15	TECHNICAL FIELDS SEARCHED (IPC) C25B
Y	US 4 638 064 A (WANG PEN-CHUNG [US] ET AL) 20 January 1987 (1987-01-20) * column 4, lines 2-11; claims 1, 8 *	1-15	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	14 September 2017	Ritter, Thomas

CATEGORY OF CITED DOCUMENTS

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US 4638064 A	20-01-1987	NONE	

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