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1 **Assessment of the photocatalytic transformation of pyridinium-based ionic liquids**
2 **in water.**

3

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15 **Abstract**

16 We studied some ionic liquids (ILs) belonging to the pyridinium class under photocatalytic treatment. In
17 particularly, we analysed how the length of the alkyl chain, the kind of inorganic ion and the type of
18 substituents could influence the disappearance rate, the mineralization extent, the acute toxicity and the
19 transformation mechanism. For such, we selected some pyridinium derivatives with different alkyl chain but
20 the same anion, namely tetrafluoroborate (1-ethylpyridinium, 1-butylpyridinium, 1-hexylpyridinium), with
21 two alkyl substituents (4-methyl-1-butylpyridium) and with a different substituent (1-
22 cyanopropylpyridinium). Then, on a selected IL (1-butylpyridinium), we evaluate the role of different
23 inorganic anions (bromine and chlorine). The results show that irrespective to the alkyl chain or the number
24 of substituents, the transformation involved an attack to the alkyl chain, proceeded through the formation
25 of harmless compounds and the mineralization was easily achieved within 4 h. Nitrogen was mainly released
26 as ammonium ion. When introducing a cyano group, the extent of nitrate ions and the number of possible
27 transformation route increased. Conversely, the type of inorganic ion deeply affected the transformation
28 pathways and the extent of mineralization. Actually, in the presence of bromide as anion, IL was only partially
29 mineralized and the formation of highly persistent transformation products occurred.

30

31 **Keywords:** TiO₂, pyridinium-based ionic liquids, photocatalysis, toxicity, transformation products

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35 1. Introduction

36 Ionic liquids (ILs) at ordinary temperature are receiving considerable attention for application in different
37 fields [1,2], i.e. lithium ion batteries [3], gas separation and handling [4,5], metal plating [6], dye sensitized
38 solar cells, and as paint or polymer additives [7,8].

39 Due to their high stability, it can be expected in the near future the presence of significant amounts of ILs in
40 wastewaters, with consequent further release into natural waters. If their low vapor pressure can preserve
41 the atmosphere from the emission of toxic vapors, on the other hand their stability could make them
42 hazardous to water and soil [9-12]. ILs partition in the environment is deeply influenced by their
43 hydrophobicity. Surface water is the first environmental compartment in which ILs are spread as a result of
44 industrial and laboratories waste. Therefore, we would expect to find more hydrophilic or polar ILs in surface
45 water, while ILs with longer side chains could be distributed preferably in soils [13]. Hydrophobic ILs are
46 linked to sediments and could behave as persistent pollutants, while hydrophilic ILs are more bioavailable
47 [11]. Derivatives with short or hydroxylated chains are less adsorbed, but become more mobile in soils and
48 can be issued more rapidly in surface waters and groundwater [14], causing contamination. The anionic
49 component can influence adsorption as well as the cationic one; in particular ionic liquids endowed with
50 anions able to form ion pairs show a greater adsorption in the soil [15].

51 Among the various biotic and abiotic transformation processes [16-18], photochemistry is a potentially
52 important attenuation route influencing ILs fate in surface waters [19, 20]. Moreover, some studies showed
53 that ILs are more toxic for cells in comparison to conventional solvents; in particular, the most common
54 imidazolium based compounds showed high resistance toward microbial degradation [10].

55 Thus, it is important to develop efficient methods for a complete and safe ILs removal [21-23]. Recently,
56 several studies describe the use of advanced oxidation processes towards ILs decomposition [24-31], while
57 at present studies on the identification of their transformation product are scarce [30].

58 In this study, we investigated about the efficiency of heterogeneous photocatalysis toward the degradation
59 of ILs holding different hydrophilicity and inorganic ions by assessing their transformation mechanisms and
60 the extent of the mineralization process. The mutual influence of anion and cation was studied in detail. An
61 hybrid linear trap-high resolution orbitrap was employed to identify the intermediate products formed during
62 the course of ionic liquid degradation.

63

64 2. Experimental section

65 2.1. Materials and Reagents

66 1-Ethylpyridinium tetrafluoroborate (**EP-TFB**) (98%), 1-butylpyridinium bromide (**BP-Br**) ($\geq 99\%$), 1-(3-
67 cyanopropyl)pyridinium chloride (**CPP-Cl**) (98.5%), 1-butyl-4-methylpyridinium tetrafluoroborate (**4-BMP-**

68 **TFB**) ($\geq 97.0\%$), acetonitrile ($\geq 99.9\%$), formic acid (99%) and phosphoric acid were purchased from Sigma
69 Aldrich, Milan, Italy.

70 1-Butylpyridinium chloride (**BP-Cl**) (99%), 1-butylpyridinium tetrafluoroborate (**BP-TFB**) ($\geq 98\%$), 1-
71 hexylpyridinium tetrafluoroborate (**HP-TFB**) (99%) and 1-butyl-3-methylpyridinium bromide (**3-BMP-Br**)
72 (99%) were purchased from IoLiTec Ionic Liquids Technologies GmbH (Deutschland).

73 All aqueous solutions were prepared with ultrapure water Millipore Milli-Q™. TiO₂P25 (Evonik Industries,
74 Italy) was used as photocatalyst.

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76

2.2. Irradiation procedures

77 Irradiation experiments were performed in stirred cylindrical Pyrex cells containing 5 ml of aqueous
78 dispersions with 20 mg L⁻¹ of analyte and 200 mg L⁻¹ of TiO₂. A Blacklight Philips TLK 05 (40W) lamp source
79 with emission maximum at 360 nm was employed for irradiation. The dispersions at the end of the irradiation
80 were filtered through 0.45 μ m Millex LCR hydrophilic PTFE membranes (Millipore) before the analysis.

81

2.3. Analytical procedures

2.3.1. Liquid Chromatography-MS

84 All samples were analyzed by HPLC/HRMS. The chromatographic separations, monitored using an MS
85 analyzer, were carried out with a Phenomenex Gemini NX C18 150 \times 2.1 mm \times 3 μ m particle size
86 (Phenomenex, Bologna, Italy), using an Ultimate 3000 HPLC instrument (Dionex, Thermo Scientific, Milan,
87 Italy). The Injection volume was 20 μ L and the flow rate 200 μ L/min. The following gradient mobile phase
88 composition was adopted: 5/95 to 95/5 in 27 min acetonitrile/5 mM heptafluorobutanoic acid in water.

89 A LTQ Orbitrap mass spectrometer (Thermo Scientific, Milan, Italy) equipped with an ESI ion source was used.
90 The LC column effluent was delivered into the ion source using nitrogen as both sheath and auxiliary gas. The
91 capillary voltage and tube lens voltage in the ESI source were maintained at 28 V and 70 V, respectively. The
92 source voltage was set to 4.5 kV (in positive ion mode). The capillary temperature was maintained at 270°C.
93 The acquisition method used was optimized beforehand in the tuning sections for the parent compound
94 (capillary, magnetic lenses and collimating octapole voltages) to achieve maximum sensitivity. Mass accuracy
95 of recorded ions (vs calculated) was ± 10 millimass units (mmu, without internal calibration).

96 Analyses were run using full scan MS (50-1000 m/z range), MS² acquisition in the positive ion mode, with a
97 resolution of 30000 (500 m/z FWHM) in FTMS (full transmission) mode. The ions submitted to MS² acquisition
98 were chosen on the base of full MS spectra abundance without using automatic dependent scan. Collision
99 energy was set to 30 % for all of the MS² acquisition methods. MS² acquisition range was between the values
100 of ion trap cut-off and m/z of the (M+H)⁺ ion. Xcalibur (Thermo Scientific, Milan, Italy) software was used
101 both for acquisition and data analysis.

102 2.3.2. Ion chromatography

103 A Dionex instrument equipped with a conductimeter detector was used. Cations were analysed with and a
104 CS12A column using methanesulphonic acid (20 mM) as eluent at a flow rate of 1 mL min⁻¹. In such conditions,
105 the retention time of the ammonium ion was 4.7 min. Anions were analysed with an AS9HC column and
106 K₂CO₃ (9 mM) as eluent at a flow rate of 1 mL min⁻¹. Under these conditions, the retention times for nitrite
107 and nitrate were 6.83 and 9.51, respectively.

108

109 2.3.3. Total organic carbon analyzer

110 Total organic carbon (TOC) was measured in filtered suspensions using a Shimadzu TOC-5000 analyzer
111 (catalytic oxidation on Pt at 680°C). The calibration was performed using potassium phthalate standards.

112

113 2.3.4. Toxicity Measurements

114 The toxicity was evaluated with a Microtox Model 500 Toxicity Analyzer (Milan, Italy). Acute toxicity was
115 evaluated with a bioluminescence inhibition assay using the marine bacterium *Vibrio fischeri* by monitoring
116 changes in the natural emission of the luminescent bacteria when challenged with toxic compounds. Freeze-
117 dried bacteria, reconstitution solution, diluent (2% NaCl) and an adjustment solution (non-toxic 22% sodium
118 chloride) were obtained from Azur (Milan, Italy). Samples were tested in a medium containing 2% sodium
119 chloride, in five dilutions, and luminescence was recorded after 5, 15, and 30 min of incubation at 15°C. Since
120 no substantial change in luminescence was observed between 5 and 30 minutes, only the percent toxicity
121 recorded at 15 minutes will be discussed. Inhibition of luminescence, compared with a toxic-free control to
122 give the percentage inhibition, was calculated following the established protocol using the Microtox
123 calculation program.

124

125

126 3. Results and discussion

127 3.1. Ionic liquids degradation and mineralization

128 Direct photolysis contribution was negligible for all ILs in the considered time window. Considering ILs
129 degradation in the presence of TiO₂, Figure 1 shows ILs holding the same anion (BF₄⁻), while Figure 2 displays
130 ILs with different anions. Analyzing data of Fig. 1, **BP-TFB**, **HP-TFB** and **4-BMP-TFB** show easier disappearance
131 than **EP-TFB** and their complete degradation occurred within 30 min. Compared to **EP-TFB**, the other three
132 ILs examined show a wide time delay between the substrate disappearance (ca 30 min) and the complete
133 mineralization (ca 120-150 min). The difference between the two curves has to be attributed to the TPs
134 formation.

135 The release of nitrogen over time is very similar (and inverse) to TOC profile. Within 1 h, only a small
136 percentage of nitrogen is released; afterward, a sharp increase was observed between one and 2 h and then
137 the complete mineralization was achieved within 3h of irradiation. No nitrite traces were detected under the
138 employed experimental conditions. The nitrogen reaches the stoichiometric amount within 2h and it is
139 mainly released as ammonium ions in all cases (80-90%). Pyridine is known to degrade by giving aliphatic
140 intermediates with one to five C atoms, all containing C=O groups. Whenever the N atom subsists, it is in
141 amide form, so implying a prevalent conversion of nitrogen into ammonium [32]. Taking into account the
142 nitrogen evolution, the formation of TPs more persistent than the parent compounds, still containing N in
143 the structure, can be hypothesized.

144 The results obtained for **BP-Cl**, **BP-Br**, **BMP-Br** and **CPP-Cl** are reported in Figure 2. The two ILs with bromide
145 present similar degradation curves and disappeared within 2h of treatment. Conversely, in the presence of
146 bromide (**BP-Br** and **BMP-Br**), TOC profile was strongly modified and, even if a sharp decrease was achieved
147 within 4 h of irradiation, at longer irradiation times (16 h) no more degradation occurred and almost 20% of
148 the initial TOC persisted. The fate of nitrogen for **BP-Br** and **BMP-Br** was deeply modified as well. In the case
149 of **BP-Br** the measured $\text{NH}_4^+/\text{NO}_3^-$ ratio is close to 1, whereas the ammonium represents the most abundant
150 product of nitrogen mineralization for **BMP-Br** degradation, for which the ratio is close to 3. For **BP-Br**, the
151 stoichiometric release was not achieved, so implying that persistent TPs still containing the nitrogen were
152 formed.

153 Analyzing **CPP-Cl**, the TOC disappearance was complete after 4h of irradiation and almost 85% was abated
154 within 3h. The fate of nitrogen is rather interesting. Within 2h, nitrogen was mainly released as ammonium
155 ions (55%), while for longer irradiation times it was released as nitrate ions. This behavior is well matched
156 with the formation of cyanate at early stage, then slowly oxidized to give nitrate ion formation [33,34].

157

158 3.2. Acute toxicity

159 Acute toxicity was evaluated by monitoring changes in the natural emission of the luminescent bacteria *Vibrio*
160 *fischeri*. Initially, EC_{50} values were calculated for all ILs and they are collected in Table 1. These values show a
161 correlation between the number of carbons of the alkyl chain and the acute toxicity, as plotted in Figure 3.
162 Analyzing ILs with the same anion (TFB), EC_{50} value increases from about 7 g/l for **EP-TFB**, holding two carbon
163 atoms in the chain, to 95 mg/l for **HP-TFB**, with six carbon atoms, in agreement with literature data [35]. An
164 increase of toxicity was also observed when a second aliphatic substituent (CH_3) is present in the aromatic
165 structure, exhibiting an intermediate value between **BP-TFB** and **HP-TFB**.

166 The presence of a hydrophilic group (i.e. a cyano group) on butyl chain significantly decreases ILs toxicity, as
167 assessed by $EC_{50} > 10$ g/l. In fact, the lower hydrophobicity of the cation hinders the molecule capability to
168 pass through the cell membranes and exert acute toxicity on bacteria [35].

169 As reported in previous studies, the length of the alkyl chain had a significant influence on the toxicity of IL
170 and also the methyl groups appended to a pyridinium cation showed the same effect on toxicity [35].

171 Since the trend of increased growth inhibition with hydrophobicity had been demonstrated for other
172 microorganisms, the mechanism of toxicity of ILS may be explained through the membrane disruption
173 because of the ILs structural similarity to detergents, pesticides and antibiotics.

174 Another studies suggested mechanism of IL toxicity is related to acetylcholinesterase inhibition in more
175 complex test organisms [36 and references within].

176 Conversely, ILs toxicity was less influenced by the type of anion. For BP, the following order of toxicity was
177 observed: **BP-Br** < **BP-Cl** < **BP-TFB** in agreement with literature data [35].

178 Acute toxicity was monitored as well during the photocatalytic degradation for all of the compounds and the
179 percentage of inhibition effect is collected in Figure 4. For all ILs the initial inhibition percentage is worthless,
180 but a different toxicity is observed during the photocatalytic treatment.

181 The photocatalytic degradation of ILs holding TFB as inorganic ion proceeded through the formation of rather
182 harmless compounds. **EP-TFB** and **BMP-TFB** transformation proceeds through the formation of harmless
183 compounds as a very slight inhibition increase occurred from 30 min onward (10-15%) TPs. While the presence
184 of short-chain groups seems to avoid the formation of harmful compounds, some toxicity was exhibited by
185 longer chain ILs **HP-TFB** and **BP-TFB** (inhibition percentages up to 30-40%),

186 As far as the behavior of **CPP-Cl**, initially it does not display any toxicity, but later on its transformation
187 proceeds through the formation of toxic compounds. The inhibition percentage increases up to 80 % after
188 60-120 min and then slows down. This trend closely resembles to the TPs temporal profiles as most of the
189 identified TPs greatly decrease from 120 to 240 min. So, it was not possible to assess which of the formed
190 TPs are the most hazardous.

191 For **BP-Br** and **BMP-Br** the toxicity increased from 15 min onward and became maximum after 4h of
192 irradiation. This could to be attributed to the formation of toxic and persistent TPs, whose formation has to
193 be ascribed to the presence of bromide as anion and is not directly related to the ILs organic moiety. As blank
194 analysis, a solution of NaBr was subjected to irradiation under the same experimental conditions aimed to
195 assess the contribution of bromide derivatives to the toxicity arising from photocatalytic treatment. As it can

196 be seen in the Figure S1, the toxicity increases with time of irradiation. Therefore, the detected toxicity has
197 to be chiefly ascribed to the formation of inorganic brominated species rather than to organic compounds.

198

199 3.3. Characterization of transformation products

200 TPs formed along with ILs photocatalysed degradation were detected *via* HPLC-MS, ESI positive mode.
201 Analyzing short chain ILs, 1-ethylpyridinium tetrafluoroborate (**EP-TFB**) shares with 1-cyanopropylpyridinium
202 chloride (**CPP-Cl**) several transformation routes as assessed in Scheme 1. **EP-TFB** transformation proceeds
203 through the formation of seven TPs, all already recognized during UV-B photolysis [20] and their MS and MS²
204 ions are collected in Table S1. The recognized TPs involved hydroxylation (**TP-124** (1-
205 (hydroxyethyl)pyridinium) and **TP 140** (dihydroxyethyl-pyridinium)) hydroxylation/oxidation (**TP-122** and
206 **138**), detachment of the ethyl chain (**TP 80**, pyridinium ion) and ring opening (**TP 84**). The evolution profiles
207 over time for **EP-TFB** are shown in Figure 5. Most of TPs reached the maximum amount within 30-60 min,
208 with the only exception of **TP-138**. This is not surprising as its formation involved several steps, as assessed
209 by the transformation pathways collected in Scheme 1.

210 **CPP-Cl** transformation produced eleven TPs and their MS² ions are collected in Table S2, while the evolution
211 profiles over time are collected in Figure S2. Nine of them have been already detected under UV-B light and
212 their characterization is reported elsewhere [20]. They comprise **TP-163**, attributed to the monohydroxyl
213 derivative, **TP-136**, **TP-154** and **TP-152**, all formed through the detachment of the cyano group, **EP**, **TP-138**
214 and **TP-140** formed through the detachment of the methylcyano group. **TP-140** was formed through a bi-
215 hydroxylation, further transformed into **TP-138** through the oxidation of one of the two alcoholic groups to
216 a keto group; it matches with the monohydroxyl/keto derivative holding the OH group on the alkyl chain,
217 already detected with **EP-TFB**. **TP-94** and **TP-80** correspond to 1-methyl pyridinium ion and pyridinium ion,
218 respectively. Two additional TPs were detected during the photocatalytic treatment, **TP-130** and **TP-84**, both
219 involving the ring opening.

220 Butyl pyridinium derivatives share most of the formed TPs, but with some peculiar differences evidenced in
221 Scheme 2. **BP-TFB**, **BP-Cl** and **BP-Br** transformation involved the formation of fourteen, twelve and fifteen
222 TPs respectively. Three of them involved chain shortening (**TP-138** and **TP-140**) and chain detachment (**TP-**
223 **80**), and match with TPs already detected from **EP-TFB** and **CPP-Cl**. Their ions, detected by MS, are collected
224 in Table S3-S5, while the evolution profiles over time are collected in Figures S3-S5.

225 Considering **BP-Cl**, all the detected TPs match with those formed from **BP-TFB**, with only exception of **TP-**
226 **166-D**, and are completely degraded within 120 min. **TP-168-B**, **TP-134**, **TP-150C** and **TP-152B** were easily

227 formed and reached the maximum after 15 min of irradiation, while **TP-166-A** and **B** and **TP-80** achieved the
228 maximum after 30 min; **TP-138** was slowly formed and is maximum at 60 min.

229 Following **BP-Br** degradation, the evolution profiles over time for most abundant and persistent TPs are
230 reported in Figure 6, while the other TPs are collected in Figure S5. Almost all TPs disappear within 4h, with
231 **TP-150-A** and **C** only exception, which persist and contribute to the lack of mineralization described in 3.1.

232 Three isobaric species at 152.1073 m/z with empirical formula $C_9H_{14}ON$ were formed and attributed to
233 hydroxyl derivatives. In all cases, MS^2 spectra allowed to locate the OH group on the alkyl chain (**TP-152 A-**
234 **C**).

235 Six isobaric species at 150.0892 m/z were detected and attributed to keto derivatives or hydroxylated with a
236 double bond (**TP-150 A-F**). **TP-150-C** and **F** hold the keto group on the butyl chain, as assessed by the
237 formation of the pyridinium ion in MS^2 spectrum. Furthermore, the loss of formaldehyde for **TP-150-F** allows
238 to locate the keto group on C4. For the other isomers, no specific information can be deduced by MS^2 spectra.

239 Three isobaric species at 168.1025 m/z were formed and attributed to bi-hydroxyl derivatives (**TP-168-A-C**).
240 For **TP-168-A** and **B**, both OH groups are located on the alkyl chain. In the case of **TP-168-B** the loss of
241 methanol combined with the loss of $C_2H_6O_2$ suggested to locate the two OH groups on the C3 and C4. For **TP-**
242 **168-C** an OH group was located on C3 (loss of C_2H_4O combined with the absence of methanol loss).

243 Four species at 166.0867 m/z were detected and attributed to the bihydroxylated/oxidized compounds; in
244 all cases, the groups were located on the alkyl chain. **TP-166-A** exhibits the loss of formaldehyde, so
245 permitting to assess the presence of the carbonyl group on C4. Reasonably, it comes from the oxidation of
246 the species **TP-168-C**.

247 A TP with 134.0967 m/z (**TP-134**) could be attributed to the formation of a double bond in the chain or to the
248 chain closure to give a ring. MS^2 is not useful to assess which of the two routes occurred.

249 Scheme 3 collects TPs formed from **4-BMP-TFB** and **3-BMP-Br**, while their evolution profiles as a function of
250 irradiation time are shown in Figure S6 and 7, respectively. Thirty-two TPs were detected during **4-BMP-TFB**
251 degradation, all summarized in Table S6, eighteen of which already recognized and characterized during the
252 UV-B photolysis [20]. **3-BMP-Br** transformation proceeds through the formation of nineteen TPs, all collected
253 in Table S7.

254 Both compounds share some transformation pathways involving oxidation and/or oxidation and the side
255 chain reduction, but they show also some peculiar routes. First of all, the presence of bromide as anion leads
256 again to the formation of some highly persistent TPs. Secondly, the position of methyl group on the pyridine
257 ring seems to affect the extent of different pathways. With **4-BMP-TFB** TPs formed at higher amount comes

from hydroxylation (**TP-182**), reduction (**TP-148**) and reduction/hydroxylation (**TP-164**). For **3-BMP-Br**, **TPs-164-B,D,F** were the most prominent. **TP-164** and **TP-150** were particularly persistent and these should be the same structures already evidenced from **BP-Br** plus a methyl group. Besides, while for **4-BMP-TFB** the detachment/shortening of alkyl chains prevails, for **3-BMP-Br** this route is absent and only the ring-opening occurred.

Analyzing different **TPs**, a first group of **TPs** comprises mono and dihydroxylated derivatives and their oxidation products. Four or two monohydroxyl derivatives with 166.1233 m/z (**TP-166-A-D** for **4-BMP-TFB** and **TP-166-E,F** for **3-BMP-Br**) were formed. **TP-166-E,F** were recognized also during biodegradation [37]. For isomer **D** the OH group can be located on the butyl chain [20], while for **TP-166-C** on C₂ or C₃ due to the loss of C₃H₆O. In both cases the absence of methanol loss in MS² spectra allowed to exclude a hydroxylation on C₄.

Twelve isobaric species with m/z 164.1078 and empirical formula C₁₀H₁₄ON (**TP-164**) were formed from **4-BMP-TFB** and **3-BMP-Br**. Nine of them matched with keto derivatives, four of which already detected *via* direct photolysis (**TP-164-A, C, D** and **F**) [20]. For **TP-164-B** the loss of C₃H₆ permitted to exclude the presence of a keto group on C₂-C₄. For **164-E** the loss of C₂H₄O allowed to locate the keto group on C₃. **TP-164-B, G** and **I** were well matched with the presence of a double bond in the alkyl chain plus an hydroxyl group.

Two species rather stable were formed with 162.0891 and 148.1126 m/z . For **TP-162** (formed from **4-BMP-TFB**), the most abundant ion exhibited in MS² the loss of C₄H₄; this peculiar loss allowed to propose an insaturation/cyclization of the butyl chain. Conversely, **TP-162** produced from **3-BMP-Br** presented 3-methylpyridinium as product ion in MS² spectrum, thus allowing to locate an oxygen on the butyl chain. **TP-148-A-C** with empirical formula C₁₀H₁₄N presented an insaturation/cyclization as well; **TP-148-A** and **C**, losing acetylene, suggested the presence of a double bond on C₃-C₄ on the butyl chain.

Six dihydroxyderivatives with 182.1184 m/z were formed from **4-BMP-TFB**; isomers **B, C** and **D** were also formed during direct photolysis [20]. For **3-BMP-Br**, only three isomers (**TP-182-G,H, I**) were detected. **TP-182-A** holds an OH group on butyl chain and the other one on the ring, as assessed by the product ion C₆H₈ON. For **TP-182-F** the losses of C₂H₆O and C₃H₇O₂ allowed to position the two OH groups on C₂ and C₃. This hypothesis is confirmed by the loss of CO in MS³ spectra. For **TP-182-E** no structurally-diagnostic ions were present in MS² spectrum. **TP-182-G** holds the two OH groups on carbon 3 and 4 thanks to the loss of methanol and C₂H₃O₂. This was further confirmed by the formation of 3-methylpyridium as product ion (m/z 94.0655). For **TP-182-H**, the loss of C₄H₈ permitted to exclude a hydroxylation on the butyl chain.

Eight bihydroxylated/oxidized **4-BMP-TBF** with 180.0995 m/z were formed, three of them already detected *via* direct photolysis (**TP-180-A,C** and **E**) [20]. **TP-180-F** holds both groups on the butyl chain. **TP-180-B** and **H** hold a keto group on the butyl chain and the OH group on the other part of the molecule, as assessed by the

loss of C_4H_6O in MS^2 spectrum. **TP-180-D** could hold the keto group on the methyl or butyl C4, as due the formaldehyde loss; the combined loss of H_2O in MS^2 and formaldehyde in MS^3 permitted to exclude the involvement of the methyl group. **3-BMP-Br** produced an isomer only (**TP-180-I**), also detected via biodegradation [37]. It was further oxidized to produce **TP-178** with m/z 178.0869 and empirical formula $C_{10}H_{12}O_2N$.

Three compounds at m/z 134.0967, 150.0891 and 168.0996 were formed through the detachment of the methyl group and were only detected from **4-BMP-TFB**. **TP-134** presented a double bond (or a ring closure). **TP-150** showed a demethylation and a carbonyl group; its intensity was too low to permit MS^2 analysis. **TP-168** involved a demethylation and a bihydroxylation.

For **4-BMP-TFB** only, two TPs involving chain shortening and two hydroxyl group were detected (**TP-154**). MS^2 product ions did not allow to properly locate them. **TP-124** could be formed by the detachment of the butyl chain together with the methyl oxidation and hydroxylation. For **3-BMP-Br**, **TP-94** matched with 3-methylpyridinium, confirmed by the injection of a standard solution and already detected via biodegradation [37].

Few TPs involved the ring opening and the first one was **TP-102** with m/z 102.0912 and empirical formula $C_5H_{12}ON$ that involved ring opening and hydroxylation. The formation of a compound at 76.0391 m/z with empirical formula $C_2H_6O_2N$ occurred and its formation involved the pyridinium ring opening. **TP 84** with m/z 84.0806 and empirical formula $C_5H_{10}N$, derived from ring opening and partial of alkyl chain conservation.

1-Hexylpyridinium tetrafluoroborate (**HP-TFB**) produced 46 TPs, whose MS and MS^2 ions are collected in Table S8 and 9 and the proposed structure are shown in Scheme 4. TPs temporal profiles are plotted in Figure S8.

The main TPs were **TP-196-D** and **TP-180**, implying mono and dihydroxylation, and **TP-162**, involving a reduction on the alkyl chain. Besides, the pathways involving the chain shortening, chain detachment and ring cleavage played a minor role. **HP-TFB** shares with other ILs **TP-80** (pyridinium ion), formed though the detachment of alkyl chain, three species characterized by chain shortening, mono or dihydroxylation and oxidation (**TP-148**, **TP-166** and **TP 140**) and two TPs involved the ring opening, namely **TP-84** and **TP-102**. Furthermore, two TPs **TP-154** and **TP-152** with empirical formula $C_8H_{12}O_2N$ and $C_8H_{10}O_2N$ were in common with TPs coming from **CPP-Cl** transformation and involved chain shortening, hydroxylation and oxidation.

Analyzing **HP-TFB** peculiar TPs, the first group comprises mono, di and trihydroxylated/oxidized derivatives. Nine isobaric species with m/z 178.1234 and empirical formula $C_{11}H_{16}ON$ (**TP-178**) were formed. Isomers **178-B**, **C**, **D**, **E** and **G** hold the keto group on the alkyl chain. Furthermore, in the case of **TP-178-B**, the loss of C_2H_4O , combined with the absence of formaldehyde loss, allowed us to locate the group on C5. In all cases,

the formation of the pyridinium ion (m/z 80.0492) as product ion allowed us to locate the OH group on the alkyl chain. The fragmentation of TP-178-F and G can be justified by the hydroxylation of parent molecule and oxidation of alkyl chain, whereas no useful information to elucidate the structure of TP-178A and B was obtained.

Five isobaric species with m/z 196.1341 (**TP-196**) and empirical formula $C_{11}H_{18}O_2N$, were detected and attributed to bihydroxylated-HP. **TP196-A** and **196-C**, hold both OH groups on the alkyl chain, as assessed by the product ion at 80.0460 m/z ; furthermore, the loss of C_2H_6O , combined with the absence of the methanol loss, permits to locate one of the two hydroxyls on the C5. Ten isobaric species with 194.1187 m/z and empirical formula $C_{11}H_{16}O_2N$ (**TP-194**) were formed and attributed to bihydroxylation/oxidation processes. Two isobaric species with m/z 192.1030 and empirical formula $C_{11}H_{14}O_2N$ (**TP-192**), due to a bihydroxylation/oxidation process were then detected. Two **TP-210** and a **TP-208** were detected and involved trihydroxylation with oxidation of one (or two) hydroxyl group to keto groups; the formation of pyridinium ion in their MS^2 allows to locate these groups in the alkyl chain.

The second group comprises **TP-162**, **TP-160** and **TP-176** with empirical formula $C_{11}H_{16}N$, $C_{11}H_{14}N$ and $C_{11}H_{14}ON$, respectively, that are well matched with structure holding double bond(s) in the alkyl chain.

It can be concluded that the type of anion does not influence deeply the degradation pathway of ILs and all BP share most of the intermediates arising from mono and dihydroxylation of molecule and detachment of the alkyl chain. The presence of TPs showing the alkyl chain shortening is peculiar for **BP-TFP**, **BP-Cl**, **EP-TFB** and **CPP-Cl**, whereas in the case of **BP-Br** the formation of TPs holding the keto group on the butyl chain was observed. Also for ILs with a second alkyl chain (i.e a methyl group), the main pathways of degradation are hydroxylation, reduction and reduction/hydroxylation. On the other hand, the presence of a longer chain involves the formation of TPs of holding double bond(s) in the alkyl chain.

Conclusions

In the case of ILs containing TFB as anion, even if some differences in the time trend occurred, neither the alkyl chain length or the presence of more than one substituent does significantly affect the mineralization process. In all cases, the complete mineralization was easily achieved within 2-3 h of irradiation and nitrogen is mainly released as ammonium ions. Conversely, for ILs with bromide as anion, a lack of mineralization was assessed.

All ILs share some transformation pathways but present also some peculiar routes. In the case of **4-BMP-TFB** and **3-BMP-Br**, TPs formed at higher amount comes from hydroxylation (**TP-182**), reduction (**TP-148**) and reduction/hydroxylation (**TP-164-B**). Compared to other ILs, the mechanism of reduction plays a key role in

355 the **HP-TFB** degradation, with the formation of TPs holding two double bonds in the alkyl chain, while the
356 ring opening plays a minor role. The three BP ILs share most of the transformation pathways, with some
357 differences. **BP-TFB** and **BP-Cl** exhibit a chain shortening with the formation of **TP-138** and **TP-140**, two
358 transformation products already recognized from **EP-TFB** and **CPP-Cl**. Conversely, **BP-Br** degradation formed
359 some persistent TPs.

360 The photocatalytic degradation of ILs holding TFB as inorganic ion proceeded through the formation of rather
361 harmless compounds, while **CPP-Cl**, **BP-Br** and **3-BMP-Br** transformation involved the formation of hazardous
362 products.

363

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Figure captions

Figure 1. ILs disappearance curves, TOC evolution profile and inorganic ions release over time for ILs with BF_4^- as anion (**EP-TFB** 1-ethylpyridinium, **BP-TFB** 1-butylpyridinium, **HP-TFB** 1-hexylpyridinium, **4-BMP-TFB** 1-butyl-4-methylpyridinium).

Figure 2. ILs disappearance curve, TOC evolution profile and inorganic ions release over time for ILs with other anions (**BP-Cl** 1-butylpyridinium chloride, **BP-Br** 1-butylpyridinium bromide, **3-BMP-Br** 1-butyl-3-methylpyridinium bromide and **CPP-Cl** 1-cyanopropyl chloride).

Figure 3. Relation between $\text{Log}_{10}(\text{EC}_{50})$ (mg/l) and the number of carbon on alkyl chains.

Figure 4. Acute toxicity for ILs during the photocatalytic treatment; (top) **EP-TFB**, **BP-TFB**, **HP-TFB**, **BMP-TFB**; (bottom) **BP-Cl**, **BP-Br**, **BMP-Br** and **CPP-Cl**.

Figure 5. Transformation products formed from compound **EP-TFB** degradation in the presence of TiO_2 .

Figure 6. Persistent and more abundant transformation products formed from compound **BP-Br** degradation in the presence of TiO_2 .

Scheme 1. Proposed transformation pathways followed by compound **EP-TFB** and **CPP-Cl** in the presence of TiO_2 (200 mg/l).

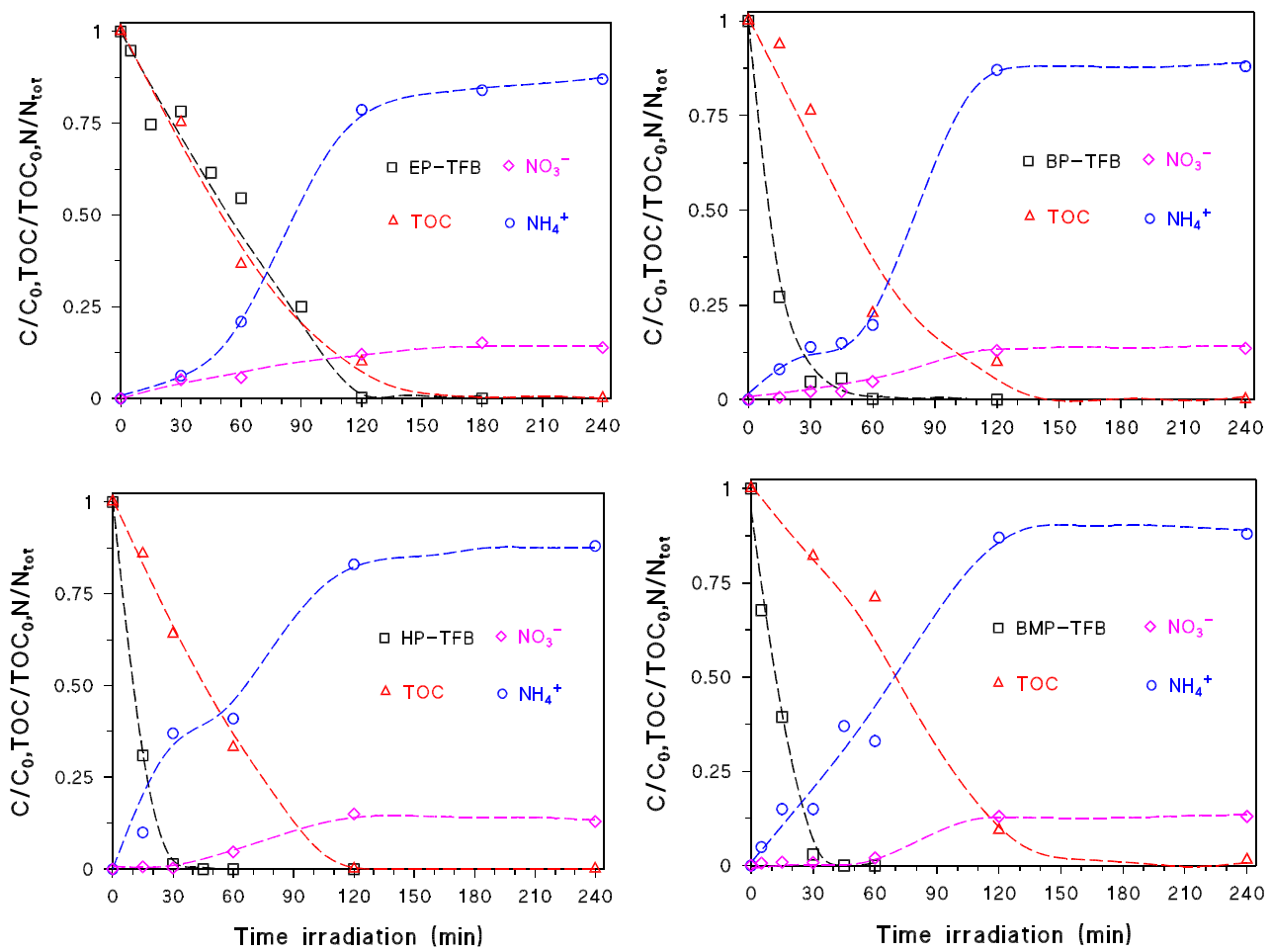
Scheme 2. TPs formed from butyl-pyridine (**BP-TFB**, **BP-Cl**, **BP-Br**). TPs formed from all BP derivatives are marked with one asterisk, with two those formed from **BP-Cl** and **BP-TFB** only, with three those with **BP-Br** only, with four in the case of **BP-Br** and **BP-TFB** only, with five the TPs for **BP-TFB** only and with six asterisks the one obtained from **BP-Br** and **BP-Cl** only.

Scheme 3. Proposed transformation pathways followed by **4-BMP-TFB** and **3-BMP-Br** under photocatalytic treatment. With one asterisk are indicated TPs formed from **4-BMP-TFB** only and with two the ones TPs formed from **3-BMP-Br** only.

501 **Scheme 4.** Proposed transformation pathways followed by **HP-TFB** under photocatalytic treatment.

502 **Table 1.** EC₅₀ values for the investigated ILs.

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504

505 **Figure 1.**

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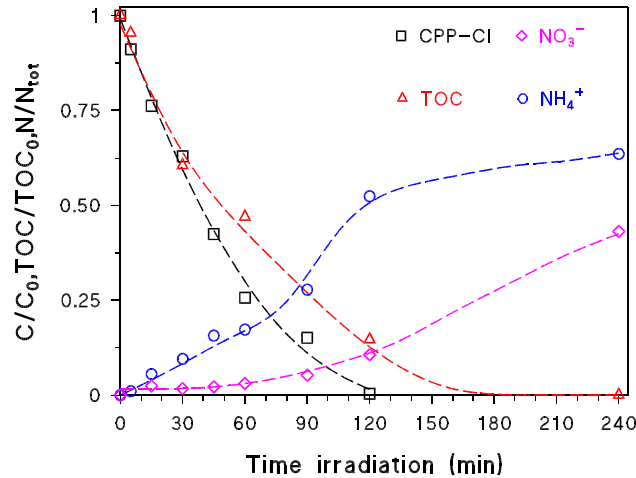
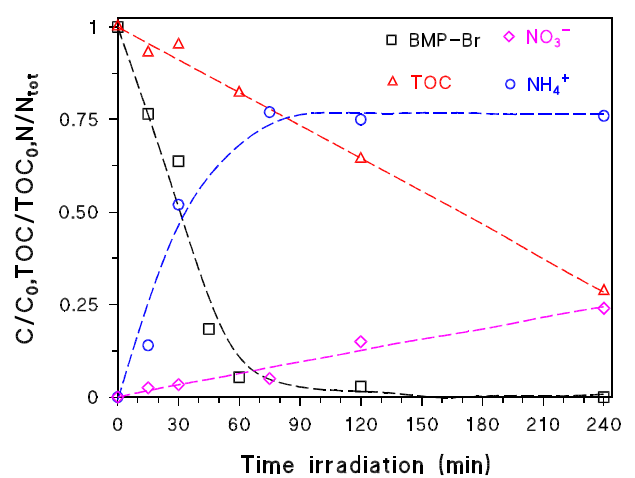
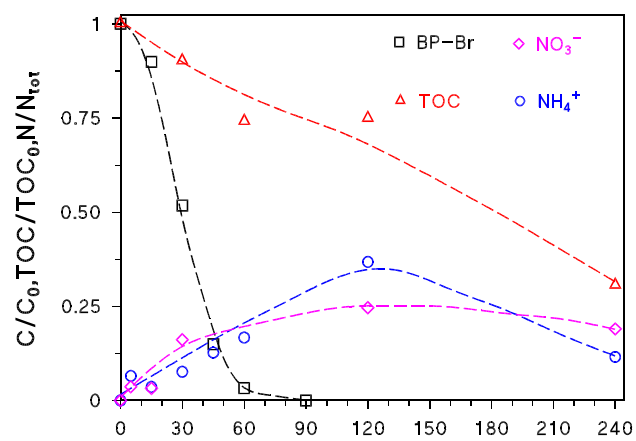
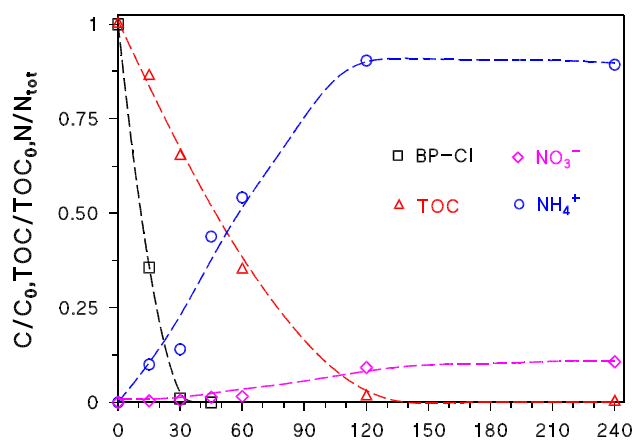
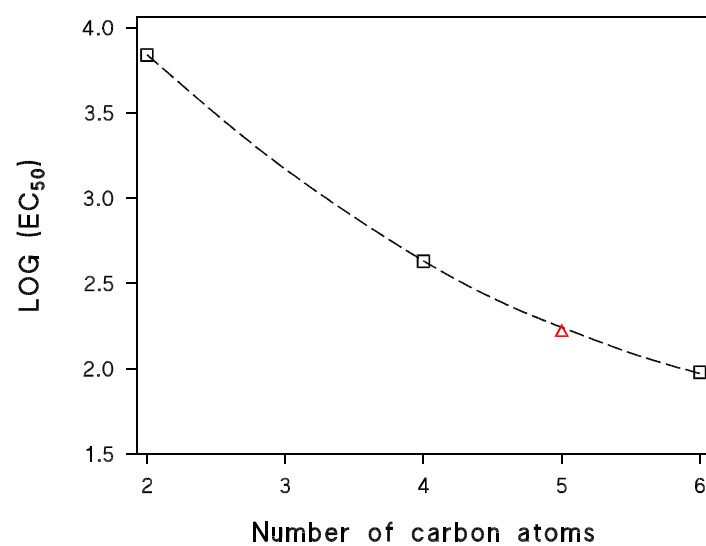


Figure 2.



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512 **Figure 3.**

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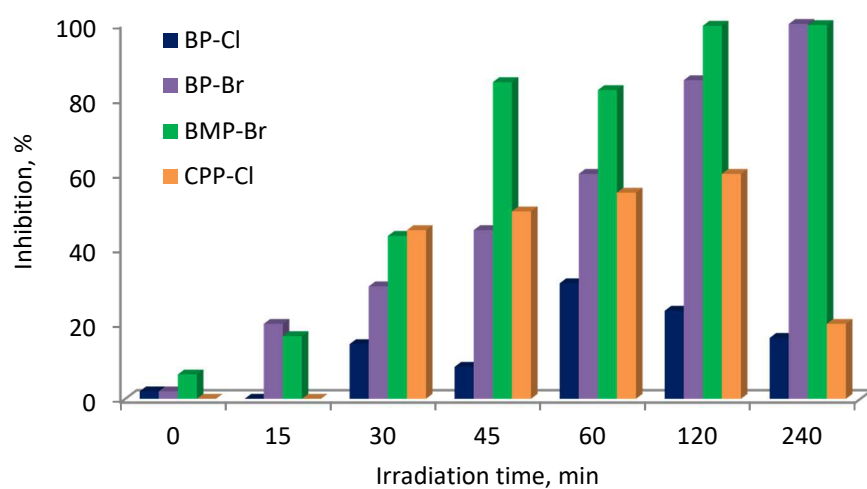
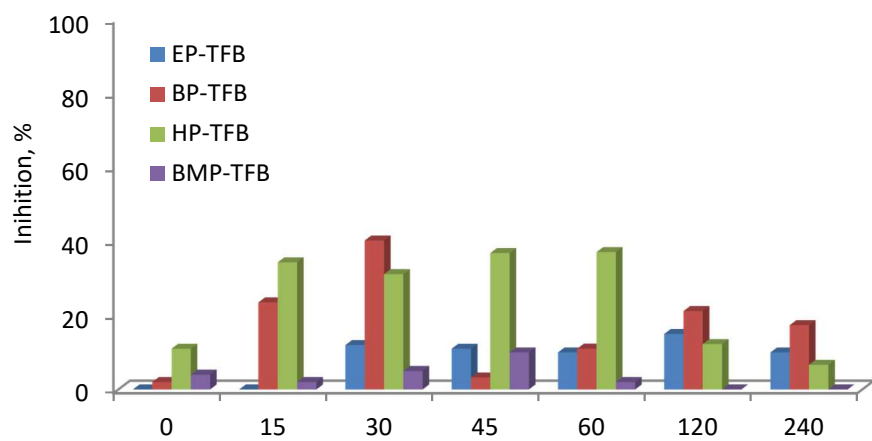


Figure 4.

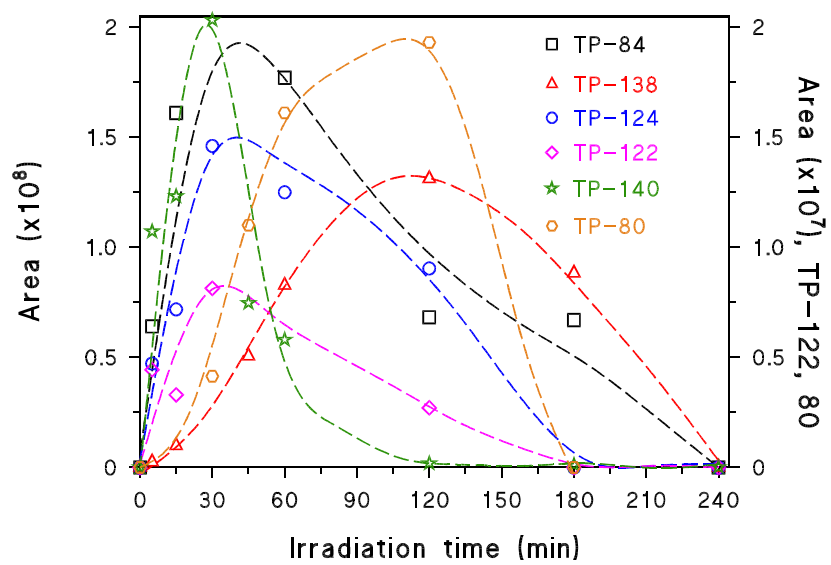


Figure 5.

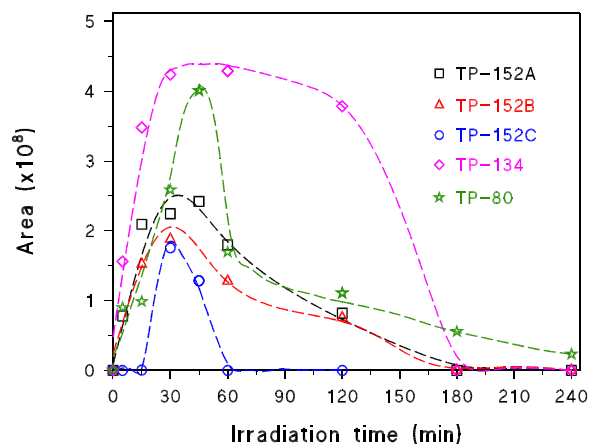
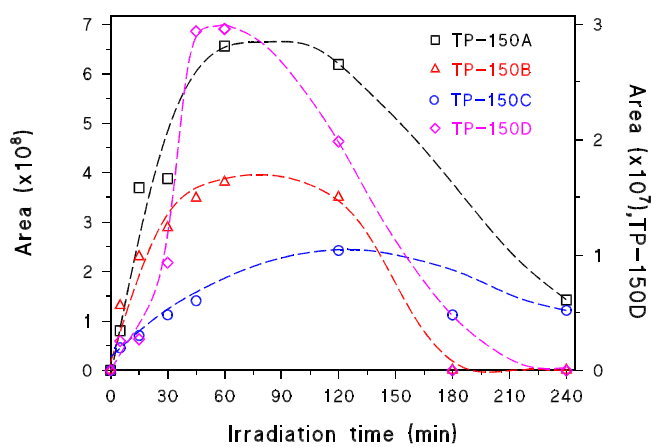
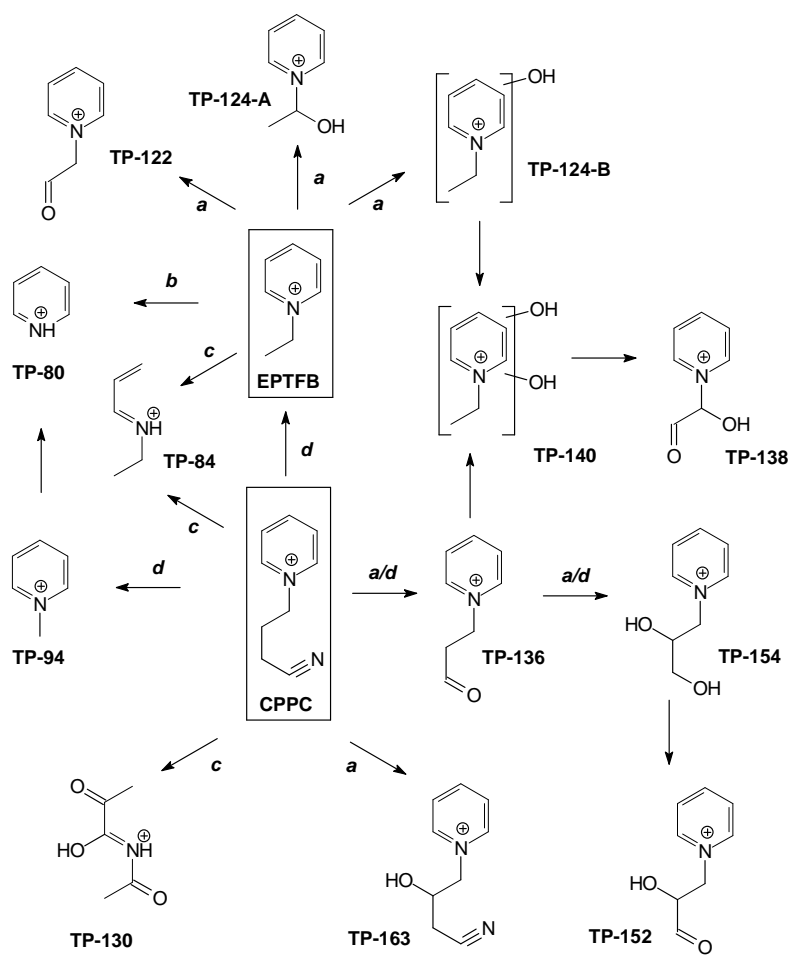
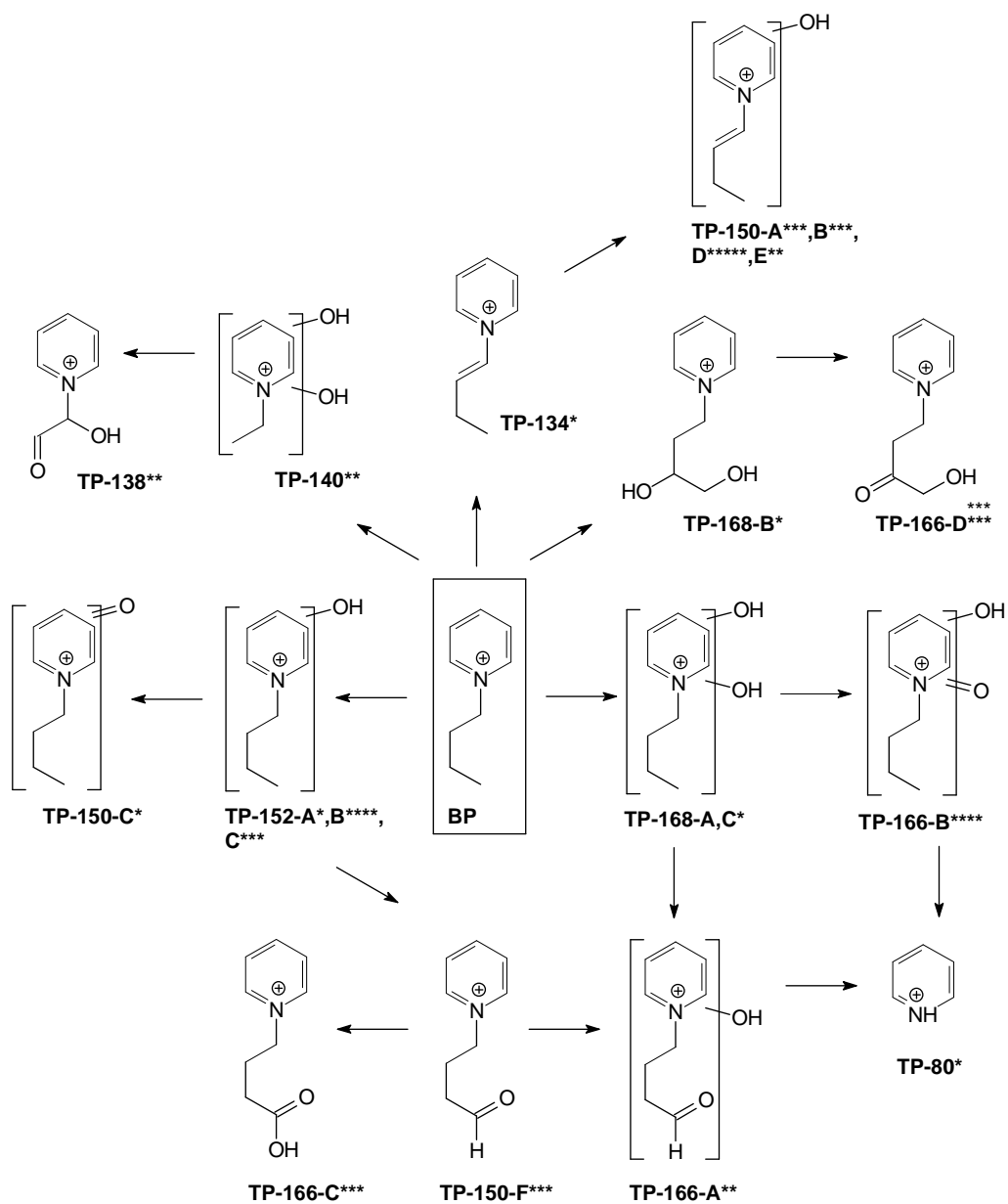


Figure 6.



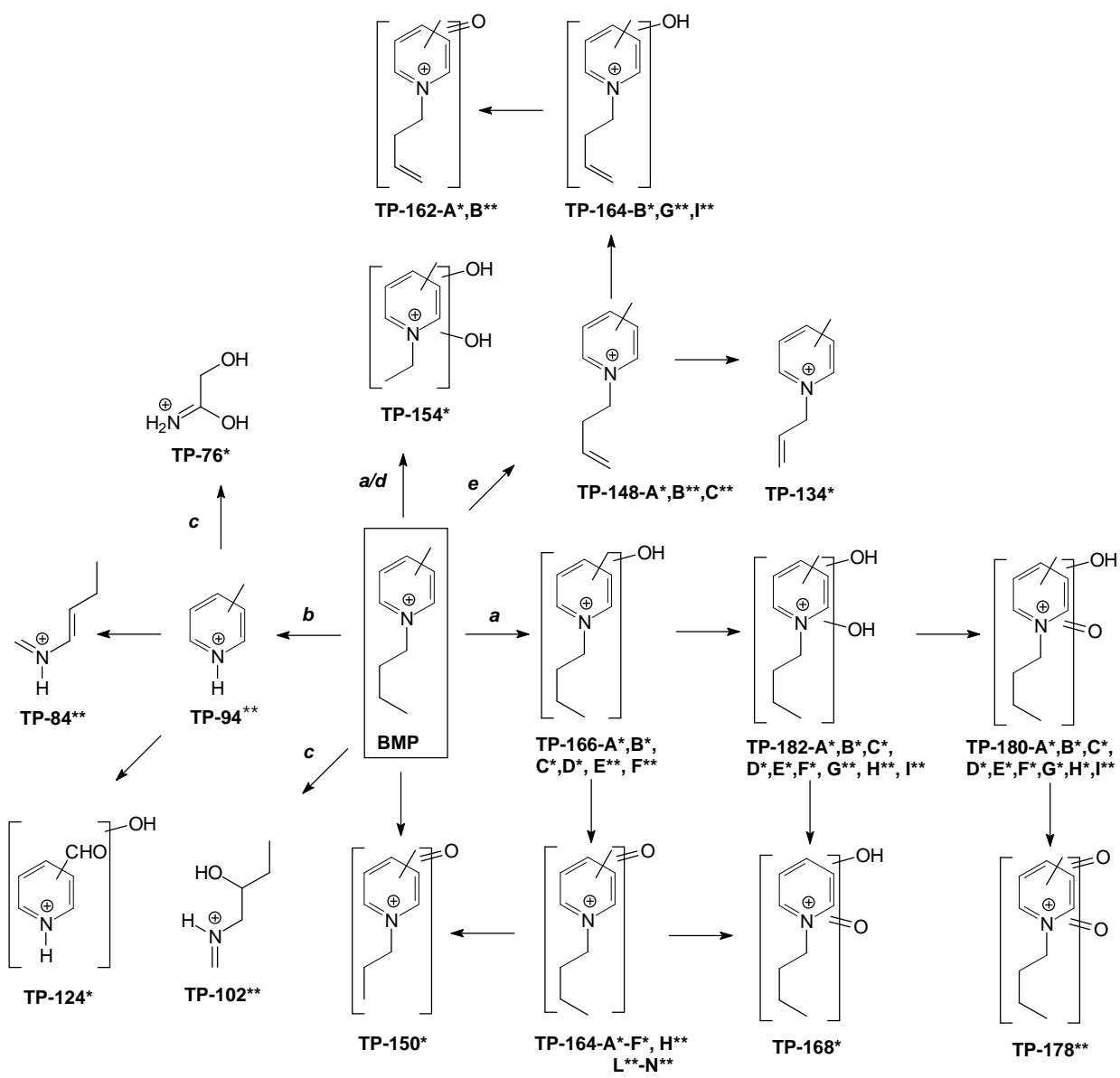
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525 **Scheme 1.**



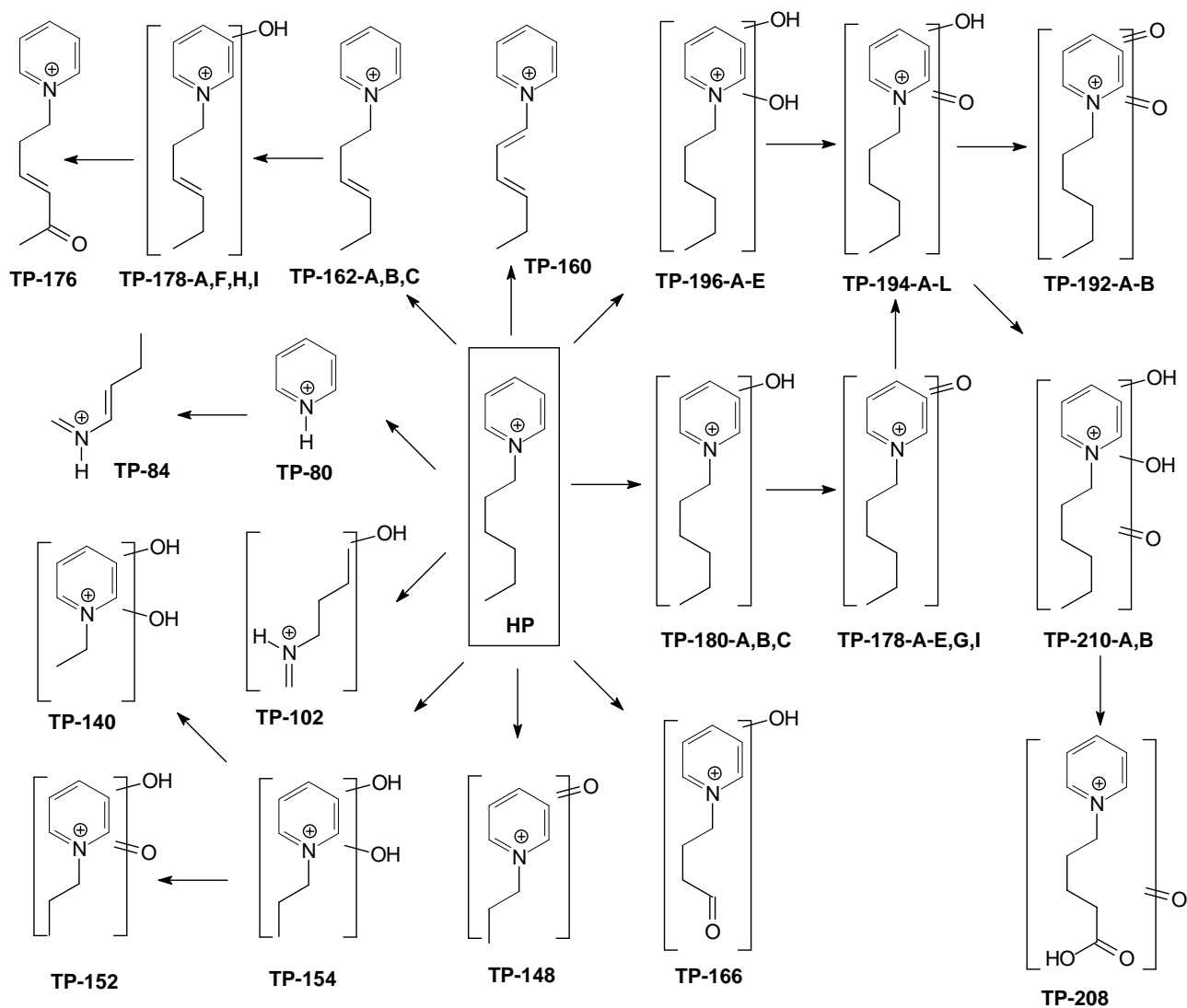
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527 Scheme 2.



528

529 **Scheme 3.**



Scheme 4.

533 **Table 1.** EC50 values for the investigated ILs.

	EP-TFB	BP-TFB	BP-Cl	BP-Br	BMP-TFB	BMP-Br	HP-TFB	CPP-Cl
EC50 (mg/L)	6988	423,5	494,6	539,6	164,0	139,04	94,89	>10000

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