Furan containing ammonium salts from furfural: synthesis and properties evaluation†

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Furan-containing quaternary ammonium iodides, bis(trifluoromethane)sulfonimides, and tetrafluoroborates are obtained in good overall yield with mild operation conditions starting from furfural, a cheap chemical substance obtainable from crop residue feedstocks. The application of these new ion pairs can be envisioned in the fields of ionic liquid solvents, of surfactants and of biocides in analogy with benzyl quaternary ammonium salts. In view of practical applications, the determination of the thermal properties of new ion pairs together with preliminary ecotoxicological evaluation of some representative products has also been performed.

Introduction

Obtaining chemicals from renewable material is of growing importance in facing environmental concerns over fossil fuels consumption. Biomass is the most important renewable resource available both for energy and chemical compounds production; the treatment of the biomass affords a large number of oxygenated compounds, such as anhydrosugars and furans, which can be used in different chemical applications.[1]

Furfural **1** (2-furaldehyde), in particular, is a cheap chemical which is industrially obtained in a large amount from the treatment of lignocellulosic materials, derived from agricultural or forestry wastes, with acidic water at high temperatures. It is currently produced in more than 25 000 tons/year globally, with a 10% yield of the original biomass. It can be also recovered in the liquid fraction obtained from the pyrolysis of wood and cellulose.[2]

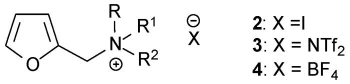
Here we present the synthesis, starting from **1**, of a class of furan-containing quaternary ammonium iodides **2a–i**, bis(trifluoromethane)sulfonimides (NTf_2 salts) **3a–h**, and tetrafluoroborates (BF_4 salts) **4a–h** whose application can be envisioned in the fields of ionic liquid solvents, of surfactants and of biocides in analogy with benzyl quaternary ammonium salts (Table 1).

Long-chain ammonium salts, such as benzalkonium chloride (BAC), show antimicrobic and tensioactive features so that they are largely employed as surfactants and biocides.[3] Moreover, the use of quaternary ammonium salts with low melting points as room-temperature ionic liquids (RTILs) is of growing importance.[4] Ionic liquids are a promising class of alternative solvents for many applications; nowadays, either commonly used ionic liquids or quaternary ammonium surfactants are synthesized from petroleum derivatives with polluting methodologies; therefore, the synthesis of those chemical commodities from renewable raw materials, such as furfural, can be of great potential impact.[5]

Some examples of furan-containing ammonium salts are present in the literature. The first example dates to 1940 by Nabenhauer[6] who prepared some short chain dimethylalkyl furan ammonium salts, called furtrethoniums, showing cholinergic or muscarinic properties.[7] Furmethide (2-*N*,*N*,*N*-trimethylfurfurylammonium iodide) in particular is the most studied furan-containing ammonium salts among the short chain dimethylalkyl furans synthesized since now,[8] because of its high similarity with the alkaloid muscarine. In 1945 Weilmuenster and co-workers[9] proposed a synthetic method whose key step is the reaction of a large excess of *N*,*N*-dialkylformamide with furfural at 170 °C, followed by quenching with very strong alkaline solutions.

Our approach to the synthesis of quaternary ammonium salts **2**, **3** and **4** combines the use of a starting material obtainable from renewable resources with mild operation

Table 1 Furan-derived quaternary ammonium salts **2a–i**: X = I, **3a–h**: X = NTf_2, **4a–h**: X = BF_4



Compd.	R	R¹	R²
a	Butyl	Butyl	Methyl
b	Butyl	Dodecyl	Methyl
c	Octyl	Butyl	Methyl
d	Octyl	Dodecyl	Methyl
e	Butyl	Methyl	Methyl
f	Butyl	Butyl	Butyl
g	Octyl	Methyl	Methyl
h	Octyl	Butyl	Butyl
i	Hexyl	Methyl	Methyl

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conditions; in view of practical applications, the evaluation of the thermal properties of new ion pairs **2**, **3** and **4** together with preliminary ecotoxicological evaluation of some representative products is also presented here.

Results and discussion

Synthesis of furan-based ammonium salts iodides 2a–i

Ammonium iodides **2a–i** are synthesized through a solventless procedure at room temperature in three or four steps according to the general route described in the Scheme 1: furfural imines **5a**, **5b** and **5c** are quantitatively obtained from **1** and butylamine, octylamine or hexylamine, respectively, and then reduced using hydrogen (1 atm on Pd/C, 10%) to give secondary amines **6a**, **6b** and **6c**. Alkylation with bromobutane or bromododecane gives the tertiary amines **7a–d** which are finally converted into **2a–d** by treatment with iodomethane. Products **2e–i** can be obtained directly from secondary amines **6a**, **6b** and **6c** and 2.2 equivalents of iodomethane or iodobutane. Although the synthesis is multistep, the overall yields from **1** to **2a–i** are very good and range from 75 to 90% for **2a–i** (see also ESI† for details). Purity of compounds is generally very good, when necessary, especially for toxicity tests, ion pairs can be further purified by flash chromatography on a short silica gel column, or, for solid compounds **2a**, **2e**, **2f** and **2i** by grinding in ethyl acetate. Purity was assessed by means of quantitative ^{1}H NMR with internal standard.

Ion pairs **2a**, **2e**, **2f** and **2i** with short lateral chains or high degree of symmetry are solid with melting points around 100 °C, whereas iodide salts with four different substituents on ammonium (**2c**) or long lateral chains (**2b** and **2d**, **2g** and **2h**) are viscous liquids at room temperature (see Table 2).

Preparation of 3a–h and 4a–h

The iodide anion can be exchanged with several inorganic salts: we tested two anion metathesis in water to give tetrafluoroborates (BF_4^-) and bis(trifluoromethane)sulfonimides (NTf_2^-).

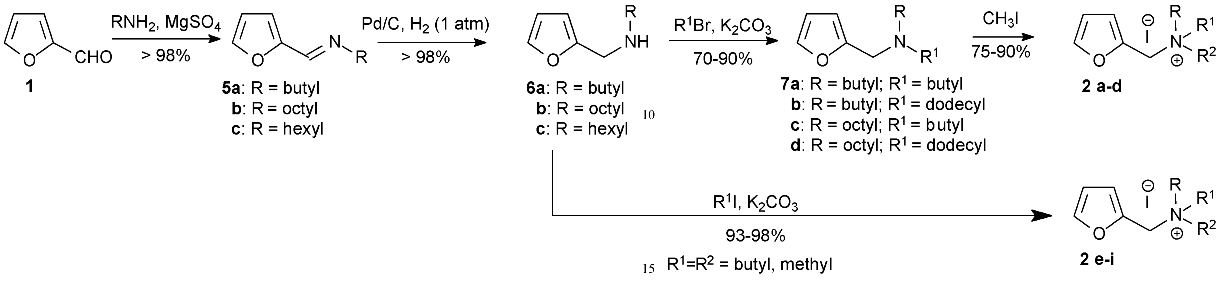
According to the general procedure described in Scheme 2, the ammonium iodides **2a–h** are converted in to **3a–h** upon treatment with $LiNTf_2$ in water.[10] Ion pairs **3a–h** are liquid at room temperature, except for compound **3f**, and insoluble in water; the presence of NTf_2 anion, in fact strongly lowers the melting point with respect to the corresponding iodides and increases the fluidity of viscous ones as a general feature.

We also performed the exchange with $NaBF_4$ in water to obtain ionic salts **4a–h**; except for compound **4e** which is solid, tetrafluoroborate ammonium salts are all liquid at room temperature. The yields of the exchange reactions are always close to 100%.

Analyzing the sustainability of the whole process several aspects can be pointed out: (i) all the reactions depicted in Scheme 1 are solvent free and performed at room temperature; (ii) the overall yields are high (iii) the atom economies (AE) of the five steps are 90, 100, 72, 100 and 64% (for BF_4 salts) or 78% (NTf_2 salts), respectively. The use of alkyl halides in the quaternization step has the advantages of producing ammonium salts with anions easily exchangeable in water but sensibly reduces the sustainability of the process.

Properties of ion pairs 2a–i, 3a–h, 4a–h

We checked the solubility of quaternary ammonium salts prepared in some common solvents: all salts are highly soluble in acetone, ethanol, methanol, dichloromethane and chloroform, but insoluble in diethyl ether and cyclohexane. Solubility in water and in ethyl acetate, however, heavily depends on the anion and other structural features (Table 2). For example, iodides and tetrafluoroborates with short lateral chains such as **2a**, **2e**, **2f** and **4a**, **4e**, **4f**, do not dissolve in ethyl acetate whereas those bearing longer chains, such as **2b** and **4b**, are soluble. An opposite behaviour is found in water: **2a**, **2e**, **2f**, and **4a**, **4e**, **4f** are water soluble while compounds with longer chains are not. The partial solubility of compounds **2g** and **4g** in water was quantitatively measured by ^{1}H NMR in D_2O, being 40 and 28 mg L^{-1}, respectively. All the ionic liquids **3a–h** with hydrophobic NTf_2 anion are totally miscible with ethyl acetate and water insoluble. Thermal analysis data, essential to establish the temperature range of use of the prepared organic salts, are also collected in Table 2. Melting temperature and glass transition temperature were established by differential scanning calorimetry (DSC), while decomposition temperatures were obtained through thermogravimetric analysis. Furan iodides **2a–i** are stable from room temperature to at least 170 °C, moreover no significant material loss due to water or other volatile impurities has been observed in this region; at higher temperatures they show three thermal decomposition steps: the first (T_1) ranges from 162 °C (**2h**) to 196 °C (**2e**), the second (T_2) from 225 °C (**2h**) to 266 °C (**2b**), and the third (T_3) from 264 °C (**2f**) to 308 °C (**2i**); all of them are in the same range of decomposition temperatures of other quaternary ammonium compound reported in the literature.[11]

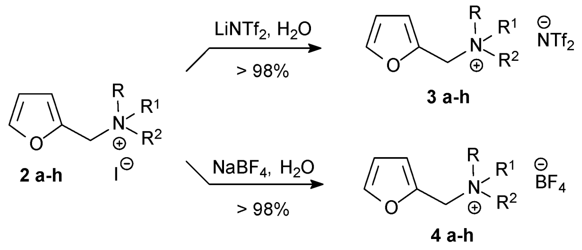


Scheme 1 Synthesis of furan-based ammonium salts.

Table 2 Thermal analysis data, phase state and selected solubility properties of furan-based ionic pairs **2a–h**, **3a–h**, **4a–h**[a]

	T_{dec}						Solubility			T_{dec}						Solubility	
Salt	T_1	T_2	T_3	T_g	T_m	State	H_2O	AcOEt	Salt	T_1	T_2	T_3	T_g	T_m	State	H_2O	AcOEt
2a	187	264	303	−46	102	s	+	–	**3d**	252	378	433	−47		l	–	+
2b	190	266	306	−47		vl	–	+	**3e**	—	353	400	−46		l	–	+
2c	187	229	288	−47		l	–	+	**3f**	—	345	403	−47	66	s	–	+
2d	187	261	298	−47		vl	–	+	**3g**	291	360	393	−46		l	–	+
2e	196	264	—	−47	110	s	+	–	**3h**	290	366	391	−46		l	–	+
2f	173	228	264	−47	107	s	+	–	**4a**	192	267	—	−47		l	+	–
2g	192	262	296	−47		l	40 mg L^{-1}	+	**4b**	184	260	—	−47		vl	–	+
2h	162	225	—	−47		l	–	+	**4c**	191	275	—	−47		l	–	+
2i	195	251	308	−47	78	s	+	–	**4d**	182	271	—	−47		vl	–	+
TBAI	223	—	—	−47	141[b]	s	+	–	**4e**	198	264	—	−47	57	s	+	–
BTBAI	187	—	—	−46	143[b]	s	+	–	**4f**	187	263	—	−46		l	+	–
3a	250	377	—	−46		l	–	+	**4g**	189	260	—	−47		l	28 mg L^{-1}	+
3b	246	287	415	−47		l	–	+	**4h**	165	254	—	−47		l	–	+
3c	318	367	387	−47		l	–	+									

[a] T_{dec}: temperatures of decomposition (°C); T_g: glass transition temperature (°C); T_m: melting temperature (°C); s: solid; l: liquid; vl: viscous liquid. [b] Source: Individual Material Safety Data Sheets; +: soluble, –: not soluble



Scheme 2 Anion exchange with $LiNTf_2$ and $NaBF_4$.

To understand the thermogravimetric behaviour of furan-based iodides we have analyzed also two commercially available ammonium salts, tetrabutylammonium iodide (TBAI) and benzyltributylammonium iodide (BTBAI): they have only one decomposition temperature at 223 and at 187 °C, respectively, in the same range of the first and second decomposition temperatures T_1 and T_2 of iodides **2a–i**. We therefore suppose that the higher T_3 temperatures of furan-containing iodides **2a–i** could be correlated with the decomposition of the aromatic furan ring. The bis(trifluoromethane)sulfonimides **3a–h** are more stable than the corresponding iodides, in fact they show a first irreversible loss of mass at higher temperature: T_1, ranging from 246 °C (**3b**) to 318 °C (**3c**), a second decomposition temperature T_2 from 287 °C (**3b**) to 378 °C (**3d**), and a third, T_3, between 387 °C (**3c**) and 433 °C (**3d**). It is reasonable to think that the poorly basic NTf_2 anion is less prone to promote elimination reactions.

The tetrafluoroborate ammonium salts have only two decomposition temperatures: the first, T_1, ranges from 165 °C (**4h**) to 198 °C (**4e**), and the second, T_2, from 254 °C (**4e**) to 275 °C (**4c**), displaying a thermogravimetric behaviour similar to the corresponding iodides.

Other thermal properties of the ion pairs have been evaluated by DSC, cooling the samples at −90 °C and then heating them to 130 °C at a rate of 10 °C min^{-1}, in two cycles. All the salts show a glass transition temperature (T_g) at around −47 °C, as the conventional ammonium based ion pairs[12] such as TBAI do, independently on the anion type. The melting points (T_m) of the four solid iodides range from 78 °C (**2i**) to 110 °C (**2e**), with a reduction of the temperatures of melting when increasing the length of the alkyl chain.

By exchanging the anion from I^- to BF_4^-, ammonium salts with lower melting temperatures are obtained. For example, compounds **2a** and **2f** afford liquids **4a** and **4f** at room temperature, and compound **4e** has a substantially lower melting point than **2e**: from 110 °C to 57 °C.

Comparing TBAI and BTBAI with compound **2f**, it is possible to note that the furan moiety causes a decrease in the melting point, relative to an alkyl or benzyl substituent, with a T_m reduction of about 40 °C (the temperature of melting of **2f** is 107 °C). The melting point of the only solid bis(trifluoromethane)sulfonimide salt (**3f**) is 66 °C, lower than those of the other two classes (**2f** and **4f**), according to the general behaviour of the NTf_2 anion.

As most of the obtained furan-ammonium salts are liquid at room temperature, the application as alternative reaction media can be envisaged, in particular NTf_2 salts possess the best physical properties for a use as solvents, since they combine a low melting point with a high decomposition temperature and a reduced viscosity.

In order to investigate the chemical stability of the prepared ammonium salts to different conditions, we have checked the behaviour of **2e**, chosen as a model compound, in four solutions at different pH (<1, 2, 7 and 11) recording quantitative ^1H NMR spectra in acetone-d_6 with a known amount of tetrakis(trimethylsilyl)silane (TTMS) as internal standard. While **2e** was find to be stable under basic and weakly acidic conditions for at least 24 h; on the contrary, fast decomposition occurs at very low pH.

Evaluation of acute ecotoxicity

Benzalkonium chlorides (BAC) are among the most used and efficient antimicrobic agents in the biocides field; however, the acute toxicity towards non-target living organisms is quite high (for example the EC_{50} values towards both the crustacean *Daphnia magna* at 48 h and the bacterium *Vibrio fischeri* at 15 min depend on the length of the lateral chain and range from 0.02 to 0.22 mg L^{-1},[13] and from 0.06 to 0.15 mg L^{-1},[14] respectively) and recent studies have demonstrated that they cause genotoxic effects in mammalian and plant cells at environmentally relevant concentrations.[15]

The toxicological studies developed in recent years have demonstrated that short chain furan-based ammonium salts, such as furmethide, have a deep interaction with biological systems, so the toxicity and the environmental fate of the ammonium ion pairs we have synthesized needs to be evaluated.

Accordingly, we have evaluated the acute ecotoxicity towards *Daphnia magna* and *Vibrio fischeri* of the water-soluble iodides **2a**, **2e**, **2f**, **2g** and **2i**. In addition, the toxicity of TBAI and BTBAI was assessed for comparison. *D. magna* and *V. fischeri* were selected because they are among the most widely used species in aquatic toxicity studies, allowing comparison with a large number of substances. Toxicity to the marine planctonic bacterium *V. fischeri* can also be considered a preliminary, aspecific measure of biocidal activity both toward pathogens and non-target bacteria. The freshwater planktonic crustacean *D. magna* is representative of eukaryotic non-target species.

The toxicity to *D. magna* was assessed using a 48 h static acute immobilization test, according to the procedures set out in the Organization for Economic Co-operation and Development (OECD) guideline 202.[16]

Toxicity to *V. fischeri* was measured as inhibition of bioluminescence using Microtox® M500 Rapid Toxicity Testing System (Azur Environmental, Strategic Diagnostics, Newark, DE) equipment and consumables. The assay was carried out in accordance with the 90% basic test for pure compounds protocol, as described in the Microtox user's manual.[17]

For each substance three trials of both the toxicity tests were carried out; details are described in the Experimental section. Concentration–response curves are reported in Fig. 1 and 2 of ESI† and main results are presented in Table 3.

The EC_{50} values of the tested ammonium salts for *D. magna* range from 1.7 to 2.8 mg L^{-1}. The differences tested by ANOVA are significant ($P = 0.016$), however the *post-hoc* SNK test only discriminates **2g**, the most toxic compound, from **2a** and TBAI, the least toxic; other substances are not significantly different from each other or from **2g**, **2a** and TBAI.

The EC_{50} values of the tested ammonium salts for *V. fischeri* range from 1.3 to 284 mg L^{-1}. The differences tested by ANOVA are highly significant ($P < 0.001$), moreover, the *post-hoc* test indicates that any compound is significantly different from all the others.

Thus, while *D. magna* is in general more sensitive to the tested ammonium salts, toxicity to *V. fischeri* is more influenced by the characteristics of the lateral chains of the cation. In particular, **2e** has the lowest toxicity to *V. fischeri*. EC_{50} dramatically decreases (*i.e.* toxicity increases) as a single lateral chain is lengthened from butyl (**2e**) to hexyl (**2i**) to octyl (**2g**). This trend is shown also by *D. magna*, however differences are much less marked and not statistically significant.

Substitution of a methyl with a second butyl (from **2e** to **2a**) also greatly increases toxicity to *V. fischeri*; yet, substitution of the last methyl with a third butyl (from **2a** to **2f**) slightly reduces toxicity. Substitution of the benzyl ring with a furyl ring (from BTBAI to **2a**) slightly decreases toxicity. On the other hand, substitution of an aromatic ring with a butyl (from **2f** or BTBAI to TBAI) produces a larger reduction of toxicity.

Even if preliminary, these results indicate that toxicity of furan-based quaternary ammonium salts is comparable to the analogous benzyl-based salts, in particular the toxicity profile towards *V. fischeri* indicate potentially the same applications as biocides.

Conclusions

The synthesis of furan-based ion pairs from furfural has been accomplished in very good yields, good purity of the products and wide versatility. The main goal of preparing RTILs suitable to be used as reaction and general-purpose solvents

Table 3 The 50% effect concentrations (EC_{50}) of the ammonium salts TBAI, BTBAI, **2a**, **2e–i** to *Daphnia magna* in a 48 h immobilization test and to *Vibrio fischeri* in a 15 min inhibition of bioluminescence test

	Daphnia magna			*Vibrio fischeri*		
	EC_{50}/mg L^{-1}	EC_{50}/μmol L^{-1}	SNK[a] test	EC_{50}/mg L^{-1}	EC_{50}/μmol L^{-1}	SNK[b] test
TBAI	2.8 (2.4–3.2)	7.6 (6.6–8.7)	a	284 (241–336)	769 (652–908)	a
BTBAI	2.6 (0.7–9.8)	6.3 (1.6-24.3)	ab	64 (46–88)	158 (115–218)	b
2f	2.3 (1.4–3.8)	6.0 (3.6–9.8)	ab	95 (66–136)	240 (167–345)	c
2a	2.4 (2.3–2.5)	6.7 (6.4–7.0)	a	37 (29–47)	105 (82–135)	d
2e	2.0 (1.6–2.4)	6.3 (5.1–7.8)	ab	677 (473–968)	2189 (1530–3129)	e
2i	2.0 (1.3–3.1)	6.0 (4.0–9.1)	ab	11.6 (8.9–15.2)	34 (26–45)	f
2g	1.7 (1.2–2.4)	4.6 (3.3–6.5)	b	1.3 (0.6–2.5)	3.5 (1.7–6.9)	g

[a] The reported values are means of three independent trials (in parenthesis: lower and upper limits of the confidence interval). [b] Results of the Student–Newman–Keuls *post-hoc* statistical test for pairwise comparison of EC_{50} (μmol L^{-1}). Substances sharing the same letter are not significantly different.

has been also attained, specially for NTf_2 salts **3a–h** that combine low melting points with high decomposition temperatures and reduced viscosities. Regarding the possible applications as surfactants and biocides, furan-based salts could be a valuable alternative to benzyltributylammonium salts and benzalkonium chloride, that are produced from non-renewable resources. Further studies are in progress, in particular to characterize biocidal efficiency toward pathogens and other non-target organisms and to eliminate the use of alkyl halide in the alkylation step.

Experimental

General

Most chemicals are purchased from Sigma-Aldrich and used without further purification. Reactions are monitored by means of TLC using silica gel sheets (Merck 60 F_{254}); the products are separated by flash chromatography on silica gel (Aldrich, 230–400 mesh). NMR spectra are recorded using a 5 mm probe on a Varian Inova 200, Varian Inova 300, Varian Mercury 400 or Varian Inova 600 spectrometer, all chemical shifts are quoted relative to deuterated solvent signals with chemical shifts (δ) given in ppm and coupling constants (J) values given in Hz. GC-MS spectra are obtained using a AGILENT 6850 gas chromatograph on a SUPELCO SPB-5 capillary column (temperature programme: 50 °C for 5 min then 10 °C min^{-1} up to 300 °C) coupled with a mass spectrometer (quadrupole) AGILENT 5975. Thermogravimetric measurements (TGA) are carried out using a TA-SDT Q600. The analyses were performed at 10 °C min^{-1} from room temperature to 500 °C under N_2 flow. Differential scanning calorimetry (DSC) was performed using TA-DSC Q100 in the temperature range from −90 to 130 °C under N_2 flow, at an heating rate of 10 °C min^{-1}.

The purity of the new compounds was established to be at least 98% through proton nuclear magnetic resonance (^1H NMR) spectra by integration of proton signals with respect to an internal standard; consistently, by integration of its peak (1.56 ppm in $CDCl_3$), the residual water was in the range 0.5–2 wt%. The spectral data were acquired in deuterated solvent with a known amount of tetrakis(trimethylsilyl)silane (TTMS) as an internal standard and a delay time between successive scans of 20 s to ensure complete proton relaxation and therefore quantitative integration.[18] Purity was confirmed by elemental analysis on a Perkin Elmer 2400 Series II CHNS/O Analyzer equipped with a Perkin AD-4 Autobalance. Experimental procedures and characterization of products **5a–5c**, **6a–c**, and **7a–7d** are reported in the ESI.†

***N*,*N*-Dibutyl-*N*-methyl-2-furfurylammonium iodide 2a.** Tertiary amine **7a** (2.0 g, 10 mmol) and iodomethane (6.9 cm^3, 11.1 mmol) were stirred at room temperature for 24 h. The excess of iodomethane was evaporated under vacuum and the solid obtained was recrystallized from ethyl acetate and ethanol (3.0 g, 85% yield). Found: C, 47.18; H, 7.36; N, 4.43; $C_{14}H_{26}INO$ requires C, 47.87; H, 7.46; N, 3.99%. ^1H NMR (400 MHz, $CDCl_3$): δ 0.99–1.03 (m, 6H, 2 × $N(CH_2)_3CH_3$), 1.40–1.49 (m, 4H, 2 × $N(CH_2)_2CH_2CH_3$), 1.75–1.84 (m, 4H, 2 × $NCH_2CH_2(CH_2)_2CH_3$), 3.29 (s, 3H, NCH_3), 3.33–3.51 (m, 4H, 2 × $NCH_2(CH_2)_2CH_3$), 4.99 (s, 2H, NCH_2-furan), 6.49 (dd, ^3J(H, H) = 2.0 Hz, ^3J(H, H) = 3.2 Hz, 1H, 4-H furan), 7.06 (d, ^3J(H, H) = 3.2 Hz, 1H, 3-H furan), 7.59 ppm (d, ^3J(H, H) = 2.0 Hz, 1H, 5-H furan); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6 (×2C), 19.7 (×2C), 24.5 (×2C), 48.5, 57.9, 61.2 (×2C), 111.7, 117.9, 142.0, 145.4 ppm.

***N*-Butyl-*N*-dodecyl-*N*-methyl-2-furfurylammonium iodide 2b.** Prepared starting from tertiary amine **7b** with the same procedure reported for **2a**. The viscous liquid obtained can be purified by a short flash chromatography eluting with CH_2Cl_2–acetone (1 : 1) (3.5 g, 75% yield). Found: C, 56.84; H, 9.02; N, 3.25; $C_{22}H_{42}INO$ requires C, 57.01; H, 9.13; N, 3.02%. ^1H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, ^3J(H, H) = 6.4 Hz, 3H, $CH_3(CH_2)_{11}N$), 0.99 (t, ^3J(H, H) = 7.2 Hz, 3H, $CH_3(CH_2)_3N$), 1.24–1.30 (m, 16H, $CH_3(CH_2)_8(CH_2)_3N$), 1.34–1.38 (m, 4H, $CH_3(CH_2)_8CH_2(CH_2)_2N$, $CH_3CH_2(CH_2)_2N$), 1.76–1.83 (m, 4H, $CH_3(CH_2)_9CH_2CH_2N$, $CH_3CH_2CH_2CH_2N$), 3.27 (s, 3H, NCH_3), 3.32–3.47 (m, 4H, $CH_3(CH_2)_{10}CH_2N$, $CH_3(CH_2)_2CH_2N$), 4.96 (s, 2H, NCH_2-furan), 6.46 (dd, ^3J(H, H) = 2 Hz, ^3J(H, H) = 3.6 Hz, 1H, 4-H furan), 7.03 (d, ^3J(H, H) = 3.6 Hz, 1H, 3-H furan), 7.51 ppm (d, ^3J(H, H) = 2 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 14.0, 19.6, 22.5, 22.6, 24.5, 26.2, 29.0, 29.2, 29.3, 29.3, 29.5 (×2C), 31.8, 48.5, 57.7, 61.2, 61.4, 111.5, 117.7, 142.0, 145.2 ppm.

***N*-Butyl-*N*-methyl-*N*-octyl-2-furfurylammonium iodide 2c.** Prepared starting from tertiary amine **7c** with the same procedure reported for **2a**. The viscous liquid obtained can be purified by flash chromatography eluting with CH_2Cl_2–acetone (1 : 1) (3.2 g, 78% yield). Found: C, 52.85; H, 8.45; N, 3. 28; $C_{18}H_{34}INO$ requires C, 53.07; H, 8.41; N, 3.44%. ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, ^3J(H, H) = 6.8 Hz, 3H, $N(CH_2)_7CH_3$), 1.01 (t, ^3J(H, H) = 7.6 Hz, 3H, $N(CH_2)_3CH_3$), 1.23–1.47 (m, 12H, $CH_3CH_2(CH_2)_2N$, $CH_3(CH_2)_5(CH_2)_2N$), 1.77–1.81 (m, 4H, $CH_3CH_2CH_2CH_2N$, $CH_3(CH_2)_5CH_2CH_2N$), 3.29 (s, 3H, NCH_3), 3.31–3.48 (m, 4H, $CH_3(CH_2)_2CH_2N$, $CH_3(CH_2)_6CH_2N$), 5.00 (s, 2H, NCH_2-furan), 6.49 (dd, ^3J(H, H) = 1.6 Hz, ^3J(H, H) = 3.4 Hz, 1H, 4-H furan), 7.07 (d, ^3J(H, H) = 3.4 Hz, 1H, 3-H furan), 7.52 ppm (d, ^3J(H, H) = 1.6 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 14.0, 19.6, 22.5, 22.6, 24.5, 26.2, 28.9, 29.0, 31.5, 48.4, 57.8, 61.2, 61.3, 111.6, 117.9, 142.0, 145.3 ppm.

***N*-Dodecyl-*N*-methyl-*N*-octyl-2-furfurylammonium iodide 2d.** Prepared starting from tertiary amine **7d** with the same procedure reported for **2a**. The viscous liquid obtained can be purified by flash chromatography eluting with CH_2Cl_2–acetone (1 : 1) (4.6 g, 90% yield). Found: C, 59.95; H, 9.73; N, 2.58; $C_{26}H_{50}INO$ requires C, 60.10; H, 9.70; N, 2.70%. ^1H NMR (400 MHz, $CDCl_3$): δ 0.83 (t, ^3J(H, H) = 6.4 Hz, 6H, $CH_3(CH_2)_{11}N$, $CH_3(CH_2)_7N$), 1.24–1.35 (m, 28H, $CH_3(CH_2)_9(CH_2)_2N$, $CH_3(CH_2)_5(CH_2)_2N$), 1.75–1.77 (m, 4H, $CH_3(CH_2)_9CH_2CH_2N$, $CH_3(CH_2)_4CH_2CH_2N$), 3.23 (s, 3H, NCH_3), 3.30–3.40 (m, 4H, $CH_3(CH_2)_{10}CH_2N$, $CH_3(CH_2)_6CH_2N$), 4.92 (s, 2H, NCH_2-furan), 6.43 (dd, ^3J(H, H) = 1.8 Hz, ^3J(H, H) = 3.4 Hz, 1H, 4-H furan), 7.00 (d, ^3J(H, H) = 3.4 Hz, 1H, 3-H furan), 7.47 ppm (d, ^3J(H, H) = 1.8 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 13.9, 22.4, 22.5, 22.5, 26.1, 28.8, 28.8, 28.9, 29.1, 29.2, 29.2, 29.4 ($\times$4C), 31.4, 31.7, 48.5, 57.7, 61.2, 61.4 , 111.4, 117.5, 141.9, 145.1 ppm.

***N*-Butyl-*N*,*N*-dimethyl-2-furfurylammonium iodide 2e.** *N*-Butylfurfurylamine **6a** (1.5 g, 10 mmol) and K_2CO_3 (3.0 g, 22 mmol) were charged in a two-neck round bottom flask, then iodomethane (1.3 cm^3, 22 mmol) was added and the reaction was stirred at room temperature for 24 h. K_2CO_3 was filtered off and the excess of iodomethane evaporated under vacuum. The solid obtained was crystallized from ethanol and ethyl acetate (3.1 g, 98% yield). Found: C, 42.10; H, 6.50; N, 5.11; $C_{11}H_{20}INO$ requires C, 42.73; H, 6.52; N, 4.53%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (t, ^3J(H, H) = 7.2 Hz, 3H, $N(CH_2)_3CH_3$), 1.43–1.48 (m, 2H, $N(CH_2)_2CH_2CH_3$), 1.82–1.86 (m, 2H, $NCH_2CH_2CH_2CH_3$), 3.36 (s, 6H, 2 $\times$ NCH_3), 3.50–3.54 (m, 2H, $NCH_2(CH_2)_2CH_3$), 5.04 (s, 2H, NCH_2-furan), 6.05 (dd, ^3J(H, H) = 3.4 Hz, ^3J(H, H) = 2 Hz, 1H, 4-H furan), 7.05 (d, ^3J(H, H) = 3.4 Hz, 1H, 3-H furan), 7.54 ppm (d, ^3J(H, H) = 2 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.3, 19.1, 24.3, 50.3 ($\times$2C), 59.4, 63.8, 111.1, 117.2, 141.9, 145.1 ppm.

***N*,*N*,*N*-Tributyl-2-furfuryl ammonium iodide 2f.** *N*-Butylfurfuryl amine **6a** (1.5 g, 10 mmol) and K_2CO_3 (3.0 g, 22 mmol); were charged in a two-neck round bottom flask, then iodobutane (2.5 cm^3, 22 mmol) was added and the reaction was stirred at 50 °C for 24 h. K_2CO_3 was filtered off and the oil extracted with H_2O/diethyl ether; the water phase was concentrated and the solid crystallized from ethyl acetate and ethanol (3.6 g, 93% yield). Found: C, 51.32; H, 8.34; N, 3.84; $C_{17}H_{32}INO$ requires C, 51.91; H, 8.20; N, 3.56.%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00–1.04 (m, 9H, 3 $\times$ $N(CH_2)_3CH_3$), 1.42–1.48 (m, 6H, 3 $\times$ $N(CH_2)_2CH_2CH_3$), 1.77–1.85 (m, 6H, 3 $\times$ $NCH_2CH_2CH_2CH_3$), 3.29–3.34 (m, 6H, 3 $\times$ $NCH_2CH_2)_2CH_3$), 4.90 (s, 2H, NCH_2-furan), 6.49 (dd, ^3J(H, H) = 2 Hz, ^3J(H, H) = 3.2 Hz, 1H, 4-H furan), 6.96 (d, ^3J(H, H) = 3.2 Hz, 1H, 3-H furan), 7.52 ppm (d, ^3J(H, H) = 2 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6 ($\times$3C), 19.7 ($\times$3C), 24.4 ($\times$3C), 55.6, 59.2 ($\times$3C), 111.6, 117.3, 141.9, 145.2 ppm.

***N*-Octyl-*N*,*N*-dimethyl-2-furfurylammonium iodide 2g.** Prepared starting from amine **6b** with the same procedure reported for **2e**. The liquid obtained was purified by flash chromatography eluting with CH_2Cl_2–acetone (1/1) (3.5 g, 96% yield). Found: C, 49.11; H, 7.68; N, 3.92; $C_{15}H_{28}INO$ requires C, 49.32; H, 7.73; N, 3.83%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, ^3J(H, H) = 6.4 Hz, 3H, $N(CH_2)_7CH_3$), 1.27–1.37 (m, 10H, $N(CH_2)_2(CH_2)_5CH_3$), 1.83–1.85 (m, 2H, $NCH_2CH_2(CH_2)_5CH_3$), 3.36 (s, 6H, 2 $\times$ NCH_3), 3.46–3.51 (m, 2H, $NCH_2(CH_2)_6CH_3$), 5.05 (s, 2H, NCH_2-furan), 6.49 (dd, ^3J(H, H) = 3.4 Hz, ^3J(H, H) = 2 Hz, 1H, 4-H furan), 7.05 (d, ^3J(H, H) = 3.4 Hz, 1H, 3-H furan), 7.54 ppm (d, ^3J(H, H) = 2 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 13.9, 19.6, 22.4, 24.3, 26.3, 28.9, 31.5, 55.5, 59.1, 59.3, 111.5, 117.2, 141.9, 145.1 ppm.

***N*,*N*-Dibutyl-*N*-octyl-2-furfurylammonium iodide 2h.** Prepared starting from amine **6b** with the same procedure reported for **2f**. The liquid obtained can be purified by flash chromatography eluting with CH_2Cl_2–acetone (1 : 1) (4.2 g, 95% yield). Found: C, 56.01; H, 8.93; N, 2.98; $C_{21}H_{40}INO$ requires C, 56.12; H, 8.97; N, 3.12%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, ^3J(H, H) = 6.8 Hz, 3H, $N(CH_2)_7CH_3$), 1.02 (t, ^3J(H, H) = 7.2 Hz, 6H, 2 $\times$ $N(CH_2)_3CH_3$), 1.24–1.38 (m, 14H, 2 $\times$ $CH_3CH_2(CH_2)_2N$, $CH_3(CH_2)_5(CH_2)_2N$), 1.78–1.82 (m, 6H, 2 $\times$ $CH_3CH_2CH_2CH_2N$, $CH_3(CH_2)_5CH_2CH_2N$), 3.27–3.34 (m, 6H, 2 $\times$ $CH_3(CH_2)_2CH_2N$, $CH_3(CH_2)_6CH_2N$), 4.92 (s, 2H, NCH_2-furan), 6.50 (dd, ^3J(H, H) = 1.6 Hz, ^3J(H, H) = 3.2 Hz, 1H, 4-H furan), 6.97 (d, ^3J(H, H) = 3.2 Hz, 1H, 3-H furan), 7.52 ppm (d, ^3J(H, H) = 1.6 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5 ($\times$2C), 13.9, 19.6 ($\times$2C), 22.4 ($\times$2C), 24.3 ($\times$2C), 26.2, 28.8, 28.8, 31.4, 55.4, 59.1, 59.3 ($\times$2C), 111.5, 117.1, 141.9, 145.1 ppm.

***N*-Hexyl-*N*,*N*-dimethyl-2-furfurylammonium iodide 2i.** Prepared starting from amine **6c** with the same procedure reported for **2e**. The solid obtained was recrystallized from ethanol and ethyl acetate (2.8 g, 97% yield). Found: C, 46.17; H, 7.07; N, 4.31; $C_{15}H_{28}INO$ requires C, 46.30; H, 7.17; N, 4.15%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, ^3J(H, H) = 6.8 Hz, 3H, $N(CH_2)_5CH_3$), 1.29–1.35 (m, 6H, $N(CH_2)_2$-$(CH_2)_3CH_3$), 1.82–1.86 (m, 2H, $NCH_2CH_2(CH_2)_3CH_3$), 3.36 (s, 6H, 2 $\times$ NCH_3), 3.47–3.56 (m, 2H, $NCH_2(CH_2)_4CH_3$), 5.04 (s, 2H, NCH_2-furan), 6.48 (dd, ^3J(H, H) = 3.4 Hz, ^3J(H, H) = 1.8 Hz, 1H, 4-H furan), 7.04 (d, ^3J(H, H) = 3.4 Hz, 1H, 3-H furan), 7.54 ppm (d, ^3J(H, H) = 1.8 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7 ($\times$2C), 22.2, 22.7, 25.7 31.0, 50.6, 59.6, 64.4, 111.4, 117.6, 142.1, 145.3 ppm.

***N*,*N*-Dibutyl-*N*-methyl-2-furfurylammonium bis(trifluoromethane)sulfonimide 3a.** According to the general procedure reported in the literature,[11] ammonium salt **2a** (0.35 g, 1 mmol) was dissolved in deionized water (1 cm^3) and then an aqueous solution of $LiN(SO_2CF_3)_2$ (0.28 g, 1 mmol) was added. The reaction was stirred at room temperature for 24 h, the product was extracted with ethyl acetate and the solvent was evaporated under vacuum (0.50 g, 99% yield). Found: C, 37.95; H, 5.26; N, 5.38; $C_{16}H_{26}F_6N_2O_5S_2$ requires C, 38.09; H, 5.19; N, 5.55%.^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (t, ^3J(H, H) = 7.2 Hz, 6H, 2 $\times$ $N(CH_2)_3CH_3$), 1.39–1.44 (m, 4H, 2 $\times$ N $(CH_2)_2CH_2CH_3$), 1.73–1.78 (m, 4H, 2 $\times$ $NCH_2CH_2CH_2CH_3$), 3.00 (s, 3H, NCH_3), 3.14–3.18 (m, 4H, 2 $\times$ $NCH_2CH_2)_2CH_3$), 4.46 (s, 2H, NCH_2-furan), 6.51 (dd, ^3J(H, H) = 2 Hz, ^3J(H, H) = 3.4 Hz, 1H, 4-H furan), 6.80 (d, ^3J(H, H) = 3.4 Hz, 1H, 3-H furan), 7.56 ppm (d, ^3J(H, H) = 2 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.3 ($\times$2C), 19.4 ($\times$2C), 24.1 ($\times$2C), 48.0, 57.7, 61.5 ($\times$2C), 111.6, 117.3, 119.7 (q, *J* 318, CF_3), 141.5, 145.6 ppm.

***N*-Butyl-*N*-dodecyl-*N*-methyl-2-furfurylammonium bis(trifluoromethane)sulfonimide 3b.** Prepared starting from ammonium iodide **2b** (0.46 g, 1 mmol) with the same procedure reported for **3a** (0.61 g, 99% yield). Found: C, 46.68; H, 6.79; N, 4.61; $C_{24}H_{24}F_6N_2O_5S_2$ requires C, 46.74; H, 6.86; N, 4.54%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, ^3J(H, H) = 6.4 Hz, 3H, $CH_3(CH_2)_{11}N$), 1.00 (t, ^3J(H, H) = 7.2 Hz, 3H,

$C\mathit{H}_3(CH_2)_3N$), 1.24–1.28 (m, 16H, $CH_3(C\mathit{H}_2)_8(CH_2)_3N$), 1.32–1.35 (m, 4H, $CH_3(CH_2)_8C\mathit{H}_2(CH_2)_2N$, $CH_3C\mathit{H}_2(CH_2)_2N$), 1.75–1.77 (m, 4H, $CH_3(CH_2)_9C\mathit{H}_2CH_2N$, $CH_3CH_2C\mathit{H}_2CH_2$), 3.00 (s, 3H, $NC\mathit{H}_3$), 3.13–3.20 (m, 4H, $CH_3(CH_2)_{10}C\mathit{H}_2N$, $CH_3(CH_2)_2C\mathit{H}_2N$), 4.48 (s, 2H, $NC\mathit{H}_2$-furan), 6.51 (dd, ^3J(H, H) = 2 Hz, ^3J(H, H) = 3.4 Hz, 1H, 4-H furan), 6.81 (d, ^3J(H, H) = 3.4 Hz, 1H, 3-H furan), 7.56 ppm (d, ^3J(H, H) = 2 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.4, 14.1, 19.5, 22.3, 22.6, 24.2, 26.1, 28.9, 29.2 (×2C), 29.3, 29.5 (×2C), 31.8, 48.1, 57.8, 61.4, 61.6, 111.8, 117.5, 119.8 (q, J 319, CF_3), 141.5, 145.6 ppm.

***N*-Butyl-*N*-methyl-*N*-octyl-2-furfurylammonium bis(trifluoromethane)sulfonimide 3c.** Prepared starting from ammonium iodide **2c** (0.40 g, 1 mmol) with the same procedure reported for **3a** (0.56 g, 99% yield). Found: C, 42.73; H, 6.03; N, 4.92; $C_{20}H_{34}F_6N_2O_5S_2$ requires C, 42.85; H, 6.11; N, 5.00%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, ^3J(H, H) = 6.4 Hz, 3H, $N(CH_2)_7C\mathit{H}_3$), 1.00 (t, ^3J(H, H) = 7.2 Hz, 3H, $N(CH_2)_3C\mathit{H}_3$), 1.28–1.44 (m, 12H, $CH_3C\mathit{H}_2(CH_2)_2N$, $CH_3(C\mathit{H}_2)_5(CH_2)_2N$), 1.73–1.77 (m, 4H, $CH_3CH_2C\mathit{H}_2CH_2N$, $CH_3(CH_2)_5C\mathit{H}_2CH_2N$), 2.99 (s, 3H, $NC\mathit{H}_3$), 3.15–3.19 (m, 4H, $CH_3(CH_2)_2C\mathit{H}_2N$, $CH_3(CH_2)_6C\mathit{H}_2N$), 4.47 (s, 2H, $NC\mathit{H}_2$-furan), 6.50 (dd, ^3J(H, H) = 1.6 Hz, ^3J(H, H) = 3.2 Hz, 1H, 4-H furan), 6.80 (d, ^3J(H, H) = 3.2 Hz, 1H, 3-H furan), 7.55 ppm (d, ^3J(H, H) = 1.6 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.3, 14.9, 19.5, 22.3, 22.5, 24.2, 26.1, 28.8, 28.9, 31.5, 48.0, 57.7, 61.5, 61.6, 111.7, 117.4, 119.8 (q, J 319, CF_3), 141.5, 145.6 ppm.

***N*-Dodecyl-*N*-methyl-*N*-octyl-2-furfurylammonium bis(trifluoromethane)sulfonimide 3d.** Prepared starting from ammonium iodide **2d** (0.51 g, 1 mmol) with the same procedure reported for **3a** (0.67 g, 99% yield). Found: C, 49.81; H, 7.45; N, 4.24; $C_{28}H_{50}F_6N_2O_5S_2$ requires C, 49.98; H, 7.49; N, 4.16%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, ^3J(H, H) = 6.8 Hz, 3H, $C\mathit{H}_3(CH_2)_{11}N$), 1.01 (t, ^3J(H, H) = 7.2 Hz, 3H, $N(CH_2)_7C\mathit{H}_3$), 1.24–1.36 (m, 28H, $CH_3(C\mathit{H}_2)_9(CH_2)_2N$, $CH_3(C\mathit{H}_2)_5(CH_2)_2N$), 1.74–1.78 (m, 4H, $CH_3(CH_2)_9C\mathit{H}_2CH_2N$, $CH_3CH_2C\mathit{H}_2CH_2N$), 3.01 (s, 3H, $NC\mathit{H}_3$), 3.14–3.20 (m, 4H, $CH_3(CH_2)_{10}C\mathit{H}_2N$, $CH_3(CH_2)_2C\mathit{H}_2N$), 4.48 (s, 2H, $NC\mathit{H}_2$-furan), 6.52 (dd, ^3J(H, H) = 1.6 Hz, ^3J(H, H) = 3.2 Hz, 1H, 4-H furan), 6.82 (d, ^3J(H, H) = 3.2 Hz, 1H, 3-H furan), 7.56 ppm (d, ^3J(H, H) = 1.6 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.4, 14.0, 19.5, 22.3, 22.5, 24.2, 26.1, 28.8 (×10C), 31.5, 48.1, 57.9, 61.4, 61.6, 111.8, 117.5, 119.6 (q, J 318, CF_3), 141.4, 145.7 ppm.

***N*-Butyl-*N*,*N*-dimethyl-2-furfurylammonium bis(trifluoromethane)sulfonimide 3e.** Prepared starting from ammonium iodide **2e** (0.30 g, 1 mmol) with the same procedure reported for **3a** (0.46, 99% yield). Found: C, 33.61; H, 4.29; N, 6.18; $C_{13}H_{20}F_6N_2O_5S_2$ requires C, 33.76; H, 4.36; N, 6.06%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (t, ^3J(H, H) = 7.2 Hz, 3H, $N(CH_2)_3C\mathit{H}_3$), 1.39–1.44 (m, 2H, $N(CH_2)_2C\mathit{H}_2CH_3$), 1.78–1.82 (m, 2H, $NCH_2C\mathit{H}_2CH_2CH_3$), 3.07 (s, 6H, 2 × $NC\mathit{H}_3$), 3.21–3.24 (m, 2H, $NC\mathit{H}_2(CH_2)_2CH_3$), 4.48 (s, 2H, $NC\mathit{H}_2$-furan), 6.51 (dd, ^3J(H, H) = 3.6, ^3J(H, H) = 1.8 Hz, 1H, 4-H furan), 6.82 (d, ^3J(H, H) = 3.6 Hz, 1H, 3-H furan), 7.57 ppm (d, ^3J(H, H) = 1.8 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.3, 19.3, 24.5, 50.4 (×2C), 60.0, 64.4, 111.7, 117.4, 119.7 (q, J 319, CF_3), 141.6, 145.8 ppm.

***N*,*N*,*N*-Tributyl-2-furfurylammonium bis(trifluoromethane)sulfonimide 3f.** Prepared starting from ammonium iodide **2f** (0.39 g, 1 mmol) with the same procedure reported for **3a** (0.54 g, 99% yield). Found: C, 41.72; H, 5.98; N, 4.97; $C_{19}H_{32}F_6N_2O_5S_2$ requires C, 41.75; H, 5.90; N, 5.13%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00–1.04 (m, 9H, 3 × $N(CH_2)_3C\mathit{H}_3$), 1.40–1.45 (m, 6H, 3 × $N(CH_2)_2C\mathit{H}_2CH_3$), 1.70–1.76 (m, 6H, 3 × $NCH_2C\mathit{H}_2CH_2CH_3$), 3.09–3.13 (m, 6H, 3 × $NC\mathit{H}_2(CH_2)_2CH_3$), 4.48 (s, 2H, $NC\mathit{H}_2$-furan), 6.52 (dd, ^3J(H, H) = 2 Hz, ^3J(H, H) = 3.4 Hz, 1H, 4-H furan), 6.75 (d, ^3J(H, H) = 3.4 Hz, 1H, 3-H furan), 7.56 ppm (d, ^3J(H, H) = 2 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.3 (×3C), 19.4 (×3C), 23.7 (×3C), 54.5, 58.5 (×3C), 111.5, 116.7, 119.8 (q, J 319, CF_3), 141.5, 145.5 ppm.

***N*-Octyl-*N*,*N*-dimethyl-2-furfurylammonium bis(trifluoromethane)sulfonimide 3g.** Prepared starting from ammonium salt **2g** (0.36 g, 1 mmol) with the same procedure reported for **3a** (0.51 g, 99% yield). Found: C, 39.75; H, 5.29; N, 5.26; $C_{17}H_{28}F_6N_2O_5S_2$ requires C, 39.38; H, 5.44; N, 5.40%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, ^3J(H, H) = 6.8 Hz, 3H, $N(CH_2)_7C\mathit{H}_3$), 1.23–1.34 (m, 10H, $N(CH_2)_2(C\mathit{H}_2)_5CH_3$), 1.78–1.82 (m, 2H, $NCH_2C\mathit{H}_2(CH_2)_5CH_3$), 3.05 (s, 6H, 2 × $NC\mathit{H}_3$), 3.16–3.21 (m, 2H, $NC\mathit{H}_2(CH_2)_6CH_3$), 4.46 (s, 2H, $NC\mathit{H}_2$-furan), 6.50 (dd, ^3J(H, H) = 3.4 z, ^3J(H, H) = 1.4 Hz, 1H, 4-H furan), 6.81 (d, ^3J(H, H) = 3.4 Hz, 1H, 3-H furan), 7.56 ppm (d, ^3J(H, H) = 1.4 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9 (×2C), 22.4, 22.6, 25.9, 28.8, 28.8, 31.5, 50.4, 60.0, 64.3, 111.7, 117.4, 119.6 (q, J 319, CF_3), 141.5, 145.8 ppm.

***N*,*N*-Dibutyl-*N*-octyl-2-furfurylammonium bis(trifluoromethane)sulfonimide 3h.** Prepared starting from ammonium salt **2h** (0.44 g, 1 mmol) with the same procedure reported for **3a** (0.60 g, 99% yield). Found: C, 45.72; H, 6.63; N, 4.57; $C_{23}H_{40}F_6N_2O_5S_2$ requires C, 45.84; H, 6.69; N, 4.65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, ^3J(H, H) = 6.8 Hz, 3H, $N(CH_2)_7C\mathit{H}_3$), 1.01 (t, ^3J(H, H) = 7.6 Hz, 6H, 2 × $N(CH_2)_3C\mathit{H}_3$), 1.28–1.45 (m, 14H, 2 × $CH_3C\mathit{H}_2(CH_2)_2N$, $CH_3(C\mathit{H}_2)_5(CH_2)_2N$), 1.71–1.77 (m, 6H, 2 × $CH_3CH_2C\mathit{H}_2CH_2N$, $CH_3(CH_2)_5C\mathit{H}_2CH_2N$), 3.08–3.13 (m, 6H, $CH_3(CH_2)_2C\mathit{H}_2N$, $CH_3(CH_2)_6C\mathit{H}_2N$, 4.50 (s, 2H, $NC\mathit{H}_2$-furan), 6.51 (dd, ^3J(H, H) = 1.6 Hz, ^3J(H, H) = 3.2 Hz, 1H, 4-H furan), 6.75 (d, ^3J(H, H) = 3.2 Hz, 1H, 3-H furan), 7.54 ppm (d, ^3J(H, H) = 1.6 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.4 (×2C), 14.0, 19.5 (×2C), 21.9, 22.5, 23.9 (×2C), 26.2, 28.8, 28.9, 31.5, 54.8, 58.7 (×2C), 59.0, 111.7, 117.0, 119.3 (q, J 318, CF_3), 141.5, 145.5 ppm.

***N*,*N*-Dibutyl-*N*-methylfurfurylammonium tetrafluoroborate 4a.** Ammonium salt **2a** (0.35 g, 1 mmol) was dissolved in deionized water (1 cm^3) and then $NaBF_4$ (0.1 g, 1 mmol) added. The reaction is stirred at room temperature for 24 h. The product is extracted with ethyl acetate, the solvent is evaporated under vacuum (0.31 g, 99% yield). Found: C, 54.12; H, 8.31; N, 4.62; $C_{14}H_{26}BF_4NO$ requires C, 54.04; H, 8.42; N, 4.50%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99

(t, ^{3}J(H, H) = 7.6 Hz, 2 × 6H, N(CH$_2$)$_3$C*H*$_3$), 1.37–1.46 (m, 4H, 2 × N(CH$_2$)$_2$C*H*$_2$CH$_3$), 1.72–1.81 (m, 4H, 2 × NCH$_2$C*H*$_2$-CH$_2$CH$_3$), 3.11 (s, 3H, NC*H*$_3$), 3.20–3.33 (m, 4H, 2 × NC*H*$_2$(CH$_2$)$_2$CH$_3$), 4.68 (s, 2H, NC*H*$_2$-furan), 6.47 (dd, ^{3}J(H, H) = 1.8 Hz, ^{3}J(H, H) = 3.6 Hz, 1H, 4-H furan), 6.93 (d, ^{3}J(H, H) = 3.6 Hz, 1H, 3-H furan), 7.52 ppm (d, ^{3}J(H, H) = 1.8 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.5 (×2C), 19.6 (×2C), 24.3 (×2C), 48.1, 57.7, 61.2 (×2C), 111.6, 117.6, 142.0, 145.3 ppm.

***N*-Butyl-*N*-dodecyl-*N*-methylfurfurylammonium tetrafluoroborate 4b.** Prepared starting from ammonium salt **2b** (0.46 g, 1 mmol) with the same procedure reported for **4a** (0.42 g, 99% yield). Found: C, 62.38; H, 9.91; N, 3.48; C$_{22}$H$_{42}$BF$_4$NO requires C, 62.41; H, 10.00; N, 3.31%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.87 (t, ^{3}J(H, H) = 6.8 Hz, 3H, C*H*$_3$(CH$_2$)$_{11}$N), 1.00 (t, ^{3}J(H, H) = 7.2 Hz, 3H, C*H*$_3$(CH$_2$)$_3$N), 1.25–1.36 (m, 16H, CH$_3$(C*H*$_2$)$_8$(CH$_2$)$_3$N), 1.40–1.45 (m, 4H, CH$_3$(CH$_2$)$_8$-C*H*$_2$(CH$_2$)$_2$N, CH$_3$C*H*$_2$(CH$_2$)$_2$N), 1.74–1.78 (m, 4H, CH$_3$(CH$_2$)$_9$C*H*$_2$CH$_2$N, CH$_3$CH$_2$C*H*$_2$CH$_2$N), 3.10 (s, 3H, NC*H*$_3$), 3.20–3.30 (m, 4H, CH$_3$(CH$_2$)$_{10}$C*H*$_2$N, CH$_3$(CH$_2$)$_2$-C*H*$_2$N), 4.67 (s, 2H, NC*H*$_2$-furan), 6.48 (dd, ^{3}J(H, H) = 2.2 Hz, ^{3}J(H, H) = 3.4 Hz, 1H, 4-H furan), 6.94 (d, ^{3}J(H, H) = 3.4 Hz, 1H, 3-H furan), 7.52 ppm (d, ^{3}J(H, H) = 2.2 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.5, 14.0, 19.6, 22.4, 22.6, 24.3, 26.2, 29.0, 29.3, 29.3, 29.4, 29.5 (×2C), 31.8, 48.1, 57.8, 61.2, 61.3, 111.7, 117.8, 141.9, 145.4 ppm.

***N*-Butyl-*N*-methyl-*N*-octyl-2-furfurylammonium tetrafluoroborate 4c.** Prepared starting from ammonium salt **2c** (0.40 g, 1 mmol) with the same procedure reported for **4a** (0.36 g, 99% yield). Found: C, 58.78; H, 9.32; N, 3.71; C$_{18}$H$_{34}$BF$_4$NO requires C, 58.86; H, 9.33; N, 3.81%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.88 (t, ^{3}J(H, H) = 6.4 Hz, 3H, N(CH$_2$)$_7$C*H*$_3$), 1.00 (t, ^{3}J(H, H) = 7.2 Hz, 3H, N(CH$_2$)$_3$C*H*$_3$), 1.25–1.47 (m, 12H, CH$_3$C*H*$_2$(CH$_2$)$_2$N, CH$_3$(C*H*$_2$)$_5$(CH$_2$)$_2$N), 1.72–1.81 (m, 4H, CH$_3$CH$_2$C*H*$_2$CH$_2$N, CH$_3$(CH$_2$)$_5$C*H*$_2$CH$_2$N), 3.10 (s, 3H, NC*H*$_3$), 3.20–3.30 (m, 4H, CH$_3$(CH$_2$)$_2$C*H*$_2$N, CH$_3$(CH$_2$)$_6$-C*H*$_2$N), 4.68 (s, 2H, NC*H*$_2$-furan), 6.48 (dd, ^{3}J(H, H) = 2 Hz, ^{3}J(H, H) = 3.2 Hz, 1H, 4-H furan), 6.95 (d, ^{3}J(H, H) = 3.2 Hz, 1H, 3-H furan), 7.52 ppm (d, ^{3}J(H, H) = 2 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.5, 14.0, 19.6, 22.4, 22.5, 24.3, 26.2, 28.9 (×2C), 31.5, 48.1, 57.8, 61.1, 61.3, 111.7, 117.7, 142.1, 145.3 ppm.

***N*-Dodecyl-*N*-methyl-*N*-octyl-2-furfurylammonium tetrafluoroborate 4d.** Prepared starting from ammonium salt **2d** (0.51 g, 1 mmol) with the same procedure reported for **4a** (0.47 g, 99% yield). Found: C, 64.98; H, 10.44; N, 2.83; C$_{26}$H$_{50}$BF$_4$NO requires C, 65.13; H, 10.51; N, 2.92%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.88 (t, ^{3}J(H, H) = 6.8 Hz, 3H, C*H*$_3$(CH$_2$)$_{11}$N), 1.00 (t, ^{3}J(H, H) = 7.2 Hz, 3H, N(CH$_2$)$_7$C*H*$_3$), 1.24–1.36 (m, 28H, CH$_3$(C*H*$_2$)$_9$(CH$_2$)$_2$N, CH$_3$(C*H*$_2$)$_5$(CH$_2$)$_2$N), 1.75–1.79 (m, 4H, CH$_3$(CH$_2$)$_9$-C*H*$_2$CH$_2$N, CH$_3$ (CH$_2$)$_4$C*H*$_2$CH$_2$N), 3.09 (s, 3H, NC*H*$_3$), 3.21–3.27 (m, 4H, CH$_3$(CH$_2$)$_{10}$C*H*$_2$N, CH$_3$(CH$_2$)$_6$C*H*$_2$N), 4.64 (s, 2H, NC*H*$_2$-furan), 6.48 (dd, ^{3}J(H, H) = 2 Hz, ^{3}J(H, H) = 3.4 Hz, 1H, 4-H furan), 6.92 (d, ^{3}J(H, H) = 3.4 Hz, 1H, 3-H furan), 7.53 ppm (d, ^{3}J(H, H) = 2 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.5, 14.0, 19.6, 22.4, 22.5, 24.2, 26.2, 28.9 (×10C), 31.5, 48.0, 57.7, 61.2, 61.3, 111.7, 117.6, 142.0, 145.3 ppm.

***N*-Butyl-*N*,*N*-dimethyl-2-furfurylammonium tetrafluoroborate 4e.** Prepared starting from ammonium salt **2e** (0.30 g, 1 mmol) with the same procedure reported for **4a** (0.26 g, 99% yield). Found: C, 49.21; H, 7.58; N, 5.02; C$_{11}$H$_{20}$BF$_4$NO requires C, 49.10; H, 7.49, N, 5.21%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.99 (t, ^{3}J(H, H) = 7.2 Hz, 3H, N(CH$_2$)$_3$C*H*$_3$), 1.37–1.47 (m, 2H, N(CH$_2$)$_2$C*H*$_2$CH$_3$), 1.76–1.84 (m, 2H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 3.18 (s, 6H, 2 × NC*H*$_3$), 3.31–3.35 (m, 2H, NC*H*$_2$(CH$_2$)$_2$CH$_3$), 4.70 (s, 2H, NC*H*$_2$-furan), 6.48 (dd, ^{3}J(H, H) = 3.2 Hz, ^{3}J(H, H) = 2 Hz, 1H, 4-H furan), 6.93 (d, ^{3}J(H, H) = 3.2 Hz, 1H, 3-H furan), 7.53 ppm (d, ^{3}J(H, H) = 2 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.5, 19.5, 24.6, 50.4 (×2C), 59.7, 64.3, 111.6, 117.6, 141.9, 145.5 ppm.

***N*,*N*,*N*-Tributyl-2-furfurylammonium tetrafluoroborate 4f.** Prepared starting from ammonium salt **2f** (0.39 g, 1 mmol) with the same procedure reported for **4a** (0.35 g, 99% yield). Found: C, 57.71; H, 9.12; N, 3.98; C$_{17}$H$_{32}$BF$_4$NO requires C, 57.80; H, 9.13; N, 3.97%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.00 (t, ^{3}J(H, H) = 7.2 Hz, 9H, 3 × N(CH$_2$)$_3$C*H*$_3$), 1.39–1.45 (m, 6H, 3 × N(CH$_2$)$_2$C*H*$_2$CH$_3$), 1.73–1.77 (m, 6H, 3 × NCH$_2$C*H*$_2$CH$_2$CH$_3$), 3.18 (t, ^{3}J(H, H) = 8.8 Hz, 6H, 3 × NC*H*$_2$(CH$_2$)$_2$CH$_3$), 4.62 (s, 2H, NC*H*$_2$-furan), 6.49 (dd, ^{3}J(H, H) = 2 Hz, ^{3}J(H, H) = 3.2 Hz, 1H, 4-H furan), 6.83 (d, ^{3}J(H, H) = 3.2 Hz, 1H, 3-H furan), 7.52 ppm (d, ^{3}J(H, H) = 2 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.5 (×3C), 19.6 (×3C), 23.9 (×3C), 54.9, 58.9 (×2C), 111.7, 117.1, 141.9, 145.3 ppm.

***N*-Octyl-*N*,*N*-dimethyl-2-furfurylammonium tetrafluoroborate 4g.** Prepared starting from ammonium salt **2g** (0.36 g, 1 mmol) with the same procedure reported for **4a** (0.32 g, 99% yield). Found: C, 55.33; H, 8.09; N, 4.58; C$_{15}$H$_{28}$BF$_4$NO requires C, 55.40; H, 8.14; N, 4.71%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.86–0.90 (m, 3H, N(CH$_2$)$_7$C*H*$_3$), 1.27–1.35 (m, 10H, N(CH$_2$)$_2$(C*H*$_2$)$_5$CH$_3$), 1.79–1.82 (m, 2H, NCH$_2$C*H*$_2$-(CH$_2$)$_5$CH$_3$), 3.19 (s, 6H, 2 × NC*H*$_3$), 3.30–3.34 (m, 2H, NC*H*$_2$(CH$_2$)$_6$CH$_3$), 4.73 (s, 2H, NC*H*$_2$-furan), 6.49 (dd, ^{3}J(H, H) = 3.6 Hz, ^{3}J(H, H) = 1.8 Hz, 1H, 4-H furan), 6.96 (d, ^{3}J(H, H) = 3.6 Hz, 1H, 3-H furan), 7.53 ppm (d, ^{3}J(H, H) = 1.8 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.5, 13.6, 19.7, 22.5, 22.8, 26.2, 29.0, 31.5, 50.5, 59.8, 64.2, 111.7, 117.8, 141.9, 145.5 ppm.

***N*,*N*-Dibutyl-*N*-octyl-2-furfurylammonium tetrafluoroborate 4h.** Prepared starting from ammonium salt **2h** (0.44 g, 1 mmol) with the same procedure reported for **4a** (0.40 g, 99% yield). Found: C, 61.51; H, 9.81; N, 3.30; C$_{21}$H$_{40}$BF$_4$NO requires C, 61.62; H, 9.85; N, 3.42%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.88 (t, ^{3}J(H, H) = 6.6 Hz, 3H, N(CH$_2$)$_7$C*H*$_3$), 1.01 (t, ^{3}J(H, H) = 7.2 Hz, 6H, 2 × N(CH$_2$)$_3$C*H*$_3$), 1.26–1.44 (m, 14H, 2 × CH$_3$C*H*$_2$(CH$_2$)$_2$N, CH$_3$(C*H*$_2$)$_5$(CH$_2$)$_2$N), 1.74–1.76 (m, 6H, 2 × CH$_3$CH$_2$C*H*$_2$CH$_2$N, CH$_3$(CH$_2$)$_5$C*H*$_2$CH$_2$N), 3.13–3.19 (m, 6H, CH$_3$(CH$_2$)$_2$C*H*$_2$N, CH$_3$(CH$_2$)$_6$C*H*$_2$N), 4.59 (s, 2H, NC*H*$_2$-furan), 6.49 (dd, ^{3}J(H, H) = 1.6 Hz, ^{3}J(H, H) = 3.2 Hz, 1H, 4-H furan), 6.81 (d, ^{3}J(H, H) = 3.2 Hz, 1H, 3-H furan), 7.53 ppm (d, ^3J(H, H) = 1.6 Hz, 1H, 5-H furan). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.5 ($\times$2C), 14.0, 19.6 ($\times$2C), 22.0, 22.5, 23.9 ($\times$2C), 26.3, 28.8, 28.9, 31.5, 54.8, 58.8 ($\times$2C), 59.0, 111.7, 117.0, 142.0, 145.2 ppm.

Solubility in water

To verify the miscibility in water of the compounds **2g** and **4g** we recorded two ^{1}H NMR spectra in D_2O (5 mm probe on a Varian Inova 600 spectrometer) with a known amount of 3-(trimethylsilyl)propionic acid-d_4 sodium salt (TSP) (28.9 μmol for each proton in 1 cm^3 of D_2O) as internal standard and a delay time between successive scans of 20 s to ensure complete proton relaxation and, therefore, quantitative integration.

The samples has been prepared by sonication of the NMR tube, charged with D_2O, TSP and ammonium salts **2g** or **4g** with three ultrasound cycles of 30 min. Then the spectra have been recorded and the integrals have been calculated respect to the TSP signal.

Test of 2e stability to different pH conditions

pH stability has been established recording quantitative ^{1}H NMR spectra in acetone-d_6 (5 mm probe on a Varian Mercury 400 spectrometer) with a known amount of tetrakis(trimethylsilyl)silane (TTMS) as internal standard and a delay time between successive scans of 20 s to ensure complete proton relaxation and, therefore, quantitative integration.

Four solutions of the compound **2e** have been prepared in acetone-d_6: neutral pH, basic pH with triethylamine, weakly acidic pH with acetic acid and strongly acidic pH with hydrochloric acid.

After 24 h the spectra were recorded and the integrals have been calculated respect to TTMS signal.

Toxicity tests

Daphnia magna. The essay was carried out according to the procedures set out in the Organization for Economic Co-operation and Development (OECD) guideline 202.[16] Five neonates (age <24 h; born from parthenogenic females grown in a batch culture) have been placed in each 100 ml beaker, containing 40 ml of test solution; two replicate beakers for each of eight treatment concentrations (control plus seven toxicant concentrations) have been used. Test concentrations, identified through a preliminary range finding test, were arranged in a geometric series. Three consecutive trials were carried out for each substance, for a total of six replicates at each concentration. Substances **2a**, **2e**, **2f**, **2g** and **2i**, were tested simultaneously; this was not possible for TBAI and BTBAI that were tested some weeks later.

The temperature was 20 ± 1 °C, with a 16/8 h light/dark photoperiod. Each test vessel was checked for immobilized individuals at 24 and 48 h after the beginning of the test. Animals not able to swim within 15 s after gentle agitation of the test vessel have been considered immobilized, even though they could still move their antennae. The endpoint used to establish the concentration-response relationship was the number of individuals still active after 48 h of exposure.

Vibrio fischeri. The assay was carried out in accordance with the 90% basic test for pure compounds protocol.[17] Three trials were carried out for each substance using three vials of Microtox® "reagent" (lyophilized *V. fischeri*) from the same lot. Nine concentrations of each substance were tested in a 1 : 2 dilution series and a control. Due to constraints imposed by the protocol, it was not possible to test the substances simultaneously or to test all the substance using a single vial of bacteria. To approximate simultaneous testing, substances were tested according to a rotation scheme: the first trials for all the substances were carried out sequentially; when all the substances were tested once, the second trials were carried out and then the third. Light emission of the bacteria was measured after 0, 5 and 15 min of exposure using a Microtox® Model 500 Toxicity Analyzer.

The endpoint used to establish the concentration-response relationship was the bioluminescence of the bacteria, measured at each concentration as the ratio between the light emission after 15 min of exposure and the emission at time 0, expressed as a percentage of the same ratio in the control:

$$100\frac{I_{15}/I_0}{I^c_{15}/I^c_0}$$

Here: I_0: light emission at time 0; I_{15}: emission after 15 min, I^c: emission of the control treatment.

Data analysis. The 50% effect concentration (EC$_{50}$) of each substance for *D. magna* and *V. fischeri* was estimated by fitting the experimental concentration-response curves to a logistic model:

$$y = \frac{a}{1 + \left(\frac{x}{\mathrm{EC}_{50}}\right)^b}$$

Here: y = endpoint value; x = substance concentration; a = expected endpoint value in absence of toxic effect; b = slope parameter. The parameters of the equation, including the EC$_{50}$, were estimated using the non-linear regression procedures implemented in Statistica (Statsoft, Tulsa, OK, USA). An independent estimate of EC$_{50}$ was obtained for each of the three experimental trials. The statistical significance of the differences among EC$_{50}$ values was tested by one-way analysis of variance (ANOVA). Once ANOVA was established to be significant, the *post-hoc* Student–Newman–Keuls (SNK) test was carried out to identify which substances were significantly different from each other. The statistical tests were performed on log transformed data to achieve homogeneity of variances.

Concentration–response curves for toxicity texts have been reported in the ESI.†

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