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Ionic liquid forms of the herbicide dicamba with increased efficacy and reduced volatility

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Twenty eight new dicamba (3,6-dichloro-2-methoxybenzoic acid)-based herbicidal salts, have been synthesized and characterized in order to attempt to improve the efficacy of this widely known herbicide used to protect maize, grassland, and other cultures. The new compounds, most of which are ionic liquids by definition and three of which are solids melting above 100 °C, were prepared by pairing quaternary tetraalkyl- or alkoxyammonium, piperidinium, imidazolium, pyridinium, morpholinium, quinolinium, and phosphonium cations with the dicamba anion. Growth chamber and field test data suggested that ionic liquid forms of dicamba offer substantially increased efficacy which would allow less to be applied in the field. Compared to the commercial dicamba free acid product, improved physical properties were observed including higher decomposition temperatures and reduced volatilities, suggesting a potential reduction of overall environmental impact of this herbicide.

Introduction

Many herbicides, widely used in agriculture to eliminate unwanted species of plants, have secondary environmental impacts due to their high volatility,[1–3] water solubility,[4] and droplet drift[5] during application. DuPont's Imprelis herbicide, for example, was removed from commercial use[6] based on concerns suggesting a link between the herbicide's use and a negative impact on neighboring conifers, deciduous trees, and shrubs.[7]

Dicamba free acid (3,6-dichloro-2-methoxybenzoic acid) is a selective systemic herbicide, absorbed by the plants' leaves and roots, with ready translocation throughout the plant *via* both the symplastic and apoplastic systems. Dicamba acts as an auxin-like growth regulator. Dicamba is the active ingredient in the commercial herbicide Banvel®, and one of the most widely used agrochemicals.[8] This herbicide exhibits all the disadvantages previously mentioned. Dicamba has been reported to have a high water solubility (and therefore persists in groundwater),[9] and does not bind to soil particles (soil sorption coefficient normalized to organic carbon, $K_{oc} = 2\ \mathrm{g\ mL^{-1}}$) which leads to a high leaching rate. Its leaching potential increases with the volume of the herbicide applied.

The vapor pressure of dicamba acid is 2.6×10^{-8} atm at 25 °C, indicating substantial volatilization after application.[10] Burnside *et al.*[11] studied dicamba volatility under laboratory conditions, finding that as high as 29% of dicamba acid volatilized from planchets at 35 °C, after 7 days. Similar studies by Baur *et al.*[12] reported 58% volatilization loss from glass beakers in 4 days at 30 °C.

Volatility, of course, differs from glass beakers, soil, and plant surfaces. Burnside and Lavy[11] established that evaporative losses of dicamba from soil were very small compared to losses from planchets due to herbicide binding to soil particles. However, dicamba is often applied as an aerial spray and losses can occur from a variety of surfaces such as plant leaf or foliage. In one study, volatilization injury to soybean has been reported to be 37% and 48% after the 1st and 2nd application, respectively,[13] due to dicamba evaporation from the leaf surface.

Any modification or new formulations of such a widely utilized herbicide will need to reduce the potential for environmental exposure, while increasing efficacy in order to reduce the application rates. Current approaches include the use of emulsified esters, ammonium salts, metal salts, or additives.[14] However these methods have only minimally improved the reported environmental impact.[15]

Dicamba, a benzoic acid derivative with a pK_a of 1.9, fits the normal design rules for choosing ions to generate ionic liquids (ILs), generally defined as salts that melt below 100 °C and composed of at least two ions.[16] Both ions comprising an IL can independently and/or simultaneously introduce a specific functionality or property beyond low melting character.

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Applying the IL concept to herbicides should allow controlled modification of important properties such as thermal stability, volatility, and water solubility.[17]

Herbicidal ionic liquids (HILs) have been previously synthesized from 2,4-dichlorophenoxyacetic acid (2,4-D),[18] *N*-(phosphonomethyl)glycine (glyphosate),[19] 3,5,6-trichloro-2-pyridinyloxyacetic acid (triclopyr),[18a] (*R*)-2-[4-(4-cyano-2-fluorophenoxy)phenoxy]propionic acid (cyhalofop),[18a] and 2-methyl-4-chlorophenoxyacetic acid (MCPA).[18d] Dicamba ILs have been reported in a recent patent application from Dow Agrosciences[18a] that described pairing acidic herbicides with inert amines to create quaternary ammonium salts for overcoming volatility problems of the parent herbicides. The patent examples suggested that ILs formed by combining dicamba with certain amines possessed herbicidal activity on an acid equivalent basis, but substantially less volatile.[18a] However, Dow Agrosciences did not take into the account that there are a number of key differences between the usually higher volatility of protic ILs *vs.* aprotic ILs. For example, Baur *et al.*[12] compared dimethylammonium dicamba herbicides (a protic cation) with tetramethylammonium dicamba (an aprotic cation) and found 70% injury to grapes from vapor exposure of $[N(CH_3)_2H_2]^+$ salt *vs.* only 12% injury to grapes, with the $[N(CH_3)_4]^+$ salt.[12] With judicious selection of appropriate aprotic (so-called "permanent") biologically active cations, liquid salt forms might not only allow for modified physical properties, but also for dual functional performance[20,21] or even synergistic effects by the incorporation of two biologically active ions into a single IL. Such herbicidal ILs should not only retain their biological activity, but also introduce new herbicidal/fungicidal/antimicrobial properties not inherent in the pure neutral forms,[22] and even potentially increase efficacy through, for example, better leaf transport or reduced rain wash-off.[19]

In the study we report here, we have combined the hydrophilic dicamba anion with hydrophobic, antimicrobial/antifungal ammonium cations to produce hydrophobic ILs (Fig. 1). Several criteria were taken into consideration for the choice of the cations to be paired with dicamba.

It is known that when surfactants are added to dicamba, total absorption (the amount of herbicide in the plant) increases compared to dicamba without surfactant.[23] Therefore, we chose cations with surfactant character (hydrophobic agents which also decrease water solubility).

We also focused on cations with additional biological activity (*e.g.*, fungicidal or antibacterial activity to complement the herbicidal activity) and cations of low toxicity (*e.g.*, cations from the GRAS, 'generally regarded as safe' list[24–26]). Quaternary tetraalkylammonium,[27] imidazolium,[28] and pyridinium cations,[28] especially those with longer alkyl chain lengths, were selected for their antimicrobial effects. These cations are active against both gram-positive and gram-negative bacteria, yeast, mold, viruses, protozoans, and fungi. The same activity is observed for piperidinium and morpholinium cations, where in general, most active compounds are compounds with longer *N*-alkyl group substituents (*n* = 8–16).[29] *N*,*N*-Dialkylmorpholinium and -piperidinium cations additionally display herbicidal activity which is the greatest in the compounds with alkyl chains from 12 to 16 atoms.[29] 8-Hydroxyquinolines (8HQs) cations possess diverse biological properties such as being antibacterial and antifungal.[30] In addition, many of the cations that have been used possess surfactant/membrane-disruptive properties due to the presence of the long alkyl chains.

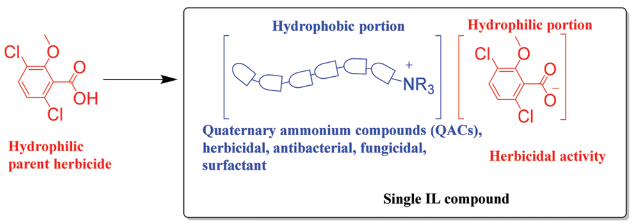
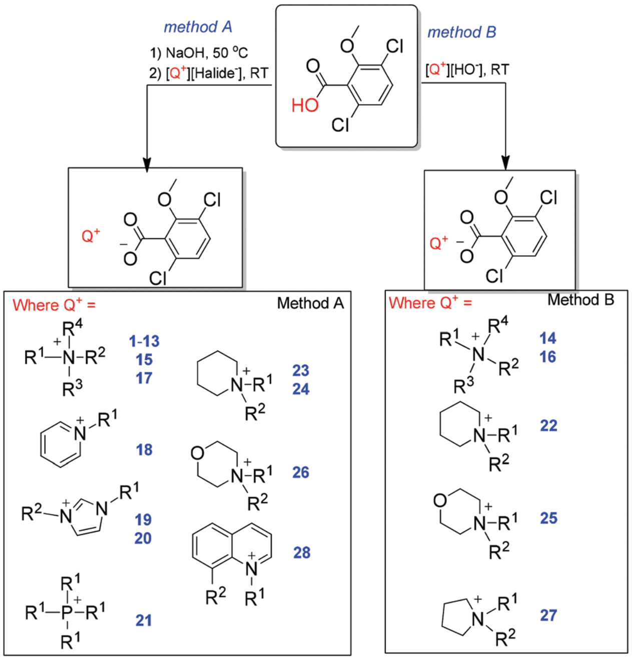


Fig. 1 Hydrophilic dicamba *vs.* hydrophobic dicamba HILs.

Results and discussion

Synthesis of dicamba ILs

Twenty eight dicamba-based salts utilizing eight different classes of cations were synthesized (Scheme 1). To test different strategies for pairing the dicamba with different cations, two different approaches were attempted: (a) *metathesis reactions* between the sodium/potassium salt of dicamba and quaternary tetraalkylammonium, pyridinium, imidazolium, quinolinium, isoquinolinium, piperidinium, morpholinium, and phosphonium halides, and (b) *acid–base reactions* between dicamba free acid and the ammonium, piperidinium, morpholinium, and pyrrolidinium hydroxides.



Scheme 1 General synthesis of HILs derived from dicamba (for substituents on the cation see Table 1).

Both approaches resulted in successfully obtaining the salts (Table 1) that were isolated in excellent yields (>90%). All isolated compounds were of high purities (98–99.5%), with water content below 0.5% (measured *via* Karl-Fischer titration).

The formation of the desired compounds was proven *via* spectroscopy (NMR and FT-IR). Particularly, in the ^1H NMR spectra, the disappearance of the acidic –CO*OH* peak, corresponding to the dicamba free acid, and an upfield chemical shift for the aromatic protons from dicamba (due to an increase of electron density on the ring from the formation of the dicamba anion) support the fully ionized nature of the compounds. In the FT-IR spectra, a blue shift of the carboxylic acid C=O stretch from *ca.* 1700 cm^{-1} to the carboxylate at ~1600 cm^{-1} is also characteristic of the formation of the carboxylate anion.

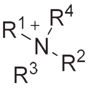
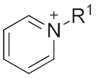
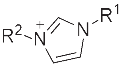
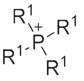
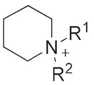
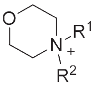
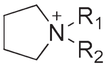
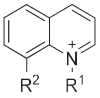
Representative examples of salts with the different cation classes are presented below, while the synthetic and characterization data for all compounds are provided in the Experimental section.

Thermal analysis

Thermal transitions for selected compounds were determined using differential scanning calorimetry (DSC), while the melting points for the solid compounds were determined using a Fisher-Johns melting point apparatus. Decomposition temperatures ($T_{5\%\ \mathrm{onset}}$, onset for 5% decomposition, and T_{dec}, decomposition temperature) were determined using thermal gravimetric analysis (TGA). All data are presented in Table 2.

Most of the synthesized compounds are liquids or waxes with melting points or glass transitions below 100 °C, being classified as ILs (dicamba-HILs); only three compounds have

Table 1 New dicamba herbicidal compounds

Cation		R^1	R^2	R^3	R^4	State[a]
	**1**	CH_3	CH_3	$C_{12}H_{25}/C_{14}H_{29}$	$CH_2C_6H_5$	Liquid
	2	CH_3	CH_3	$C_{10}H_{21}$	$C_{10}H_{21}$	Solid
	3	CH_3	CH_3	$C_{12}H_{25}$	$CH_2CH_2OC_6H_5$	Liquid
	4	CH_3	CH_3	CH_3	Coco-[b]	Wax
	5	CH_3	Tallow	—[d]	—[d]	Liquid
	6	CH_3	CH_2CH_2OH	Coco-[b]	CH_2CH_2OH	Wax
	7	CH_3	CH_3	$(CH_2)_2OH$	$CH_2O{-}C_{11}H_{21}$	Liquid
	8	CH_3	CH_3	$(CH_2)_2OH$	$CH_2O{-}C_{12}H_{23}$	Wax
	9	CH_3	CH_3	$(CH_2)_2OH$	$C_{10}H_{21}$	Wax
	10	CH_3	CH_3	H-Tallow[e]	H-Tallow[e]	Wax
	11	CH_3	Oleyl[f]	$(CH_2)_2OH$	$(CH_2)_2OH$	Wax
	12	CH_3	CH_3	CH_3	Soya-[c]	Wax
	13	CH_3	CH_3	$(CH_2)_2OCOR$	CH_2CH_2OCOR	Wax
	14	CH_3	CH_3	$CH_2CH{=}CH_2$	$CH_2CH{=}CH_2$	Wax
	15	CH_3	CH_3	CH_3	$(CH_2)_2OH$	Solid
	16	CH_3	CH_3	CH_3	$C_{14}H_{29}$	Solid
	17	C_4H_9	C_4H_9	C_4H_9	C_4H_9	Solid
	**18**	$C_{12}H_{25}$	—	—	—	Liquid
	**19**	CH_3	$CH_2OC_{18}H_{17}$	—	—	Liquid
	20	$C_{10}H_{21}$	$C_{10}H_{21}$	—	—	Liquid
	**21**	C_4H_9	—	—	—	Solid
	**22**	CH_3	CH_3	—	—	Liquid
	23	CH_3	$C_{10}H_{21}$	—	—	Liquid
	24	$C_{10}H_{21}$	$C_{10}H_{21}$	—	—	Wax
	**25**	CH_3	C_4H_9	—	—	Wax
	26	CH_3	C_4H_9	—	—	Wax
	**27**	CH_3	C_4H_9	—	—	Liquid
	**28**	H	OH	—	—	Glass

[a] State is shown at 25 °C. [b] Cocoalkyl chain distribution C_8H_{16} – 5, $C_{10}H_{21}$ – 6, $C_{12}H_{25}$ – 50, $C_{14}H_{29}$ – 19, $C_{16}H_{33}$ – 10, $C_{18}H_{37}$ – 10%. [c] Soyaalkyl chain distribution, $C_{14}H_{29}$ – 6, $C_{16}H_{33}$ – 14, $C_{18}H_{37}$ – 80%. [d] $(CH_2CH_2O)_{(x\ \mathrm{or}\ y)}H$ with $x + y = 15$. [e] Alkyl hydrogenated tallow chain distribution $C_{12}H_{25}$ – 1, $C_{14}H_{29}$ – 4, $C_{16}H_{33}$ – 31, $C_{18}H_{37}$ – 64%. [f] Oleyl chain distribution $C_{12}H_{25}$ – 1, $C_{14}H_{29}$ – 4, $C_{16}H_{33}$ – 12, $C_{18}H_{37}$ – 82%.

Table 2 Thermal analysis (DSC and TGA) for selected dicamba-HILs and dicamba salts

Compound	#	T_g[a] [°C]	T_m[b] [°C]	$T_{5\%\ \mathrm{onset}}$[c] [°C]	T_{dec}[d] [°C]
Dicamba free acid	—	−78.8	114–116	132.5	150
Dicamba HILs **2–28**	**2**	−47	86	178	232
	4	−47	—	187	213, 312[e]
	6	−40	37	200	260
	18	−25	—	187	210, 355[e]
	21	6	64–65	180	232, 355[e]
	23	−31	—	188	240
	26	−20	—	185	240
	27	−41	—	185	215
	28			190	215
Dicamba salts **15–17**	**15**	—	105	177	181
	16	—	179–180	191	206
	17	—	126–127	154	156

[a] T_g – glass transition. [b] T_m – melting point. [c] $T_{5\%\ \mathrm{onset}}$ – decomposition of 5% of the sample. [d] T_{dec} – decomposition. [e] Two step decomposition observed.

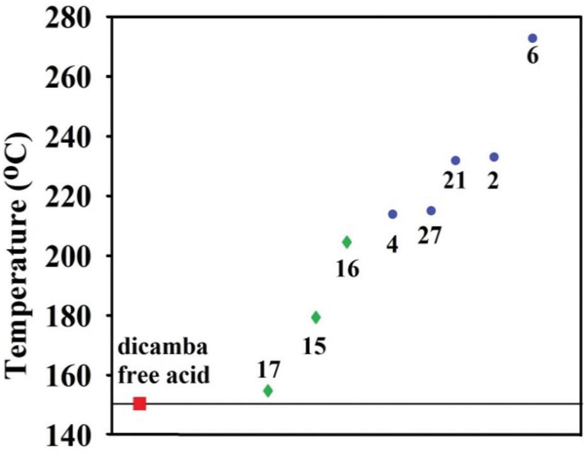


Fig. 2 Decomposition temperatures for dicamba free acid (■), several dicamba HILs (○), and the three higher melting crystalline dicamba salts (◊).

melting points above 100 °C, being classified here as "higher melting crystalline salts" (dicamba salts). Out of 28 compounds, 17 belong to the tetraalkylammonium class, with three salts **15**, **16**, and **17** being solids. Yet, most of tetraalkylammonium compounds are liquids or waxes with a melting point that decreases with an increase in the substituent alkyl chain length. The presence of as many as three *N*-methyl groups in the **16** and **17** results in melting point enhancement (the effect is not observed in the presence of long coco- or soya-substituted **4** and **12** as they are in fact mixtures of different alkyl chain lengths).

Similarly, tetrabutylphosphonium dicamba **21** was a solid with mp of 65 °C, probably due to all four alkyl chains being relatively short identical 4 carbon ones resulting in a symmetric cation. All of the pyridinium, piperidinium, morpholinium, and imidazolium compounds were liquids or waxes, though more compounds of the same class have to be prepared to statistically verify the trend.

As predicted,[31] the general trends in the melting points of the solid salts show that the presence of a hydroxyethyl-group decreases the temperature of melting transitions when compared to the alkyl substituents.

All the liquids or waxes show a glass transition below 0 °C. The lowest glass transition temperature, as well as the lowest melting point was observed for tetraalkylammonium dicamba **5**, with two polyethylene glycol (PEG)-like substituents and a "tallow" tail, a mixture of different alkyl chain lengths. Unfortunately, there were not enough compounds synthesized to determine a trend in T_g data for other compound classes.

All the new dicamba derived compounds exhibited improved thermal stabilities when compared to the neutral dicamba acid. Many ILs showed improved thermal stability when compared to parent neutral compounds, and similarly, dicamba HILs showed an improved thermal stability ($T_{dec} >$ 200 °C) when compared to dicamba free acid. They were also more stable than higher melting dicamba salts **15**, **16**, and **17** ($T_{dec} \leq$ 200 °C; Fig. 2).

In general, differences in T_{dec} were observed by changing the alkyl substituents in tetraalkylammonium dicamba. Previously, Prasad *et al.* studied the thermal decomposition temperatures for ammonium salts and showed that, as the size of the substituted alkyl group increases, the thermal stability of these compounds decreases.[32] However, in our case, tetrabutylammonium **17** bearing four relatively short butyl groups had the lowest decomposition temperature, only 10 °C above that of the dicamba free acid.

Decomposition temperatures T_{dec} for all other tested compounds were higher by at least 30 °C when compared to the free acid starting material. Tetraalkylammonium **6** bearing two hydroxyethyl-substituents and a long coco-alkyl has a decomposition temperature as high as 260 °C; while pyrrolidinium dicamba **27** and morpholinium dicamba **25** bearing the same substituents have exactly the same decomposition temperatures. However, a complete analysis of these trends is difficult, since the choice of cation targets was based on their biological properties rather than structural similarities.

Tetraalkylammonium with coco-, soya-, and tallow-substituents **4**, **12**, and **5** underwent two-step and three-step decomposition, due to the presence of a mixture of different alkyl chains. A similar observation was made for the phosphonium salt that underwent a two-step decomposition, potentially due to release of the volatile tributyl phosphine and/or tributyl phosphine oxide above 250 °C.[33] 1-Dodecylpyridinium dicamba also had a two-step decomposition event. The highest overall decomposition point was observed for *N*-methyl-*N*,*N*-dihydroxyethyl-*N*-cocoammonium dicamba.

Volatility

It is generally believed that reducing a herbicide's volatility should reduce the impact of the herbicide on environment by minimizing its vapor drift. Dicamba in its acid form has a vapor pressure of 2.0 × 10^{-5} mm Hg at 25 °C and volatilization is substantial.[34,35] Relative volatility rates of the acid form of dicamba and its ammonium salts, namely the dimethylammonium, tallowammonium, and diethanolammonium salts were reported previously[36] and it was shown that after plant exposure to 40 °C for 12 h, volatility depended on alkylammonium substituent length, and decreased in the order: dicamba > dicamba dimethylammonium salt (DMA) ≫ dicamba diethanolammonium salt (DEOA) ≫ dicamba tallowammonium salt (DT) (92%, 43%, 4%, and 2%, respectively).

We have measured the relative volatility rates of both dicamba-ILs and dicamba salts after 12 h, and compared these with reported values for the acid form of dicamba and its dimethylammonium salts. The dicamba ammonium and phosphonium HILs **2** and **21**, and dicamba tetraalkylammonium salts **15**, **16**, and **17** were subjected to thermogravimetric analysis (TGA) with isothermal heating at 75 °C for 12 h. All the compounds were thoroughly characterized to ensure the absence of any residual water or solvent that would interfere with the study. Volatility was defined as the weight loss of the herbicide when it was held under isothermal conditions at 75 °C for a period of 12 h under a constant flow of nitrogen. (It should be noted that this test does expose the herbicidal IL to relatively high temperatures, much higher than operational conditions, and exceeds the temperature conditions in the area around a plant.)

The HILs **2** and **21** showed less than 2.5% mass loss (2.4% for **2** and 1.6% for **21**; Table 3). The higher melting salts **15**, **16**, and **17**, exhibited less than 0.7% mass loss. Dicamba free acid, however, lost more than 10% of its mass during the 12 h of this test.

Table 3 Mass loss after 12 h isotherms at 75 °C

Compound		Mass loss (12 h; 75 °C; %)
Dicamba free acid	—	10.6
Dicamba HILs	**2**	2.4
	21	1.6
Higher melting dicamba salts	**15**	0.7
	16	0.7
	17	0.5

Efficacy

Growth chamber experiments. Initial efficacy tests were conducted in a growth chamber as typically approval for field testing is granted only after growth chamber test results are available. These experiments were performed under controlled environmental conditions (20 °C, 60% humidity, 16/8 h day/night photoperiod). Common lambsquarters (*Chenopodium album*) and white mustard (*Sinapis alba*) were used as test plants, because both plants are typically controlled *via* dicamba applications. Plants seeds were placed into soil-filled containers, at planting depths of 1 cm. After producing leaves, only 5 plants were left in each pot; other plants were removed. At the time of herbicide application, both types of plants were at the 3 leaves developmental phase.

HIL **2**, [DDA][Dicamba], was selected for efficacy comparison against dicamba free acid. The plants were separated into three main groups, where Group I was treated with HIL of three different concentrations, Group II was treated with dicamba free acid of three different concentrations, and Group III was a control. Specifically, Group I was treated with dicamba HIL **2** solution in water–DMSO (2 : 1 v/v); concentrations of active compound were (i) 0.001 mol L^{-1} (1 equiv., 0.546 g L^{-1}), (ii) 0.002 mol L^{-1} (2 equiv., 1.092 g L^{-1}), and (iii) 0.004 mol L^{-1} (4 equiv., 2.184 g L^{-1}), respectively. In turn, Group II was treated with Banvel® (dicamba free acid) solution in water–DMSO (2 : 1 v/v). Concentrations of active applied were (i) 0.001 mol L^{-1} (1 equiv., 0.221 g L^{-1}), (ii) 0.002 mol L^{-1} (2 equiv., 0.442 g L^{-1}), and (iii) 0.004 mol L^{-1} (4 equiv., 0.884 g L^{-1}) of active component, respectively. Group III was sprayed with a control solution of water–DMSO (2 : 1 v/v). The study was carried out in 4 replications in a completely randomized setup.

The application was performed using a sprayer equipped with a flat fan Tee Jet 1103 XR nozzle, using a steady pressure of 0.2 MPa at 200 L ha^{-1} application rate. After spraying the plants, the pots were placed back into a growth chamber at the same controlled environmental conditions as before spraying (20 °C, 60% humidity, 16/8 h day/night photoperiod). After a period of 2 weeks, the plants were cut right to the soil level and weighed (0.1 g accuracy). The reduction of plant fresh weight as compared to control (no sprayed plants) was measured.

In growth chamber experiments, dicamba HIL **2** showed an improved efficacy over dicamba free acid (Banvel®). Results for the tests on *Sinapis alba* species showed a better activity of [DDA][Dicamba] **2** than of Banvel® on the fresh weight reduction, while no reduction was observed when dicamba free acid was used. The activity of **2** was dependent on the concentration used, increasing from 6.8% (for a concentration of 0.001 M) to 18.5% (for 0.002 M) and to 27.1% (for 0.004 M). However, the activity of **2** was comparable to the activity of dicamba free acid when lambsquarters (*Chenopodium album*) species were used (the results are presented in Table 4 and Fig. 3).

Initial field experiments (visual evaluation). The research was conducted in the Field Experimental Station of the Institute of Plant Protection in Winna Gora in 1.5 m × 5 m areas. The test plants were common lambsquarters (*Chenopodium album*) and cornflower (*Centaurea cyanus*). At the time of herbicide application, common lambsquarters were at 4–10 leaves developmental phase and cornflower was a fully-formed rosette.

Didecyldimethylammonium 3,6-dichloro-2-methoxybenzoate ([DDA][Dicamba]) **2** was chosen for the initial testing. For application, **2** was dissolved in a mixture of water and ethanol (1 : 1 v/v) in an amount corresponding to a concentration of 0.01 and 0.02 mol L^{-1}. Dicamba solution was prepared in pure water with no ethanol added, also at 0.01 and 0.02 mol L^{-1} concentration.

Plants were separated into three groups. Group I was sprayed using HIL **2** and Group II was sprayed using dicamba

Table 4 Growth chamber experiments for dicamba HIL **2** and commercial Banvel® (dicamba free acid active ingredient)

Herbicide	Conc.[a] (mol L^{-1})	White mustard (*Sinapis alba*)[b]	Lambsquarters (*Chenopodium album*)[b]
		Fresh weight reduction (%)	
[DDA]	0.001	6.8	16.7
[Dicamba], **2**	0.002	18.5	41.7
	0.004	27.1	45.7
Banvel®[c]	0.001	No reduction	20.9
	0.002	No reduction	49.2
	0.004	No reduction	60.2

[a] Other conditions included 2 weeks after treatment (2 WAT); temperature of 20 °C (±2 °C), humidity 60%, illumination time 16/24. [b] Plants were grown under identical conditions and differed only in herbicidal treatment. [c] Banvel® commercial herbicide containing active ingredient as a pure acid.

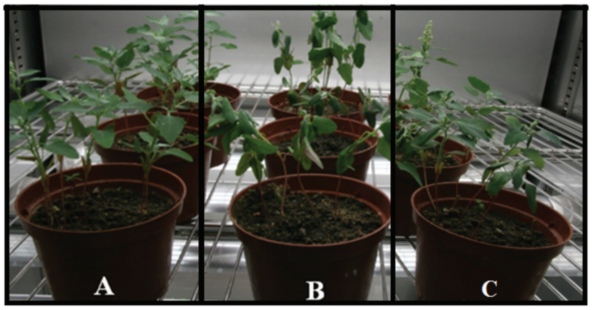


Fig. 3 Comparison (5 days after treatment) between treatment of lambsquarters with different forms of dicamba (0.001 M active): A – no treatment, B – treatment with dicamba HIL **2**, C – treatment with dicamba free acid as commercial Banvel®.

Table 5 Efficacy tests for dicamba HIL **2** and commercial Banvel® (dicamba free acid active ingredient) conducted on lambsquarters (*Chenopodium album*) and cornflower (*Centaurea cyanus*) species in the field experiments

Herbicide[a]	Lambsquarters (*Chenopodium album*)[b]	Cornflower (*Centaurea cyanus*)[b]
	Effectiveness of weed eradication (%) (visually determined)	
[DDA][Dicamba], **2**	92	95
Banvel®[c]	83	90

[a] Conditions included 4 weeks after treatment (4 WAT). [b] Plants were grown at all otherwise identical conditions and differed in herbicidal treatment. [c] Banvel® commercial herbicide containing active ingredient as a pure acid.

free acid. Group III, a control group, was not treated with herbicide, but only with a solution of water and ethanol (1 : 1 v/v).

The application was performed using a knapsack sprayer equipped with flat fan Tee Jet 1103 nozzles, using a steady pressure of 0.2 MPa at 200 L ha^{-1} application rate. The effectiveness of weed eradication was evaluated visually by comparing the state of weeds of Groups I, II, and III twenty eight days after treatment (DAT). For that, surviving plants were counted in quadrats and percent stand reduction was calculated based on the nontreated control. The evaluation took into account the degree of soil coverage, the vigor of the weeds, and the plants' height and mass.

The effectiveness of the eradication of weeds was presented in percentage scale where 100% means the complete destruction and 0% means no action of the herbicide. Results of the efficiency of [DDA][Dicamba] and the neutral dicamba are presented as the mean estimate of weed destruction as shown in Table 5. The results indicate that the species *Chenopodium album* and *Centaurea cyanus* in field conditions, were more susceptible to treatment with HIL **2** than to dicamba free acid. These results are slightly different than the ones obtained in growth chamber experiments, probably because of a more competitive stress in the field. Nevertheless, the fresh weight reduction method was employed (see below) to quantify the visual comparisons above.

Field experiments (fresh weight reduction). The specific objective of these field experiments was to determine the exact efficacy of dicamba HILs. Five HILs were randomly chosen out of the prepared compounds for the field testing on weed species, and the results were compared with dicamba free acid. Liquid or waxy HILs of different cation classes were chosen for this test: ammonium (**6**), piperidinium (**23**), and morpholinium (**26**).

Determination of efficacy was conducted using the fresh weight reduction method. The field experiments were conducted in the Field Experimental Station on a corn field (Winna Gora, Poland, E: 17°26′, N: 52°12′), in 2011. Common lambsquarters (*Chenopodium album*) were used as test plants while corn was cultivated according to the local agricultural practice. All herbicides were applied at the 3 leaves growth stage at the application rate 200 g dicamba active per ha. Field studies were conducted as randomized complete blocks, on areas of 16.5 m^2 with at least four replications.

Similarly to the previous field studies described earlier, dicamba HILs were dissolved in water–ethanol solution (1 : 1 v/v) in an amount corresponding to 0.01 mol L^{-1} concentration. Dicamba free acid was dissolved in water (no ethanol was added) to prepare solutions of the same concentrations. Control group plants were not treated with any type of dicamba but sprayed with a water–ethanol solution (1 : 1 v/v).

The plants were sprayed using a knapsack sprayer with Tee Jet 1103 XR flat fan nozzles at 0.3 MPa with an application rate of 200 L ha^{-1}. Weed control was evaluated *via* fresh weight reduction measurements, after herbicide applications using a scale of 0 (no control) to 100% (complete weed destruction). The results indicated that the species *Chenopodium album* in field conditions, were substantially more susceptible to treatment with HILs than to dicamba free acid. Differences were found among the HILs (Table 6) however all HILs were at least 15% more effective than dicamba free acid. Similarly to the visual evaluation, these results are slightly different than the ones obtained in growth chamber experiments, probably because of a more competitive stress in field.

Table 6 Control of common lambsquarters (*Chenopodium album*) by different forms of dicamba

Herbicide	Lambsquarters (*Chenopodium album*) Fresh weight reduction (%)
6[a]	62.5
26[a]	57.5
23[a]	62.5
4[a]	62.5
11[a]	56.3
Banvel® [b]	42.5

[a] Spraying with a knapsack sprayer with Tee Jet 1103 XR flat fan nozzles at 0.3 MPa. [b] Commercial product containing 480 g of dicamba per 1 L.

Conclusions

New dicamba-based HILs were synthesized and analyzed for volatility, thermal stability, and efficacy in both growth chamber and field trials. These new compounds demonstrate increased thermal stability, reduced volatility, and substantially improved efficacy over dicamba free acid, indicating that HILs may offer significant advantages over and be viable alternatives to other currently used forms of dicamba. In addition, the HIL strategy offers a way to access dual functional herbicidal ILs by combining the herbicidal activity of the dicamba anion with fungicidal, antibacterial, and/or herbicidal activity of the cation; an area that is currently under research in our groups. Moreover, by using the IL strategy, the negative impacts of dicamba free acid on the environment caused by runoff, vapor drift, and the need to use higher concentrations, might be reduced or eliminated.

Experimental

General methods

All chemicals, unless otherwise stated, were purchased from Aldrich Chemical Company (Saint Louis, MO) in reagent grade ≥98% and used without further purification. Dicamba free acid and dicamba sodium salt were provided by Monsanto Co. Quaternary ammonium chlorides with soya, oleyl, hydrogenated tallow, and coco alkyl groups were purchased from AkzoNobel, The Netherlands.

The ^{1}H and ^{13}C NMR spectra were collected utilizing a Bruker spectrometer 500 MHz Bruker Avance Spectrometer Bruker/Magnex UltraShield 500 MHz magnet (Madison, WI) operating at 500 MHz for ^{1}H spectra and 125 MHz for ^{13}C spectra, respectively.

Thermogravimetric analyses were performed on a TA Instruments (New Castle, DE) model 2950 thermogravimetric analyzer. The experiments were performed under nitrogen atmosphere. Samples between 5–10 mg were placed on a platinum pan and were heated from 25 °C to 800 °C with a heating rate of 5 °C min^{-1}. Decomposition temperatures are reported as $T_{5\%\ \mathrm{onset}}$ (onset for 5% decomposition) and T_{dec} (decomposition temperature).

Thermal transitions (melting point and glass transitions) were determined on a Mettler Toledo Star^e DSC1 (Columbus, OH) unit, under nitrogen. Samples between 5–15 mg were placed on an aluminium pan and were heated from 25 °C to 120 °C with a heating rate of 10 °C min^{-1} and cooled to −100 °C min^{-1} with an intracooler with a cooling rate of 10 °C min^{-1}. Melting points were determined using a Fisher-Johns Melting Point Apparatus.

Syntheses

Synthesis by metathesis reactions (method A)

*Method A1 (**1–13, 15, 17–21, 23, 24, 26**).* 0.01 mol of dicamba acid, 20 mL distilled water, and 0.011 mol of 10% aqueous solution of NaOH were mixed in a round-bottom flask, equipped with a magnetic stir bar, a reflux condenser, and an addition funnel. The mixture was heated at 50 °C until a clear solution was obtained. After that 0.01 mol of ammonium chloride or bromide dissolved in 30 mL water was added and stirred for 30 min at room temperature. The resulting product was extracted from the aqueous phase with 50 mL of chloroform and washed with distilled water until chloride or bromide ions were no longer detected using $AgNO_3$ test. After removal of chloroform the product was dried under reduced pressure at 60 °C for 24 h.

*Method A2 (**28**).* Stoichiometric amounts of sodium/potassium salt of dicamba and quinolinium hydrochloride were mixed in water and stirred at room temperature for 24 h. After evaporation of water, the reaction product was extracted with anhydrous acetone. The precipitate (NaCl) was filtered by gravity and the filtrate was evaporated under reduced pressure. Finally, the product was dried at 60 °C under reduced pressure.

Synthesis by acid–base reactions (method B) (14, 16, 22, 25, 27). 0.011 mol of a 40% aqueous solution of ammonium hydroxide was mixed with 0.011 mol dicamba free acid. The excess of dicamba acid was filtered out, and the water was evaporated. The product was dried under reduced pressure at 60 °C for 24 h. The ammonium hydroxide was used as received or prepared *via* ion exchange (an amount of 0.01 mol of piperidinium, morpholinium, or pyrrolidinium halide (chloride, bromide or iodide) was passed through an OH anion exchange resin Dowex-Monosphere 550A (OH)).

Characterization

Benzalkonium 3,6-dichloro-2-methoxybenzoate (1). Liquid, 92% yield, 99.5% purity, ^{1}H NMR ($CDCl_3$) δ ppm = 0.88 (t, J = 6.7 Hz, 3H), 1.26 (m, 20H), 1.71 (q, J = 6.8 Hz, 2H), 3.22 (s, 6H), 3.34 (t, J = 4.3 Hz, 2H), 3.92 (s, 3H), 4.86 (s, 2H), 6.99 (d, J = 8.5 Hz, 1H), 7.09 (d, J = 8.8 Hz, 1H), 7.38 (d, J = 6.3 Hz, 2H), 7.41 (t, J = 2.8 Hz, 1H), 7.55 (t, J = 3.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ ppm = 14.0, 22.6, 22.7 26.1, 29.1, 29.21, 29.24, 29.29, 29.34, 29.47, 29.52, 29.56, 31.8, 49.6, 61.6, 63.2, 67.4, 125.4, 126.0, 127.4, 127.6, 127.9, 129.0, 130.4, 133.1, 139.8, 151.8, 168.3; T_g = −26 °C; $T_{5\%\ \mathrm{onset}}$ = 175 °C; T_{dec} = 212 °C.

Didecyldimethylammonium 3,6-dichloro-2-methoxybenzoate (2). Liquid, 99% yield, 99.0% purity, ^{1}H NMR ($CDCl_3$) δ ppm =

0.88 (t, J = 6.7 Hz, 6H), 1.25 (m, 28H), 1.61 (q, J = 6.8 Hz, 4H), 3.34 (s, 6H), 3.39 (t, J = 6.3 Hz, 4H), 3.95 (s, 3H), 6.99 (d, J = 8.5 Hz, 1H), 7.08 (d, J = 8.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ ppm = 14.0, 22.5, 26.1, 29.1, 29.25, 29.27, 31.7, 50.9, 61.5, 63.1, 125.3, 125.9, 127.0, 127.8, 140.2, 151.7, 167.9; Anal. Calcd for: $C_{30}H_{53}O_3NCl_2$: C 65.90, H 9.79, N 2.56; Found: C 65.62, H 9.65, N 2.33; T_g = −47 °C, T_m = 86 °C, $T_{5\%\ \mathrm{onset}}$ = 178 °C; T_{dec} = 232 °C.

Dodecyldimethylphenoxyethylammonium 3,6-dichloro-2-methoxybenzoate (3). Liquid, 99% yield, 99.5% purity. ^{1}H NMR (CDCl$_3$) δ ppm = 0.88 (t, J = 6.7 Hz, 3H), 1.25 (m, 18H), 1.75 (q, J = 6.8 Hz, 2H), 3.44 (s, 6H), 3.55 (t, J = 8.4 Hz, 2H), 3.94 (s, 3H), 4.18 (t, J = 6.5 Hz, 2H), 4.43 (t, J = 6.6 Hz, 2H), 6.88 (d, J = 7.7 Hz, 2H), 7.00 (d, J = 8.5 Hz, 1H), 7.07 (d, J = 5.2 Hz, 1H), 7.26 (t, J = 2.2 Hz, 2H), 7.29 (t, J = 3.4 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ ppm = 14.1, 22.6, 22.9, 26.16, 26.19, 29.2, 29.33, 29.38, 29.49, 29.50, 31.8, 51.7, 61.6, 62.0, 62.1, 65.6, 114.1, 121.8, 125.3, 125.9, 127.1, 127.7, 129.6, 140.0, 151.5, 156.7, 167.8; Anal. Calcd for: $C_{30}H_{45}O_4NCl_2$: C 64.96, H 8.19, N 2.53; Found: C 65.12, H 8.38, N 2.41; T_g = −18 °C; $T_{5\%\ \mathrm{onset}}$ = 177 °C; T_{dec} = 236 °C.

Cocotrimethylammonium 3,6-dichloro-2-methoxybenzoate (4). Wax, 75% yield, 99.0% purity, ^{1}H NMR (CDCl$_3$) δ ppm = 0.88 (t, J = 6.7 Hz, 3H), 1.26 (m, 20H), 1.60 (q, J = 7.3 Hz, 2H), 3.27 (s, 9H), 3.30 (t, J = 8.5 Hz, 2H), 3.91 (s, 3H), 6.97 (d, J = 8.5 Hz, 1H), 7.08 (d, J = 8.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ ppm = 14.1, 22.7, 23.1, 26.2, 29.25, 29.32, 29.4, 29.5, 29.6, 31.9, 53.1, 61.7, 66.5, 125.3, 126.0, 127.4, 127.6, 139.6, 151.6, 168.1; T_g = −12 °C; $T_{5\%\ \mathrm{onset}}$ = 187 °C; T_{dec} = 213 °C, 312 °C.

Polyoxyethylene(15)(hydrogenatedtallow)methylammonium 3,6-dichloro-2-methoxybenzoate (5). Liquid, 89% yield, 99.0% purity, ^{1}H NMR (CDCl$_3$) δ ppm = 0.88 (t, J = 6.7 Hz, 3H), 1.26 (m, 28H), 1.71 (m, 2H), 3.29 (s, 3H), 3.38 (s, 3H), 3.62 (t, J = 6.6 Hz, 2H), 3.64 (m, 44H), 3.65 (m, 8H), 3.95 (m, 8H), 6.97 (d, J = 8.5 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ ppm = 14.1, 22.6, 26.3, 29.2, 29.3, 29.50, 29.59, 29.64, 31.8, 49.2, 61.4, 61.6, 63.8, 64.8, 70.1, 70.4, 72.5, 125.1, 125.8, 127.1, 127.8, 139.6, 151.6, 168.2; T_g = −57 °C, T_m = −36 °C; $T_{5\%\ \mathrm{onset}}$ = 170 °C; T_{dec} = 200 °C, 322 °C, 387 °C.

Cocodi(2-hydroxyethyl)methylammonium 3,6-dichloro-2-methoxybenzoate (6). Wax, 99% yield, 98.0% purity, ^{1}H NMR (CDCl$_3$) δ ppm = 0.88 (t, J = 6.6 Hz, 3H), 1.26 (m, 20H), 1.61 (q, J = 7.3 Hz, 2H), 3.19 (s, 3H), 3.37 (t, J = 8.0 Hz, 2H), 3.58 (t, J = 4.0 Hz, 4H), 3.91 (s, 3H), 3.99 (t, J = 4.0 Hz, 4H), 7.01 (d, J = 8.5 Hz, 1H), 7.13 (d, J = 8.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ ppm = 14.1, 22.4, 22.5, 22.6, 26.3, 29.2, 29.3, 29.5, 29.6, 31.8, 50.0, 55.6, 61.7, 63.6, 64.1, 125.4, 126.0, 127.5, 127.9, 138.5, 151.6, 168.9; T_g = −12 °C; $T_{5\%\ \mathrm{onset}}$ = 208 °C; T_{dec} = 274 °C.

(2-Hydroxyethyl)dimethyl(undecyloxymethyl)ammonium 3,6-dichloro-2-methoxybenzoate (7). Liquid, 92% yield, 98.0% purity, ^{1}H NMR (CDCl$_3$) δ ppm = 0.88 (t, J = 6.7 Hz, 3H), 1.26 (m, 16H), 1.55 (q, J = 6.2 Hz, 2H), 3.19 (s, 6H), 3.57 (t, J = 4.4 Hz, 2H), 3.69 (t, J = 6.6 Hz, 2H), 3.92 (s, 3H), 4.04 (t, J = 4.5 Hz, 2H), 4.76 (s, 2H), 5.14 (s, 1H), 7.01 (d, J = 8.5 Hz, 1H), 7.12 (d, J = 8.8 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ ppm = 14.1, 22.6, 25.7, 29.3, 29.47, 29.54, 31.8, 48.1, 55.5, 61.7, 62.9, 73.3, 91.2, 125.4, 126.0, 127.6, 127.8, 138.6, 151.6, 168.9; Anal. Calcd for $C_{24}H_{41}O_5NCl_2$: C 58.28, H 8.37, N 2.83; Found: C 58.57, H 8.16, N 2.59.

Cyclododecyloxymethyl(2-hydroxyethyl)dimethylammonium 3,6-dichloro-2-methoxybenzoate (8). Wax, 95% yield, 99.0% purity, ^{1}H NMR (CDCl$_3$) δ ppm = 1.31 (m, 18H), 1.47 (m, 2H), 1.61 (m, 2H), 3.20 (s, 6H), 3.60 (t, J = 4.7 Hz, 2H), 3.78 (q, J = 3.7 Hz, 1H), 3.93 (s, 3H), 4.06 (t, J = 4.5 Hz, 2H), 4.74 (s, 2H), 5.58 (s, 1H), 7.01 (d, J = 8.5 Hz, 1H), 7.13 (d, J = 8.8 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ ppm = 19.8, 22.5, 22.6, 24.7, 24.9, 28.4, 48.2, 55.7, 61.7, 63.0, 81.5, 89.9, 125.5, 126.1, 127.8, 128.0, 138.5, 151.8, 169.0; Anal. Calcd for $C_{25}H_{41}O_5NCl_2$: C 59.27, H 8.17, N 2.77; Found: C 59.11, H 8.23, N 2.83.

Decyl(2-hydroxyethyl)dimethylammonium 3,6-dichloro-2-methoxybenzoate (9). Wax, 79% yield, 98.5% purity, ^{1}H NMR (CDCl$_3$) δ ppm = 0.88 (t, J = 6.9 Hz, 3H), 1.20 (m, 16H), 1.24 (q, J = 6.2 Hz, 2H), 3.19 (s, 6H), 3.29 (t, J = 5.9 Hz, 2H), 3.55 (t, J = 4.6 Hz, 2H), 3.89 (s, 3H), 4.04 (t, J = 4.5 Hz, 2H), 4.69 (s, 1H), 7.01 (d, J = 8.6 Hz, 1H), 7.12 (d, J = 8.6 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ ppm = 14.0, 22.56, 22.62, 26.2, 29.1, 29.2, 29.4, 31.8, 51.6, 55.7, 61.7, 65.5, 65.6, 125.5, 126.1, 127.7, 128.6, 138.7, 151.8, 168.9; Anal. Calcd for $C_{22}H_{37}O_4NCl_2$: C 58.65, H 8.30, N 3.11; Found: C 58.17, H 8.42, N 2.99.

Di(hydrogenatedtallowalkyl)dimethylammonium 3,6-dichloro-2-methoxybenzoate (10). Wax, 98% yield, 99.5% purity, ^{1}H NMR (CDCl$_3$) δ ppm = 0.88 (t, J = 6.7 Hz, 6H), 1.26 (m, 49H), 1.61 (q, J = 6.8 Hz, 4H), 3.31 (s, 6H), 3.35 (t, J = 6.3 Hz, 4H), 3.93 (s, 3H), 6.98 (d, J = 8.5 Hz, 1H), 7.10 (d, J = 8.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ ppm = 14.0, 22.5, 26.1, 29.1, 29.25, 29.29, 29.37, 29.50, 29.55, 29.59, 31.8, 51.03, 61.6, 63.2, 125.3, 126.0, 127.6, 128.0, 139.1, 51.99, 168.0.

Oleyldi(2-hydroxyethyl)methylammonium 3,6-dichloro-2-methoxybenzoate (11). Wax, 92% yield, 99.0% purity, ^{1}H NMR (CDCl$_3$) δ ppm = 0.88 (t, J = 5.3 Hz, 3H), 1.26 (m, 26H), 1.59 (q, J = 7.3 Hz, 2H), 2.01 (m, 3H), 3.19 (s, 3H), 3.34 (t, J = 8.4 Hz, 2H), 3.55 (t, J = 4.0 Hz, 4H), 3.89 (s, 3H), 4.01 (t, J = 4.0 Hz, 4H), 5.35 (m, 2H), 7.01 (d, J = 8.7 Hz, 1H), 7.12 (d, J = 8.7 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ ppm = 14.1, 22.4, 22.6, 26.3, 27.17, 27.19, 29.17, 29.27, 29.29, 29.41, 29.44, 29.49, 29.63, 29.72, 31.85, 31.89, 50.0, 55.6, 61.8, 63.6, 64.1, 125.6, 126.2, 127.7, 128.2, 129.6, 130.0, 138.5, 151.8, 169.5.

Soyatrimethylammonium 3,6-dichloro-2-methoxybenzoate (12). Wax, 97% yield, 99.0% purity, ^{1}H NMR (CDCl$_3$) δ ppm = 0.88 (t, J = 6.6 Hz, 3H), 1.26 (m, 24H), 1.59 (q, J = 7.3 Hz, 2H), 2.02 (m, 3H), 3.22 (s, 9H), 3.28 (t, J = 8.5 Hz, 2H), 3.88 (s, 3H), 5.39 (m 2H), 6.98 (d, J = 8.6 Hz, 1H), 7.11 (d, J = 8.6 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ ppm = 14.0, 18.9, 22.5, 22.6, 23.0, 26.1, 27.1, 28.97, 29.12, 29.16, 29.23, 29.28, 29.38, 29.40, 29.45, 29.53, 29.58, 29.63, 31.81, 31.83, 32.50, 32.53, 35.58, 53.1, 61.8, 66.6, 125.5, 126.1, 127.8, 128.1, 129.9, 130.0, 130.2, 130.3, 130.4, 138.3, 151.9, 168.8.

Dialkanoyloxyethyldimethylammonium 3,6-dichloro-2-methoxybenzoate (13). Wax, 96% yield, 99.5% purity, ^{1}H NMR (CDCl$_3$) δ ppm = 0.88 (t, J = 6.6 Hz, 6H), 1.26 (m, 42H), 1.57 (q, J = 6.9 Hz, 4H), 2.29 (m, 4H), 2.32 (t, J = 9.3 Hz, 4H), 3.41 (s, 6H), 3.90 (s, 3H), 3.97 (t, J = 4.6 Hz, 4H), 4.52 (t, J = 4.6 Hz, 4H), 5.34 (m 2H), 7.00 (d, J = 8.6 Hz, 1H), 7.12 (d, J = 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ ppm = 14.1, 22.6, 24.6, 27.1, 27.2, 28.9, 29.03, 29.08, 29.15, 29.25, 29.30, 29.45, 29.60, 29.65, 29.69, 31.83, 31.86, 33.9, 52.2, 57.6, 61.8, 63.5, 125.6, 126.2, 127.9, 128.2, 129.6, 130.0, 138.2, 151.9, 168.8, 172.7.

Diallyldimethylammonium 3,6-dichloro-2-methoxybenzoate (14). Wax, 95% yield, ^{1}H NMR (D_2O) δ ppm = 3.00 (s, 6H), 3.88 (d, J = 7.4 Hz, 4H), 4.85 (s, 3H), 5.65 (m, 2H), 5.73 (m, 2H), 6.02 (m, 2H), 7.22 (d, J = 8.7 Hz, 1H), 7.38 (d, J = 8.7 Hz, 1H); ^{13}C NMR (D_2O) δ ppm = 52.2 (t, J = 4.2 Hz), 64.7, 68.8 (t, J = 3.2 Hz), 127.0, 128.7, 128.9, 130.1, 131.9, 132.3, 138.9, 153.7, 174.4; Anal. Calcd for $C_{16}H_{21}O_3NCl_2$: C 55.49, H 6.13, N 4.05; Found: C 55.55, H 6.24, N 3.98.

Choline-3,6-dichloro-2-methoxybenzoate (15). Solid, 90% yield, 99.0% purity, ^{1}H NMR (DMSO-d_6) δ ppm = 3.12 (s, 9H), 3.42 (m, 2H), 3.80 (s, 3H), 3.85 (m, 2H), 7.05 (d, J = 8.8 Hz, 2H), 7.17 (d, J = 8.8 Hz, 2H); ^{13}C NMR (DMSO-d_6) δ ppm = 53.53, 55.54, 61.45, 67.53, 125.58, 125.76, 127.13, 127.90, 141.31, 151.60, 166.09; T_m = 105 °C; $T_{5\%\ onset}$ = 177 °C; T_{dec} = 181 °C.

Trimethyltetradecylammonium-3,6-dichloro-2-methoxybenzoate (16). Solid, ^{1}H NMR ($CDCl_3$) δ ppm = 0.88 (t, J = 6.6 Hz, 6H), 1.26 (m, 42H), 1.57 (q, J = 6.9 Hz, 4H), 2.29 (m, 4H), 2.32 (t, J = 9.3 Hz, 4H), 3.41 (s, 6H), 3.90 (s, 3H), 3.97 (t, J = 4.6 Hz, 4H), 4.52 (t, J = 4.6 Hz, 4H), 5.34 (m 2H), 7.00 (d, J = 8.6 Hz, 1H), 7.12 (d, J = 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ ppm = 14.1, 22.6, 24.6, 27.1, 27.2, 28.9, 29.03, 29.08, 29.15, 29.25, 29.30, 29.45, 29.60, 29.65, 29.69, 31.83, 31.86, 33.9, 52.2, 57.6, 61.8, 63.5, 125.6, 126.2, 127.9, 128.2, 129.6, 130.0, 138.2, 151.9, 168.8, 172.7; T_m = 179–180 °C; $T_{5\%\ onset}$ = 191 °C; T_{dec} = 206 °C.

Tetrabutylammoniun-3,6-dichloro-2-methoxybenzoate (17). Solid, ^{1}H NMR (DMSO-d_6) δ ppm = 0.93 (t, 12H); 1.30 (m, 8H); 1.55 (m, 8H); 3.17 (m, 8H); 3.79 (s, 3H); 7.00 (d, 1H); 7.12 (d, 1H); ^{13}C NMR (DMSO-d_6) δ ppm = 13.93, 19.67, 23.55, 58.01, 61.20, 125.34, 125.48, 126.41, 128.03, 142.11, 151.53, 164.96; T_m = 126–127 °C; $T_{5\%\ onset}$ = 154 °C; T_{dec} = 156 °C.

1-Dodecylpyridinium 3,6-dichloro-2-methoxybenzoate (18). Liquid, 91% yield, 99.0% purity, ^{1}H NMR ($CDCl_3$) δ ppm = 0.87 (t, J = 6.7 Hz, 3H), 1.24 (m, 18H), 1.94 (q, J = 6.6 Hz, 2H), 3.91 (s, 3H), 4.82 (t, J = 7.4 Hz, 2H), 6.98 (d, J = 8.8 Hz, 1H), 7.21 (d, J = 8.5 Hz, 1H), 8.10 (t, J = 7.0 Hz, 2H), 8.41 (t, J = 7.7 Hz, 1H), 9.46 (d, J = 6.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ ppm = 14.1, 22.6, 26.0, 29.0, 29.2, 29.3, 29.4, 29.5, 31.8, 31.9, 61.7, 61.9, 125.3, 125.9, 127.9, 128.2, 138.3, 144.4, 145.2, 151.7, 168.1; Anal. Calcd for $C_{25}H_{35}O_3NCl_2$: C 64.09, H 7.54, N 2.99; Found: C 64.28, H 7.42, N 2.89; T_g = −25 °C; $T_{5\%\ onset}$ = 187 °C; T_{dec} = 210 °C, 355 °C.

1-Methyl-3-octyloxymethylimidazolium 3,6-dichloro-2-methoxybenzoate (19). Liquid, 74% yield, 98.0% purity, ^{1}H NMR ($CDCl_3$) δ ppm = 0.87 (t, J = 6.7 Hz, 3H), 1.23 (m, 10H), 1.51 (q, J = 6.3 Hz, 2H), 3.48 (t, J = 6.5 Hz, 2H), 3.91 (s, 3H), 4.03 (s, 3H), 5.64 (s, 2H), 6.99 (d, J = 8.5 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H), 7.40 (t, J = 1.8 Hz, 1H), 7.46 (t, J = 1.8 Hz, 1H), 10.37 ((t, J = 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ ppm = 14.1, 22.6, 25.8, 29.2, 29.3, 29.4, 31.8, 36.4, 61.7, 70.3, 79.0, 120.5, 123.7, 125.3, 125.9, 127.8, 127.9, 138.1, 138.6, 151.7, 168.6; Anal. Calcd for $C_{21}H_{30}O_4N_2Cl_2$: C 56.62, H 6.80, N 6.29; Found: C 56.18, H 6.15, N 6.23.

1,3-Didecylimidazolium 3,6-dichloro-2-methoxybenzoate (20). Liquid, 77% yield, 99.5% purity, ^{1}H NMR ($CDCl_3$) δ ppm = 0.88 (t, J = 6.7 Hz, 6H), 1.24 (m, 24H), 1.84 (q, J = 6.3 Hz, 4H), 3.95 (s, 3H), 4.27 (t, J = 7.4 Hz, 4H), 6.98 (d, J = 8.5 Hz, 1H), 7.08 (d, J = 8.6 Hz, 1H), 7.40 (t, J = 1.8 Hz, 1H), 7.41 (t, J = 1.7 Hz, 1H), 10.57 (t, J = 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ ppm = 13.9, 22.5, 26.1, 26.3, 28.9, 29.1, 29.2, 29.3, 30.1, 31.7, 46.9, 49.7, 61.5, 121.6, 125.2, 125.9, 127.4, 128.0, 138.2, 139.3, 151.7, 168.5; Anal. Calcd for $C_{31}H_{50}O_3N_2Cl_2$: C 65.38, H 8.86, N 4.92; Found: C 65.69, H 8.99, N 4.78.

Tetrabutylphosphonium 3,6-dichloro-2-methoxybenzoate (21). Wax, 84% yield, ^{1}H NMR ($CDCl_3$) δ ppm = 0.94 (t, J = 6.9 Hz, 12H), 1.47 (m, 16H), 2.34 (m, 8H), 3.98 (s, 3H), 6.95 (d, J = 8.5 Hz, 1H), 7.04 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ ppm = 13.3, 18.4 (d, J^{CP} = 47.4 Hz), 23.6 (d, J^{CP} = 4.9 Hz), 23.9, 61.3, 124.8, 125.5, 126.4, 127.8, 140.2, 151.4, 167.3; Anal. Calcd for $C_{24}H_{41}O_3PCl_2$: C 60.11, H 8.64; Found: C 60.25, H 8.52; T_g = 6 °C; T_m = 64–65 °C; $T_{5\%\ onset}$ = 180 °C; T_{dec} = 232 °C, 355 °C.

1,1-Dimethylpiperidinium 3,6-dichloro-2-methoxybenzoate (22). Liquid, 99% yield, ^{1}H NMR (DMSO-d_6) δ ppm = 1.50 (q, J = 5.9 Hz, 2H), 1.75 (q, J = 5.2 Hz, 4H), 3.08 (s, 6H), 3.33 (t, J = 5.9 Hz, 4H), 3.80 (s, 3H), 7.28 (d, J = 8.6 Hz, 1H), 7.80 (d, J = 8.6 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ ppm = 19.7, 20.6, 50.9, 61.0, 61.5, 125.0, 125.2, 126.5, 127.4, 140.9, 151.0, 165.2; Anal. Calcd for $C_{15}H_{21}O_3NCl_2$: C 53.89, H 6.35, N 4.19; Found: C 53.59, H 6.16, N 4.27; T_g = −54 °C; $T_{5\%\ onset}$ = 195 °C; T_{dec} = 240 °C.

1-Decyl-1-methylpiperidinium 3,6-dichloro-2-methoxybenzoate (23). Wax, 92% yield, 98.5% purity, ^{1}H NMR ($CDCl_3$) δ ppm = 0.88 (t, J = 6.8 Hz, 3H), 1.25 (m, 14H), 1.63 (q, J = 7.4 Hz, 2H), 1.72 (q, J = 5.9 Hz, 4H), 1.82 (q, J = 5.9 Hz, 4H), 3.25 (s, 3H), 3.51 (t, J = 8.6 Hz, 4H), 3.62 (t, J = 8.7 Hz, 2H), 3.95 (s, 3H), 6.98 (d, J = 8.6 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ ppm = 13.9, 20.0, 20.5, 21.8, 22.4, 26.2, 29.0, 29.1, 29.2, 31.6, 48.0, 60.5, 61.5, 62.5, 125.2, 125.9, 127.0, 127.8, 140.1, 151.6, 167.7; Anal. Calcd for $C_{24}H_{39}O_3NCl_2$: C 62.59, H 8.55, N 3.04; Found: C 62.21, H 8.39, N 2.93.

1,1-Didecylpiperidinium 3,6-dichloro-2-methoxybenzoate (24). Wax, 78% yield, 99.5% purity, ^{1}H NMR ($CDCl_3$) δ ppm = 0.88 (t, J = 6.7 Hz, 6H), 1.26 (m, 28H), 1.32 (q, J = 7.4 Hz, 2H), 1.59 (q, J = 5.9 Hz, 4H), 1.82 (q, J = 5.9 Hz, 4H), 3.37 (t, J = 8.4 Hz, 4H), 3.65 (t, J = 8.7 Hz, 4H), 3.97 (s, 3H), 6.96 (d, J = 8.5 Hz, 1H), 7.05 (d, J = 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ ppm = 13.9, 19.7, 20.4, 21.4, 22.4, 26.1, 28.95, 29.00, 29.14, 29.16, 31.6, 57.8, 58.6, 61.4, 125.0, 125.7, 126.7, 127.9, 140.1, 151.6, 167.6; Anal. Calcd for $C_{33}H_{57}O_3NCl_2$: C 67.54, H 9.81, N 2.39; Found: C 67.99, H 9.43, N 2.45.

4-Butyl-4-methylmorpholinium 3,6-dichloro-2-methoxybenzoate (25). Wax, 99% yield, ^{1}H NMR (DMSO-d_6) δ ppm = 0.92 (t, J = 7.3 Hz, 3H), 1.29 (sex, J = 7.4 Hz, 2H), 1.65 (q, J = 4.0 Hz, 2H), 3.15 (s, 3H), 3.43 (t, J = 7.1 Hz, 4H), 3.71 (t, J = 4.4 Hz, 2H), 3.80 (s, 3H), 3.91 (t, J = 4.9 Hz, 4H), 7.06 (d, J =

8.4 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (DMSO-d$_6$) δ ppm = 13.6, 19.2, 22.8, 45.8, 58.9, 59.9, 61.0, 63.6, 125.0, 125.2, 126.7, 127.4, 140.2, 151.0, 165.1; Anal. Calcd for $C_{17}H_{25}O_4NCl_2$: C 53.97, H 6.67, N 3.70; Found: C 53.62, H 6.44, N 3.85; T_g = −16 °C; $T_{5\%\ \mathrm{onset}}$ = 187 °C; T_{dec} = 215 °C.

4-Decyl-4-ethylmorpholinium 3,6-dichloro-2-methoxybenzoate (26). Liquid, 88% yield, 99.0% purity, ^{1}H NMR (D_2O) δ ppm = 0.98 (t, *J* = 6.0 Hz, 3H), 1.13 (m, 14H), 1.21 (t, *J* = 6.0 Hz, 3H), 1.49 (q, *J* = 4.0 Hz, 2H) 3.22 (t, *J* = 4.4 Hz, 2H), 3.44 (t, *J* = 4.4 Hz, 2H), 3.49 (t, *J* = 4.4 Hz, 4H), 3.86 (s, 3H), 3.99 (t, *J* = 4.9 Hz, 4H), 7.07 (d, *J* = 8.6 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (D_2O) δ ppm = 8.7, 16.1, 23.1, 24.9, 28.3, 31.3, 31.7, 31.8, 34.2, 55.9, 59.7, 60.5, 62.3, 64.0, 127.7, 128.0, 130.1, 130.3, 140.3, 153.9, 171.9; Anal. Calcd for $C_{24}H_{39}O_4NCl_2$: C 60.49, H 8.27, N 2.94; Found: C 60.01, H 8.00, N 2.79.

1-Butyl-1-methylpyrrolidinium 3,6-dichloro-2-methoxybenzoate (27). Liquid, 99% yield, ^{1}H NMR (DMSO-d$_6$) δ ppm = 0.91 (t, *J* = 7.3 Hz, 3H), 1.28 (sex, *J* = 7.4 Hz, 2H), 1.65 (q, *J* = 4.1 Hz, 2H), 2.05 (m, 4H), 2.99 (s, 3H), 3.33 (t, *J* = 8.5 Hz, 2H), 3.51 (m, 4H), 3.80 (s, 3H), 7.04 (d, *J* = 9.3 Hz, 1H), 7.16 (d, *J* = 9.3 Hz, 1H); ^{13}C NMR (DMSO-d$_6$) δ ppm = 13.6, 19.3, 21.0, 25.0, 47.2, 60.8, 62.7, 63.2, 124.9, 125.0, 126.1, 127.3, 141.3, 150.8, 164.7; Anal. Calcd for $C_{17}H_{25}O_3NCl_2$: C 56.35, H 6.97, N 3.87; Found: C 55.01, H 6.79, N 3.99; T_g = −41 °C; $T_{5\%\ \mathrm{onset}}$ = 185 °C; T_{dec} = 215 °C.

8-Hydroxyquinolinium 3,6-dichloro-2-methoxybenzoate (28). Glass, 94% yield, ^{1}H NMR (DMSO-d$_6$) δ ppm = 3.84 (s, 3H), 4.85 (s, 1H), 7.12 (dd, *J* = 1.6 Hz, *J* = 5.6 Hz, 1H), 7.32 (d, *J* = 8.7 Hz, 1H), 7.40 (d, *J* = 1.5 Hz, 1H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.53 (d, *J* = 3.8 Hz, 1H), 7.56 (d, *J* = 4.3 Hz, 1H), 8.33 (dd, *J* = 1.6 Hz, *J* = 6.7 Hz, 1H), 8.85 (dd, *J* = 1.6 Hz, *J* = 2.6 Hz, 1H); ^{13}C NMR (DMSO-d$_6$) δ = 62.1 ppm, 111.5, 117.8, 121.8, 126.0, 126.1, 127.6, 128.0; 128.8, 131.5, 131.7, 136.5, 137.9, 147.9, 152.4, 153.0, 165.1; Anal. Calcd for $C_{17}H_{13}O_4NCl_2$: C 55.75, H 3.59, N 3.83; Found: C 55.98, H 3.63, N 3.73; $T_{5\%\ \mathrm{onset}}$ = 190 °C; T_{dec} = 215 °C.

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