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Biodegradable Naphthenic Acid Ionic Liquids: Synthesis, Characterization, and Quantitative Structure–Biodegradation Relationship

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Abstract: It has been confirmed that commonly used ionic liquids are not easily biodegradable. When ultimately disposed of or accidentally released, they would accumulate in the environment, which strongly restricts large-scale industrial applications of ionic liquids. Herein, ten biodegradable ionic liquids were prepared by a single, one-pot neutralization of choline and surrogate naphthenic acids. The structures of these naphthenic acid ionic liquids (NAILs) were characterized and confirmed by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, and elemental analysis, and their physical properties, such as densities, viscosities, conductivities, melting points (T_m), glass transition points (T_g), and the onset temperatures of decomposition (T_d), were determined. More importantly, studies showed that these NAILs would be rapidly and completely biodegraded in aquatic environments under aerobic conditions, which would make them attractive candidates to be utilized in industrial processes. To explore the underlying mechanism involved in the NAIL biodegradation reaction and seek prediction of their biodegradability under environmental conditions, four molecular descriptors were chosen: the logarithm of the n-octanol/water partition coefficient ($\log P$), van der Waals volume (V_{vdW}), energies of the highest occupied molecular orbital (E_{HOMO}), and energies of the lowest unoccupied molecular orbital (E_{LUMO}). Through multiple linear regression, a general and qualified model including the biodegradation percentage for NAILs after the 28-day OECD 301D test ($\%B_{28}$) and molecular descriptors was developed. Regression analysis showed that the model was statistically significant at the 99% confidence interval, thus indicating that the $\%B_{28}$ of NAILs could be explained well by the quantum chemical descriptor E_{HOMO}, which might give some important clues in the discovery of biodegradable ionic liquids of other kinds.

Keywords: biodegradability · green chemistry · ionic liquids · molecular descriptors · reaction mechanisms

Introduction

Due to their unique physicochemical characteristics, room-temperature ionic liquids (RTILs) were designed as greener solvents to replace conventional volatile solvents that were believed to result in photochemical smog, ozone depletion, and global climate change.[1] RTILs are showing more and more promising perspectives in the diverse fields of synthesis,[2] catalysis or biocatalysis,[3–7] materials science,[8] electrochemistry,[9] and separation technology[10–13] at the laboratory level and even on the industrial scale.[14,15] With some achievement of industrial processes and commercial applications, certain factors that used to be neglected in the whole life cycle[16] of RTILs, such as ultimate disposal and environmental risk assessment, have to be taken into account. One of the most important factors in risk assessment is the biodegradability of RTILs, because biodegradation is a main process for removal of chemicals from the environment.[17] However, several studies[1,18,19] have shown that conventional or "first generation" RTILs are not biodegradable, which means that when accidentally released, these ionic liquids will stay intact and accumulate in the environment. This is obviously against the tenth of the 12 Green Chemistry prin-

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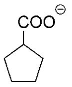
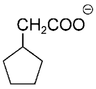
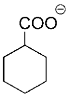
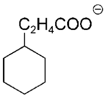
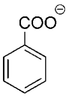
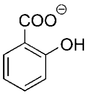
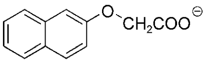
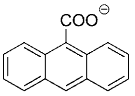
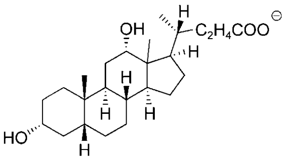
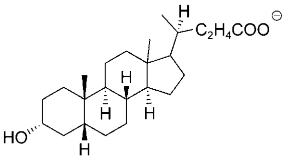
ciples[20] and will strongly restrict the large-scale industrial applications of RTILs.

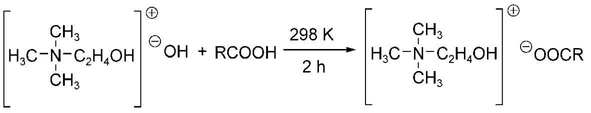
Fortunately, according to several reviews,[16,21,22] we might find a way to improve the biodegradability of RTILs through rational molecular design,[23] structural adjustment, and natural-sources screening. To produce biodegradable ionic liquids, Gathergood et al.[24–27] attached an ether side chain to the cationic core, Stolte et al.[28] introduced an octyl group and its hydroxylated and carboxylated derivatives into the side chain, and Harjani et al.[29] chose nicotinic acid, an inexpensive natural product, as starting material, which gives us a helpful hint to carry on our research.

Naphthenic acids, usually found in oil, were originally defined as a complex mixture of monocarboxylic acids with single or multiple rings, which comprise five or six carbon atoms.[30–33] Previous studies[34–36] had shown that naphthenic acids, especially low-molecular-weight surrogate naphthenic acids, could be almost completely biodegraded to CO_2 or CH_4 just by natural aging or by microbial activity in laboratory cultures.

Herein, we chose ten surrogate naphthenic acids as anions and biodegradable choline[37,38] as cation to prepare naphthenic acid ionic liquids (NAILs). The structures of the anions and the abbreviations of the synthesized NAILs are presented in Table 1. In view of the fact that halogen contaminations introduced by metathesis routes would dramatically affect the physicochemical properties of the ionic liquids, a neutralization method[39–41] was adopted to prepare the desired ionic liquids from a single, one-pot reaction (see Scheme 1). The biodegradability of the obtained NAILs was studied by means of the closed-bottle test (OECD 301D).[42] Furthermore, based on four molecular descriptors, a biodegradation model for NAILs was established to identify the rate-limiting step and explore the underlying mechanism involved in the NAILs biodegradation reaction.

Table 1. Structures of anions and the abbreviations used for the synthesized NAILs.

Anions	Ionic liquids	Abbreviations
 [CPC]	choline cyclopentane carboxylate	[Ch][CPC]
 [CPA]	choline cyclopentyl acetate	[Ch][CPA]
 [CHC]	choline cyclohexane carboxylate	[Ch][CHC]
 [CHP]	choline 3-cyclohexyl propionate	[Ch][CHP]
 [Be]	choline benzoate	[Ch][Be]
 [Sa]	choline salicylate	[Ch][Sa]
 [NOA]	choline 2-naphthoxyacetate	[Ch][NOA]
 [AC]	choline anthracene-9-carboxylate	[Ch][AC]
 [DOC]	choline deoxycholate	[Ch][DOC]
 [LC]	choline lithocholate	[Ch][LC]



$$[H_3C-N(CH_3)_2-C_2H_4OH]^{\oplus}\,{}^{\ominus}OH + RCOOH \xrightarrow[2\,h]{298\,K} [H_3C-N(CH_3)_2-C_2H_4OH]^{\oplus}\,{}^{\ominus}OOCR$$

Scheme 1. Synthesis of NAILs.

Results and Discussion

Density, viscosity, and conductivity: The densities, viscosities, and conductivities of six NAILs that are liquid at room temperature are presented in Table 2. Their densities range from 1.03 to 1.18 $g\,cm^{-3}$ at 40 °C. It can be seen that: 1) $\rho_{[Ch][CPC]} > \rho_{[Ch][CPA]}$ and $\rho_{[Ch][CHC]} > \rho_{[Ch][CHP]}$: this may be attributed to the incorporation of longer alkyl chains into the rings, which results in the increasing disruption of crystal effective packing; 2) $\rho_{[Ch][Sa]} > \rho_{[Ch][Be]}$: introduction of the OH group into the ring can generate hydrogen bonds between the anions, then increase the density of [Ch][Sa]; and 3) ionic liquids with aromatic naphthenic acids as anions were much denser than their aliphatic naphthenic acid counterparts, due to their planar phenyl groups which resulted in stacking effects and interactions between them.

The viscosity of an ionic liquid appears to be governed essentially by van der Waals interactions and hydrogen bonds.[43] Table 2 shows that increased van der Waals interactions between the alkyl chains contribute to higher viscosities of both [Ch][CPA] and [Ch][CHP] compared with those of their homologues without alkyl chains. Similarly,

Table 2. Some properties of six room-temperature NAILs.

Ionic liquids	$\rho^{[a]}$ [g cm^{-3}]	$\rho^{[b]}$ [g cm^{-3}]	$\eta^{[c]}$ [mPa s]	$\sigma^{[d]}$ [S m^{-1}]	$M_w^{[e]}$	$R_-^{-1[f]}$ [$\times 10^9$ m^{-1}]
[Ch][CPC]	1.087904	1.081890	172.7103	0.0958	217	2.192
[Ch][CPA]	1.068976	1.062376	249.7639	0.0653	231	1.990
[Ch][CHC]	1.064432	1.061194	292.3849	0.0497	231	1.999
[Ch][CHP]	1.046285	1.038349	676.9422	0.0117	259	1.680
[Ch][Be]	1.138713	1.131199	1096.7305	0.0139	225	2.269
[Ch][Sa]	1.174111	1.168177	1192.3123	0.0101	241	2.082

[a] Density at 25 °C. [b] Density at 40 °C. [c] Viscosity at 40 °C. [d] Conductivity at 40 °C. [e] Molar mass. [f] Inverse of the anionic radius. In the case of choline it is a cation (R_+^{-1}): inverse of choline's radius; $R_+^{-1} = 1.955 \times 10^9$ m^{-1}. R_-^{-1} and R_+^{-1} were calculated with the program Gaussian 03.

hydrogen bonding between the anions increases the viscosity of [Ch][Sa] over [Ch][Be]. Generally, for the same cation, the smaller the size of the anion, the lower the viscosity. However, strong stacking effects and interactions between aromatic rings dramatically increase the viscosities of NAILs with an aromatic carboxylate as anion compared with their aliphatic-ring counterparts, as is also the case for the densities.

The conductivity is usually influenced by viscosity, density, molecular weight, and ion size. Among these, viscosity plays a dominating role; normally, the larger the viscosity, the lower the conductivity. Besides the obvious influence of viscosity, the effects of density and ion size must be stressed. [Ch][Be], for instance, is more conducting than [Ch][CHP], in spite of its much higher viscosity. This might combine the advantages of a larger density and a smaller anion size. Additionally, the negative charge is delocalized more widely over aromatic rings than aliphatic rings. The aromatic-ring NAILs will therefore dissociate more easily than the corresponding aliphatic-ring NAILs, which is another contributor to higher conductivity.[44]

Abbott et al.[45–47] used the Stokes–Einstein relation to derive an expression for the conductivity of ionic liquids. In this study, the conductivities σ of NAILs are also calculated by using Equation (1):

$$\sigma = \frac{z^2 Fe}{6\pi\eta}\frac{\rho}{M_w}(R_+^{-1} + R_-^{-1}) \tag{1}$$

where F is the Faraday constant, e is the electronic charge, and z is the charge on the ion; ρ, η, M_w, R_+^{-1}, and R_-^{-1} are all listed in Table 2. The relationship between calculated and experimental conductivities is illustrated in Figure 1. An excellent correlation is observed, which means the conductivity of NAILs can be predicted with Equation (1) very well.

Melting and glass transition temperatures: Several studies[48–50] assumed that the introduction of carboxylic acid groups to ionic liquids would readily produce strong hydrogen bonds, and thus result in high melting points (T_m) or glass transition temperatures (T_g), so it was not appropriate for carboxylic acid groups to be incorporated into the ions. The fact is that all ten NAILs are obtained with the T_m or T_g below 100 °C, and six of them (shown in Table 2) are liquid at room temperature. The T_m and T_g values of the NAILs are listed in Table 3, and Figure 2 shows their differential scanning calorimetry (DSC) traces. In most cases, the glass transition temperatures are in the region of −85 to −50 °C for a wide range of anions. The results indicate that an increase of ion size and incorporation of an alkyl chain into the ring will result in a gradual increase of T_g. This confirms the increasing importance of van der Waals forces over Coulomb attractions because the latter decrease with increasing size of the ions.[51–53] It is expected at first that the T_g of [Ch][Be] and [Ch][Sa] should increase dramatically, presumably as a consequence of the phenyl ring component in this anion structure. Surprisingly, the opposite is observed, which could probably be attributed to larger electron delocalization.[49]

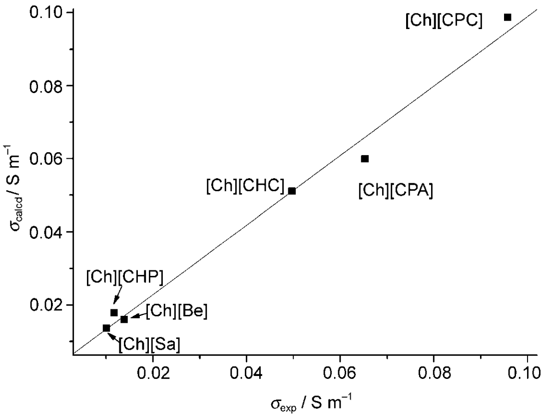


Figure 1. Conductivities calculated from Equation (1) (σ_{calcd}) versus those measured in the experiment (σ_{exp}).

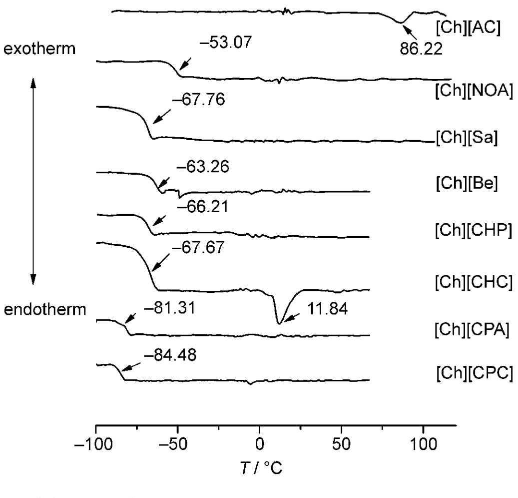


Figure 2. DSC curves for NAILs.

Table 3. Thermal properties of ten NAILs.

Ionic liquids	[Ch][CPC]	[Ch][CPA]	[Ch][CHC]	[Ch][CHP]	[Ch][Be]	[Ch][Sa]	[Ch][NOA]	[Ch][AC]	[Ch][DOC]	[Ch][LC]
T_g [°C]	−84.48	−81.31	−67.67	−66.21	−63.26	−67.76	−53.07	–	–	–
T_m [°C]	–	–	11.84	–	–	–	–	86.22	70.72	88.45
T_d [°C]	178.76	180.63	177.64	175.73	203.15	230.43	210.20	201.35	232.45	218.50

Thermal stability: The onset points of decomposition (T_d) for the ten NAILs are given in Table 3, and Figure 3 shows their thermogravimetric analysis traces. The four single-aliphatic-ring NAILs show only very minor weight loss until above 175 °C; from that point, a rapid and complete decomposition is observed. As for the aromatic-ring NAILs, that point is above 200 °C, the highest being 230 °C for [Ch][Sa]. The thermal decomposition traces of [Ch][DOC] and [Ch][LC] are a little different from those of the ionic liquids mentioned above. These compounds decompose initially at the first point (232 °C for [Ch][DOC] and 218 °C for [Ch][LC]); after that, they have parallel humps in the decomposition traces, perhaps indicating a similar decomposition mechanism and products. Yoshizawa-Fujita et al.[54] found that the thermal stability of an ionic liquid was primarily related to the nature of the anion, including the nucleophilicity and Lewis basicity. They found that a stronger Lewis basicity of the anion tended to induce thermal decomposition of RTILs at a lower temperature compared with typical ionic liquids. In this study, the electron is delocalized more widely over aromatic rings than aliphatic rings, so the aliphatic-ring anions have stronger Lewis basicity, which leads to the lower onset temperatures of decomposition.

Ultimate biodegradability: The biodegradability of the ten NAILs was studied by means of the closed-bottle test (OECD 301D).[42] In this test, sodium dodecyl sulfate (SDS) was used as reference compound. Other ionic liquids were [BMIM][BF_4] (BMIM: 1-butyl-3-methylimidazolium), [BMIM][PF_6], [BMIM][HSO_4], [BMIM][CHC], [BMIM][Sa], and [BMIM][NOA]; some common volatile organic solvents (toluene, methylene chloride, acetonitrile, and ethanol) were tested for comparison. A test substance whose biodegradation percentage after 28 days of incubation (%B_{28}) is higher than 60 % is referred to as readily biodegradable; therefore, it should be assumed that such a chemical will be rapidly and completely biodegraded in aquatic environments under aerobic conditions.[18,42] The biodegradation data of all the test substances are illustrated in Figure 4, which shows that almost all the NAILs pass the closed-bottle test (%B_{28} > 60 %) during a 28-day incubation period, except for [Ch][NOA] and [Ch][AC]. Notably, as the number of rings increases, biodegradability generally decreases; yet the two- and three-ring NAILs failed in the closed-bottle test, but both of the four-ring NAILs passed. Similar results[55] were obtained from naphthalene and phenanthrene under the MITI test, another aerobic biodegradation test method adopted by the Japanese Ministry of International Trade and Industry. The negative results of [Ch][NOA] and [Ch][AC] may be attributed to their toxicity to microorganisms because only these two had lag phases (0–14 days) in their incubation curves, although the test substance concentration is only about 2 mg L^{-1}. Another reason might be the poor solubility of [Ch][NOA] and [Ch][AC] in the test medium, which results in a decrease of the actual uptake of dissolved molecular oxygen.[19]

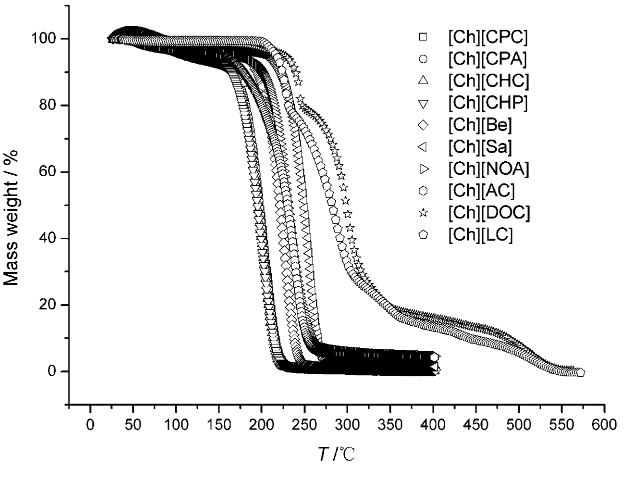


Figure 3. Thermogravimetric analysis traces for NAILs.

Under the same conditions, [BMIM][BF_4] and [BMIM][PF_6] show a %B_{28} value lower than 25 %. The %B_{28} of [BMIM][HSO_4] is even negative, which is probably due to its strong inhibition of endogenous respiration of the microorganisms. The ultimate biodegradability of [BMIM][CHC], [BMIM][Sa], and [BMIM][NOA] is much lower than that of their [Ch] counterparts but significantly higher than that of [BMIM][BF_4], [BMIM][PF_6], and [BMIM][HSO_4]. To some extent, it might help us to conclude that the synthesized ionic liquids would be biodegradable if the anions and cations are both easily biodegraded. Three out of four chosen organic solvents pass the closed-bottle test. Except for ethanol, whose %B_{28} value reaches 95.1 %, the biodegradability of eight NAILs which pass the test is equivalent to or even higher than that of the chosen common volatile solvents, so the NAILs can be competent as greener solvents to replace conventional volatile ones.

To identify the rate-limiting step and explore the underlying mechanism involved in the NAIL biodegradation reaction, four molecular descriptors were chosen and calculated; the results, together with the %B_{28} values of the NAILs, are listed in Table 4. Through stepwise regression analysis carried out by SPSS software, the regression equation for %B_{28} can be expressed as Equation (2):

$$\%B_{28} = 119.294 + 37.821E_{\mathrm{HOMO}} \qquad (2)$$

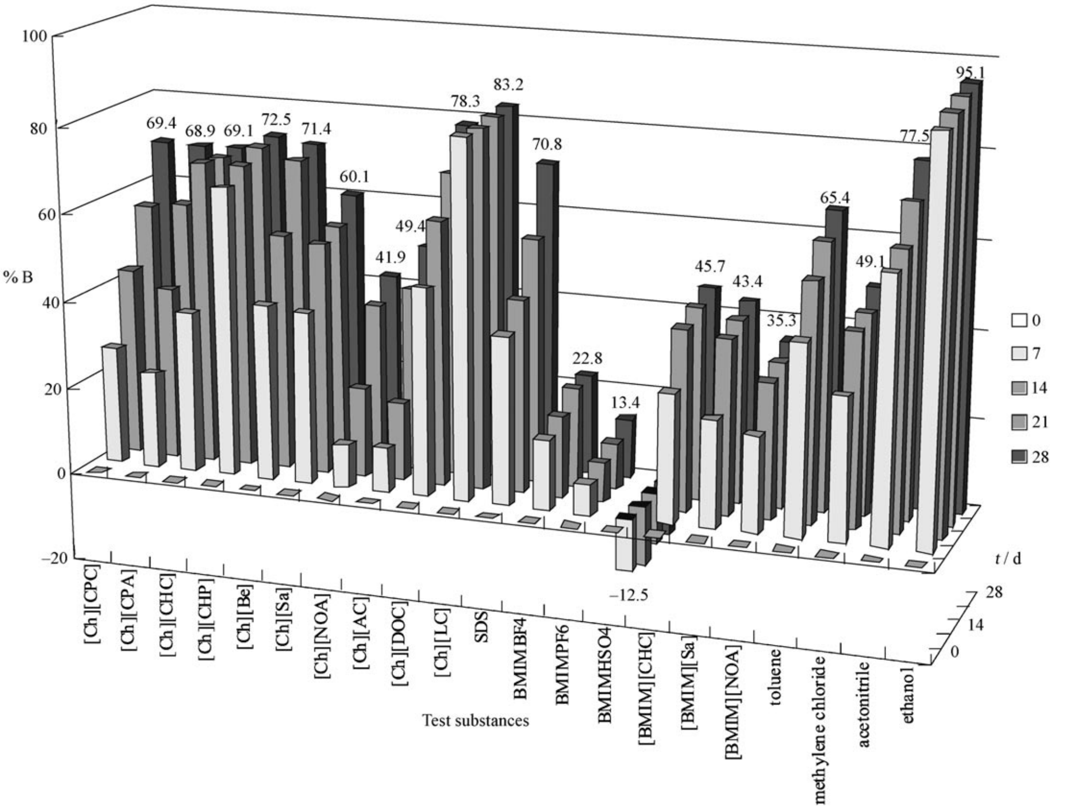


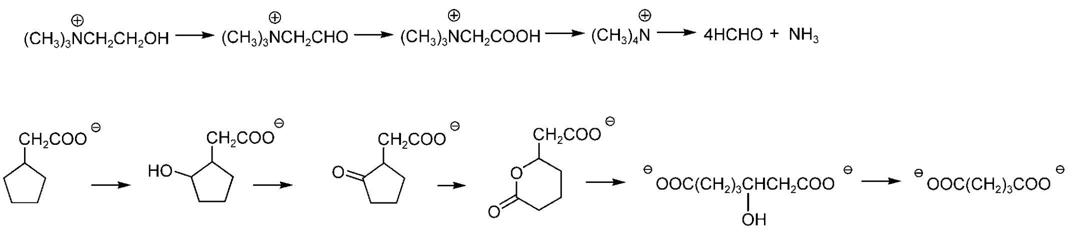
Figure 4. Biodegradation of all test substances; the $\%B_{28}$ values are given on the corresponding columns.

Table 4. $\%B_{28}$ values and some descriptors of ten NAILs.

Ionic liquids	$\%B_{28}$	E_{LUMO} [eV]	E_{HOMO} [eV]	$\log P$	V_{vdW} [Å^3]
[Ch][CPC]	69.4	2.88	−1.20	0.59	110.41
[Ch][CPA]	68.9	2.64	−1.22	1.33	126.89
[Ch][CHC]	69.1	2.64	−1.22	1.33	126.86
[Ch][CHP]	72.5	2.20	−1.22	1.99	159.68
[Ch][Be]	71.4	2.67	−1.61	1.56	110.01
[Ch][Sa]	60.1	2.45	−1.47	1.50	119.01
[Ch][NOA]	41.9	1.50	−1.90	1.96	178.56
[Ch][AC]	49.4	1.17	−1.85	3.30	196.08
[Ch][DOC]	78.3	0.95	−1.12	2.89	390.75
[Ch][LC]	83.2	1.12	−1.17	3.70	381.91

$n=10$, $R=0.875$, S.E.$=6.48$, $F=26.210>F_{0.01}\ (1,8)=11.93$, and $p=0.001$, where n is the number of observations, R is the correlation coefficient, S.E. is the standard error, F is the Fisher criterion, and p is the significance level. Multiple linear regression analysis shows that the model is statistically significant at the 99% confidence interval, thus indicating that the $\%B_{28}$ of NAILs can be explained well by the quantum chemical descriptor E_{HOMO}. Under aerobic conditions, the percentage of biodegradation is mainly governed by three factors: hydrophobic, steric, and electronic parameters. If a molecule or compound has proper hydrophobicity and molecular volume, it will easily penetrate the membrane of the cell, arrive at the active site of oxygenase, and then be oxidized and degraded. In the model, E_{HOMO} plays an important role in the biodegradation reaction of NAILs. We can conclude that the rate-limiting step of aerobic biodegradation of NAILs may be the attack on the ions by the electrophilic oxygen of a monoxygenase or dioxygenase, because E_{HOMO} usually directs the nucleophilic reactivity of a compound in the frontier molecular orbital theory. So the higher the E_{HOMO}, the easier it is for the compound to be attacked by electrophilic oxygen, and the larger the $\%B$ value. Our study and some others[56,57] on quantitative structure–biodegradation relationships (QSBRs) confirmed that.

We can also explore the underlying mechanism and predict the most probable biodegradation procedure with the frontier molecular orbital theory. Take [Ch][CPA], for example: complete dissociation is presumed due to its low starting concentration (about 2 mg L^{-1}), so the interactions between the cation and anion are not considered. According to its structure, generally, the cation [Ch] does not have other biodegradation pathways than the one illustrated in Scheme 2. As for the anion [CPA], when attacked by electrophilic oxygen there are six positions available. By analyzing the HOMO surfaces (Figure 5, left), we find that only three positions (1–3) are easily attacked, because these positions have higher E_{HOMO} values. Combined with atomic charge analysis (Figure 5, right), we know that the most probable position to be attacked is position 3, because it has the highest electron density. The most probable biodegradation pathway of [Ch][CPA] is illustrated in Scheme 2, which needs to be proved further.



Scheme 2. Most probable biodegradation pathway of [Ch][CPA].

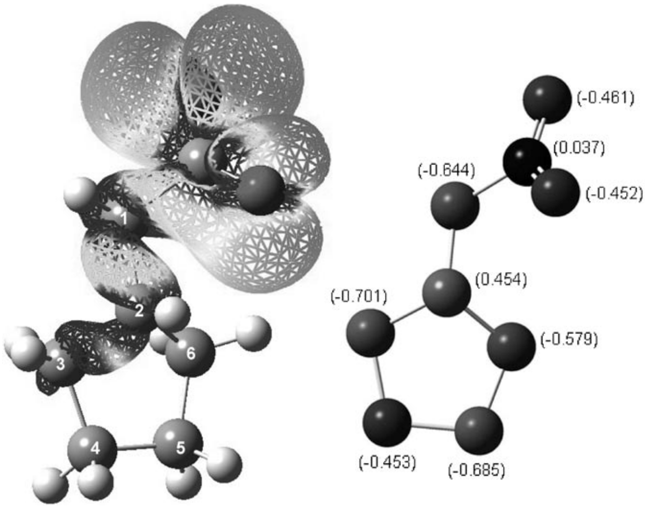


Figure 5. HOMO surfaces (left) and atomic charges (right) of [Ch][CPA].

Conclusion

Ten NAILs have been synthesized by neutralization of the respective acid with choline hydroxide. The overall neutralization process is atom efficient and produces no waste. Compared with metathesis routes, the neutralization method provides a guideline for the synthesis of ionic liquids in a very pure state without any halogen contamination. Furthermore, the simple preparation involved encourages commercial applications of NAILs.

The densities, viscosities, conductivities, glass transition/melting temperatures, and decomposition temperatures of NAILs were measured. Studies indicate that these properties of NAILs are more influenced by van der Waals forces and stacking effects of phenyl groups than Coulomb attractions and electron interactions. In addition, similar to other ionic liquids, NAILs also have designable characteristics. Their physicochemical properties can be adjusted by changing the following four factors: the alkyl chain connected to the rings, the carbon number in the rings, the number of rings, and whether aromatic or aliphatic rings. Therefore, NAILs are more designable than common ionic liquids, which can be adjusted just by the side chains connected to the core.

In the closed-bottle test, the biodegradation values of most NAILs are higher than 60 % during a 28-day incubation period. That means the NAILs will be rapidly and completely biodegraded under environmental conditions. One point we should keep in mind is that the closed-bottle test method is extremely stringent (relatively low density of microorganism, relatively short incubation period, absence of other carbon and nitrogen sources), so that biodegradation values lower than 60 % (larger than 40 %) do not necessarily mean the test compound will persist under environmental conditions; it may be sufficiently removed by using an appropriate treatment system.[58] Due to their good biodegradability, we anticipate that these new NAILs will be attractive in large-scale industrial processes and commercial applications in the near future. By comparing the biodegradability of NAILs with that of other ionic liquids and some common organic solvents, we can conclude that biodegradable ionic liquids can be designed as successful substitutes for volatile solvents through natural-sources (biodegradable cations and anions) screening.

Although the biodegradation reaction is complicated, influenced by many factors, and hard to interpret in a simple equation, through descriptor selection, regression analysis, and model development we can draw the conclusion that E_{HOMO} is a dominant parameter governing the biodegradability of NAILs, which gives us a clear direction to discover biodegradable ionic liquids of other kinds.

Experimental Section

Materials

Chemicals used in the synthesis of NAILs: Cyclopentane carboxylic acid, cyclopentyl acetic acid, 3-cyclohexyl propionic acid, 2-naphthoxyacetic acid, and anthracene-9-carboxylic acid were purchased from Lancaster. Cyclohexane carboxylic acid, benzoic acid, salicylic acid, deoxycholic acid, and choline hydroxide (45 wt. % aqueous solution) were purchased from Acros Organics, and lithocholic acid was purchased from Fluka.

Chemicals used for comparison in the ultimate biodegradability test: SDS, toluene, methylene chloride, acetonitrile, and ethanol were all analytical grade and produced by the Sinopharm Chemical Reagent Beijing Co., Ltd. [BMIM][BF_4], [BMIM][PF_6], and [BMIM][HSO_4] were supplied by Henan Lihua Pharmaceutical Co., Ltd. We synthesized [BMIM]-[CHC], [BMIM][Sa], and [BMIM][NOA] and their preparation and characterization can be found in the Supporting Information. All reagents purchased were used as received without further purification.

General methods: Densities of NAILs were measured at 25 and 40 °C by using a DMA 5000 density meter (Anton Parr) with a precision of $\pm 10^{-6}$ $g\,cm^{-3}$. Viscosities were measured at 40 °C by using an automated microviscometer (Anton Parr) with an uncertainty in experimental measurement of ± 0.0001 mPa s. Conductivities were measured with a DDS-

307 conductometer (Shanghai Precision & Scientific Instruments). The glass transition and melting temperatures were determined from DSC thermograms during heating scans (heating rate of 10 °C min^{-1} from −120 to +100 °C) on a modulated DSC 2910 apparatus (TA Instruments). Thermogravimetric analyses were conducted in an air atmosphere on a TGA 2050 thermogravimetric analyzer (TA Instruments) between 25 and 400 °C (570 °C for [Ch][DOC] and [Ch][LC]) at a heating rate of 5 °C min^{-1}. The ^{1}H NMR spectra were recorded on an ARX400 NMR spectrometer (Bruker) at 400 MHz with dimethyl sulfoxide (DMSO) as solvent and TMS as internal standard. ^{13}C NMR spectra were recorded on the same instrument at 100 MHz. IR studies were conducted with a Nicolet 380 FTIR spectrometer (Thermo Nicolet). Elemental analyses were conducted with a Vario EL elemental analyzer (Elementar).

Synthesis: The obtained NAILs were prepared by neutralization of the respective surrogate naphthenic acids dissolved in ethanol with choline hydroxide. As an example, the synthesis procedure of [Ch][CPC] is as follows. Cyclopentane carboxylic acid (17.12 g, about 0.15 mol) dissolved in ethanol (50 mL) was loaded into a flask (250 mL) with a magnetic stirrer, and then, under vigorous stirring, an equimolar amount of choline hydroxide aqueous solution was added dropwise to the flask in about 20 min. The reaction lasted for 2 h at 25 °C. The solvent was removed in vacuo at or below 50 °C in a rotary evaporator. The resultant residue was dried under vacuum over P_2O_5 for 48 h at 80 °C to afford a colorless product.

Characterization

[Ch][CPC]: ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 7.75 (br, 1 H; $\mathit{H}\mathrm{OCH_2CH_2}$), 3.87 (m, 2 H, ^3J(H,H) = 15.1 Hz; $\mathrm{HOC}\mathit{H}_2\mathrm{CH_2}$), 3.46 (t, 2 H, ^3J(H,H) = 9.9 Hz; $\mathrm{HOCH_2C}\mathit{H}_2$), 3.15 (s, 9 H; $\mathrm{N(C}\mathit{H}_3\mathrm{)_3}$), 2.29 (m, 1 H, ^3J(H,H) = 23.8 Hz; OC(=O)C1*H*CCCC1), 1.63 (m, 4 H, ^3J(H,H) = 15.6 Hz; $\mathrm{OC({=}O)C1C}\mathit{H}_2\mathrm{CCC1}\mathit{H}_2$), 1.52 (m, 2 H, ^3J(H,H) = 4.2 Hz; $\mathrm{OC({=}O)C1CC}\mathit{H}_2\mathrm{CC1}$), 1.40 ppm (m, 2 H, ^3J(H,H) = 11.5 Hz; $\mathrm{OC({=}O)C1CCC}\mathit{H}_2\mathrm{C1}$); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 179.31 (O*C*(=O)C1CCCC1), 67.40 ($\mathrm{HO}\mathit{C}\mathrm{H_2CH_2}$), 55.07 ($\mathrm{HOCH_2}\mathit{C}\mathrm{H_2}$), 53.19 ($\mathrm{N(}\mathit{C}\mathrm{H_3)_3}$), 47.59 (OC(=O)*C*1CCCC1), 30.61 (OC(=O)C1*C*CC*C*1), 25.71 ppm (OC(=O)C1C*CC*C1); IR: $\tilde{\nu}$ = 3381 (νOH), 2956 (νCH), 2870, 1552 (ν_{as}COO), 1479 (δCH), 1397 (ν_{s}COO), 1325, 1138 (νCN), 1089, 1007, 957, 867, 669 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{23}NO_3\cdot 2H_2O$: C 52.15, H 10.74, N 5.53; found: C 52.34, H 10.59, N 5.49.

[Ch][CPA]: ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 7.87 (br, 1 H; $\mathit{H}\mathrm{OCH_2CH_2}$), 3.86 (m, 2 H, ^3J(H,H) = 8.9 Hz; $\mathrm{HOC}\mathit{H}_2\mathrm{CH_2}$), 3.46 (t, 2 H, ^3J(H,H) = 5.0 Hz; $\mathrm{HOCH_2C}\mathit{H}_2$), 3.15 (s, 9 H; $\mathrm{N(C}\mathit{H}_3\mathrm{)_3}$), 2.12 (m, 1 H, ^3J(H,H) = 22.7 Hz; OC(=O)CC1*H*CCCC1), 1.87 (d, 2 H, ^3J(H,H) = 7.3 Hz; $\mathrm{OC({=}O)C}\mathit{H}_2\mathrm{C1CCCC1}$), 1.67 (m, 2 H, ^3J(H,H) = 7.2 Hz; $\mathrm{OC({=}O)CC1CCCC1}\mathit{H}_2$), 1.52 (m, 2 H, ^3J(H,H) = 7.7 Hz; $\mathrm{OC({=}O)CC1C}\mathit{H}_2\mathrm{CCC1}$), 1.45 (m, 2 H, ^3J(H,H) = 9.1 Hz; $\mathrm{OC({=}O)CC1CCC}\mathit{H}_2\mathrm{C1}$), 1.07 ppm (m, 2 H, ^3J(H,H) = 13.8 Hz; $\mathrm{OC({=}O)CC1CC}\mathit{H}_2\mathrm{CC1}$); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 175.81 (O*C*(=O)CC1CCCC1), 67.52 ($\mathrm{HO}\mathit{C}\mathrm{H_2CH_2}$), 55.00 ($\mathrm{HOCH_2}\mathit{C}\mathrm{H_2}$), 53.21 ($\mathrm{N(}\mathit{C}\mathrm{H_3)_3}$), 45.55 (OC(=O)*C*C1CCCC1), 37.80 (OC(=O)C*C*1CCCC1), 32.63 (OC(=O)CC1*C*CC*C*1), 24.84 ppm (OC(=O)CC1C*CC*C1); IR: $\tilde{\nu}$ = 3419 (νOH), 2952 (νCH), 2870, 1557 (ν_{as}COO), 1487 (δCH), 1398 (ν_{s}COO), 1319, 1134 (νCN), 1088, 1007, 956, 866, 667 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{25}NO_3\cdot 2H_2O$: C 53.82, H 10.16, N 5.23; found: C 53.88, H 10.61, N 5.19.

[Ch][CHC]: ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 7.90 (br, 1 H; $\mathit{H}\mathrm{OCH_2CH_2}$), 3.96 (m, 2 H, ^3J(H,H) = 15.6 Hz; $\mathrm{HOC}\mathit{H}_2\mathrm{CH_2}$), 3.41 (t, 2 H, ^3J(H,H) = 10.0 Hz; $\mathrm{HOCH_2C}\mathit{H}_2$), 3.08 (s, 9 H; $\mathrm{N(C}\mathit{H}_3\mathrm{)_3}$), 2.05 (m, 1 H, ^3J(H,H) = 11.2 Hz; OC(=O)C1*H*CCCCC1), 1.71 (m, 2 H, ^3J(H,H) = 10.4 Hz; $\mathrm{OC({=}O)C1C}\mathit{H}_2\mathrm{CCCC1}$), 1.62 (m, 2 H, ^3J(H,H) = 7.6 Hz; $\mathrm{OC({=}O)C1CCCCC1}\mathit{H}_2$), 1.21 ppm (m, 6 H, ^3J(H,H) = 12.0 Hz; $\mathrm{OC({=}O)C1CC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C1}$); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 178.86 (O*C*(=O)C1CCCCC1), 67.47 ($\mathrm{HO}\mathit{C}\mathrm{H_2CH_2}$), 55.03 ($\mathrm{HOCH_2}\mathit{C}\mathrm{H_2}$), 53.18 ($\mathrm{N(}\mathit{C}\mathrm{H_3)_3}$), 46.73 (OC(=O)*C*1CCCCC1), 30.55 (OC(=O)C1*C*CCC*C*1), 26.36 (OC(=O)C1CC*C*CC1), 26.13 ppm (OC(=O)C1C*C*C*C*C1); IR: $\tilde{\nu}$ = 3419 (νOH), 3025, 2928 (ν_{as}CH), 2852 (ν_{s}CH), 1567 (ν_{as}COO), 1539, 1404 (ν_{s}COO), 1279, 1221, 1137 (νCN), 1087, 960, 930, 892, 721, 668 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{25}NO_3\cdot H_2O$: C 57.80, H 10.91, N 5.62; found: C 57.81, H 10.69, N 5.51.

[Ch][CHP]: ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 7.70 (br, 1 H; $\mathit{H}\mathrm{OCH_2CH_2}$), 3.87 (m, 2 H, ^3J(H,H) = 15.2 Hz; $\mathrm{HOC}\mathit{H}_2\mathrm{CH_2}$), 3.50 (t, 2 H, ^3J(H,H) = 4.4 Hz; $\mathrm{HOCH_2C}\mathit{H}_2$), 3.14 (s, 9 H; $\mathrm{N(C}\mathit{H}_3\mathrm{)_3}$), 1.84 (t, 2 H, ^3J(H,H) = 15.6 Hz; $\mathrm{OC({=}O)C}\mathit{H}_2\mathrm{CC1CCCCC1}$), 1.66 (m, 5 H, ^3J(H,H) = 19.3 Hz; $\mathrm{OC({=}O)CCC1}\mathit{H}\mathrm{C}\mathit{H}_2\mathrm{CCCC1}\mathit{H}_2$), 1.33 (m, 2 H, ^3J(H,H) = 22.3 Hz; $\mathrm{OC({=}O)CC}\mathit{H}_2\mathrm{C1CCCCC1}$), 1.14 (m, 4 H, ^3J(H,H) = 16.4 Hz; $\mathrm{OC({=}O)CCC1CC}\mathit{H}_2\mathrm{CC}\mathit{H}_2\mathrm{C1}$), 0.81 ppm (m, 2 H, ^3J(H,H) = 10.8 Hz; $\mathrm{OC({=}O)CCC1CCC}\mathit{H}_2\mathrm{CC1}$); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 176.73 (O*C*(=O)CCC1CCCCC1), 67.39 ($\mathrm{HO}\mathit{C}\mathrm{H_2CH_2}$), 55.05 ($\mathrm{HOCH_2}\mathit{C}\mathrm{H_2}$), 53.28 ($\mathrm{N(}\mathit{C}\mathrm{H_3)_3}$), 37.38 (OC(=O)*C*CC1CCCCC1), 36.13 (OC(=O)CC*C*1CCCCC1), 34.39 (OC(=O)C*C*C1CCCCC1), 33.05 (OC(=O)CCC1*C*CCC*C*1), 26.43 (OC(=O)CCC1CC*C*CC1), 26.07 ppm (OC(=O)CCC1C*C*C*C*C1); IR: $\tilde{\nu}$ = 3234 (νOH), 3026, 2923 (ν_{as}CH), 2851 (ν_{s}CH), 1558 (ν_{as}COO), 1447 (δCH), 1394 (ν_{s}COO), 1297, 1124 (νCN), 1092, 1008, 957, 887, 668 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{29}NO_3\cdot H_2O$: C 60.61, H 11.26, N, 5.05; found: C 59.99, H 10.81, N 4.93.

[Ch][Be]: ^{1}H NMR (400 MHz, D_2O, 25 °C, TMS): δ = 7.75 (d, 2 H, ^3J(H,H) = 9.6 Hz; OC(=O)c1c*H*cccc1*H*), 7.38 (t, 1 H, ^3J(H,H) = 8.8 Hz; OC(=O)c1ccc*H*cc1), 7.34 (t, 2 H, ^3J(H,H) = 16.4 Hz; OC(=O)c1cc*H*cc*H*c1), 3.81 (m, 2 H, ^3J(H,H) = 15.6 Hz; $\mathrm{HOC}\mathit{H}_2\mathrm{CH_2}$), 3.23 (t, 2 H, ^3J(H,H) = 10.0 Hz; $\mathrm{HOCH_2C}\mathit{H}_2$), 2.91 ppm (s, 9 H; $\mathrm{N(C}\mathit{H}_3\mathrm{)_3}$); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 169.21 (O*C*(=O)c1ccccc1), 140.76 (OC(=O)c1cc***c***cc1), 129.05 (OC(=O)c1***c***ccc***c***1), 128.66 (OC(=O)***c***1ccccc1), 127.21 (OC(=O)c1c***c***c***c***c1), 67.42 ($\mathrm{HO}\mathit{C}\mathrm{H_2CH_2}$), 55.16 ($\mathrm{HOCH_2}\mathit{C}\mathrm{H_2}$), 53.25 ppm ($\mathrm{N(}\mathit{C}\mathrm{H_3)_3}$); IR: $\tilde{\nu}$ = 3203 (νOH), 1598 (ν_{as}COO), 1558, 1486 (δCH), 1373 (ν_{s}COO), 1136 (νCN), 1089, 1023, 957, 867, 829, 725, 672 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{19}NO_3\cdot H_2O$: C 59.24, H 8.74, N 5.76; found: C 59.46, H 8.55, N 5.78.

[Ch][Sa]: ^{1}H NMR (400 MHz, D_2O, 25 °C, TMS): δ = 7.69 (d, 1 H, ^3J(H,H) = 9.6 Hz; OC(=O)c1c*H*cccc1O), 7.31 (t, 1 H, ^3J(H,H) = 10.0 Hz; OC(=O)c1cccc*H*c1O), 6.84 (m, 2 H, ^3J(H,H) = 23.6 Hz; OC(=O)c1cc*H*c*H*cc1O), 3.87 (m, 2 H, ^3J(H,H) = 15.6 Hz; $\mathrm{HOC}\mathit{H}_2\mathrm{CH_2}$), 3.29 (t, 2 H, ^3J(H,H) = 10.0 Hz; $\mathrm{HOCH_2C}\mathit{H}_2$), 2.97 ppm (s, 9 H; $\mathrm{N(C}\mathit{H}_3\mathrm{)_3}$); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 171.75 (O*C*(=O)c1ccccc1O), 162.86 (OC(=O)c1cccc***c***1O), 131.56 (OC(=O)c1cc***c***cc1O), 130.09 (OC(=O)c1***c***cccc1O), 120.59 (OC(=O)c1c***c***ccc1O), 116.20 (OC(=O)***c***1ccccc1O), 115.94 (OC(=O)c1ccc***c***c1O), 67.20 ($\mathrm{HO}\mathit{C}\mathrm{H_2CH_2}$), 55.27 ($\mathrm{HOCH_2}\mathit{C}\mathrm{H_2}$), 53.28 ppm ($\mathrm{N(}\mathit{C}\mathrm{H_3)_3}$); IR: $\tilde{\nu}$ = 3296 (νOH), 1633, 1589 (ν_{as}COO), 1486 (δCH), 1385 (ν_{s}COO), 1140 (νCN), 1087, 1028, 956, 859, 810, 766, 707, 666 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{19}NO_4\cdot 0.85H_2O$: C 56.25, H 8.20, N 5.47; found: C 56.10, H 8.21, N 5.51.

[Ch][NOA]: ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 7.80 (t, 2 H, ^3J(H,H) = 16.6 Hz; OC(=O)COc1ccc2c*H*ccc*H*c2c1), 7.73 (d, 1 H, ^3J(H,H) = 8.1 Hz; OC(=O)COc1cc*H*c2ccccc2c1), 7.42 (t, 1 H, ^3J(H,H) = 13.9 Hz; OC(=O)COc1ccc2ccc*H*cc2c1), 7.31 (t, 1 H, ^3J(H,H) = 13.8 Hz; OC(=O)COc1ccc2cc*H*ccc2c1), 7.13 (dd, 1 H, ^3J(H,H) = 11.3 Hz; OC(=O)COc1ccc2ccccc2c1*H*), 7.08 (d, 1 H, ^3J(H,H) = 2.3 Hz; OC(=O)COc1c*H*cc2ccccc2c1), 6.73 (br, 1 H; $\mathit{H}\mathrm{OCH_2CH_2}$), 4.24 (s, 2 H; $\mathrm{OC({=}O)C}\mathit{H}_2\mathrm{Oc1ccc2ccccc2c1}$), 3.84 (m, 2 H, ^3J(H,H) = 9.5 Hz; $\mathrm{HOC}\mathit{H}_2\mathrm{CH_2}$), 3.42 (t, 2 H, ^3J(H,H) = 9.8 Hz; $\mathrm{HOCH_2C}\mathit{H}_2$), 3.10 ppm (s, 9 H; $\mathrm{N(C}\mathit{H}_3\mathrm{)_3}$); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 170.09 (O*C*(=O)COc1ccc2ccccc2c1), 157.04 (OC(=O)CO***c***1ccc2ccccc2c1), 134.31 (OC(=O)COc1c***c***c2ccccc2c1), 128.77 (OC(=O)COc1cc***c***2ccccc2c1), 128.10 (OC(=O)COc1ccc2cccc***c***2c1), 127.41 (OC(=O)COc1ccc2***c***cccc2c1), 126.45 (OC(=O)COc1ccc2ccc***c***c2c1), 126.11 (OC(=O)COc1ccc2cc***c***cc2c1), 123.01 (OC(=O)COc1ccc2c***c***ccc2c1), 119.04 (OC(=O)COc1***c***cc2ccccc2c1), 106.63 (OC(=O)COc1ccc2ccccc2***c***1), 67.98 (OC(=O)*C*Oc1ccc2ccccc2c1), 67.16 ($\mathrm{HO}\mathit{C}\mathrm{H_2CH_2}$), 55.02 ($\mathrm{HOCH_2}\mathit{C}\mathrm{H_2}$), 53.07 ppm ($\mathrm{N(}\mathit{C}\mathrm{H_3)_3}$); IR: $\tilde{\nu}$ = 3362 (νOH), 1605 (ν_{as}COO), 1471 (δCH), 1393 (ν_{s}COO), 1260, 1216, 1179, 1121 (νCN), 1053, 953, 842, 752, 665 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_{23}NO_4\cdot 1.1H_2O$: C 62.73, H 7.75, N 4.31; found: C 2.89, H 8.00, N 4.33.

[Ch][AC]: ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 8.29 (s, 1 H; OC(=O)c1c2ccccc2c*H*c3ccccc13), 8.18 (d, 2 H, ^3J(H,H) = 3.3 Hz; OC(=

O)c1c2c*H*cccc2cc3cccc*H*c13), 7.99 (d, 2H, ^{3}J(H,H) = 4.8 Hz; OC(=O)c1c2cccc*H*c2cc3c*H*cccc13), 7.43 (t, 2H, ^{3}J(H,H) = 12.2 Hz; OC(=O)c1c2cc*H*c*H*cc2cc3ccccc13), 7.40 (t, 2H, ^{3}J(H,H) = 9.8 Hz; OC(=O)c1c2ccccc2cc3cc*H*c*H*cc13), 6.86 (br, 1H; $H\mathrm{OCH_2CH_2}$), 3.79 (m, 2H, ^{3}J(H,H) = 9.6 Hz; $\mathrm{HOC}H_2\mathrm{CH_2}$), 3.36 (t, 2H, ^{3}J(H,H) = 9.9 Hz; $\mathrm{HOCH_2C}H_2$), 3.07 ppm (s, 9H; $\mathrm{N(C}H_3)_3$); ^{13}C NMR (100 MHz, [D_6]DMSO, 25 °C, TMS): δ = 171.10 (O*C*(=O)c1c2ccccc2cc3ccccc13), 134.58 (OC(=O)c1c2cccc***c***2c***c***3ccccc13), 131.20 (OC(=O)***c***1c2ccccc2cc3ccccc13), 127.96 (OC(=O)c1***c***2ccccc2cc3cccc***c***13), 126.76 (OC(=O)c1c2cccc***c***c2cc3***c***cccc13), 125.75 (OC(=O)c1c2***c***cccc2cc3cccc***c***c13), 124.91 (OC(=O)c1c2c***c***ccc2cc3cc***c***cc13), 123.91 (OC(=O)c1c2ccccc2***c***c3ccccc13), 122.35 (OC(=O)c1c2cc***c***cc2cc3c***c***ccc13), 67.08 ($\mathrm{HO}C\mathrm{H_2CH_2}$), 55.00 ($\mathrm{HOCH_2}C\mathrm{H_2}$), 53.07 ppm ($\mathrm{N(}C\mathrm{H_3)_3}$); IR: $\tilde{\nu}$ = 3423 (νOH), 1588 (ν_{as}COO), 1423 (δCH), 1387 (ν_{s}COO), 1318, 1276, 1133 (νCN), 1087, 1011, 955, 887, 861, 800, 742, 656, 559 cm^{-1}; elemental analysis calcd (%) for $C_{20}H_{23}NO_3 \cdot 1.3\,H_2O$: C 68.80, H 7.34, N 4.01; found: C 68.93, H 7.47, N 3.98.

[Ch][DOC]: ^{1}H NMR (400 MHz, [D_6]DMSO, 25 °C, TMS): δ = 7.30 (br, 1H; $H\mathrm{OCH_2CH_2}$), 4.26 (br, 1H), 3.85 (m, 2H, ^{3}J(H,H) = 6.6 Hz; $\mathrm{HOC}H_2\mathrm{CH_2}$), 3.79 (br, 1H), 3.56 (m, 1H, ^{3}J(H,H) = 11.2 Hz), 3.44 (t, 2H, ^{3}J(H,H) = 5.0 Hz; $\mathrm{HOCH_2C}H_2$), 3.41 (m, 2H, ^{3}J(H,H) = 13.1 Hz), 3.12 (s, 9H; $\mathrm{N(C}H_3)_3$), 1.85 (m, 2H, ^{3}J(H,H) = 13.3 Hz), 1.77 (m, 2H, ^{3}J(H,H) = 3.9 Hz), 1.69 (m, 2H, ^{3}J(H,H) = 8.2 Hz), 1.61 (m, 2H, ^{3}J(H,H) = 10.0 Hz), 1.55 (m, 2H, ^{3}J(H,H) = 7.7 Hz), 1.47 (m, 2H, ^{3}J(H,H) = 5.2 Hz), 1.43 (m, 2H, ^{3}J(H,H) = 4.1 Hz), 1.36 (m, 3H, ^{3}J(H,H) = 7.1 Hz), 1.31 (m, 2H, ^{3}J(H,H) = 7.6 Hz), 1.19 (m, 2H, ^{3}J(H,H) = 14.7 Hz), 1.07 (m, 2H, ^{3}J(H,H) = 9.5 Hz), 1.04 (m, 2H, ^{3}J(H,H) = 14.0 Hz), 0.99 (m, 2H, ^{3}J(H,H) = 5.4 Hz), 0.88 (m, 4H, ^{3}J(H,H) = 6.5 Hz), 0.84 (d, 3H, ^{3}J(H,H) = 5.6 Hz), 0.58 ppm (s, 3H); ^{13}C NMR (100 MHz, [D_6]DMSO, 25 °C, TMS): δ = 176.79 (CC(CC*C*(O)=O)C1CCC2C3CCC4CC(O)CCC4(C)C3CC(O)C12C), 71.16 (CC(CCC(O)=O)C1CCC2C3CCC4CC(O)CCC4(C)C3C*C*(O)C12C), 70.01 (CC(CCC(O)=O)C1CCC2C3CCC4C*C*(O)CCC4(C)C3CC(O)C12C), 67.27 ($\mathrm{HO}C\mathrm{H_2CH_2}$), 55.06 ($\mathrm{HOCH_2}C\mathrm{H_2}$), 53.22 ($\mathrm{N(}C\mathrm{H_3)_3}$), 47.50, 46.61, 46.01, 41.69, 36.32, 35.84, 35.72, 35.21, 33.87, 32.97, 30.24, 28.65, 27.05, 26.16, 23.63, 23.13, 17.32, 12.57 ppm; IR: $\tilde{\nu}$ = 3239 (νOH), 3030, 2939, 2850, 1576 (ν_{as}COO), 1452 (δCH), 1379 (ν_{s}COO), 1291, 1215, 1093 (νCN), 1078, 1052, 1014, 958, 922, 866, 781, 714, 618, 607 cm^{-1}; elemental analysis calcd (%) for $C_{29}H_{53}NO_5 \cdot 1.0\,H_2O$: C 67.73, H 10.71, N 2.73; found: C 67.68, H 10.65, N 2.71.

[Ch][LC]: ^{1}H NMR (400 MHz, [D_6]DMSO, 25 °C, TMS): δ = 7.50 (br, 1H; $H\mathrm{OCH_2CH_2}$), 3.84 (m, 2H, ^{3}J(H,H) = 9.7 Hz; $\mathrm{HOC}H_2\mathrm{CH_2}$), 3.53 (m, 1H, ^{3}J(H,H) = 9.2 Hz), 3.41 (t, 2H, ^{3}J(H,H) = 14.7 Hz; $\mathrm{HOCH_2C}H_2$), 3.33 (m, 1H, ^{3}J(H,H) = 4.7 Hz), 3.28 (m, 1H, ^{3}J(H,H) = 5.5 Hz), 3.11(s, 9H; $\mathrm{N(C}H_3)_3$), 1.93 (m, 1H, ^{3}J(H,H) = 6.4 Hz), 1.81 (m, 3H, ^{3}J(H,H) = 15.3 Hz), 1.65 (m, 2H, ^{3}J(H,H) = 4.3 Hz), 1.61 (m, 2H, ^{3}J(H,H) = 5.2 Hz), 1.59 (m, 2H, ^{3}J(H,H) = 5.7 Hz), 1.35 (m, 4H, ^{3}J(H,H) = 14.1 Hz), 1.28 (m, 4H, ^{3}J(H,H) = 10.6 Hz), 1.24 (m, 4H, ^{3}J(H,H) = 6.0 Hz), 1.19 (m, 2H, ^{3}J(H,H) = 7.6 Hz), 1.15 (m, 3H, ^{3}J(H,H) = 10.0 Hz), 0.87 (m, 4H, ^{3}J(H,H) = 6.9 Hz), 0.83 (d, 3H, ^{3}J(H,H) = 6.6 Hz), 0.59 ppm (s, 3H); ^{13}C NMR (100 MHz, [D_6]DMSO, 25 °C, TMS): δ = 176.60 (CC(CC*C*(O)=O)C1CCC2C3CCC4CC(O)CCC4(C)C3CCC12C), 72.20, 70.03 (CC(CCC(O)=O)C1CCC2C3CCC4C*C*(O)CCC4(C)C3CCC12C), 67.20 ($\mathrm{HO}C\mathrm{H_2CH_2}$), 64.63, 64.19, 60.07, 56.27, 55.19 ($\mathrm{HOCH_2}C\mathrm{H_2}$), 53.29 ($\mathrm{N(}C\mathrm{H_3)_3}$), 42.35, 41.67, 36.38, 35.67, 35.53, 34.32, 30.45, 27.93, 27.01, 26.28, 24.02, 23.38, 20.53, 18.60, 12.05 ppm; IR: $\tilde{\nu}$ = 3280 (νOH), 2926, 2862, 1564 (ν_{as}COO), 1467 (δCH), 1398 (ν_{s}COO), 1341, 1256, 1242, 1167, 1088 (νCN), 1071, 1046, 1013, 964, 950, 869, 786, 723, 617 cm^{-1}; elemental analysis calcd (%) for $C_{29}H_{53}NO_4 \cdot H_2O$: C 69.97, H 11.14, N 2.81; found: C 71.20, H 10.87, N 2.80.

Ultimate biodegradability testing: The ultimate biodegradability of NAILs was evaluated using the closed-bottle test (OECD 301D).[42] In this test, solutions of test substances were added to an aerobic aqueous medium inoculated with microorganisms derived from the second effluents of a local sewage treatment plant. The aerobic aqueous medium was transferred into completely full, closed biochemical oxygen demand (BOD) bottles. All transfer and filling operations were conducted by the use of siphons to make the medium bubble-free. The closed BOD bottles were kept in the dark and incubated at 25 °C at a rotation rate of 150 rpm in an incubator. The depletion of dissolved molecular oxygen was measured at the desired test intervals (0, 7, 14, 21, and 28 days) with a JPSJ-605 dissolved oxygen analyzer (Shanghai Precision & Scientific Instruments). The depletion data were corrected for uptake by the use of a blank inoculum run in parallel and then expressed as a percentage of the theoretical oxygen demand to give the percentage of biodegradation (%*B*).

Calculation of descriptors—statistical analysis: The logarithm of the *n*-octanol/water partition coefficient ($\log P$) and van der Waals volume (V_{vdW}) of the anions were calculated by using Molecular Modeling Pro Plus (ChemSW, Inc.); energies of the highest occupied molecular orbital (E_{HOMO}) and energies of the lowest unoccupied molecular orbital (E_{LUMO}) of the anions were all calculated with the program Gaussian 03 (Gaussian, Inc.). E_{HOMO} and E_{LUMO} were calculated at the B3LYP/6-311+G* level so that the overlap of the orbitals was considered.

All statistical analyses to develop the biodegradation model were carried out by SPSS software (version 14.0, SPSS Inc.). Multiple linear regression analysis with the stepwise method was used. The criterion for descriptors to enter the model is the probability of $F <= 0.050$; to remove, the probability of $F >= 0.100$. Model quality was characterized by the number of observations (n), the correlation coefficient (R), the standard error (S.E.), the Fisher criterion (F), and the significance level (p).

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