A series of dicaticonic ionic liquids (DILs) including \([\text{PF}_6]\)[(PYR)C4(PYR)][Cl], \([\text{PF}_6]\)[(PYR)C5(PYR)][Cl], \([\text{PF}_6]\)[(PYR)C2COOH][PF6], \([\text{PF}_6]\)[(PYR)C5(MIM)][Cl], and \([\text{PF}_6]\)[(PYR)C5(MIM)][Cl], and \([\text{PF}_6]\)[(PYR)C5(PYR)][Cl], and monocationic ILs including \([\text{PYR}C4\text{Cl}]\)[PF6], \([\text{PYR}C5\text{Cl}]\)[PF6], \([\text{MIM}C2\text{COOH}]\)[PF6] and \([\text{PYR}C2\text{COOH}]\)[PF6] were synthesized. Their thermal stability and melting points were determined. Their solubility with organic solvents and the miscibility with water were investigated. These functional ILs are hydrophilic at high temperatures and they are hydrophobic at low temperatures, which enable the effective isolation of the resulting reducing sugar. High yields of reducing sugar were obtained for corn stalk after 8 h (20.73%) and potato starch after 6 h (72.50%) by the treatment with the mixture of \([\text{PF}_6]\)[(PYR)C4(PYR)][Cl] and \([\text{PF}_6]\)[(PYR)C2COOH][PF6]. The reuse of dicaticonic and monocationic ILs was successfully performed and no significant reduction in yields of reducing sugar was observed. These functional ILs have important implications in the design of homogeneous and heterogeneous systems with water and organic solvents, which could be used to satisfy some specific applications.

Introduction

Ionic liquids (ILs) generally consist of organic cations such as imidazolium, pyridinium, ammonium and phosphonium cations with inorganic or organic anions such as halogen, tetrafluoroborate, and hexafluorophosphate anions.\(^1\) ILs have several superior properties including extremely low vapor pressure, excellent thermal and chemical stability, and a large liquid temperature range.\(^3,4\) Therefore, ILs have been reported in a variety of applications, such as separation processes, organic synthesis, and biomass pretreatment.\(^3,4\)

Recently, dicaticonic ionic liquids (DILs) that are composed of two mono-cations have been reported.\(^5\)–\(^10\) DILs have been classified as symmetrical DILs (two mono-cations are identical) and unsymmetrical DILs (two mono-cations are different). In particular, imidazolium and pyridinium based DILs have shown greater promising physicochemical properties.\(^11\)–\(^14\) DILs can be adjusted by changing their cations, anions, and the length of linker chains between the two cations to achieve significant properties to satisfy some specific chemical task.\(^15\)–\(^17\)

Over the years, ILs-pretreatment of biomass has received dominant attention. ILs are described to be capable to decrease the crystallinity of cellulose and to reduce the portions of hemicellulose and lignin.\(^18\)–\(^20\) In recent years, ILs as pretreated solvents followed by the enzymatic hydrolysis, are widely utilized in academic and industrial applications.\(^21\)–\(^23\) The pretreatment of cotton stalk was performed at 150 °C for 30 min in 1-ethyl-3-imidazolium acetate ([EMIM]CH3COO) to release 65% of reducing sugars after 72 h of enzymatic hydrolysis.\(^24\) The saccharification degree of [EMIM]CH3COO-pretreated corn stalk by the crude enzyme of Penicillium oxalicum HC6 and the cellulase from Trichoderma reesei ATCC26921 were determined as 24.58% and 21.40%, respectively.\(^25\)

Currently, functional acidic ILs as catalysts and solvents become potentially a sustainable approach, which avoid the addition of mineral acid in the hydrolysis process of lignocelluloses. As reported, hydrolysis of fiber sludge using hydroxymethylimidazolium hydrogen sulphate produced 29% of reducing sugars at 100 °C for 30 min.\(^26\) Hydrolysis of switchgrass in 1-(sulfobutyl)-3-methylimidazolium chloride resulted in 58.1% reducing sugars under thermal and microwave conditions for the pretreatment for 1 h at 70 °C followed by treatment with the addition of water for another 1 h at 70 °C.\(^27\)

Although ILs-pretreatment of lignocelluloses are successfully utilized, the low rate and high cost of cellulase limit their industrial utilization. The addition of a large amount of corrosive inorganic acid may cause environmental problems. Actually, all the ILs for lignocellulose treatment are hydrophilic in current studies, thus it is much difficult to separate reducing sugar from the common ILs and also functional acidic ILs. The recovery and reuse of hydrophilic ILs become a problem.\(^28,29\) The alternative techniques are still necessary to achieve the sugars in the conversion of biomass to biofuels.
In this study, a series of novel functional ionic liquids were synthesized. These ILs are hydrophilic at high temperatures and they are hydrophobic at low temperatures, which provide an opportunity to improve the isolation of sugars and the reuse of ILs. Both dicatonic ILs and monocatonic ILs were investigated for their physicochemical properties including thermal stability, the melting points, the solubility in water and organic solvents. The ILs were investigated for the first time in the conversion of potato starch and corn stalk to prepare reducing sugar.

Results and discussion

Synthesis of ionic liquids

Ionic liquids were synthesized using quaternization reaction followed by anion metathesis. The synthetic route for dicatonic ionic liquids (DILs) was shown in Scheme 1. Initially, \([\text{PYR}]\text{CnCl}[\text{PF}_6]\) was prepared by heating one equivalent of pyridine with one equivalent of dichloroalkane in solvent-free conditions, followed by the anion exchange reaction with \(\text{KPF}_6\). After that, DILs were obtained by the alkylation of \([\text{PYR}]\text{C}_n\text{Cl}[\text{PF}_6]\) with one equivalent of 1-methylimidazole or pyridine to afford symmetrical and unsymmetrical dicatonic compounds such as \([\text{PF}_6][\text{PYR}]\text{C}_n\text{Cl}[\text{PYR}][\text{Cl}]\) and \([\text{PF}_6][\text{PYR}]\text{C}_n\text{Cl}[\text{MIM}][\text{Cl}]\). Monocatonic acidic ILs were obtained by the alkylation of 1-methylimidazole or pyridine with 3-chloropropionic acid, followed by the anion metathesis with \(\text{KPF}_6\) to give \([\text{PYR}]\text{C}_2\text{COOH}[\text{PF}_6]\) and \([\text{MIM}]\text{C}_2\text{COOH}[\text{PF}_6]\) (Scheme 2).

In the synthetic process of DILs, pyridine as the weak nucleophile was used in the first step, because it replaced only one chloride of dichloroalkane, whereas stronger nucleophiles such as 1-methylimidazole would attach both sides of the dichloroalkane. However, a yield of product, for example, \([\text{Cl}][\text{PYR}]\text{C}_n\text{Cl}[\text{PYR}][\text{Cl}]\) was still observed, which was isolated by the column chromatography (\(\text{CH}_2\text{Cl}_2/\text{MeOH} = 3/1\)).

Thermal stability

Thermal stability and melting points of ILs were determined and the results were presented in Table 1 and Fig. 1. Generally, unsymmetrical dicatonic ILs containing 1-methylimidazolium group, e.g. \([\text{PF}_6][\text{PYR}]\text{C}_n\text{Cl}[\text{MIM}][\text{Cl}]\) (237 °C) were more stable than those symmetrical dicatonic ILs containing the pyridinium ring, e.g. \([\text{PF}_6][\text{PYR}]\text{C}_n\text{Cl}[\text{PYR}][\text{Cl}]\) (235 °C), possibly due to the better nucleophilic capability of 1-methylimidazolium than pyridinium.\(^{32-36}\) A similar study showed that the thermal stability of \([\text{PF}_6][\text{PYR}]\text{C}_n\text{Cl}[\text{MIM}][\text{Br}]\) was 252 °C, which was higher than that of \([\text{C}_n\text{Cl}[\text{PYR}][\text{Cl}]\) (240 °C).\(^{37}\) Less thermal stability was also obtained for \([\text{PYR}]\text{C}_2\text{COOH}[\text{PF}_6]\) compared with \([\text{MIM}]\text{C}_2\text{COOH}[\text{PF}_6]\) in this work. The low thermal stability was caused for monocatonic acidic ILs by introducing the carboxyl group.

In addition, an impact of the symmetry of the linkage chain of the dication on the thermal stability was observed.\(^{38}\) A slight decrease of thermal stability was obtained for \([\text{PF}_6][\text{PYR}]\text{C}_n\text{Cl}[\text{MIM}][\text{Cl}]\) and \([\text{PF}_6][\text{PYR}]\text{C}_n\text{Cl}[\text{PYR}][\text{Cl}]\) than that of \([\text{PF}_6][\text{PYR}]\text{C}_n\text{Cl}[\text{MIM}][\text{Cl}]\) and \([\text{PF}_6][\text{PYR}]\text{C}_n\text{Cl}[\text{PYR}][\text{Cl}]\).

Melting points

As shown in Table 1, symmetrical dicatonic ILs containing pyridinium group \([\text{PF}_6][\text{PYR}]\text{C}_n\text{Cl}[\text{PYR}][\text{Cl}]\) (160.9 °C) have higher melting points than unsymmetrical dicatonic ILs with imidazolium ring \([\text{PF}_6][\text{PYR}]\text{C}_n\text{Cl}[\text{MIM}][\text{Cl}]\) (98.3 °C). As suggested by Welton and Wasserscheid, this may be attributed to the relative degree of charge dispersion around the cation. Imidazolium has good charge dispersion compared with pyridine.\(^{35,39}\) A low symmetry of dication of \([\text{PF}_6][\text{PYR}]\text{C}_n\text{Cl}[\text{MIM}][\text{Cl}]\) also assisted the low melting point.

Previous reports indicated that the melting points of dicatonic ILs decreased with the increase of alkyl linkage chain.\(^{40}\) It was described that the melting point of \([\text{C}_n\text{Cl}[\text{MIM}][\text{Cl}]\) was 131 °C, which was higher that of \([\text{C}_n\text{Cl}[\text{MIM}][\text{Cl}]\) (120 °C).\(^{27,37}\) In this study, \([\text{PYR}]\text{C}_n\text{Cl}[\text{PF}_6]\) that generated longer linkage chain displayed a lower melting point than that of \([\text{PYR}]\text{C}_n\text{Cl}[\text{PF}_6]\) in addition, the symmetry of the linkage chain of the dication has a significant effect on the melting points. A reduced symmetry of linkage caused decreased melting points. As a result, \([\text{PF}_6][\text{PYR}]\text{C}_n\text{Cl}[\text{MIM}][\text{Cl}]\) and \([\text{PF}_6][\text{PYR}]\text{C}_n\text{Cl}[\text{PYR}][\text{Cl}]\)

Table 1 Thermal decomposition temperature and melting points of ILs

| ILs | \(T_d\) (°C) | \(M_p\) (°C) |
|-----|-------------|-------------|
| \([\text{PYR}]\text{C}_n\text{Cl}[\text{PF}_6]\) | 238 | 49.6 |
| \([\text{PYR}]\text{C}_n\text{Cl}[\text{PF}_6]\) | 248 | 40.7 |
| \([\text{C}_n\text{Cl}[\text{PYR}][\text{Cl}]\) | 237 | 98.3 |
| \([\text{C}_n\text{Cl}[\text{PYR}][\text{Cl}]\) | 235 | 160.9 |
| \([\text{C}_n\text{Cl}[\text{PYR}][\text{Cl}]\) | 232 | 81.5 |
| \([\text{C}_n\text{Cl}[\text{PYR}][\text{Cl}]\) | 230 | 97.3 |
| \([\text{MIM}]\text{C}_2\text{COOH}[\text{PF}_6]\) | 215 | 91.7 |
| \([\text{PYR}]\text{C}_n\text{Cl}[\text{PYR}][\text{Cl}]\) | 190 | 101.3 |

\(T_d\) decomposition temperature; \(M_p\) melting points.
exhibited lower melting points than that of \([PF_6]_2[(PYR)C_4(MIM)][Cl]\) and \([PF_6]_2[(PYR)C_4(PYR)][Cl]\).

### Solubility of ionic liquids with organic solvents

The synthesized ILs were determined in several representative solvents at room temperature. As summarized in Table 2, both dicationic and monocationic ILs exhibited good solubility in high polar solvents, e.g. dimethyl sulfoxide (DMSO), but they were not soluble in non-polar solvents, e.g. diethyl ether (Et₂O).

In this work, monocationic ILs generated better solubility than dicationic ILs. Monocationic ILs were soluble in most organic solvents. Dicationic ILs were not dissolved in methanol (MeOH), ethanol (EtOH), and dichloromethane (CH₂Cl₂). However, monocationic acidic ILs with carboxyl group were soluble in MeOH, EtOH, but they were not soluble in CH₂Cl₂.

Particularly, imidazolium-based ILs displayed good solubility compared with pyridinium-based ILs. Dicationic ILs with imidazolium group were dissolved in acetonitrile (CH₃CN) and acetone (DMK). In contrast, dicationic ILs with pyridinium ring were not soluble in CH₃CN and DMK. Moreover, \([MIM]C_2COOH][PF_6]\) was soluble in CH₃CN and DMK, whereas \([PYR]C_2COOH][PF_6]\) was not soluble in these two organic solvents.

### Miscibility of ionic liquids with water

Generally, ILs with the anions of PF₆⁻ and NTf₂⁻ are water-immiscible, whereas others are water-miscible. Interestingly, these dicationic and monocationic ILs are miscible with water at high temperatures and they are immiscible with water at low temperatures. It was found that dicationic ILs could form a homogeneous or heterogeneous system with water, depending on the dealing temperature.

As illustrated in Fig. 2, when the temperature was higher, the miscibility of dicationic ILs with water was better with a reduced amount of water. For example, 1.0 g of \([PF_6]_2[(PYR)C_4(MIM)][Cl]\) was miscible with 4 mL of water at 100 °C. However, 105 mL of water was required at room temperature. Similarly, 6 mL of water was used to dissolve 1.0 g of \([PF_6]_2[(PYR)C_4(PYR)][Cl]\) at 100 °C, whereas 232 mL of water was employed at room temperature.

Monocationic ILs were more soluble with water than dicationic ILs. For instance, 1.0 g of \([MIM]C_2COOH][PF_6]\) was miscible with 61 mL of water at room temperature, whereas 105 mL and 232 mL of water for \([PF_6]_2[(PYR)C_4(MIM)][Cl]\) and \([PF_6]_2[(PYR)C_4(PYR)][Cl]\) were required, respectively. Meanwhile, good miscibility was observed with imidazolium-based dicationic ILs than pyridinium-based dicationic ILs. Moreover, monocationic

In current studies, the reported ILs were insoluble in ethyl acetate (EtOAc), because of their polar properties. Interestingly, \([PF_6]_2[(PYR)C_4(MIM)][Cl]\) and \([PF_6]_2[(PYR)C_4(PYR)][Cl]\) with haloalkyl chain were readily dissolved in EtOAc. Therefore, these ILs with different solubility could be selected and employed in various areas to satisfy different requirements.

### Table 2 Solubility of ILs in various organic solvents

|          | DMSO | MeOH | EtOH | CH₃CN | DMK | EtOAc | CH₂Cl₂ | Et₂O |
|----------|------|------|------|-------|-----|-------|--------|------|
| IL1      | ++   | +    | +    | +++   | +++ | ++    | +      | –    |
| IL2      | +    | +    | +    | +++   | +++ | ++    | +      | –    |
| IL3      | –    | –    | –    | +     | –   | –     | –      | –    |
| IL4      | +    | –    | –    | –     | –   | –     | –      | –    |
| IL5      | +    | –    | +    | –     | +   | –     | –      | –    |
| IL6      | +    | –    | –    | –     | –   | –     | –      | –    |
| IL7      | +    | +    | +    | +     | +   | +     | –      | –    |
| IL8      | +    | +    | –    | –     | –   | –     | –      | –    |

* IL1: \([PF_6]_2[(PYR)C_4(MIM)][Cl]\); IL2: \([PF_6]_2[(PYR)C_4(PYR)][Cl]\); IL3: \([PF_6]_2[(PYR)C_4(MIM)][Cl]\); IL4: \([PF_6]_2[(PYR)C_4(PYR)][Cl]\); IL5: \([PF_6]_2[(PYR)C_4(MIM)][Cl]\); IL6: \([PF_6]_2[(PYR)C_4(PYR)][Cl]\); IL7: \([MIM]C_2COOH][PF_6]\); IL8: \([PYR]C_2COOH][PF_6]\).

Fig. 1 Thermogravimetry curves of ILs.

Fig. 2 Miscibility of ILs with water at different temperature.
Hydrolysis of corn stalk and potato starch in ILs

Currently, ILs with the addition of mineral acids or functional acidic ILs for the treatment of biomass were reported. Hernoux-Villière et al.\(^\text{43}\) found that the treatment of potato starch in aqueous 1-(4-sulfobutyl)-3-methylimidazolium chloride at 80 °C for 2 h produced 43% of the total reducing sugar. Seddon et al.\(^\text{44}\) reported that the total yield of reducing sugar for potato starch was 54% with the Brønsted-acidic ionic liquids and was 6% with the 1-allyl-3-methylimidazolium chloride at 80 °C for 1 h. In this study, a high yield of reducing sugar (72.50%) for potato starch was achieved with the treatment of the mixture of [PF\(_6\)][(PYR)C\(_4\)(MIM)][Cl] at room temperature. And yet, 45 mL was required for 1.0 g of [PF\(_6\)][(PYR)C\(_2\)COOH][PF\(_6\)] because an increase of the of the linkage chain of dication improved the hydrophilic properties of dicationic ILs.

Initially, as the treatment time was increased, the total yield of reducing sugar was increased (Fig. 4). When the treatment time for potato starch was increased from 2 h to 6 h, the yield of reducing sugar was improved from 47.60% to 72.50% with the mixture of [PF\(_6\)][(PYR)C\(_4\)(PYR)][Cl] and [(PYR)C\(_2\)COOH][PF\(_6\)]. With the same ILs, as the treatment time for corn stalk was increased from 4 h to 8 h, the yield of reducing sugar was improved from 5.87% to 20.73%. However, the yields of reducing sugar were reduced as the treatment time was increased from 4 h to 8 h for both potato starch and corn stalk.

Obviously, high yields of reducing sugar were obtained from potato starch and corn stalk with the mixture of dicationic ILs and monocationic acidic ILs. Monicationic ILs provided the acidic nature to assist the hydrolysis of potato starch and corn stalk. The basicity of one of the anion (Cl\(^-\)) of dicationic ILs made it more efficient at disrupting inter- and intra-molecular hydrogen bonding in polymers. The other anion ([PF\(_6\)]) of dicationic ILs provided the hydrophobic and hydrophilic properties at different temperature. In current studies, all the ILs used for polymers-hydrolysis and biomass-treatment are hydrophilic, which increase the difficulty of the isolation of sugar and reuse of ILs. The variable miscibility of these functional ILs with water in this work provided the opportunity for hydrolysis of various carbohydrate polymers.

**Reuse of ionic liquids**

The feasibility and sustainable development of any catalytic process depends on the reusability of catalysts and solvents. Generally, after ILs-treatment of biomass, reducing sugar was readily extracted by the addition of water at a low temperature. However, a yield of monocationic acidic ILs would be lost in the aqueous layer. Further work will focus on the design of functional acidic ILs to increase their hydrophobic property. Alternatively, both of [PF\(_6\)][(PYR)C\(_4\)(MIM)][Cl] and [(MIM)C\(_2\)COOH][PF\(_6\)] could be simply extracted with acetonitrile, which were readily reused after the removal of acetonitrile. Otherwise, monocationic acidic [(PYR)C\(_2\)COOH][PF\(_6\)] or [(MIM)C\(_2\)COOH][PF\(_6\)] could be extracted with methanol. After the isolation of reducing sugar with water at room temperature, an amount of deionized water was added into the mixture with heating and cooling for the isolation of ILs.
stirring to provide \([\text{PF}_6][(\text{PYR})\text{C}_4(\text{PYR})]\)[Cl]. As shown in Fig. 5, high re-covery of ILs including \([\text{PF}_6][(\text{PYR})\text{C}_4(\text{PYR})]\)[Cl] and \([\text{PYR})\text{C}_4\text{COOH}][\text{PF}_6]\) were obtained in the range of 80.20% to 88.37% for potato starch and 80.73% to 85.27% for corn stalk. Good recovery of ILs including \([\text{PF}_6][(\text{PYR})\text{C}_4(\text{MIM})]\)[Cl] and \([\text{MIM})\text{C}_2\text{COOH}][\text{PF}_6]\) were achieved in the range of 81.45% to 94.49% for potato starch and 80.73% to 85.27% for corn stalk. Similarly, the rates of reducing sugar for potato starch were 100% (1st run), 82.41% (2nd run) and 73.69% (3rd run) with the treatment of \([\text{PF}_6][(\text{PYR})\text{C}_4(\text{PyR})]\)[Cl] and \([\text{PYR})\text{C}_2\text{COOH}][\text{PF}_6]\) (Fig. 6). The rates of reducing sugar after three cycles.

### Experimental

**Materials**

1-Methylimidazole (99%), pyridine (99%), 1,4-dichlorobutane (99%), 1,5-dichloropentane (99%), 3-chloropropionic acid (99%), potassium hexafluorophosphate (99%) were purchased from Aldrich Reagent Co., Ltd (Shanghai, China). All the reagents were used without further purification. Corn stalk was supplied by local farm in Harbin City (China), milled to pass through 40 mesh sieves and dried at 60 °C for 24 h. Potato starch was purchased from Tianjin Kaitong Chemical Reagent Co., Ltd (Tianjin, China).

**Synthesis of ionic liquids**

1-(4-Chlorobutyl) pyridinium hexafluorophosphate \([\text{PYR})\text{C}_4\text{Cl}][\text{PF}_6]\). Pyridine (1.0 mmol) and 1,4-dichlorobutane (1.2 mmol) were stirred at 60 °C for 4 days. The resulting precipitate was filtered and washed with ethyl acetate, which was further purified by silica column chromatography (CH$_2$Cl$_2$/MeOH = 3/1) and was dried at 60 °C under vacuum for 4 h. After that, the precipitate (1.0 mmol) was reacted with KPF$_6$ (1.5 mmol) in deionized water at room temperature for 3 h. The resulting product was washed with deionized water and was dried in a vacuum for 12 h. 1-(5-Chloropentyl) pyridinium hexafluorophosphate \([\text{PYR})\text{C}_5\text{Cl}][\text{PF}_6]\) was prepared using a similar method as \([\text{PYR})\text{C}_4\text{Cl}][\text{PF}_6]\).

\([\text{PYR})\text{C}_4\text{Cl}][\text{PF}_6]\): 1H-NMR (400 MHz, DMSO-d$_6$) (ppm): 9.34 (m, 2H), 8.63 (t, 1H), 8.19 (m, 2H), 4.77 (t, 2H), 3.66 (t, 2H), 2.03 (m, 2H), 1.71 (m, 2H).

\([\text{PYR})\text{C}_5\text{Cl}][\text{PF}_6]\): 1H-NMR (400 MHz, DMSO-d$_6$) (ppm): 9.09 (d, 2H), 8.60 (t, 1H), 8.17 (t, 2H), 4.61 (t, 2H), 3.65 (t, 2H), 1.95 (quint, 2H), 1.76 (m, 2H), 1.39 (m, 2H).

**Hexafluorophosphate**

1-(1-pyridinium-yl-buty1)-4-methylimidazolium chloride \([\text{PF}_6][(\text{PYR})\text{C}_4\text{MIM})][\text{Cl}]\). \([\text{PYR})\text{C}_4\text{Cl}][\text{PF}_6]\) (3.16 g) and 1-methylimidazolium (0.1 mmol) were added into 2 mL of ethyl acetate. The reaction proceeded at 60 °C for 24 h. The desired product was purified by recrystallization of acetoni-trile/ethyl acetate (1/10) and then was dried in a vacuum at 60 °C for 4 h. Hexafluorophosphate \([1-(1-\text{pyridinium-yl-pentyl})-5\text{-methylimidazolium)}\] chloride \([\text{PF}_6]\) \([\text{PYR})\text{C}_5\text{Cl}][\text{Cl}]\) was synthesized using a similar method as \([\text{PF}_6][(\text{PYR})\text{C}_4\text{MIM})][\text{Cl}]\).

\([\text{PF}_6][(\text{PYR})\text{C}_4\text{MIM})][\text{Cl}]\): 1H-NMR (400 MHz, DMSO-d$_6$) (ppm): 9.42 (s, 1H), 9.26 (d, 2H), 8.60 (t, 1H), 8.16 (t, 2H), 7.84 (s, 1H), 7.74 (s, 1H), 4.74 (t, 2H), 4.27 (t, 2H), 3.85 (s, 3H), 1.92 (quint, 2H), 1.83 (quint, 2H).

\([\text{PF}_6][(\text{PYR})\text{C}_5\text{MIM})][\text{Cl}]\): 1H-NMR (400 MHz, DMSO-d$_6$) (ppm): 9.43 (s, 1H), 9.27 (d, 2H), 8.59 (m, 1H), 8.14 (m, 1H), 7.84 (s, 1H), 7.72 (s, 1H), 4.67 (m, 2H), 4.19 (m, 2H), 3.85 (s, 3H), 1.96 (m, 2H), 1.83 (m, 2H), 1.23 (m, 2H).

**Hexafluorophosphate**

1-(1-pyridinium-yl-buty1)-4-pyridinium chloride \([\text{PF}_6][(\text{PYR})\text{C}_4\text{PYR})][\text{Cl}]\). \([\text{PYR})\text{C}_4\text{Cl}][\text{PF}_6]\) (0.1 mmol) was reacted with pyridinium (0.12 mmol) at 80 °C for 24 h. Following that, the product was recrystallized with acetonitrile/ethyl acetate (1/10) and dried in a vacuum at 60 °C for 4 h. Hexafluorophosphate \([1-(1-\text{pyridinium-yl-pentyl})-5\text{-pyridinium)}\] chloride \([\text{PF}_6]\) \([\text{PYR})\text{C}_5\text{Cl}][\text{Cl}]\) was prepared using a similar method as \([\text{PF}_6][(\text{PYR})\text{C}_4\text{PYR})][\text{Cl}]\).

\([\text{PF}_6][(\text{PYR})\text{C}_4\text{PYR})][\text{Cl}]\): 1H-NMR (400 MHz, DMSO-d$_6$) (ppm): 9.19 (m, 4H), 8.62 (t, 2H), 8.17 (t, 4H), 4.69 (t, 4H), 1.97 (quint, 4H).

\([\text{PF}_6][(\text{PYR})\text{C}_5\text{PYR})][\text{Cl}]\): 1H-NMR (400 MHz, DMSO-d$_6$) (ppm): 9.25 (d, 4H), 8.60 (t, 2H), 8.17 (t, 4H), 4.67 (t, 4H), 1.99 (quint, 4H), 1.31 (t, 2H).
Reducing sugar
Yields of reducing sugar after any treatment

$\text{Reducing sugar (mg)} = \frac{\text{Reducing sugar (mg)}}{\text{Sample subjected to treatment (mg)}} \times 100 \tag{1}$

Reuse of ionic liquids
Corn stalk or potato starch (200 mg) was treated with the mixture containing the dicaticonic ILs (3 g), monocationic acidic ILs (1 g) and deionized water (1.5 mL) at 100 °C for 6 h in a reaction kettle in an oil bath. After that, the mixture in a kettle was dried at 60 °C for 6 h. 20 mL of acetonitrile was added into the mixture. The filtrate was collected and methanol was evaporated to give [(MIM)C₂COOH][PF₆] and [(PYR)C₄(MIM)][Cl]. The reducing sugar was then obtained by the addition of deionized water (20 mL). Otherwise, 20 mL of methanol was added into the mixture. The filtrate was collected and methanol was evaporated to give [(PYR)C₂COOH][PF₆]. The reducing sugar was then obtained by the addition of deionized water (20 mL). Following that, 60 mL of deionized water was added into the mixture. The rates of reducing sugar were calculated as eqn (2):

$\text{Rate of reducing sugar (\%)} = \frac{\text{Yields of reducing sugar after any treatment (mg)}}{\text{Yields of reducing sugar after first treatment (mg)}} \times 100 \tag{2}$

Conclusions
Dicaionic and monocationic ILs with variable miscibility with water at different temperatures were synthesized. These functional ILs have important implications in the design of homogeneous and heterogeneous system with water and organic solvents, which will greatly benefit some specific applications. Particularly, the mixture of [(PF₆)][(PYR)C₄(MIM)][Cl] and [(PYR)C₂COOH][PF₆] played a crucial effect on the hydrolysis of carbohydrate polymers. Total reducing sugar was up to 72.50% for potato starch after 6 h and 20.73% for corn stalk after 8 h, respectively. The recovery of ILs were higher than 80% and the rates of reducing sugar were more than 70% after three cycles. The variable miscibility of these functional ILs with water provides the possibility for polymers-hydrolysis, biomass-treatment and other industrial specific utilizations.

Conflicts of interest
There are no conflicts to declare.
Acknowledgements

This work was financially supported by University Nursing Program for Young Scholars with Creative Talents in Heilongjiang Province (UNPYSCT-2017021).

Notes and references

1. K. K. Laali and K. Kenneth, *Synthesis*, 2003, **11**, 1752.
2. P. L. Verma and S. P. Gejji, *J. Mol. Graphics Modell.*, 2018, **85**, 304–315.
3. K. J. Stevenson, *J. Am. Chem. Soc.*, 2005, **127**, 11878.
4. S. Letaief and C. Detellier, *J. Mater. Chem.*, 2007, **17**, 1476–1484.
5. F. Guo, S. Zhang, J. Wang, B. Teng, T. Zhang and M. Fan, *Curr. Org. Chem.*, 2015, **19**, 455–468.
6. Z. S. Qureshi, K. M. Deshmukh and B. M. Bhanage, *Clean Technol. Environ. Policy*, 2013, **16**(8), 1487–1513.
7. H. T. Xu, C. H. Zhang, G. Chen, R. P. Shen and A. G. Ying, *Chin. J. Chem.*, 2016, **36**, 2353.
8. C. Yue, D. Fang, L. Liu and T. F. Yi, *J. Mol. Liq.*, 2011, **163**, 99–121.
9. A. S. Khan, Z. Man, A. Arvina, M. A. Bustam, A. Nasrullah and Z. Ullah, *J. Mol. Liq.*, 2017, **227**, 98–105.
10. M. G. Montalbán, G. Villora and P. Licence, *Data in Brief*, 2018, **19**, 769–788.
11. T. Payagala, J. Huang, Z. S. Breitbach, P. S. Sharma and D. W. Armstrong, *Chem. Mater.*, 2007, **19**, 5848–5850.
12. Z. Zeng, B. S. Phillips, J. C. Xiao and J. M. Shreeve, *Chem. Mater.*, 2008, **20**, 2719–2726.
13. S. B. Aher and P. R. Bhagat, *Res. Chem. Intermed.*, 2016, **42**, 5587–5596.
14. R. Kore and R. Srivastava, *J. Mol. Catal. A: Chem.*, 2003, **345**, 117–126.
15. U. Domańska, E. V. Lukoshko and M. Królikowski, *Chem. Eng. J.*, 2012, **183**, 261–270.
16. V. Misuk, D. Breuch and H. Löwe, *Chem. Eng. J.*, 2011, **173**, 536–540.
17. S. A. Shamsi and N. D. Danielson, *J. Sep. Sci.*, 2007, **30**, 1729–1750.
18. A. M. Da Costa Lopes, K. G. João, A. R. C. Morais, E. Bogel-Lukasik and R. Bogel-Lukasik, *Sustainable Chem. Processes*, 2013, **1**, 3.
19. A. P. Dadi, C. A. Schall and S. Varanasi, *Appl. Biochem. Biotechnol.*, 2007, **137**–140, 407–421.
20. F. L. Wang, S. Li, Y. X. Sun, H. Y. Han, B. X. Zhang and B. Z. Hu, *RSC Adv.*, 2017, **7**, 47990–47998.
21. J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508–3576.
22. S. H. Lee, T. V. Doherty, R. J. Linhardt and J. S. Dordick, *Biotecnol. Bioeng.*, 2009, **102**, 1368–1376.
23. H. T. Tan and K. T. Lee, *Chem. Eng. J.*, 2012, **183**, 448–458.
24. Z. C. Zhang, *Adv. Catal.*, 2006, **49**, 153–237.
25. H. Zhao, *Chem. Eng. Commun.*, 2006, **193**, 1660–1677.
26. N. I. Haykir, E. Bahcegul, N. Bicak and U. Bakir, *Ind. Crops Prod.*, 2013, **41**, 430–436.
27. Y. X. Sun, Y. Y. Wang, B. B. Shen, B. X. Zhang and X. M. Hu, *R. Soc. Open Sci.*, 2018, **5**, 181230.
28. Y. Dong, J. Holm, J. Karkkainen, J. Nowicki and U. Lassi, *Biomass Bioenergy*, 2014, **70**, 461–467.
29. A. S. Amarasekara and P. Shanbhag, *BioEnergy Res.*, 2012, **6**, 719–724.
30. Y. X. An, M. H. Zong, H. Wu and N. Li, *Bioresour. Technol.*, 2015, **192**, 165–171.
31. L. Bai, X. L. Wang, Y. Nie, H. F. Dong and X. P. Zhang, *Sci. China Chem.*, 2013, **56**, 1811–1816.
32. A. H. Jadhav and H. Kim, *Chem. Eng. J.*, 2012, **200–202**, 264–274.
33. M. Talebi, R. A. Patil and D. W. Armstrong, *J. Mol. Liq.*, 2018, **256**, 247–255.
34. J. F. Vélez, L. V. Álvarez, C. del Rio, B. Herradón, E. Mann and E. Morales, *Electrochim. Acta*, 2017, **241**, 517–525.
35. H. Zhang, M. Li and B. Yang, *J. Phys. Chem. C.*, 2018, **122**, 2467–2474.
36. B. S. Wang, L. Qin, T. C. Mu, Z. M. Xue and G. H. Gao, *Chem. Rev.*, 2017, **10**, 7113–7313.
37. J. C. Chang, W. Y. Ho, I. W. Sun, Y. L. Tung, M. C. Tsui, T. Y. Wu and S. S. Liang, *Tetrahedron*, 2010, **66**, 6150–6155.
38. Z. M. Xue, L. Qin, J. Y. Jiang, T. C. Mu and G. H. Gao, *Phys. Chem. Chem. Phys.*, 2018, **20**, 8382–8402.
39. A. Chinnappan and H. Kim, *Chem. Eng. J.*, 2012, **187**, 283–288.
40. Y. S. Ding, M. Zha, J. Zhang and S. S. Wang, *Colloids Surf., A*, 2007, **298**, 201–205.
41. Y. Chen, Y. Y. Cao, X. F. Sun and T. C. Mu, *J. Mol. Liq.*, 2014, **190**, 151–158.
42. Y. Y. Cao, Y. Chen, X. F. Sun, Z. M. Zhang and T. C. Mu, *Phys. Chem. Chem. Phys.*, 2012, **14**, 12252–12262.
43. A. Hernoux-Villiére, J. M. Lévéque, J. Kärkkäinen, N. Papaiconomou, M. Lajunen and U. Lassi, *Catal. Today*, 2014, **223**, 11–17.
44. K. R. Seddon, A. Stark, M. J. Torres and T. María-José, *Pure Appl. Chem.*, 2000, **72**, 2275–2287.
45. C. Z. Li, Q. Wang and Z. B. K. Zhao, *Green Chem.*, 2008, **2**, 177–182.
46. H. H. Ma, B. X. Zhang, P. Zhang, S. Li, Y. F. Gao and X. M. Hu, *Fuel Process. Technol.*, 2016, **148**, 138–145.
47. P. Zhang, S. J. Dong, H. H. Ma, B. X. Zhang, Y. F. Wang and X. M. Hu, *Ind. Crops Prod.*, 2015, **76**, 688–696.
48. J. L. Anderson, R. Ding, A. Ellern and D. W. Armstrong, *J. Am. Chem. Soc.*, 2005, **127**, 593–604.
49. M. Moniruzzaman and T. Ono, *Bioresour. Technol.*, 2013, **127**, 132–137.
50. J. Salgado, M. Villanueva, J. J. Parajo and J. Fernández, *J. Chem. Thermodyn.*, 2013, **65**, 184–190.
51. G. Yu, S. Yan, F. Zhou, X. Liu, W. Liu and Y. Liang, *Tribol. Lett.*, 2006, **25**, 197–205.