# Catalytic Conversion of Carbohydrates to Levulinate Ester over Heteropolyanion-Based Ionic Liquids

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An efficient one-pot approach for the production of levulinate ester from renewable carbohydrates is demonstrated over heteropolyanion-based ionic liquid (IL-POM) catalysts with alcohols as the promoters and solvents. The relationships between the structure, acidic strength, and solubility of the IL-POM in methanol and the catalytic performance were studied intensively. A cellulose conversion of 100% could be achieved with a 71.4% yield of methyl levulinate over the catalyst [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> [PyPS=1-(3-sulfopropyl)pyridinium] at 150°C

for 5 h. This high efficiency is ascribed to the reasonably high activity of the ionic liquid (IL) catalyst and reaction coupling with rapid in situ esterification of the generated levulinic acid with the alcohol promoter, which allows the insolubility of cellulose encountered in biomass conversion to be overcome. Furthermore, the present process exhibits high feedstock adaptability for typical carbohydrates and handy catalyst recovery by a simple self-separation procedure through temperature control.

geneous catalysts have been pursued as alternatives. For ex-

#### Introduction

The overexploration of petroleum resources and the deterioration of the environment have spurred the exploration of green processing from nonedible biomass to biofuels and biochemicals.<sup>[1]</sup> Numerous studies have focused on the one-pot conversion of carbohydrates to value-added and versatile chemical platforms, such as 5-hydroxymethylfurfural (5-HMF),<sup>[2]</sup> levulinic acid (LA),<sup>[3]</sup> and 2,5-furandicarboxylic acid (FDCA),<sup>[4]</sup> to support the sustainable production of valuable compounds, fuel, and power.<sup>[5]</sup> In this context, LA and its esters have been highlighted for their high potential as substitutes for current petrochemicals.<sup>[6]</sup> For example, diphenolic acid, synthesized by the condensation of LA with phenols, has been envisaged as a desirable substitute for 4,4'-(propane-2,2-diyl)diphenol in the polycarbonate and epoxy-resin industries.<sup>[7]</sup> Similarly, methyl levulinate (ML) has found application in the synthesis of  $\gamma$ -valerolactone,<sup>[8]</sup> which is used as a solvent and an alternative fuel additive.<sup>[9]</sup> Furthermore, ethyl levulinate (EL) is considered as a new biobased diluent for biodiesel owing to its high saturated fatty acid content.[10]

Generally, the conventional production of LA and its esters is achieved through acid-catalyzed processes with mineral acids, such as  $H_2SO_4$ , HCl, and HBr, as homogenous catalysts;<sup>[6b, 11]</sup> unfortunately, problems such as environmental pollution, catalyst separation issues, and corrosion are encountered. Thus, hetero-

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ample, various solid acid catalysts, such as sulfonated metal oxides, acidic resins, and zeolites, have been explored widely.<sup>[6b, 12]</sup> However, it should be noted that solid acids showed lower activities for cellulose in comparison with their superior catalytic performances for glucose and fructose.<sup>[13]</sup> This can be ascribed to the limited contact between the solid catalysts and the water-insoluble cellulose,<sup>[14]</sup> and the insolubility is attributed to the presence of inter- and intramolecular hydrogen bonding in the stabilized twofold-helix conformation of cellulose.<sup>[15]</sup> Therefore, ecofriendly and easily regenerated catalysts with desirable activities should be explored. Furthermore, an appropriate acidic strength and reaction temperature are crucial to the conversion of carbohydrates to LA and its esters, especially in the rate-determining opening of the H-bonded cellulose structure. As the acidity of the catalyst employed and the temperature increase, the hydrolysis rate can be enhanced. However, a common problem is that an elevated temperature and a higher acid concentration facilitate the formation of humins,<sup>[16]</sup> which is regarded as a main byproduct in the carbohydrate industry. Thus, an acid catalyst with a tunable acidic strength should be devised and coupled with an intensified process to replace the use of higher reaction temperatures to accelerate the depolymerization of cellulose.

lonic liquids (ILs), which combine the advantages of homogenous and heterogeneous catalysts with tunable structures and physiochemical properties, are considered to be a promising solution.<sup>[17]</sup> For example, the use of acidic ILs is an efficient and sustainable approach for cellulose and lignocellulosic biomass conversion, and ILs containing SO<sub>3</sub>H groups have attracted considerable attention owing to their strong Brönsted acidities.<sup>[18]</sup> In 2009, the first use of Brönsted acidic ILs, namely, 1-methyl-3-(3-sulfopropyl)imidazolium chloride ([MIMPS]Cl) and 1-methyl-3-(3-sulfobutyl)imidazolium chloride ([MIMBS]Cl), to



dissolve cellulose was reported by Amarasekara and Owereh.<sup>[19]</sup> Then, Liu et al. proposed the use of HSO<sub>3</sub>-functional ILs based on imidazolium and quaternary ammonium cations in the hydrolysis of cellulose, and 1-(3-sulfopropyl)triethylammonium hydrogen sulfate ([TEAPS]HSO₄) gave a maximum total reducing sugar yield of 99% at 100°C.<sup>[20]</sup> The IL 1-methyl-3-(3sulfobutyl)imidazolium hydrogen sulfate ([MIMBS]HSO<sub>4</sub>) is a robust and efficient catalyst for cellulose degradation and biomass liquefaction that demonstrates better catalytic activity compared with those of conventional imidazolium ILs.<sup>[21]</sup> Recently, Siankevich et al. reported that the mixture of the ILs 1-(2-hydroxyethyl)-3-methylimidazolium chloride ([C<sub>2</sub>OHmim]Cl) and 1-methyl-3-(3-sulfobutyl)imidazolium trifluoromethanesulfonate ([MIMBS]CF<sub>3</sub>SO<sub>3</sub>) was a powerful system for the production of 5-HMF from cellulose.<sup>[22]</sup> Numerous studies of the production of LA and its esters have also been reported. Ren et al. showed that the IL 1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate ([MIMPS]HSO<sub>4</sub>) was an efficient catalyst for the conversion of cellulose to LA with a yield of 55.0% under the assistance of microwave heating.<sup>[23]</sup> Amarasekara and Wiredu found that [MIMPS]Cl was an efficient catalyst in cellulose decomposition, and an EL yield of 19.0% was obtained for a reaction performed at 170°C for 12 h in a water-ethanol medium.<sup>[24]</sup> Shen et al. showed that a 39.4% LA yield could be achieved with the acidic IL catalyst [MIMBS]HSO4.[25] In our recent work, we also demonstrated that 98.4% of cellulose could be converted into 31.1% butyl levulinate (BL) with the SO<sub>3</sub>H-functionalized [MIMBS]HSO<sub>4</sub> IL catalyst.<sup>[26]</sup> However, the yield and selectivity of the target products in the aforementioned processes should be enhanced.

Recently, heteropolyacid-based catalysts with agreeable catalytic behavior have been applied widely in reactions such as esterification,<sup>[27]</sup> hydrogenation,<sup>[28]</sup> and oxidation.<sup>[29]</sup> Owing to their intrinsic structures and physiochemical properties, heteropolyanion-based ionic liquid (IL-POM) catalysts are generally immiscible with polar solvents at ambient temperatures but miscible at elevated temperatures;<sup>[30]</sup> thus, they can act as homogeneous catalysts at suitable temperatures and then precipitate as gelatinous solids at low temperatures to provide remarkably convenient catalyst separation and recycling. Furthermore, the acidic strength of IL-POMs can be fine-tuned by variation of the cation and anion. Therefore, a series of IL-POMs catalysts with tunable acidity were designed and synthesized for the conversion of carbohydrates to levulinate ester in an efficient and intensified process. During the reaction, the alcohol acts as both promoter and solvent and can esterify the generated LA rapidly to accelerate the whole carbohydrate conversion process through reaction coupling. Additionally, the relationships between the structure, acidic strength, and solubility in methanol of the IL and the catalytic activity are evaluated and discussed.

#### **Results and Discussion**

#### Determination of acidic strengths of IL-POM catalysts

In this work, a series of typical IL-POMs with similar structures were designed and synthesized (Scheme 1), and their acidities were characterized by the Hammett method<sup>[31]</sup> and pH measurement. As depicted in Table 1 and Figure S7, [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> [PyPS = 1-(3-sulfopropyl)pyridinium], [EIMPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> [EIMPS = 1-ethyl-3-(3-sulfopropyl)imidazolium], [TEAPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and [MIMPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> have strong Hammett acidic strengths, whereas [PyPS]<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub>, [Py]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (Py = pyridinium), [*i*-PIMPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> [*i*-PIMPS = 1-isopropyl-3-(3-sulfopropyl)imidazolium], and [PyPS]H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub> have moderate Hammett acidic strengths. The results from pH determination show a similar trend, except for [Py]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and [IMPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> owing to their poor solubilities at room temperature.

#### Solubilities of IL-POM catalysts in methanol

The UV/Vis spectra of saturated solutions of various IL-POMs are depicted in Figure 1, and the solubilities of the IL-POMs in methanol are listed in Table 2. The prominent peaks at  $\lambda \approx 210$  nm are associated with the O $\rightarrow$ P transition, and those at  $\lambda \approx 265$  nm are assigned to the ligand-to-metal charge transfer (O<sup>2-</sup> $\rightarrow$ W<sup>6+</sup>).<sup>[32]</sup> It should be noted that the imidazole rings of the IL-POMs generally show UV/Vis absorption at  $\lambda = 210$  nm,<sup>[33]</sup> which is overlapped by the O $\rightarrow$ P transition. Therefore, the O<sup>2-</sup> $\rightarrow$ W<sup>6+</sup> absorption band ( $\lambda = 260$  nm) was selected for the solubility determination of the IL-POMs in saturated methanol solution. The UV/Vis absorbance results and those





C: [TEAPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>

Scheme 1. Structures of the as-synthesized IL-POM catalysts.

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Entry	IL-POM	A <sub>max</sub>	[I] [%]	[IH+] [%]	H <sub>o</sub>	рН С <sub>1</sub> [0.10 mм]	С <sub>2</sub> [1.0 mм]	С <sub>3</sub> [10 mм]
1	_	3.210	100	0	-	_	_	-
2	[PyPS]H <sub>2</sub> PW <sub>12</sub> O <sub>40</sub> (A <sub>1</sub> )	1.607	50.07	49.93	0.991	3.22	2.30	1.44
3	$[PyPS]_{2}HPW_{12}O_{40}(A_{2})$	1.625	50.63	49.37	1.001	3.30	2.39	1.48
4	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (A <sub>3</sub> )	1.640	51.08	48.92	1.009	3.28	2.39	1.47
5	[Py] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (A <sub>4</sub> )	1.623	50.55	49.45	0.999	4.32	3.80	3.63
6	$[PyPS]HSO_4 (A_5)^{[b]}$	1.480	46.12	53.88	0.922	3.88	2.70	1.71
7	[IMPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (B <sub>1</sub> )	1.610	50.17	49.83	0.993	4.98	4.55	4.27
8	[MIMPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (B <sub>2</sub> )	1.632	50.84	49.16	1.005	3.33	2.41	1.50
9	[EIMPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (B <sub>3</sub> )	1.638	51.03	48.97	1.008	3.32	2.36	1.47
10	[ <i>i</i> -PIMPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (B <sub>4</sub> )	1.620	50.47	49.53	0.998	3.36	2.50	1.67
11	[BnIMPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (B <sub>5</sub> )	1.579	49.19	50.81	0.976	3.32	2.47	1.69
12	[TEAPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (C)	1.635	50.94	49.06	1.006	3.35	2.38	1.43



Figure 1. UV/Vis spectra of methanol solutions saturated with IL-POMs. A1: [PyPS]H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>; A<sub>2</sub>: [PyPS]<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub>; A<sub>3</sub>: [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>; A<sub>4</sub>: [Py]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>; B1: [IMPS]3PW12O40; B2: [MIMPS]3PW12O40; B3: [EIMPS]3PW12O40; B4: [i- $PIMPS]_{3}PW_{12}O_{40}$ ; B<sub>5</sub>: [BnIMPS]\_{3}PW\_{12}O\_{40}; and C: [TEAPS]\_{3}PW\_{12}O\_{40}.

Table 2. Solubilities of IL-POMs in methanol, as determined by ICP-OES

and UV/Vi	s spectroscopy methods.								
Entry	IL-POM	Solubility [g S <sub>ICP</sub> <sup>[a]</sup>	J L <sup>-1</sup> ] S <sub>UV</sub> <sup>[b]</sup>						
1	[PyPS]H <sub>2</sub> PW <sub>12</sub> O <sub>40</sub> (A <sub>1</sub> )	58.4	59.8						
2	$[PyPS]_2HPW_{12}O_{40}(A_2)$	62.5	63.1						
3	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (A <sub>3</sub> )	68.7	71.3						
4	[Py] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (A <sub>4</sub> )	1.98	2.88						
5	[IMPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (B <sub>1</sub> )	53.1	53.1						
6	$[MIMPS]_{3}PW_{12}O_{40}$ (B <sub>2</sub> )	50.8	51.5						
7	[EIMPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (B <sub>3</sub> )	54.5	55.5						
8	[ <i>i</i> -PIMPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (B <sub>4</sub> )	50.3	52.3						
9	[BnIMPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (B <sub>5</sub> )	60.6	62.0						
10	[TEAPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (C)	48.1	49.4						
11 <sup>[c]</sup>	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (A <sub>3</sub> )	0	0						
[a] Solubility of IL-POM from the W content detected by ICP-OES									
(Table S1).	(Table S1). [b] Solubility of IL-POM from the UV/Vis spectra result.								
[c] [PyPS] <sub>3</sub>	[c] $[PyPS]_3PW_{12}O_{40}$ content in the chloroform-soluble fraction from the								
product congration (Scheme S1), the "O" value is defined as "not detect									

ed".

from the determination of the W content are in accordance with each other. Most of the IL-POMs have moderate solubilities in the range 48.1 ([TEAPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) to 68.7 g  $L^{-1}$ ([PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) at room temperature. However, it is noteworthy that only a trace amount of W was detected in a saturated methanol solution of [Py]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, which exhibits a very weak absorption band; this clearly indicates that [Py]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> is only slightly soluble in methanol at room temperature (Table 2, Entry 4).

#### Catalytic conversion of cellulose to levulinate ester

Microcrystalline cellulose was selected for the IL-POM catalytic activity test, and the results are listed in Table 3. In the absence of catalyst, the cellulose conversion was only 3.6% without any detectable ML production (Table 3, Entry 1); therefore, the thermal chemical reaction at 150°C and the autocatalytic performance of the solvent are negligible. As shown in Table 3, it is interesting that the conversion of cellulose and the yield of ML are promoted significantly by the addition of the IL-POMs containing cationic sulfonic groups coupled with POM functional anions. For example, 100% cellulose conversion was achieved with 71.4% ML yield and 79.7% process efficiency over  $[PyPS]_3PW_{12}O_{40}$  (Table 3, Entry 4). Generally, the domino processes for the formation of ML from cellulose, including the hydrolysis of cellulose to glucose, the dehydration/rehydration process from glucose to LA, and the subsequent esterification of LA with methanol, can be enhanced by acidic catalysts. On the other hand, direct cellulose methanolysis, which also contributes to ML production, is promoted in the presence of an acid catalyst. Hence, the integration of these typical acidcatalyzed processes over IL-POMs with high acidic strengths can promote cellulose degradation and ML generation.

The substitution of the IL-POM cation has a pronounced effect on the ML yield, as is demonstrated clearly by two systems with the same anion, that is, [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and [MIM-PS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, which yielded similar apparent acidic strengths (Table 1). However, the catalytic activities of these IL-POMs are remarkably different. The highest ML yield of 71.4% was ach-

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Entry	Catalyst	Promoter/solvent	Conversion [%]	Yield of lev product	vulinate ester yield [%]	Y <sub>LA</sub> [%]	Y <sub>glucose</sub> [%]	Efficiency [%]
1	blank	methanol	3.6±0.1	ML	not detected	0.9±0.01	0.2±0.02	0.9±0.01
2	[PyPS]H <sub>2</sub> PW <sub>12</sub> O <sub>40</sub> (A <sub>1</sub> )	methanol	100	ML	$48.4 \pm 1.9$	$6.8\pm1.0$	$1.5\pm0.2$	$55.2\pm2.0$
3	[PyPS] <sub>2</sub> HPW <sub>12</sub> O <sub>40</sub> (A <sub>2</sub> )	methanol	100	ML	$53.4\pm2.9$	$6.5\pm1.2$	$1.6 \pm 0.4$	$59.9 \pm 2.9$
4	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (A <sub>3</sub> )	methanol	100	ML	$71.4 \pm 1.7$	$8.3\pm0.5$	$0.3\pm0.02$	$79.7 \pm 1.8$
5	[Py] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (A <sub>4</sub> )	methanol	$3.2 \pm 0.2$	ML	not detected	$1.2\pm0.1$	$1.0\pm0.1$	$1.2\pm0.1$
6	[PyPS]HSO <sub>4</sub> (A <sub>5</sub> )	methanol	$88.9 \pm 1.3$	ML	$11.1\pm0.3$	$1.2\pm0.2$	$0.2\pm0.01$	$12.3\pm0.4$
7	[IMPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (B <sub>1</sub> )	methanol	100	ML	$26.2\pm1.1$	$1.7\pm0.03$	$15.5\pm0.4$	$27.9 \pm 1.1$
8	[MIMPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (B <sub>2</sub> )	methanol	100	ML	$\textbf{36.5} \pm \textbf{1.8}$	$4.4\pm0.1$	$3.1\pm0.5$	$40.9\pm1.7$
9	$[EIMPS]_{3}PW_{12}O_{40}(B_{3})$	methanol	100	ML	$45.8\pm2.9$	$8.8\pm0.4$	$1.1\pm0.2$	$54.6\pm3.0$
10	[ <i>i</i> -PIMPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (B <sub>4</sub> )	methanol	100	ML	$38.8\pm2.1$	$6.0\pm0.9$	$1.9\pm0.2$	$44.8\pm1.9$
11	[BnIMPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (B <sub>5</sub> )	methanol	100	ML	$33.9 \pm 1.4$	$13.5\pm0.9$	$0.5\pm0.2$	$47.4 \pm 1.6$
12	[TEAPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (C)	methanol	100	ML	$29.0\pm0.9$	$2.9\pm0.1$	$3.5\pm0.3$	$31.9\pm0.9$
13	$H_{3}PW_{12}O_{40}$	methanol	100	ML	$29.7 \pm 1.3$	$3.0\pm0.8$	$3.4 \pm 0.2$	$32.7 \pm 1.2$
14 <sup>[b]</sup>	$H_2SO_4$	methanol	100	ML	$41.6\pm1.9$	$5.0\pm1.1$	$3.1\pm0.1$	$46.6\pm2.2$
15	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (A <sub>3</sub> )	<i>n</i> -hexane	$0.3\pm0.1$	LA	not detected	not detected	not detected	-
16	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (A <sub>3</sub> )	H₂O	$71.4 \pm 1.3$	-	-	$18.1 \pm 1.5$	$32.9 \pm 0.5$	$18.1 \pm 1.5$
17	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (A <sub>3</sub> )	ethanol	100	EL	$57.5\pm2.8$	$3.9\pm0.1$	$0.5\pm0.1$	$61.4 \pm 2.8$
18	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (A <sub>3</sub> )	<i>n</i> -propanol	100	<i>n</i> -PL	$37.0 \pm 1.4$	$4.0\pm0.1$	$1.5\pm0.4$	$41.0\pm1.4$
19	$[PyPS]_{3}PW_{12}O_{40}(A_{3})$	2-propanol	100	<i>i</i> -PL	$21.5\pm1.4$	$9.4\pm0.1$	$1.0\pm0.01$	$30.9 \pm 1.3$

ieved with [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, whereas a yield of only 36.5% was obtained in the presence of [MIMPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>. Imidazole is considerably more basic than pyridine, though both of them are aromatic heterocyclic compounds. As the lone pair of the Hbearing N atom in imidazole is required to maintain aromaticity, the other N atom with a lone pair in its sp<sup>2</sup> orbital, perpendicular to the aromatic system, is the basic one.<sup>[34]</sup> Thus, compared with that of [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, the acidity of [MIM- $\mathsf{PS}]_3\mathsf{PW}_{12}\mathsf{O}_{40}$  is partly compensated by its basic N atom, and this results in lower catalytic activity. To verify this assumption, H, ethyl, isopropyl, and benzyl substituents were grafted onto the basic N atom to adjust the basicity of the IL in the control experiments (Table 3, Entries 7 and 9-11, respectively). As the electron-donating ability increases in the order benzyl < H < methyl < ethyl < isopropyl,<sup>[35]</sup> theoretically, the basicity of the mentioned N atom in imidazole should increase in the order  $[BnIMPS]^+ > [IMPS]^+ > [MIMPS]^+ > [EIMPS]^+ > [i-PIMPS]^+.$ The catalytic performance of the IL-POMs containing an imidazole ring follows the sequence  $[EIMPS]_3PW_{12}O_{40} >$  $[i-PIMPS]_{3}PW_{12}O_{40} \approx [MIMPS]_{3}PW_{12}O_{40} > [IMPS]_{3}PW_{12}O_{40} >$ 

 $[BnIMPS]_{3}PW_{12}O_{40}, which accords well with their acidic-strength sequence (Table 1 and Figure S7). The catalytic activity of [$ *i* $-PIMPS]_{3}PW_{12}O_{40} is lower than that of [EIMPS]_{3}PW_{12}O_{40}, and this can be ascribed to the steric hindrance of the isopropyl group in cellulose conversion.$ 

The effect of the SO<sub>3</sub>H functional group in the cation of the pyridine-based IL-POMs on cellulose conversion and ML yield was also studied. Clearly, more ML production can be achieved with an increasing number of coordinated [PyPS]<sup>+</sup> groups. For example, the ML yield increases from 48.4 to 53.4 and 71.4% as the number of coordinated [PyPS]<sup>+</sup> groups increases from one to two and three. As shown in Table 1 (Entries 2–4), the substitution of the H<sup>+</sup> ion in the heteropolyacid by the [PyPS]<sup>+</sup>

cation can enhance the acidic strength of the as-synthesized IL-POMs, though the acidity of heteropolyacid is normally stronger than that of a sulfonated acid. The results indicate that a stronger acidic strength of the IL-POM is desirable to trigger the reaction. The  $H_3PW_{12}O_{40}$  catalyst exhibits a significantly lower ML yield of 29.7%, which implies that protons from the sulfonic-containing cation favor ML formation more than those from the parent heteropolyacid. On the other hand, the catalytic activity of the IL-POM without a propanesulfonate group ([Py]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) was also investigated, and this catalyst resulted in 3.2% cellulose conversion and no detectable ML formation (Table 3, Entry 5). The poor solubility of [Py]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> is considered to be the main reason for this result owing to solid-to-solid contact limitations. However, it is also plausible that the weaker acidic strength (Table 1, Entry 5) may also contribute to the seemingly poor catalytic activity exhibited by this system.

To determine whether the heteropolyanion is indispensable to the achievement of a high yield of ML, the catalytic performance of [PyPS]HSO<sub>4</sub> was tested. In general, the Keggin heteropolyacids and their salts are strong acids,<sup>[36]</sup> and the relatively higher acidic strength of the heteropolyacid anion makes a bigger contribution to the acidities of these IL-POMs than the  $HSO_4^-$  ion; therefore,  $[PyPS]_3PW_{12}O_{40}$  has a much higher acidic strength than that of [PyPS]HSO<sub>4</sub>. In the catalyticperformance comparison, 11.1% yield of ML was obtained at 88.9% cellulose conversion with [PyPS]HSO<sub>4</sub> as the catalyst (Table 3, Entry 6), whereas all of the  $PW_{12}O_{40}^{3-}$ -coupled IL-POMs exhibited complete cellulose conversions with moderate-tohigh ML yields. Thus, on the basis of the aforementioned results, it is hypothesized that intensive synergistic effects between the sulfonic-functionalized cation and the heteropolyanion of [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> are responsible for the high ML yield.



Furthermore, this IL-POM with an appropriate acidic strength accelerates cellulose hydrolysis, LA generation, and finally esterification to realize a coupled and intensified process. The rapid in situ esterification of LA not only slows the depolymerization equilibrium of cellulose but also protects ML from side reactions owing to the immiscibility of  $[PyPS]_3PW_{12}O_{40}$  with apolar esters;<sup>[30a]</sup> therefore, it is of benefit for enhanced ML selectivity. Furthermore,  $[PyPS]_3PW_{12}O_{40}$  shows significantly enhanced catalytic activity relative to that of the conventional acid  $H_2SO_4$  (Table 1, Entry 14). This suggests that the present IL catalysts have great potential as promising alternatives to conventional acids in ML production owing to their high activities and reduced corrosiveness.

The effects of the reaction medium and promoter were also investigated. As shown in Table 3, if the cellulose depolymerization is conducted in the nonpolar solvent *n*-hexane, both the cellulose conversion and the LA yield are negligible (Table 3, Entry 15). The presence of water is beneficial for cellulose hydrolysis, and 71.4% cellulose conversion and 18.1% LA yield could be attained (Table 3, Entry 16). However, if alcohols are used, the cellulose is converted completely at process efficiencies in the range 30.9 to 79.7% (Table 3, Entries 17-19). In these systems, the in situ esterification of the generated LA with the alcohol promoter can be catalyzed by the acid catalyst, and this shifts the equilibrium of LA production through reaction coupling and, thus, enhances the process. This intensification effect of the in situ esterification can be further confirmed by cellulose depolymerization with various alcohols. For example, 71.4% ML yield was obtained in a methanol medium, whereas 2-propanol presents a relatively low isopropyl levulinate yield of 21.5% owing to steric hindrance from the branched alkyl chain.

#### Effect of catalyst loading

The effect of the catalyst loading on the ML generation is illustrated in Figure 2. The cellulose conversion was only 3.6% and no ML was detected in the control experiment (Table 3,



Figure 2. Effect of catalyst loading on ML production. Conditions: microcrystalline cellulose (0.162 g),  $[PyPS]_3PW_{12}O_{40\prime}$  methanol (20 mL), 2 MPa  $N_{2\prime}$  150 °C, 5 h.

Entry 1). However, the conversion of cellulose increased significantly to 100%, and the ML yield increased to 30.3% with 0.3 mmol of  $[PyPS]_3PW_{12}O_{40}$  catalyst (Figure 2). As illustrated in Figure 2, the yield of ML peaks at 71.4% if the catalyst loading is 0.5 mmol. Further increments in catalyst quantity resulted in the formation of dark brown floccule polymers and reduced ML yields. This can be ascribed to the idea that excess catalytic sites simultaneously accelerate cellulose conversion to ML and facilitate undesirable side reactions.

#### Effects of reaction temperature and time

The effects of reaction temperature and time on the conversion of cellulose to ML are depicted in Figure 3. This ML production process is highly temperature-dependent. At 130°C, the cellulose conversion increases gradually from 39.0 to 100% from 3 to 6 h reaction time. However, at elevated temperatures, 3 h is sufficient for complete cellulose conversion (Figure 3 a). Glucose is the dominant product at 130 °C (Figure 3 b), whereas ML is the major product at temperatures above this (Figure 3 d). Generally, the thermal effect is helpful for the degradation of the  $\beta$ -1,4-glycoside bonds in cellulose<sup>[37]</sup> and accelerates the reaction but is not advantageous for the exothermic esterification reaction. The use of excess alcohol not only leads to the in situ esterification of LA but also pushes the esterification equilibrium towards the product side and effectively minimizes the LA yield. At 140 and 150 °C, the LA yields increase initially and then decrease owing to the consumption of LA. In contrast, higher temperatures (160 and 170 °C) result in small increases to the LA yields as the time increases, whereas the ML yields increase and decrease accordingly (Figure 3 c and d). The results indicate that moderate temperatures are appropriate for the hydrolysis of cellulose and simultaneous in situ esterification; therefore, more complete conversion of cellulose and higher ML yields can be achieved at optimized reaction times. Excessively high reaction temperatures and times result in severe undesirable side reactions, such as repolymerization and the formation of humins,<sup>[38]</sup> and, therefore, decrease the ML yield. For example, at 150 °C, the ML yield increases gradually from 33.0 to 71.4% as the reaction time increases from 3 to 5 h and then decreases to 54.9% at 7 h. Thus, an appropriate temperature (150 °C) and time (5 h) are required to achieve excellent process efficiency.

#### Conversion of carbohydrates over $[PyPS]_3PW_{12}O_{40}$ catalyst

The catalytic activity of the optimum IL-POM  $[PyPS]_3PW_{12}O_{40}$  for ML production was studied further with various carbohydrate substrates and real biomass (Table 4 and Figure S9). The nature of the biomass has a substantial effect on the conversion and ML yield. Mono- and polysaccharides can be converted completely with suitable ML yields (51.4–76.1%) and process efficiencies (60.8–82.7%) under the optimized reaction conditions (150 °C for 4–5 h) with very low glucose yields (Table 4 and Figure S9). The raw biomasses corn straw and bagasse are partly converted at 170 °C for 4–4.5 h with ML yields of approximately 50%.



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Figure 3. Effects of temperature and time on (a) cellulose conversion, (b) glucose yield, (c) LA yield, and (d) ML yield. Conditions: microcrystalline cellulose (0.162 g), [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (0.5 mmol), methanol (20 mL), 2 MPa N<sub>2</sub>.

Table 4. Conversion of various carbohydrates over $[PyPS]_3PW_{12}O_{40}$ catalyst. <sup>[a]</sup>							
Substrate	Time [h]	Conversion [%]	Y <sub>ML</sub> [%]	Y <sub>LA</sub> [%]	Efficiency [%]		
glucose <sup>(b)</sup> sucrose <sup>(b)</sup> cellobiose <sup>(b)</sup> starch cellulose corn straw <sup>[c]</sup> bagasse <sup>(c)</sup>	4 4.5 4.5 5 5 4.5 4	$     100     100     100     100     100     100     45.9 \pm 2.9     50.2 \pm 1.8   $	$58.7 \pm 1.0 \\76.1 \pm 1.1 \\58.6 \pm 1.4 \\51.4 \pm 1.3 \\71.4 \pm 1.7 \\50.3 \pm 1.1 \\50.0 \pm 1.3$	$\begin{array}{c} 6.9 \pm 0.8 \\ 6.6 \pm 0.5 \\ 6.5 \pm 0.4 \\ 9.4 \pm 1.1 \\ 8.3 \pm 0.5 \\ 7.8 \pm 0.5 \\ 8.9 \pm 0.6 \end{array}$	$\begin{array}{c} 65.6 \pm 0.9 \\ 82.7 \pm 1.3 \\ 65.1 \pm 1.5 \\ 60.8 \pm 1.3 \\ 79.7 \pm 1.9 \\ 58.1 \pm 1.1 \\ 58.9 \pm 1.1 \end{array}$		
Conditions: [a] Cellulose or starch (0.162 g, containing 1 mmol $C_6H_6O_5$ unit), [PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (0.5 mmol), methanol (20 mL), 2 MPa N <sub>2</sub> , 150 °C. Efficiency [%] = $Y_{ML}$ [%]+ $Y_{LA}$ [%]. [b] 1 mmol substrate. [c] 0.5 g substrate, 170 °C. The ML yield was calculated from the cellulose content.							

Hemicellulose is converted to furfural and its derivatives, whereas the conversion of lignin is negligible. The three main components of real biomass (cellulose, hemicellulose, and lignin) are tightly bound through a mixture of hydrogen bonding and covalent linkages, which provide structural rigidity to the lignocellulosic matrix.<sup>[18,39]</sup> Thus, the lower ML yields observed for bagasse and corn straw are attributed to the hindered cellulose hydrolysis that occurs because of the recalcitrant structure of real biomass. Interestingly, the ML yields for starch, cellobiose, and glucose were lower than that for cellulose. This may be attributed to the significantly higher solubilities of starch, cellobiose, and glucose relative to that of cellulose during the reaction; the increased solubility can accelerate

the hydrolysis process, and this results in the promotion of undesired side reactions<sup>[16,40]</sup> and, thereby, lower ML yields. If sucrose is used as the substrate, the hydrolysis of sucrose leads to the generation of fructose, which undergoes dehydration readily to yield ML, whereas glucose isomerizes before dehydration.<sup>[41]</sup>

Summarily, with the optimum  $[PyPS]_3PW_{12}O_{40}$  loading of 0.5 mmol, cellulose can be degraded completely with 71.4% ML yield and 79.7% process efficiency at 150 °C for 5 h. This result shows the clear advantages of the IL-POM catalysts over the current technologies (Table S2), that is, the use of milder conditions (lower temperature), higher product yield, and less catalyst corrosion.

#### Reusability of [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> catalyst

Under the optimized conditions, the reusability of the IL-POM catalyst  $[PyPS]_3PW_{12}O_{40}$  was investigated, and the results are presented in Figure 4. The procedure could be repeated up to ten times without any clear loss of cellulose conversion. However, the ML yield decreased from 71.1 to 57.6% after the 10th run. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis detected no tungsten leaching into the chloroform phase (Table S1, Entry 11); therefore,  $[PyPS]_3PW_{12}O_{40}$  could not be extracted in this process. Nevertheless, there is approximately 20% weight loss of the catalyst after the 10th

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Figure 4. The recyclability of  $[PyPS]_3PW_{12}O_{40}$ . Conditions: microcrystalline cellulose (0.162 g),  $[PyPS]_3PW_{12}O_{40}$  (0.5 mmol), methanol (20 mL), 2 MPa N<sub>2</sub>, 150 °C, 5 h.

run. Therefore, 20 wt% of the fresh IL-POM [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> was supplemented in the eleventh run. Surprisingly, a ML yield of 70.1% was obtained; this suggests that mechanical loss during the separation of the product rather than catalyst deactivation is one of the reasons for the reduction of process efficiency.

To determine the structural changes between the fresh and spent catalyst after the 10th run, a series of comparative characterizations were performed through FTIR spectroscopy, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, ESI-MS, elemental analysis, and ICP-OES. As shown in Figure 5, the difference between the FTIR



Figure 5. FTIR spectra of (a) fresh and (b) spent  $[PyPS]_3PW_{12}O_{40}$  catalyst after the 10th run.

spectra of the fresh and spent IL-POM  $[PyPS]_3PW_{12}O_{40}$  is insignificant, and the characteristic absorptions of the pyridinium cation ( $\tilde{\nu} = 1633$ , 1488, 1124, and 1181 cm<sup>-1</sup>) and the Keggin heteropolyacid anion ( $\tilde{\nu} = 1080$ , 978, 896, and 804 cm<sup>-1</sup>) can be observed clearly in the spectrum of spent  $[PyPS]_3PW_{12}O_{40}$ . The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the spent IL-POM also exhibit similar chemical shifts to those of the fresh one (Figure 6 and 7). However, it should be noted that extra signals are apparent

at  $\delta = 1.83$  and 3.70 ppm in the <sup>1</sup>H NMR spectrum (Figure 6b) and at  $\delta = 25.04$  and 67.87 ppm in the <sup>13</sup>C NMR spectrum (Figure 7 b). This suggests the formation of the furan ring structure of humins,<sup>[42]</sup> a main byproduct in carbohydrate conversion. The ESI-MS spectra of the fresh and spent catalysts present similar m/z values (Figure 8). The elemental analyses show a slight increase in the carbon content (from 8.15 to 9.50%) for the spent catalyst after the 10th run in comparison with that of the fresh [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (Table S3), and this confirms further the existence of coating of humins on the IL catalyst. Additionally, the W content, determined by ICP-OES, demonstrates that the purity of the spent catalyst is 95.1% (Table S4). Therefore, we can conclude that the IL-POM [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> is highly reusable. The slight loss of activity for ML production is caused by mechanical loss during the IL-POM separation and recrystallization. On the other hand, the formation of humins, a nonvolatile and conventional byproduct from carbohydrate conversion, also contributes to the loss of catalytic activity.

#### Conclusions

A new ecofriendly and intensified strategy for the efficient conversion of carbohydrates to levulinate esters is achieved through a one-pot process over heteropolyanion ionic liquids (IL-POMs). Under mild conditions (150°C for 5 h), a cellulose conversion of 100% yields 71.4% methyl levulinate (ML) at a process efficiency of 79.7%; therefore, this process shows clear advantages over current technologies. This high efficiency is due to the excellent catalytic activity of  $[PyPS]_{3}PW_{12}O_{40}$ [PyPS = 1-(3-sulfopropyl)pyridinium] for the simultaneous cellulose depolymerization and in situ esterification of the generated levulinic acid (LA) with methanol. Furthermore, this process is efficient for the conversion of other typical carbohydrates the production of levulinate esters. Moreover, and [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> can be recovered readily by self-separation through temperature control. In addition, the IL-POM catalyst shows excellent reusability, and a satisfactory ML yield can be obtained even after the 10th run. Therefore, the presented technique will be a good reference for future biomass valorization owing to its high efficiency, simple technology, mild conditions, and simple catalyst recycling and reusability.

#### **Experimental Section**

#### Materials

Microcrystalline cellulose (Avicel PH-101, particle size  $\approx$  50 µm), soluble starch, and D-(+)-glucose were purchased from Sigma-Aldrich. The corn straw and bagasse were collected from Liaoning and Guangdong provinces, China, respectively, and then air-dried and ground to 40–50 mesh. The cellulose contents (w/w) of the corn straw and bagasse were 44.5 and 34.7%, respectively, as determined by the National Renewable Energy Laboratory (NREL) analytical method. D-(+)-Cellobiose, sucrose, 1,3-propanesultone, imidazole, 1-methylimidazole, 1-benzylimidazole, pyridine, trimethylamine, methanol (ACS/HPLC reagent), *n*-propanol, 2-propanol, THF, LA, ML, EL, and D<sub>2</sub>O (99.8 at% D) were purchased from J&K Chemical Ltd. Phosphotungstic acid hydrate (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·xH<sub>2</sub>O), 1-ethylimi-





Figure 6. <sup>1</sup>H NMR of spectra (a) fresh and (b) spent [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> catalyst after the 10th run.



Figure 7. <sup>13</sup>C NMR spectra of (a) fresh and (b) spent [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> catalyst after the 10th run.

dazole, *n*-octanol (standard for GC), potassium bromide, and 4-nitroaniline were purchased from Aladdin. 1-Isopropylimidazole was purchased from Aamas-beta. Sulfuric acid (98%), diethyl ether, ethanol, toluene, and chloroform were supplied by Guanghua Chemical Factory Co., Ltd. All chemicals were of analytical-grade and were used without further purification.

#### **Preparation of IL-POM catalysts**

The general preparation procedure for the IL-POM catalyst<sup>[30]</sup> (Scheme 1) was as follows. For  $[PyPS]_3PW_{12}O_{40^r}$  pyridine (0.11 mol) and 1,3-propanesultone (0.10 mol) were dissolved in toluene, and the mixture was stirred vigorously at 50 °C for 24 h under the pro-

tection of a nitrogen atmosphere. The obtained white precipitate, 1-(3-sulfopropyl)pyridinium (PyPS), was collected by filtration, washed with diethyl ether (3×100 mL), and finally dried under vacuum overnight. PyPS (0.06 mol) was added to an aqueous solution containing  $H_3PW_{12}O_{40}$  (0.02 mol). The mixture was stirred vigorously at room temperature for 24 h and then dried under vacuum to give the final product [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> as a light yellow powder. The other IL catalysts [PyPS]H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>, [PyPS]<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub>, [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, [PyPS]HSO<sub>4</sub>, [IMPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, [MIMPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, [EIMPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, [*i*-PIMPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, [BnIMPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, and [TEAPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> were prepared accordingly.



Figure 8. Negative-ion-mode ESI-MS spectra of (a) fresh and (b) spent [PyPS]  $_3PW_{12}O_{40}$  catalyst after the 10th run.

#### Characterization of the ILs

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker AV-400 spectrometer with  $D_2O$  as the solvent. The ESI-MS spectra were obtained with an Agilent 1290/Bruker maxis impact instrument. The FTIR spectra (KBr pellets) were recorded with a Bruker Equinox-55 FTIR instrument. The C, H, S, and N contents were measured with a Vario EL III elemental analyzer. The thermal stabilities of the ILs were studied with a NETZSCH TG 209 F3 analyzer from 30 to 800 °C at the rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. The detail catalyst characterization data can be found in the Supporting Information.

#### IL acidic strengths and their solubilities in methanol

The Brönsted acidic strengths of the as-synthesized ILs were determined by the Hammett method<sup>[31]</sup> and measurement of the pH values. The  $A_{max}$  values for the Hammett functions were obtained with a UV/Vis spectrometer (UV-3010) in the range  $\lambda = 200$  to 800 nm. 4-Nitroaniline was used as the indicator, and the Hammett acidity function ( $H_0$ ) was calculated with Equation (1). The pH values of the IL catalysts were measured with a Precision PHS-25 pH meter.

$$H_{o} = pK_{a} + \log [I] / [IH^{+}]$$
(1)

In Equation (1), I represents the indicator base, and [IH<sup>+</sup>] and [I] are the molar concentrations of the protonated and unprotonated forms of the indicator, respectively. The  $pK(I)_a$  value of 4-nitroaniline is 0.99.

The solubilities of the IL-POMs in methanol were obtained by two methods: (1) The solubilities of the IL-POMs were calculated from the W content in their saturated methanol solutions, as measured by ICP-OES analysis with a NexION 300 analyzer. (2) A standard curve-based method was employed with the intensity of the absorption band at  $\lambda \approx 260$  nm in UV/Vis spectra, and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> was employed as the standard compound for quantitative analysis. Saturated solutions of the ILs were diluted 1000 times before analysis.

#### Typical procedure for levulinate ester production

In a typical process for the conversion of cellulose to ML, microcrystalline cellulose (0.162 g), methanol (20 mL), and a given amount of the IL-POM catalyst were mixed in a 50 mL stainlesssteel autoclave. The reactor was first purged with N<sub>2</sub> three times to displace the air and then heated to the designated temperature and stirred with a magnetic stirrer (300 rpm). After the desired time, the mixture was cooled to room temperature in an ice–water bath.

#### **Product separation**

The whole procedure for product separation is shown in Scheme S1. The solid residue was first collected by filtration, washed with H<sub>2</sub>O and THF (five times each), and then dried under vacuum overnight to enable the calculation of the conversion. Deionized water (25 mL) was added to the filtrate, and then chloroform (5×5 mL) was used for the product extraction. After careful separation, an organic phase (containing levulinate ester) and an aqueous phase (containing the water-soluble fraction and the IL-POM catalyst) were obtained. The organic phase was diluted with chloroform to 50 mL for qualitative and quantitative analysis. The aqueous phase was diluted with deionized water to 100 mL for the measurement of the yields of the water-soluble products such as LA and glucose. After the removal of water at 50°C under reduced pressure, the obtained fraction was diluted with methanol (50 mL) to dissolve the IL-POM catalyst. The solvent was first removed from the methanol solution with a rotary evaporator until a light yellow solid appeared. Then, the suspension was placed in a refrigerator  $(-10 \degree C)$  to precipitate the IL-POM catalyst and to separate the residual methanol-soluble organic chemicals. The recycled and recrystallized catalyst was obtained by centrifugation and then dried at 70 °C under vacuum overnight. The catalyst was used directly for the next run without further purification.

#### Qualitative and quantitative analysis of the products

The volatile products in the chloroform (organic phase) were identified by GC-MS and quantified by GC with an Agilent 7890 GC instrument with both a 5977A MS detector and a flame ionization detector (FID). An Agilent HP-5 MS [(5% phenyl)methylpolysiloxane] capillary column (30 m  $\times 250~\mu m \times 0.25~\mu m)$  was used for chemical separation. The FID was operated at 270 °C, and the carrier gas was helium at a flow rate of 1.0 mLmin<sup>-1</sup>. The initial oven temperature was 50 °C (held for 3 min) and then it was ramped to 250 °C (held for another 1 min) at 15 °C min<sup>-1</sup>. The chemicals in the aqueous phase were analyzed with an Agilent 1200 HPLC instrument equipped with an HPX-87H column (300 mm  $\times$  7.8 mm, 5  $\mu$ m) and a refractive index detector (RID). A solution of  $5 \text{ mm H}_2\text{SO}_4$ was used as the mobile phase at a flow rate of 0.6 mLmin<sup>-1</sup>. The column oven temperature was 65 °C. Commercial chemicals were used as the standard compounds for the qualitative and quantitative analyses.

The conversion of carbohydrate was defined by Equation (2).

Conversion [%] = 
$$\frac{m_c - m_s}{m_c} \times 100\%$$
 (2)

 $m_{\rm c}$  is the mass of feed carbohydrate, and  $m_{\rm s}$  is the mass of the unreacted feedstock collected by filtration, washing, and drying.



The yields of levulinate esters, LA, and glucose and the process efficiency were defined by Equations (3)–(6), respectively.

$$Yield_{LA ester} \ [\%] = \frac{n_{LA ester}}{n(C_6H_6O_5 unit)} \times 100 \ \% \tag{3}$$

Yield<sub>LA</sub> [%] = 
$$\frac{n_{LA}}{n(C_6H_6O_5 \text{ unit})} \times 100\%$$
 (4)

$$Yield_{glucose} \ [\%] = \frac{\Pi_{glucose}}{n(C_6H_6O_5 \text{ unit})} \times 100\%$$
(5)

 $\label{eq:Process efficiency [\%] = Yield_{LA \ ester} + Yield_{LA} \eqno(6)$ 

 $n_{\text{LA ester}}$ ,  $n_{\text{LA}}$ , and  $n_{\text{glucose}}$  are the molar amounts of levulinate ester, LA, and glucose, respectively, and  $n(C_6H_6O_5 \text{ unit})$  is the molar amount of  $C_6H_6O_5$  units in the initial feedstock.

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Iconic ionic: Heteropolyanion-based ionic liquids are used as catalysts for the conversion of renewable carbohydrates to levulinate esters. The process can be operated under mild conditions, and the catalyst can be recovered readily by self-separation through temperature control. The catalyst shows excellent reusability, and a satisfactory yield can be obtained even after the 10th run.

Carbohydrates [PyPS],PW,O ed & intensified proce

C. Song, S. Liu, X. Peng, J. Long,\* W. Lou, X. Li\*

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Catalytic Conversion of Carbohydrates to Levulinate Ester over Heteropolyanion-Based Ionic Liquids