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## Introduction

Recently, ionic liquids (ILs) have been applied and shown to be effective in some catalytic conversions. They have important and unique properties such as negligible vapor pressure, excellent chemical and thermal stability, potential recoverability, and convenience for the separation of products from reactants.<sup>1-4</sup> In particular, Brønsted acid functionalized ILs (FILs) have been reported as novel ecologically benign catalysts for some acid-catalyzed reactions. Since Cole et al.<sup>5</sup> firstly described a FIL with Brønsted acidity in 2002, the research and application of various SO<sub>3</sub>H functionalized Brønsted acidic ILs have received an increased attention. In most cases, ILs were functionalized with only one sulfonic acid group and that resulted in the reduced acidity of the ILs compared to the acidities shown by conventional acid catalysts.6-8 In recent years, a series of multi-SO<sub>3</sub>H functionalized ILs have been reported and shown to be effective, strong acidic catalysts.<sup>9-11</sup> However, most of those multi-SO<sub>3</sub>H functionalized ILs are solid at room temperature and could not be administered as pure liquids, which have restricted their applications. In continuation of our studies on the preparation and application of  $SO_3H$ -functionalized ILs,<sup>12–14</sup> we herein report the synthesis

## Bi-SO<sub>3</sub>H-functionalized room temperature ionic liquids based on bipyridinium: highly efficient and recyclable catalysts for the synthesis of naphthalene-condensed oxazinone derivatives

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Several bi-SO<sub>3</sub>H-functionalized room temperature ionic liquids were synthesized and their catalytic performances for the synthesis of naphthalene-condensed oxazinone derivatives were studied theoretically, as well as experimentally. Compared with traditional single-SO<sub>3</sub>H-functionalized ionic liquids, less catalyst and higher yields are the key features of this methodology. Hammett function values and the minimum-energy geometries of bi-SO<sub>3</sub>H-functionalized ionic liquids were calculated and the results revealed that the acidities and catalytic activities of ionic liquids in the synthesis of naphthalene-condensed oxazinone derivatives were influenced by their structures. There are strong hydrogen bond networks in these bi-SO<sub>3</sub>H-functionalized ionic liquids. The H–O bond of the sulfonic acid groups was lengthened to different levels compared with the one in the isolated cation. The ionic liquid [(PS)<sub>2</sub>bPy][OTf]<sub>2</sub> with the shortest H–O bond distance had the strongest hydrogen bond and hence showed the strongest acidity and the highest catalytic activity.

of novel  $bi-SO_3H$ -functionalized ILs based on bipyridinium, which are liquid at room temperature (Scheme 1).

Multicomponent reactions (MCRs) have drawn great interest in modern organic synthesis and medicinal chemistry because of their one-pot processes about bringing together three or more components, high atom economy and high selectivity.15-17 Aromatic-condensed oxazinone derivatives are an important class of heterocyclic compounds, since many of these heterocyclic systems exhibit biological activity.<sup>18</sup> For example, naphthalene-condensed 1,3-oxazin-3-ones have been reported to act as antibacterial agents.<sup>19</sup> This class of compounds has also been used as precursors in the preparation of phosphinic ligands for asymmetric catalysis.<sup>20</sup> Naphthalene-condensed oxazinone derivatives have been synthesized through MCRs using HClO<sub>4</sub>-SiO<sub>2</sub> as a catalyst<sup>21</sup> or by the use of MW irradiation.<sup>22</sup> Although these methods are quite useful, they have limitations, such as low yields, tedious work-up procedures and harsh reaction conditions. To the best of our knowledge, there are few reports using ILs as catalysts for the synthesis of naphthalene-condensed oxazinone derivatives. We have reported the effective catalytic results of single SO<sub>3</sub>H-functionalized ILs to some organic reactions,<sup>12–14</sup> so we predicted that our bi-SO3H-functionalized ILs could also catalyze the synthesis of naphthalene-condensed oxazinone derivatives efficiently (Scheme 2).

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Scheme 1 Structures of the bi-SO<sub>3</sub>H-functionalized ILs used in this paper.

#### **Results and discussion**

The measurement of the acidic scale of bi-SO<sub>3</sub>H-functionalized ILs was conducted on an Agilent B453 UV-vis spectrophotometer with a basic indicator, crystal violet.<sup>23</sup> With the increase of the acidic scale of the ILs, the absorbance of the unprotonated form of the basic indicator decreased, whereas the protonated form of the indicator could not be observed. It is because of its small molar absorptivity and its location. The  $[I]/[IH^+]$  (I represents indicator) ratio could be determined from the measured absorbance differences after the addition of ILs and the Hammett function ( $H_0$ ) was calculated by using eqn (1). This value could be considered as the relative acidity of the ILs.

$$H_0 = pK(I)_{aq} + \log([I]/[IH^+])$$
(1)

 $H_0$  values of bi-SO<sub>3</sub>H-functionalized ILs were calculated with the same concentration of crystal violet (5 mg L<sup>-1</sup>, pK<sub>a</sub> = 0.8) and IL (25 mmol L<sup>-1</sup>) in distilled water. For comparison, we also determined the  $H_0$  values of single-SO<sub>3</sub>H-functionalized ILs based on pyridium. The maximal absorbance of the unprotonated form of the indicator was observed at 590 nm. When an acidic IL was added, the absorbance of the unprotonated form of the indicator decreased. As is shown in Fig. 1, the absorbance of the unprotonated form of the indicator on nine ILs decreased as follows: [PSPy][H<sub>2</sub>PO<sub>4</sub>] >



Scheme 2 The synthesis of naphthalene-condensed oxazinone derivatives via the condensation reaction of an aldehyde, 2-naphthol and urea catalyzed by ILs.

 $[(BS)_2 bPy][H_2 PO_4]_2 > [PSPy][HSO_4] > [PSPy][OTf]$ >  $[(PS)_2bPy][H_2PO_4]_2 > [(BS)_2bPy][HSO_4]_2 > [(PS)_2bPy][HSO_4]_2$  $> [(BS)_2 bPy][OTf]_2 > [(PS)_2 bPy][OTf]_2$ . The acidity order of these SO<sub>3</sub>H-functionalized ILs is accompanied by the following  $H_0$  values (Table 1):  $[(PS)_2 bPy][OTf]_2$  (-0.3873) >  $[(BS)_2 bPy][OTf]_2 (-0.0799) > [(PS)_2 bPy][HSO_4]_2 (-0.0411) >$  $[(BS)_2 bPy][HSO_4]_2 (0.0329) > [(PS)_2 bPy][H_2 PO_4]_2 (0.2033) >$ [PSPy][OTf]  $(0.2087) > [PSPy][HSO_4]$ (0.5707)> $[(BS)_2 bPy][H_2 PO_4]_2$  (0.7320) >  $[PSPy][H_2 PO_4]$  (1.0958). The results indicated that the acidity of ILs became stronger with the increase of the number of SO<sub>3</sub>H-functionalized groups. The acidity of bi-SO<sub>3</sub>H-functionalized ILs depended on the characteristics of both cations and anions. The ILs with a  $[(PS)_2 bPy]^+$  cation had stronger acidities than those with a  $[(BS)_2 bPy]^+$  cation. When the cations of the ILs were the same, the dependence of the acidity of the IL on the anion was significant. The acidities of the bi-SO<sub>3</sub>H-functionalized ILs with [OTf]<sup>-</sup> were stronger than those of the ILs with [HSO<sub>4</sub>]<sup>-</sup> and  $[H_2PO_4]^-$  anions (Table 1, entries 1–6).

The minimum-energy geometries of bi-SO<sub>3</sub>H-functionalized ILs were determined by performing ab initio geometry optimizations at the RHF/6-31(d, p) level. The fully optimized geometries of these ILs were presented in Fig. 2 and 3 and Table 2. It is obvious that a strong hydrogen bond network is present in the bi-SO<sub>3</sub>H-functionalized ILs. Taking the IL [(PS)<sub>2</sub>bPy][HSO<sub>4</sub>]<sub>2</sub> as an example, the anions were located on the side of the propyl sulfonic acid groups, and interacted with the propyl alkyl sulfonic acid group and bipyridinium ring in the form of C(N)-H···O or O-H···O (hydrogen bonds). There were eight hydrogen bonds in the IL [(PS)<sub>2</sub>bPy][HSO<sub>4</sub>]<sub>2</sub>, which were shorter than the van der Waals distance of 2.67 Å.<sup>24</sup> These included the hydrogen bonds C15-H18...O54, C12-H16...O54 and C<sub>1</sub>-H<sub>6</sub>…O<sub>57</sub> (bond distances are 2.474 Å, 2.181 Å and 2.392 Å) between the anions and the bipyridinium ring, as well as the C22-H26 ... O52, C31-H35 ... O57 and C30-H32 ... O57 (bond distances are 2.150 Å, 2.242 Å and 2.770 Å) hydrogen bonds between the anions and the alkyl sulfonic acid chain. Most importantly, the



Fig. 1 Absorbance spectra of crystal violet for various SO<sub>3</sub>H-functionalized ILs in distilled water.

strongest interactions between the anions and the sulfonic acid proton were O447-H48...O51 and O45-H46...O58 (bond distances are 1.435 Å and 1.388 Å). The other five bi-SO3Hfunctionalized ILs also exhibited similar strong interactions between the anions and the sulfonic acid groups. Those interactions could make the H-O bond of the sulfonic acid groups lengthen to different levels compared with the one in the isolated cation. When the cation of the ILs was the same, the H-O bond distance of the bi-SO<sub>3</sub>H-functionalized ILs decreased as follows:  $[Cation][H_2PO_4]_2 > [Cation][HSO_4]_2 >$ [Cation][OTf]<sub>2</sub>. Taking ILs based on the [(PS)<sub>2</sub>bPy]<sup>+</sup> cation as examples, the H-O bond distance of the sulfonic acid group of these ILs decreased as follows: [(PS)2bPy][H2PO4]2 (H46-O45 = 1.131 Å,  $H_{48}-O_{47} = 1.147$  Å) > [(PS)<sub>2</sub>bPy][HSO<sub>4</sub>]<sub>2</sub> (H<sub>48</sub>-O<sub>47</sub> = 1.088 Å,  $H_{46}-O_{45} = 1.105$  Å) > [(PS)<sub>2</sub>bPy][OTf]<sub>2</sub> (H46-O45 = 1.063 Å, H48–O47 = 1.073 Å), which was the reverse of their

Table 1 Calculation and comparison of  $H_0$  values of different SO<sub>3</sub>H-functionalized ILs in distilled water (20 °C)<sup>a</sup>

IL	A <sub>max</sub>	[I] (%)	$\left[\mathrm{IH}^{+}\right]\left(\%\right)$	$H_0$
a:blank	0.9516	100	0	
b:[PSPy][H <sub>2</sub> PO <sub>4</sub> ]	0.6320	66.4	33.6	1.0958
$c:[(BS)_2bPy][H_2PO_4]_2$	0.4389	46.1	53.9	0.7320
d:[PSPy][HSO4]	0.3533	37.1	62.9	0.5707
e:[PSPy][OTf]	0.1939	20.4	79.6	0.2087
$f:[(PS)_2bPy][H_2PO_4]_2$	0.1920	20.2	79.8	0.2033
g:[(BS) <sub>2</sub> bPy][HSO <sub>4</sub> ] <sub>2</sub>	0.1389	14.6	85.4	0.0329
h:[(PS) <sub>2</sub> bPy][HSO <sub>4</sub> ] <sub>2</sub>	0.1195	12.6	87.4	-0.0411
i:[(BS) <sub>2</sub> bPy][OTf] <sub>2</sub>	0.1109	11.65	88.35	-0.0799
j:[(PS) <sub>2</sub> bPy][OTf] <sub>2</sub>	0.0583	6.1	93.9	-0.3873

<sup>*a*</sup> Indicator: crystal violet (5 mg L<sup>-1</sup>, pK<sub>a</sub> = 0.8), IL (25 mmol L<sup>-1</sup>).

acidity sequence. When the anion of the ILs was the same, the H–O bond distances of bi-SO<sub>3</sub>H-functionalized ILs with the  $[(PS)_2 bPy]^{2+}$  cation were shorter than those with the  $[(BS)_2 bPy]^{2+}$  cation. Taking ILs with the  $[H_2PO_4]$  anion as examples, the H–O bond distance of the sulfonic acid group of these ILs decreased as follows:  $[(PS)_2 bPy][H_2PO_4]_2$  ( $H_{46}$ – $O_{45}$  = 1.131 Å,  $H_{48}$ – $O_{47}$  = 1.147 Å) <  $[(BS)_2 bPy][H_2PO_4]_2$  ( $H_{43}$ – $O_{42}$  = 1.209 Å,  $H_{54}$ – $O_{53}$  = 1.204 Å), which was also the reverse of their acidity sequence. The formation of a hydrogen bond was caused by a process of sharing the lone electron pair of the O or F atom with the H atom. As the hydrogen bond is stronger, the potential energy surface for the shared hydrogen is flattened, hence causing the delocalization of the shared proton, which most likely in this case, increases the acidity of the ionic liquids.<sup>25–28</sup>

The results obtained from experiments and the minimumenergy geometries of bi-SO<sub>3</sub>H-functionalized ILs revealed that the acidity and catalytic activity of the ILs were related to their structures. The bi-SO<sub>3</sub>H-functionalized ILs with a shorter H–O bond had stronger acidity and higher catalytic activity in the synthesis of  $\beta$ -acetamido ketones.

A comparative study on the catalytic activity of the novel bi-SO<sub>3</sub>H-functionalized ILs with other ILs was carried out using the reaction of 2-naphthol, benzaldehyde and urea as a model reaction (Fig. 4). Fang *et al.*<sup>29</sup> reported the application of pyridinium-based functionalized ILs in the synthesis of 1,2dihydro-1-phenylnaphtho[1,2-e][1,3]oxazine-3-one. However, those procedures encountered the problems of larger usage of the ILs and a relatively low yield of product. As shown in Fig. 4, under the same reaction conditions (150 °C, 60 min, 10 mol% IL, solvent-free), the best yield of 1,2-dihydro-1phenylnaphtho[1,2-e][1,3]oxazine-3-one was 94% in the prePublished on 10 April 2013. Downloaded by University of North Carolina at Chapel Hill on 31/10/2014 14:37:11.



Fig. 3 Molecular structures of the isolated  $[(BS)_2 bPy]^{2+}$  cation and ILs based on this cation.

sence of  $[(PS)_2bPy][OTf]_2$ . When the amount of IL dropped from 10 to 5 mol%, the yield of 2-dihydro-1-phenylnaphtho[1,2-e][1,3]oxazine-3-one could still reach as high as 92%. When  $[PSPy][HSO_4]$  was used as a catalyst, the yield was only 80% (85% reported by Fang *et al.*). It is very interesting that the sequence of catalytic activity of SO<sub>3</sub>H-functionalized ILs observed in the synthesis of 1,2-dihydro-1-phenyl-

naphtho[1,2-e][1,3]oxazine-3-one was in good agreement with the acidity order determined by the Hammett method. Therefore,  $[(PS)_2bPy][OTf]_2$  was chosen as the model catalyst for further investigation.

	$[(PS)_2 bPy]^+$	$[(PS)_2 bPy][H_2PO_4]_2$	[(PS) <sub>2</sub> bPy][HSO <sub>4</sub> ] <sub>2</sub>	$[(PS)_2bPy][OTf]_2$
H–O bond distance (Å) Distance between the anion and the sulfonic acid group (Å) Other hydrogen bonds in the ILs (Å)	H <sub>48</sub> -O <sub>47</sub> = 1.005 H <sub>46</sub> -O <sub>45</sub> = 1.006	$\begin{array}{l} H_{46} - O_{45} = 1.131 \\ H_{48} - O_{47} = 1.147 \\ H_{48} \cdots O_{50} = 1.306 \\ H_{46} \cdots O_{52} = 1.456 \\ H_{36} \cdots O_{55} = 2.297 \\ H_{9} \cdots O_{50} = 2.558 \\ H_{27} \cdots O_{52} = 2.472 \\ H_{27} \cdots O_{62} = 2.201 \end{array}$	$\begin{array}{l} H_{46} {-} O_{45} = 1.105 \\ H_{48} {-} O_{47} = 1.088 \\ H_{48} {-} O_{51} = 1.435 \\ H_{46} {-} O_{58} = 1.388 \\ H_{26} {-} O_{52} = 2.150 \\ H_{18} {-} O_{54} = 2.474 \\ H_{16} {-} O_{54} = 2.181 \\ H_{35} {-} O_{57} = 2.242 \\ H_{32} {-} O_{57} = 2.770 \\ H_{6} {-} O_{57} = 2.392 \end{array}$	$\begin{array}{l} H_{46}-O_{45}=1.063\\ H_{48}-O_{47}=1.073\\ H_{48}\cdots O_{52}=1.495\\ H_{46}\cdots O_{62}=1.530\\ H_{35}\cdots O_{53}=2.314\\ H_{6}\cdots O_{53}=2.596\\ H_{6}\cdots O_{51}=2.203\\ H_{27}\cdots O_{63}=2.173\\ H_{18}\cdots O_{63}=2.612\\ H_{18}\cdots O_{64}=1.979\end{array}$
	$\left[(BS)_2 bPy ight]^+$	$[(BS)_2 bPy][H_2 PO_4]_2$	$[(BS)_2 bPy][HSO_4]_2$	$[(BS)_2 bPy][OTf]_2$
H-O bond distance (Å) Distance between the anion and the sulfonic acid group (Å) Other hydrogen bonds in the ILs (Å)	$H_{43}-O_{42} = 0.989$ $H_{54}-O_{53} = 0.989$	$\begin{array}{l} H_{43}-O_{42}=1.209\\ H_{54}-O_{53}=1.204\\ H_{43}\cdots O_{55}=1.424\\ H_{54}\cdots O_{64}=1.226\\ H_{47}\cdots O_{58}=2.162\\ H_{17}\cdots O_{58}=1.778\\ H_{29}\cdots O_{59}=2.120\\ H_{5}\cdots O_{59}=1.697 \end{array}$	$\begin{array}{l} H_{43} {-} O_{42} = 1.141 \\ H_{54} {-} O_{53} = 1.105 \\ H_{54} {-} O_{39} = 1.399 \\ H_{43} {-} O_{34} = 1.330 \\ H_{57} {-} O_{35} = 2.670 \\ H_{56} {-} O_{35} = 2.642 \\ H_{17} {-} O_{35} = 1.890 \\ H_{14} {-} O_{36} = 1.935 \\ H_{30} {-} O_{38} = 2.079 \\ H_{6} {-} O_{38} = 2.647 \\ H_{6} {-} O_{40} = 1.812 \end{array}$	$\begin{array}{l} H_{43}-O_{42}=1.084\\ H_{54}-O_{53}=1.074\\ H_{43}\cdots O_{35}=1.340\\ H_{54}\cdots O_{59}=1.573\\ H_{29}\cdots O_{50}=1.975\\ H_{56}\cdots O_{50}=2.444\\ H_{30}\cdots O_{48}=2.322\\ H_{9}\cdots O_{48}=2.004\\ H_{64}\cdots O_{36}=2.655\\ H_{65}\cdots O_{36}=2.725\\ H_{17}\cdots O_{36}=1.871\\ H_{14}\cdots O_{37}=1.911\\ \end{array}$

To extend the preparative utility and generality of this MCR, several experimental trials illustrating this method for the synthesis of aromatic-condensed oxazinone derivatives were conducted. The results are summarized in Table 3. Benzaldehyde and other aromatic aldehydes containing electron-withdrawing groups (halide groups) or electrondonating groups (such as hydroxy, alkoxyl groups) were employed and were found to react well to give the correspond-



Fig. 4 Synthesis of 1,2-dihydro-1-phenylnaphtho[1,2-e][1,3]oxazine-3-one using different ILs.

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Table 3 Synthesis of various naphthalene-condensed oxazinone derivatives catalyzed by the IL [(PS)\_2bPy][OTf]\_2  $\,$ 



 Table 3 (Continued)



 $^a$  Isolated yield. Reaction conditions: 150 °C, 60 min, 5 mol% [(PS)\_2bPy][OTf]\_2.

ing 1,2-dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-ones in good yields.

It is well-known that the stability and reusability of a catalyst system are the two key factors that identify whether it has potential applications in industry. In order to test the catalyst reusability, the reaction was carried out in the presence of [(PS)2bPy][OTf]2 (5 mol%) under the optimal reaction conditions to synthesize 1,2-dihydro-1-phenylnaphtho[1,2-e][1,3]oxazine-3-one. When the reaction finished, the mixture was cooled to room temperature and washed with distilled water, then recrystallized from EtOAc-hexane (1:3) to afford the pure product. The catalyst was soluble in H<sub>2</sub>O and could be recovered and reused conveniently after heat treatment under vacuum at 70 °C for 2 h. The recovered rate of the catalyst could reach 95-98%. The results are shown in Fig. 5, and indicated that the isolated yield of the product 1,2dihydro-1-phenylnaphtho[1,2-e][1,3]oxazine-3-one was almost consistent after eight runs and [(PS)2bPy][OTf]2 could be reused at least eight times.

#### Conclusions

Several bi-SO<sub>3</sub>H-functionalized room temperature ILs have been synthesized, and their catalytic performances for the synthesis of naphthalene-condensed oxazinone derivatives have been studied by a combination of experimental and computational techniques. An easier synthesis procedure, reduced amount of catalyst, higher yield, wider applicability and reusability are the key features of this methodology. The results obtained from the experiments and the minimumenergy geometries of bi-SO3H-functionalized ILs revealed that the acidity and catalytic activity of ILs in the synthesis of naphthalene-condensed oxazinone derivatives were influence by their structures. The ILs with shorter H-O bond distances had stronger acidity and higher catalytic activity. These conclusions will be helpful for the detailed understanding of these bi-SO<sub>3</sub>H-functionalized ILs and will contribute to the design and synthesis of ILs in a "task specific" way.



Fig. 5 Reusability of the IL [(PS)<sub>2</sub>bPy][OTf]<sub>2</sub>

## **Experimental**

#### Synthesis and characterization of ILs

4,4'-Bis(3-sulfopropyl) bipyridinium ((PS)<sub>2</sub>bPy): 4,4'-bipyridine (1.56 g, 0.01 mol) and dimethyl sulfoxide (10 ml) were placed in a three necked flask with a stirrer. Then 1,3-propane sultone (3.05 g, 0.025 mol) was added slowly within 5 min. After that, the reaction mixture was stirred for 6 h at 80 °C. The reaction mixture was distilled under reduced pressure to remove dimethyl sulfoxide, then washed with ether five times and dried at 100 °C for 3 h. The final product (PS)<sub>2</sub>bPy was a white powder.

4,4'-Bis(4-sulfobutyl) bipyridinium ((BS)<sub>2</sub>bPy): 4,4'-bipyridine (1.56 g, 0.01 mol) and dimethyl sulfoxide (10 ml) were placed in a three necked flask with a stirrer. Then 1,4-butane sultone (3.40 g, 0.025 mol) was added slowly within 5 min. After that, the reaction mixture was stirred for 6 h at 80 °C. The reaction mixture was distilled under reduced pressure to remove dimethyl sulfoxide, then washed with ether five times and dried at 100 °C for 3 h. The final product (BS)<sub>2</sub>bPy was a white powder.

4,4'-Bis(3-sulfopropyl) bipyridinium bis(hydrogen sulfate) ([[(PS)<sub>2</sub>bPy][HSO<sub>4</sub>]<sub>2</sub>), 4,4'-bis(3-sulfopropyl) bipyridinium bis(hydrogen sulfate) ([[(PS)<sub>2</sub>bPy][H<sub>2</sub>PO<sub>4</sub>]<sub>2</sub>), 4,4'-bis(3-sulfopropyl) bipyridinium bis(trifluoromethanesulfonate) ([[(PS)<sub>2</sub>bPy] [OTf]<sub>2</sub>): under strong stirring, (PS)<sub>2</sub>bPy (0.01 mol) was dissolved in water (10 ml). 0.02 mol sulfuric acid, phosphoric acid or trifluoromethanesulfonic acid was dropped slowly into it at room temperature. After the dropping, the solution was heated up to 90 °C slowly and stirred for 2 h, then water was removed under vacuum at 70 °C for 3 h. The final products

 $[(PS)_2bPy][HSO_4]_2, [(PS)_2bPy][H_2PO_4]_2 \mbox{ and } [(PS)_2bPy][OTf]_2 \mbox{ were colorless liquids.}$ 

4,4'-Bis(4-sulfobutyl) bipyridinium bis(hydrogen sulfate) ([[BS)<sub>2</sub>bPy][HSO<sub>4</sub>]<sub>2</sub>), 4,4'-bis(4-sulfobutyl) bipyridinium bis(hydrogen sulfate) ([[BS)<sub>2</sub>bPy][H<sub>2</sub>PO<sub>4</sub>]<sub>2</sub>), 4,4'-bis(4-sulfobutyl) bipyridinium bis(trifluoromethanesulfonate) ([[BS)<sub>2</sub>bPy][OTf]<sub>2</sub>): under strong vigorous stirring, (BS)<sub>2</sub>bPy (0.01 mol) was dissolved into water (10 ml). 0.02 mol sulfuric acid, phosphoric acid or trifluoromethanesulfonic acid was dropped slowly into it at room temperature. After the dropping, the solution was slowly heated up to 90 °C and stirred for 2 h, then the water was removed under vacuum at 70 °C for 3 h. The final products [[BS)<sub>2</sub>bPy][HSO<sub>4</sub>]<sub>2</sub>, [[BS)<sub>2</sub>bPy][H<sub>2</sub>PO<sub>4</sub>]<sub>2</sub> and [[BS)<sub>2</sub>bPy][OTf]<sub>2</sub> were colorless liquids.

IR spectra and <sup>1</sup>H NMR spectra data for novel bi-SO<sub>3</sub>H-functionalized ILs were shown as follows:

[(PS)<sub>2</sub>bPy][HSO<sub>4</sub>]<sub>2</sub>: IR (KBr,  $\nu$ /cm<sup>-1</sup>): 3433, 3052, 1640, 1566, 1510, 1452, 1243, 1043, 612. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O)  $\delta$ : 2.40 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.90 (t, 4H, CH<sub>2</sub>SO<sub>3</sub>H), 4.78 (t, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 8.44 (d, 4H, py), 9.03 (d, 4H, py).

[(PS)<sub>2</sub>bPy][H<sub>2</sub>PO<sub>4</sub>]<sub>2</sub>: IR (KBr,  $\nu$ /cm<sup>-1</sup>): 3429, 3062, 1634, 1559, 1507, 1441, 1224, 1031, 616. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O)  $\delta$ : 2.38 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.85 (t, 4H, CH<sub>2</sub>SO<sub>3</sub>H), 4.76 (t, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 8.42 (d, 4H, py), 9.01 (d, 4H, py).

[(PS)<sub>2</sub>bPy][OTf]<sub>2</sub>: IR (KBr,  $\nu/cm^{-1}$ ): 3532, 3058, 1640, 1560, 1495, 1452, 1286, 1033, 643. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O)  $\delta$ : 2.37 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.85 (t, 4H, CH<sub>2</sub>SO<sub>3</sub>H), 4.73 (t, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 8.39 (d, 4H, py), 9.01 (d, 4H, py).

[(BS)<sub>2</sub>bPy][HSO<sub>4</sub>]<sub>2</sub>: IR (KBr,  $\nu$ /cm<sup>-1</sup>): 3431, 3065, 1639, 1556, 1506, 1446, 1236, 1058. 616. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O)  $\delta$ : 1.88 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.28 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 3.02 (t, 4H,

CH<sub>2</sub>SO<sub>3</sub>H), 4.81 (t, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 8.58 (d, 4H, py), 9.15 (d, 4H, py).

[(BS)<sub>2</sub>bPy][H<sub>2</sub>PO<sub>4</sub>]<sub>2</sub>: IR (KBr,  $\nu/cm^{-1}$ ): 3430, 3065, 1640, 1554, 1506, 1445, 1234, 1060, 617. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O)  $\delta$ : 1.89 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.30 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 3.04 (t, 4H, CH<sub>2</sub>SO<sub>3</sub>H), 4.83 (t, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 8.60 (d, 4H, py), 9.18 (d, 4H, py).

[(BS)<sub>2</sub>bPy][OTf]<sub>2</sub>: IR (KBr,  $\nu/cm^{-1}$ ): 3432, 3049, 1641, 1561, 1506, 1447, 1275, 1060, 638. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O)  $\delta$ : 1.87 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.28 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 3.03 (t, 4H, CH<sub>2</sub>SO<sub>3</sub>H), 4.81 (t, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 8.59 (d, 4H, py), 9.15 (d, 4H, py).

#### UV-vis acidity evaluation

ILs were dissolved into distilled  $H_2O$  and characterized by UVvis spectra with an Agilent B453 spectrophotometer.

#### **Computational methods**

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The minimum-energy geometries of  $bi-SO_3H$ -functionalized ILs and isolated  $[(PS)_2bPy]^+$ ,  $[(BS)_2bPy]^+$  cations were determined by performing *ab initio* geometry optimizations at the RHF/6–31(d, p) level using the Gaussian 03 program. A vibrational analysis was performed to ensure the absence of negative frequencies and to verify the existence of a true minimum.

#### General procedure for the synthesis of oxazinone derivatives

A mixture of an aldehyde (1 mmol), 2-naphthol (1 mmol), urea (1.3 mmol) and IL (5–10 mol%) was heated at 150  $^{\circ}$ C with stirring for one hour. After the completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and washed with distilled water, then recrystallized from EtOAc–hexane (1 : 3) to afford the pure product.

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