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# Synthesis and characterization of a new acid molten salt and the study of its thermal behavior and catalytic activity in Fischer esterification<sup>†</sup>

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A new acid molten salt was prepared and its structure elucidation was conducted by FTIR, 1D NMR, 2D NMR, and mass spectrometry. Further support to elucidate the chemical structure of the 1H,4Hpiperazine-N,N'-diium ring of the new acid molten salt was achieved by <sup>1</sup>H and <sup>13</sup>C NMR, and COSY analyses of 1H,4H-piperazine-N,N'-diium dibromide, which is synthesized and characterized for the first time in the current work. The analysis of FTIR and NMR spectra as well as pH and titrimetric analysis excluded the formation of  $[SO_4]^{2-}$  and the presence of an excess of  $H_2SO_4$ . Moreover, no distinguishing peak was detected for the acid proton of  $[HSO_4]^-$  in DMSO- $d_6$ . The thermal phase transition and thermal stability of the acid molten salt were also recorded, which approved the strong interaction between a dication and hydrogen sulfate anions. According to the acidity of the new molten salt, we encourage the study of its catalytic activity for the acetylation of n-pentanol using glacial acetic acid. Pentyl acetate was obtained in 89.0% conversion and 78.0% isolated yield. The <sup>1</sup>H NMR spectrum of the residue showed an excess of HOAc together with molten salt, whereas the <sup>1</sup>H NMR spectrum of the upper phase exhibited pure pentyl acetate. After separation of the upper phase, the residue was concentrated and used in the next run without further purification. No significant changes in the chemical structure and catalytic activity of the new molten salt were observed even after the 5th run. Two chiral alcohols, including (–)-menthol and (+)-borneol, as well as  $\alpha$ -tocopherol ( $\alpha$ -TCP) were also acetylated with acetic acid in the presence of the new acid molten salt under optimized reaction conditions, which afforded the desired acetates in high yields.

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# Introduction

The structure elucidation of new compounds is the most important part of chemistry and spectroscopy analyses are the first tool used for the characterization of chemical structures including IR, Raman, NMR, Mass, UV-Vis spectroscopy, *etc.* Hydrogen bonding (H-bonding) has been extensively studied using IR and NMR spectroscopy. The treatment of organic and inorganic bases by sulfuric acid (SA) can give acid or neutral salts containing  $[HSO_4]^-$  or  $[SO_4]^{2-}$  based on various parameters such as the mole ratio and basicity of base. <sup>1</sup>H NMR spectroscopy cannot be a key technique for differentiating species  $[HSO_4]^-$  or  $[SO_4]^{2-}$ , because the chemical shift of the acid proton of  $[HSO_4]^-$ 

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can be indistinguishable due to many parameters, for example, the poor solubility of the sample or the presence of water in the deuterated solvent, the rapid rate of proton exchange, the use of protic or aprotic deuterated solvent, H-bonding, *etc.*<sup>1</sup> Regarding the different symmetry of  $[\text{HSO}_4]^-$  or  $[\text{SO}_4]^{2-}$ ,  $C_{3v}$  and  $T_d$ , respectively, the characteristic vibrations have been displayed at different frequencies of IR spectra.<sup>2-4</sup>

Ionic liquids (ILs)/molten salts are well-known as liquids or solids containing cationic and anionic organic components. The physical and chemical properties of ILs/molten salts depend on the nature, size, and charge of cations and anions, therefore, they are tunable chemicals and can be modulated to acquire the appropriate properties. Although they were initially used as eco-friendly solvents in chemical reactions, ILs/molten salts are now employed in many fields including catalysis, electrochemistry, spectroscopy, and materials science.<sup>5</sup>

Pentyl acetate is a well-known ester in the flavoring industry due to its scent similar to those of bananas and apples.<sup>6</sup> It is also used in the coating industry for lacquers or paints, and as fuel in the Hefner lamp for photometry. Furthermore, it is a



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useful extractant in the preparation of penicillin, and a good solvent for synthetic and natural resins.<sup>7</sup> Carboxylic acid esters can be synthesized by using different catalysts in various reaction media.<sup>8</sup> Fischer esterification is the conventional and most common process for the esterification reaction.<sup>9</sup> Although numerous methods have been presented for the esterification reaction,<sup>10–18</sup> the development of practical and greener methods for the preparation of carboxylic acid esters using carboxylic acids instead of acid anhydride is still one of the challenging research topics. Therefore, developing an efficient and greener methodology to overcome some drawbacks and achieve a suitable balance between the economic and ecological aspects of the process is required.

In continuation of our interest in the synthesis of new ionic liquids/molten salts and investigation of their catalytic activity,<sup>19-22</sup> a new acid molten salt was fabricated via the reaction of piperazine (PZ) and SA in CH<sub>2</sub>Cl<sub>2</sub>. Its chemical structure was demonstrated by FTIR, 1D NMR, 2D NMR, and mass analysis. A comparison of the <sup>1</sup>H and <sup>13</sup>C NMR spectra of two new ionic liquids i.e., 1H,4H-piperazine-N,N'-diium hydrogen sulfate {(PZ-SA (1:2)} and 1H,4H-piperazine-N,N'-diium dibromide ( $[PZH_2]^{2+}-2Br^-$ ), proves the chemical structure of protonated **PZ** as a six-member ring bearing two  $> NH_2^+$  groups. Our results proved that only complementary spectral data and physical properties need to be considered for the structure elucidation of the organic salts containing sulfate or hydrogen sulfate anions. The thermal phase transition and thermal stability of a new acid molten salt were also recorded and described. Finally, the esterification of n-pentanol, two chiral alcohols, including (–)-menthol and (+)-borneol, as well as  $\alpha$ -tocopherol ( $\alpha$ -TCP) with glacial acetic acid, was studied using the new molten salt as a Brönsted acid catalyst under solvent-free conditions, which demonstrated the catalytic efficiency and high recyclability of the new molten salt.

### **Results and discussion**

### Structure elucidation of PZ-SA (1:2)

Due to rapid interconversion of the **PZ** ring at room temperature, the <sup>1</sup>H NMR spectrum of **PZ** showed only a singlet at 2.59 ppm for the axial and equatorial protons of methylene groups. Also, an extensive broadening of the N–H peak, centered at 2.04 ppm, was observed probably owing to H-bonding N–H···N and rapid **PZ** ring/nitrogen inversion (see the ESI,† Fig. S1). The formation of H-bonding between N–H groups of **PZ** and DMSO-*d*<sub>6</sub>, a good H-bond acceptor, resulted in the high field of N–H peak. One peak was detected at 46.92 ppm in the <sup>13</sup>C NMR spectrum which demonstrates a lack of a well-defined AA'BB' pattern (see the ESI,† Fig. S2).

Two different products can be formed when two equivalents of SA (98%) are added to **PZ**. The possible products contain the 1*H*,4*H*-piperazine-*N*,*N*'-diium dication together with different counterions,  $[HSO_4]^-$  or  $[SO_4]^{2-}$ , as shown in Scheme 1.

After stirring the reaction mixture in an aprotic solvent overnight, a white solid was isolated in high yield. The structure elucidation of the product was conducted by different spectroscopy analyses. In order to determine the acidity, complementary analyses including the triplet determination of pH and acid–base titration were also performed. Finally, the thermal phase transition and thermal stability of the white solid were recorded by DSC and TGA/DTA analyses, respectively, which demonstrated the strong electrostatic interaction and H-bond formation between protonated **PZ** and [HSO<sub>4</sub>]<sup>-</sup>.

The <sup>1</sup>H NMR consists of a single  $> \text{NH}_2^+$  peak at 8.96 and a single CH<sub>2</sub> at 3.33 ppm in DMSO-*d*<sub>6</sub>. The chemical shift of  $> \text{NH}_2^+$  implied the presence of weak intramolecular H-bonding in DMSO-*d*<sub>6</sub> (see the ESI,† Fig. S3). The sharp singlet at 3.33 ppm is at a higher chemical shift than **PZ** ( $\Delta \delta^1$ H = 0.72 ppm), probably due to the deshielding effect of  $> \text{NH}_2^+$ moieties and a decrease of the electron density around the protons (see the ESI,† Fig. S3). The <sup>13</sup>C NMR showed a single peak at 40.63 ppm, which is lower than that of **PZ** ( $\Delta \delta^{13}$ C = 6.29 ppm). This demonstrated the protonation of **PZ** as reported in the literature<sup>23</sup> (see the ESI,† Fig. S4).

The <sup>1</sup>H and <sup>13</sup>C NMR spectrum of the white solid was recorded in  $D_2O$  (see the ESI,† Fig. S5 and S6). The disappearance of the peak at 8.96 ppm demonstrated that the  $> NH_2^+$  protons are exchangeable and labile in  $D_2O$ .

The  ${}^{1}$ H,  ${}^{1}$ H-COSY spectrum exhibited the correlation between peaks at 3.33 and 8.96 ppm. This fact supported the formation of protonated **PZ** ring (see the ESI,† Fig. S7).

Furthermore, 1H,4H-piperazine-N,N'-diium dibromide ([PZH<sub>2</sub>]<sup>2+</sup>2Br<sup>-</sup>) was synthesized and characterized for further support of the chemical structure of the new acid molten salt. The PZ was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and two equivalents of HBr (ACS reagent, Sigma Aldrich 48 wt% in water) were added dropwise into the solution in an ice bath (Scheme 2).

After overnight stirring at room temperature, the solvent was removed by a rotary evaporator. The white waxy product was isolated during washing with  $CH_2Cl_2$ . The color changed to brown for a few hours. The brown waxy product was washed several times with  $CH_2Cl_2$ , which gave a pale brown waxy product (see the ESI,† Fig. S8). The <sup>1</sup>H, <sup>13</sup>C NMR, and <sup>1</sup>H, <sup>1</sup>H-COSY spectra of  $[PZH_2]^{2+}2Br^-$  exhibited a similar NMR pattern to those of the new molten salt (see the ESI,† Fig. S9–S11) (Table 1).



Scheme 1 The procedure, conditions, and two possible chemical structures of the reaction two equivalents of SA with PZ.

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Scheme 2 Reaction conditions for the synthesis of 1H,4H-piperazine-N,N'-diium dibromide.

Table 1 The collection of <sup>1</sup>H and <sup>13</sup>C NMR data of piperazine (**PZ**), new molten salt, and  $[PZH_2]^{2+}2Br^-$  (600 MHz, DMSO- $d_6$ )

Compound	CH-A, CH-A', CH-B and CH-B' (ax and eq) $(\delta^1$ H ppm)	>N-H (ax and eq) ( $\delta^1$ H ppm)	C-A, C-A', C-B, and C-B' $(\delta^{13}$ C ppm)
PZ New molten salt	2.59 3.33	2.04 8.96	46.92 40.36
$[PZH_2]^{2+}2Br^{-}$	3.36	9.25	40.25

In the presence of bromide anion, the methylene peak does not shift ( $\Delta \delta^1 H = 0.03 \text{ ppm}$ ), but the  $> NH_2^+$  protons shift from 8.96 ppm to 9.25 ppm ( $\Delta \delta^1 H = 0.29 \text{ ppm}$ ). This fact is probably due to stronger interactions between the dication and two bromide anions.

Further study was performed through recording and analysis of <sup>1</sup>H NMR of neat sulfuric acid (98%) and a sample of the new molten salt containing 1.0 mmol excess of SA (98%), which showed a sharp peak at 7.13 ppm and a multiplet peak in the range of 9.33–9.32 ppm, respectively (see the ESI,† Fig. S12 and S13). Based on the lack of sharp or broadened peaks in the above-mentioned range of the <sup>1</sup>H NMR spectrum of new molten salt, the presence of  $H_2SO_4$  was expelled.

An aqueous solution of the new molten salt (50 mg into 25 mL deionized water) displayed a pH of  $2.03 \pm 0.01$ , whereas a pH of  $1.69 \pm 0.01$  was detected for the same concentration of SA (98%). Also, the acid-base titration was performed using NaOH as a titrant (see the ESI,† Fig. S14). The titration result exhibited that the new acid molten salt is diprotic acid in the aqueous solution (50 mg in 25 mL) and the second acid dissociation is much weaker than the first one. Regarding the above results, the formation of  $[SO_4]^{2-}$  was also ruled out.

The absence of a sharp or broaden characterized peak for the acid proton of  $[HSO_4]^-$  in the <sup>1</sup>H NMR spectrum of the new acid molten salt could be due to various reasons, including H-bonding between DMSO- $d_6$  and the –NH and –SOH groups in the new acid molten salt or rapid proton exchange between  $[HSO_4]^-$  and residue water in DMSO- $d_6$ .<sup>24</sup>

The FTIR spectra of **PZ** and the new molten salt are depicted in Fig. 1. The new molten salt displayed a completely different IR spectrum compared with **PZ**. The **PZ** has a sharp strong peak at 3272 cm<sup>-1</sup> due to the N–H stretching vibration of two secondary amine functional groups, and this peak disappeared in the spectra of the new molten salt. The C–H stretching vibrations are assigned to peaks at 2958, 2953, 2834, and 2752 cm<sup>-1</sup>. The peaks at 1459 and 1417 cm<sup>-1</sup> were assigned to CNH deformation vibration, and the CCN deformation vibrations were displayed at 663 and 602 cm<sup>-1</sup>. The peaks at 1324 and 1270 cm<sup>-1</sup> were attributed to the C-N stretching vibration, and the asymmetric and symmetric C-C stretching vibrations of PZ were observed at 1128 and 1088 m<sup>-1</sup>.<sup>25</sup> Two peaks at 3444 and 3390 cm<sup>-1</sup> were assigned to the N-H stretching vibration of protonated piperazine ring.<sup>26</sup> The broad and medium intensity bands at 2481 and 2622 and 2790  ${
m cm}^{-1}$ are due to strong intermolecular hydrogen bonding of -NH and -SOH groups in the new molten salt.<sup>27</sup> The asymmetric and symmetric stretches of methylene groups were observed at 2997 and 2981 cm<sup>-1</sup>. Two medium intensity peaks at 1614 and 1455 cm<sup>-1</sup> were assigned to the deformation vibration modes of  $> NH_2^+$  groups.<sup>28</sup> A strong band at 995 cm<sup>-1</sup> with a shoulder at 968 cm<sup>-1</sup> is assigned to the SO<sub>2</sub> symmetric stretch vibrations. Two high-intensity bands at 1132 and 1101 cm<sup>-1</sup> are assigned to the  $SO_2$  asymmetric stretching mode. The sharp band at 870 cm<sup>-1</sup> and the strong bands at 577 and 525  $\text{cm}^{-1}$  are attributed to the deformation and bending modes of [HSO<sub>4</sub>]<sup>-.26,29,30</sup>

It is worth mentioning that the neat FTIR spectrum of molten-salt displays strong hydrogen bonds, while these hydrogen bonds are weakened due to the formation of hydrogen bonds with molecules DMSO- $d_6$  as a well-known H-bonding acceptor.

The LC-ESI-MS analysis of the new molten salt was performed at positive and negative modes. In positive ion mode, the *m/z* of 163.1083, 607.3755, 585.3944, and 563.3252 for cation species of  $[(PZ + CH_3OH + CO_2) + H]^+$ ,  $[(4PZ + 3CH_3OH + 2CO_2 + 2CO) + Na]^+$ ,  $[(4PZ + 3CH_3OH + 2CO_2 + 2CO) + H]^+$ , and  $[(3PZ + 4CH_3OH + 4CO_2) + H]^+$  were observed, respectively; as well as a dication species of  $[(4PZ + 4CH_3OH + 4CO_2) + 2H]^{2+}$  at *m/z* of 650.4174. In negative mode, the anion species of  $[PZ + HSO_4]^-$  and  $[PZ + HSO_4 + CH_3OH]^-$  were detected at *m/z* 183.0436 and 215.0698. The LC-MS results showed the presence of solvent and background gases, such as *m/z* 32 =  $[CH_3OH]^{+\bullet}$ , *m/z* 28 =  $[CO]^{+\bullet}$ , and *m/z* 44 =  $[CO_2]^{+\bullet}$  which exist often inside the mass spectrometer together with the anion and cation peaks.

Regarding the above complementary results, the structure (I) was approved for the new acid molten salt and it is being referred to as "PZ–SA (1:2)".

Ionic salts are named based on their melting points >100 °C and <100 °C as molten salts or ionic liquids, respectively,<sup>31</sup> and the melting point of PZ–SA (1:2) was in the range of 180–181 °C. Also, the PZ–SA (1:2) water content at relative humidity and the room temperature was  $2.10 \pm 0.05$  wt%.

#### Thermogravimetric analysis of PZ-SA (1:2)

Fig. 2 shows TGA/DTA curves recorded for PZ–SA (1:2) in a flow of nitrogen (20 mL min<sup>-1</sup>) at a constant heating rate of 10  $^{\circ}$ C min<sup>-1</sup> in the temperature range of 25–800  $^{\circ}$ C. A small



Fig. 1 FTIR spectra of piperazine (PZ) and the new acid molten salt.

mass loss (ca. 4.0 wt%) was observed below 150 °C which can indicate the amount of the physically adsorbed water and solvent in PZ-SA (1:2). There is no significant mass loss till ca. 296 °C. Above this temperature, PZ-SA (1:2) begins to decompose. The main stage of the thermal decomposition

takes place within the temperature range of 290-360 °C in two steps (ca. 80 wt%). Finally, the decomposition is completed at 720 °C.

It is indicated that the molecules of  $SO_{3(g)}$  and  $H_2O_{(g)}$  are released in the first stage of the thermal decomposition, which



Fig. 2 TGA/DTA of PZ-SA (1:2) under a N<sub>2</sub> atmosphere.

occurs within the temperature range 296–310 °C, and 1*H*,4*H*-piperazine-*N*,*N'*-diium sulfate is formed. This compound starts to lose the next sulfuric acid molecule as  $SO_{3(g)}$  and  $H_2O_{(g)}$  up to 360 °C. Above 360 °C a moderate decomposition of created carbon nitride takes place.

### DSC analysis of PZ-SA (1:2)

In order to study the thermal phase transition of PZ-SA (1:2), differential scanning calorimetry (DSC) was obtained in a flow of nitrogen (20 mL min<sup>-1</sup>) at a constant heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. The measurements were recorded in three sequential cycles with different initial and final heating and cooling temperatures (Fig. 3). The first cycle of heating/ cooling, in the range of 25-150 °C, has not shown any significant changes in the heat flux curve. One distinct anomaly was displayed on the second cycle of heating/cooling, at a range of 25–200 °C, which can be due to the degassing and dehydration. The sharp exothermic peak was observed at 131.7 °C with the estimated enthalpy change  $-60.9 \text{ J g}^{-1}$ . Due to the lack of mass loss in TGA around this temperature, this enthalpy was indicated as the crystallization point of PZ-SA (1:2). Also, the endothermic peak in the range of 174-182 °C was indicated as the melting point of PZ-SA (1:2) with the estimated enthalpy change of +57.4 J  $g^{-1}$ . Some weak endothermic peaks were observed that can be attributed to the degassing process and dehydration.

# Using the PZ-SA (1:2) as an acid catalyst for the esterification of *n*-pentanol with glacial acetic acid

The esterification of n-pentanol and acetic acid (HOAc) was carried out at different conditions and four parameters, including catalyst type and loading, the mole ratio of n-pentanol to HOAc, temperature, and reaction time was varied to find the optimal conditions. As the results showed (Table 2), the esterification conversion increased in the presence of the catalyst, and the

highest yield was observed in 100 mg of PZ–SA (1:2) (Table 2, entry 4). Also, the most effective mole ratio of *n*-pentanol to HOAc was 1.5 at 60  $^{\circ}$ C within 4 h (Table 2, entry 8).

Although a significant improvement was obtained in the conversion when the model reaction was carried out at higher temperatures up to 80 °C; no improvement was observed at higher temperatures (Table 2, entries 12 and 13). Due to the reversibility of the esterification process, increasing or decreasing reaction time caused a lower conversion (Table 2, entries 14–16). Based on the results in Table 2, entry 12 was indicated as the best experimental condition.

Moreover, enantioselectivity of the current protocol was studied through the acetylation of (–)-menthol ( $[\alpha]_{\rm D} = -50 \pm$ 1°, c = 10 in ethanol,  $\geq 99\%$  e.e.) and (+)-borneol ([ $\alpha$ ]<sub>D</sub> = +37  $\pm$  $2^{\circ}$ , c = 5 in ethanol, 99% e.e.). The (–)-menthyl acetate ( $[\alpha]_{D} =$  $-80^{\circ}$ , in benzene, 97% e.e.) and (+)-bornyl acetate ( $[\alpha]_{D} = +41^{\circ}$ , neat, 96% e.e.) were obtained in 68 and 71% isolated yield, respectively, with retention of the configuration at the chiral center (the optical rotation was recorded and reported based on the samples from Sigma-Aldrich) (Scheme 3). The esterification of  $\alpha$ -tocopherol ( $\alpha$ -TCP) was also carried out to investigate the potential of the current protocol for scale-up in industrial applications. Owing to the light and air sensitivity of tocopherols (TCPs) and the reduction of their antioxidant activity, they are often stabilized by the esterification reaction.<sup>32,33</sup> The esterification of the  $\alpha$ -TCP (8.61 g, ~20 mmol) and glacial acetic acid (1.71 mL, 30 mmol) was conducted in the presence of PZ-SA (1:2) (0.4 g, 1.4 mmol, 7.0 mol%) and was conducted at 80 °C. After four hours of incubation in the dark under the nitrogen atmosphere, the O-acetyl-\alpha-tocopherol (Ac-TCP) was detected in 89.2% yield by LC-MS (8.18 g).

The reusability of PZ–SA (1:2) was studied for the preparation of *n*-pentyl acetate under optimized reaction conditions. The PZ–SA (1:2), water, and unreacted HOAc form a combined



Fig. 3 DSC profile of PZ-SA (1:2) under a  $N_2$  atmosphere.

 Table 2
 Optimization of the esterification of *n*-pentanol and HOAc

Entry	Catalyst	Catalyst loading (mol%)	A mole ratio of HOAc to <i>n</i> -pentanol	Temp. (°C)	Reaction time (h)	Conversion <sup>a</sup> (%)
1	_	_	1.0:1.0	r.t.	4.0	0
2	PZ-SA (1:1)	3.5	1.0:1.0	r.t.	4.0	8
3	PZ-SA (1:2)	3.5	1.0:1.0	60	4.0	34
4	PZ-SA (1:2)	7.0	1.0:1.0	60	4.0	42
5	PZ-SA (1:2)	10.5	1.0:1.0	60	4.0	42
6	PZ-SA (1:2)	7.0	1.2:1.0	60	4.0	52
7	PZ-SA (1:2)	7.0	1.4:1.0	60	4.0	58
8	PZ-SA (1:2)	7.0	1.5:1.0	60	4.0	68
9	PZ-SA (1:2)	7.0	1.8:1.0	60	4.0	68
10	PZ-SA (1:2)	7.0	1.5:1.0	70	4.0	72
11	PZ-SA (1:2)	7.0	1.5:1.0	75	4.0	81
$12^b$	PZ-SA (1:2)	7.0	1.5:1.0	80	4.0	89
13	PZ-SA (1:2)	7.0	1.5:1.0	90	4.0	89
14	PZ-SA (1:2)	7.0	1.5:1.0	80	2.0	54
15	PZ-SA (1:2)	7.0	1.5:1.0	80	6.0	81
16	PZ-SA (1:2)	7.0	1.5:1.0	80	8.0	75



bottom phase, while *n*-pentyl acetate forms the upper phase. The PZ–SA (1:2) is not soluble in *n*-pentyl acetate, and the product can be separated from the bottom phase by simple decantation. Moreover, the formation of two phases facilitates the equilibrium to shift to the right toward a higher concentration of the product, which in turn improves the conversion in the esterification reaction. The desired product was detected in 89–82% yield during five runs.

In order to verify any advantage of using the new molten salt, a comparison of the catalytic activity of PZ–SA (1:2) and a few ionic liquids was performed for the model reaction. All mentioned ionic liquids were prepared according to previous reports in the literature. Then, the conversion of n-pentanol to *n*-pentyl acetate was

carried out using ionic liquids of PZ–HBr (1:2), TMDP-ClSO<sub>3</sub>H (1:2),<sup>21</sup> PZ–ClSO<sub>3</sub>H(1:2),34 Im-1,4-butane sultone (1:1),<sup>35</sup> and Im-1,3-propane sultone  $(1:1)^{36}$  that afford *n*-pentyl acetate in 24, 61, 59, 69, and 71% yields, respectively (monitored by GC-MS), while PZ–SA (1:2) gave 89% yield under similar conditions. It is worth mentioning that 1-bromopentane and acetyl bromide were also detected by GC-MS when PZ–HBr (1:2) was employed as a catalyst under optimized reaction conditions.

Also, the catalytic efficiency of the previous reported ionic liquids bearing hydrogen sulfate anion, including pyridinium hydrogen sulfate ( $[HPy]^+[HSO_4]^-$ ), *N*-methyl imidazolium hydrogen sulfate ( $[HMIm]^+[HSO_4]^-$ ), triethylammonium hydrogen sulfate

Table 3	Compare the catalytic efficiency of PZ-SA (1:2) and some previously reported ionic liquids					
Entry	Catalyst/amount	Temp. (°C)	Reaction time (h)	Conversion <sup><math>b</math></sup> (%)	Ref.	
$1^a$	$[HPy]^+[HSO_4]^-/25$ wt% (based on the mass of HOAc)	85	2	71	37	
$2^b$	$[HMIm]^+[HSO_4]^-/25$ wt% (based on the mass of HOAc)	85 (reflux)	2	55	38	
$3^b$	$[Et_3NH]^+[HSO_4]^-/25$ wt% (based on the mass of HOAc)	85 (reflux)	2	50	38	
$4^b$	$[N_{2224}]^+$ [HSO <sub>4</sub> ] <sup>-</sup> /25 wt% (based on the mass of HOAc)	85 (reflux)	2	39.5	38	
$5^c$	$[HMIm]^{+}[HSO_{4}]^{-}/25 \text{ wt\%}$ (based on the mass of HOAc)	80	1.5	46	39	
6 <sup>c</sup>	$[Py-(CH_2)_6-Py]^{2+2}$ 2[HSO <sub>4</sub> ] <sup>-/25</sup> wt% (based on the mass of HOAc)	80	1.5	52.3	39	
8	PZ-SA(1:2)/22.2 wt% (based on the mass of HOAc)	80	4	89	This work	

<sup>*a*</sup> Reaction conditions: acetic acid (0.20 mol), *n*-pentanol (0.20 mol). <sup>*b*</sup> Reaction conditions: acetic acid (0.02 mol), *n*-pentanol (0.02 mol). <sup>*c*</sup> Reaction conditions: acetic acid (0.25 mol), *n*-pentanol (0.25 mol).

Table 4 Corrosive study of stainless steel by PZ-SA (1:2) and SA (98%)<sup>a</sup>

		Weight of stainless steel (g)		
Entry	The duration time (h)	The solution of PZ–SA (1:2)	The solution of SA (98%)	
1	_	3.9942	3.9917	
2	2	3.4942	2.8012	
3	8	3.3638	1.3425	
4	24	3.2926	—	

<sup>*a*</sup> Two stainless steel sheets were polished, cleaned, and dried to constant weight, then placed into the solution of PZ–SA (1:2) and SA, respectively. After a mentioned time, two stainless steel sheets were pulled out carefully, washed in water, and dried and weighed.

 $([Et_3NH]^+[HSO_4]^-)$ , butyltriethylammonium hydrogensulfate  $([N_{2224}] + [HSO_4]^-)$ , and 1,1'-hexamethylene bis(pyridinium) hydrogen sulfate  $([Py-(CH_2)_6-Py]^{2+} 2[HSO_4]^-)^{36-38}$  are compared with PZ–SA (1:2) in Table 3. The results revealed that the nature and number of the cations and anions play a critical role to improve the conversion as previously reported. A key feature of PZ–SA (1:2) is that it contains two hydrogen sulfate anions which lead to a stronger acidity.

The corrosive property of catalysts is a crucial factor for acid catalytic experiments, and the reduction or elimination of corrosion plays a vital role in industrial processes. Therefore, a corrosive test was conducted with PZ–SA (1:2) and SA (98%) for a 316L austenitic stainless steel with 50, 20, and 0.5 mm in length, width, and thickness, respectively. The same amount of PZ–SA (1:2) and SA (98%) (100 mg) was added into 1 mL of deionized water, and the stainless steel plates were put into the solution. As one can see in Table 4, PZ–SA (1:2) showed a much weaker corrosion property compared with SA (98%), and the surface of stainless steel was intact even after 24 h. It seems that the formation of H-bonding between PZ and SA can lead to less corrosive acid salt.

### Experimental

### The synthesis of PZ–SA (1:2)

Piperazine (PZ) (ReagentPlus<sup>®</sup>,  $\geq$  99%, Merck, 1.723 g, 20 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (ACS grade,  $\geq$  99.5%, Sigma Aldrich, 20 mL) and stirred for 30 min. Then, sulfuric acid (SA) (98%, 2.18 mL, *ca.* 40 mmol) was added dropwise into the solution in an ice-bath. The solution was mixed by a stirrer at room temperature overnight. The upper layer was decanted and the bottom solid phase was washed several times with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). A white soluti was isolated in 94% yield (3.463 g) after removing the solvent and drying under vacuum.

### The esterification of *n*-pentanol and HOAc

Glacial acetic acid (RA grade, 100%, Friendemann Schmidt chemicals, 429  $\mu$ L, 7.5 mmol), and PZ–SA (1:2) (100 mg, 0.35 mmol, 7.0 mol%) were taken into a round-bottom flask with a side port and a capacity of 5.0 mL. The mixture was stirred, and *n*-pentanol (ReagentPlus<sup>®</sup>,  $\geq$  99%, Sigma Aldrich, 544  $\mu$ L, 5.0 mmol) was added. After four hours a few drops of deionized water were added, and the bottom phase, containing PZ-SA (1:2) and unreacted HOAc, was isolated by simple decantation or separating funnel (scale-up). To determine the conversion in the optimization step, the aliquot of the upper phase in *n*-hexane was analyzed using a GC-MS instrument. The purity of isolated ethyl pentanoate was analyzed using <sup>1</sup>H and <sup>13</sup>C NMR spectra (see the ESI,† Fig. S15 and S16). The reusability of PZ-SA (1:2) was investigated in the same procedure. After the concentration and removal of water, the residue was directly used in the next run.

### Conclusions

In conclusion, a new acid molten salt was synthesized and its chemical structure was characterized by FTIR, 1D NMR, and 2D NMR, mass spectra analyses. Moreover, 1H,4H-piperazine-N,N'diium bromide was synthesized and characterized to support the chemical structure of new acid molten salt. The pH and titrimetric results showed that the PZ-SA (1:2) is a diprotic acid salt. The thermal phase transition and thermal stability of new acid molten salt were also recorded which revealed high thermal stability of PZ-SA (1:2) as was expected due to the strong coulombic and electrostatic attractions along with H-bonding between the  $[PZH_2]^{2+}$  dication and  $[HSO_4]^-$ . Despite the pH of ca. 2.0, the corrosion property of PZ-SA (1:2) was much less than the same amount of sulfuric acid (98%), thus, PZ-SA (1:2) can be a safe and greener alternative for  $H_2SO_4$ . The PZ-SA (1:2) was employed to promote the esterification process of several alcohols such as *n*-pentanol, (–)-menthol, (+)-borneol, and  $\alpha$ -tocopherol with glacial acetic acid. Some advantages can be mentioned for the acetylation of alcohols using the new acid molten salt; for example, practical and simple procedure, good yield of the desired products, easy workup, high reusability of catalyst, avoiding catalysts containing heavy-metal, and minimizing hazardous waste generation. Our group is investigating other organic transformations in the presence of PZ-SA (1:2) with promising results.

# Conflicts of interest

There are no conflicts to declare.

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