## Pyrrolidine-based Dicationic Acidic Ionic Liquids: Efficient and **Recyclable Catalysts for Esterifications**

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A highly efficient and eco-friendly esterification was achieved by a series of novel dicationic acidic ionic liquids (DAILs) containing double  $-SO_3H$  cations. High yields of the product esters were obtained by using 2 mol% of the DAILs as catalysts and DAIL I could be reused at least ten times without appreciable loss of its efficiency.

Keywords esterification, dicationic acidic ionic liquids, pyrrolidine, reuse

#### Introduction

Esterification is one of the most significant reactions in industrial processes because of enormous practical importance and widely applications of organic esters.<sup>1</sup> Inorganic acid such as sulfuric acid, hydrochloric acid and orthophoric acid are traditional catalysts in the esters manufacturing industries. However, such acid catalytic system suffers from the problems of corrosion of equipments, contamination of water, producing large volumes of acidic wastes, and also facing the difficulty of recycling acid catalysts.<sup>2</sup> With the increasing ecological and economic concerns on the esterification process, great efforts have been made to replace the traditional inorganic acid and develop clean catalyst such as zeolite,<sup>3,4</sup> heteropoly acid,<sup>5</sup> solid superacid,<sup>6</sup> ion-exchange resin,<sup>7</sup> organic or inorganic salt for the production of esters.<sup>8</sup> Although previous-mentioned problems of corrosion and pollution have been partially solved, recycling of catalysts still remains unsatisfactory.

Ionic liquids (ILs) have attracted enough interest as catalysts and alternative solvents in green chemistry.9,10 Since Forbes and co-workers firstly reported a new approach for esterification using Brønsted acidic ILs as both solvents and catalysts, many Brønsted acidic ILs,<sup>11</sup> including SO<sub>3</sub>H-functionalized ILs,<sup>12-17</sup> ILs with acidic counteranion<sup>18</sup> and protonated acidic ILs<sup>19,20</sup> have been used in esterification reactions with satisfactory catalytic performances and stable catalyst recycling. However, most of these reports used large amounts of ILs to maintain their high catalytic efficiencies. With our continuous interest in development of novel and efficient acidic ILs for the esterification,<sup>21</sup> in this report, a series of pyrrolidine-based dicationic acidic ILs (DAILs) with double —SO<sub>3</sub>H moieties in their cations were synthesized for the first time (Scheme 1). Measurement results acidity and solubility reveal that of these SO<sub>3</sub>H-functionalized DAILs demonstrate quite strong acidities and visible hydrophilic properties, which are key factors for an efficient catalyst in esterification. These novel DAILs show good tolerance toward both aromatic- and aliphatic-acid with excellent yields of the desired esters at only 2 mol% catalyst loading. Furthermore, the separation of the product and DAILs can be facilely achieved by decantion. For comparison, the performances of monocationic acidic ILs (Figure 1, ILs V-VIII) were also tested.

Scheme 1 Synthesis of pyrrolidine-based dicationic acidic ILs



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$$V. R = CH_3, A = OTf$$

$$V. R = (CH_2)_5CH_3, A = OTf$$

$$VI. R = (CH_2)_9CH_3, A = OTf$$

$$VII. R = (CH_2)_9CH_3, A = TsO$$

Figure 1 Structures of pyrrolidine-based monocationic acidic ILs.

#### **Results and discussion**

#### Pyrrolidine-baesd acidic ionic liquids

The ILs used in this article are viscous liquids at room temperature, and some usual physicochemical properties were measured and listed in Table 1. It can be seen that both cations and anions have significant effects on their physicochemical properties. DAILs I-IV possess higher densities and viscosities than monocationic ILs V-VIII, and the viscosities of DAILs I-IV even could not be determined by the viscometer at 40 °C because of their high viscosities. As for the same cation, the ILs containing  $TsO^-$  (*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>) anion have higher densities and viscosities than the ILs containing OTf<sup>-</sup>  $(CF_3SO_3^-)$  anion. The increase of size or symmetry of the cation and anoin may lead to the interaction modification between the cation and the anion.

The phase behaviors and thermal stabilities of ILs I—VIII were investigated by DSC and thermogravimetric analysis, and the glass transition temperature  $(T_g)$  and the thermal decomposition temperatures  $(T_d)$  are shown in Table 1. ILs I—VIII have no freezing points and melting points but possess lower glass transition temperatures (-58.6—-43.0 °C). The thermal decomposition temperatures (with mass loss of 10%) of the ILs employed in this work are ranged 239.5—329.6 °C (Table 1). In comparison with monocationic ILs V—VIII, DAILs I—IV have some decrease in thermal stabilities [see *e.g.*, IL I (279.2 °C), vs. IL VI (325.6 °C)], and the ILs containing OTf<sup>-</sup> anion have higher thermal stabilities than the ILs containing TsO<sup>-</sup> anion.

Table 1 also gives the ionic conductivities of ILs I— VIII, and the data indicate that ILs I—VIII exhibit good ionic conductivities  $(1.23 \times 10^{-2} - 5.09 \times 10^{-2}$ S/m) at 25 °C. The ionic conductivities of DAILs are smaller than those of monocationic ILs, and slight decrease in ionic conductivity was also observed when OTf<sup>-</sup> anion of the IL was replaced by TsO<sup>-</sup> anion. This might be attributed to higher viscosity and larger ion size, which may reduce the rate of ion mobility.

Acidity and solubility are of great importance for acidic ILs, especially when they are used as catalysts in catalytic reactions. Table 2 shows the acidities and solubilities of ILs **I**—**VIII**. The Brønsted acidities of

| IL - | Density/(g•mL <sup><math>-1</math></sup> ) |        | Visicosity/(mPa•s) |        |          | T /°C   | Lonic conductivity $a/(\mathbf{Com}^{-1})$ |
|------|--|--------|--------------------|--------|----------|---------|--|
|      | 40 °C                                      | 100 °C | 40 °C              | 100 °C | $I_{g'}$ | $I_{d}$ | ionic conductivity /(S•m )                 |
| Ι    | —  | 1.3311 |                    | 550.8  | -56.4    | 279.2   | $2.99 \times 10^{-2}$                      |
| II   | —  | 1.3248 |                    | 611.2  | -57.2    | 294.7   | $1.68 \times 10^{-2}$                      |
| III  | _  | 1.3374 | —                  | 642.5  | -52.2    | 239.5   | $2.10 \times 10^{-2}$                      |
| IV   | —  | 1.3330 |                    | 719.8  | -52.8    | 258.1   | $1.23 \times 10^{-2}$                      |
| V    | 1.3129                                     | 1.2737 | 576.8              | 43.15  | -43.0    | 329.6   | $5.09 \times 10^{-2}$                      |
| VI   | 1.2737                                     | 1.2335 | 2988               | 138.3  | -58.4    | 325.6   | $4.28 	imes 10^{-2}$                       |
| VII  | _  | 1.1865 | —                  | 251.2  | -58.6    | 324.8   | $3.41 \times 10^{-2}$                      |
| VIII |  | 1.2007 |                    | 313.1  | -52.5    | 265.7   | $1.88 \times 10^{-2}$                      |

Table 1 Density, viscosity, glass transition temperature, thermal decomposition temperature and ionic conductivity of ILs I-VIII

<sup>*a*</sup> Measured at 25  $^{\circ}$ C.

Table 2 Acidities and solubilities of ILs I—VIII (25 °C)

| Enter | п    | $H_0^{\ a}$ | Miscibility with <sup>b</sup> |          |               |            |         |         |  |
|-------|------|-------------|-------------------------------|----------|---------------|------------|---------|---------|--|
| Enuy  | IL   |             | Water                         | Methanol | Ethyl acetate | Chloroform | Toluene | Diethyl |  |
| 1     | Ι    | -0.727      | +++                           | ++       | —             |            | —       | _       |  |
| 2     | II   | -0.202      | +++                           | ++       | —             |            | —       |         |  |
| 3     | III  | 0.607       | +++                           | ++       | —             |            | —       |         |  |
| 4     | IV   | 0.838       | +++                           | +++      | —             | +          | +       | +       |  |
| 5     | V    | 0.412       | +++                           | +++      | —             |            | +       | -       |  |
| 6     | VI   | 0.434       | +++                           | +++      | +             |            | +       | +       |  |
| 7     | VII  | 0.531       | +++                           | +++      | ++            | +          | ++      | +       |  |
| 8     | VIII | 1.273       | +++                           | +++      | ++            | +          | ++      | ++      |  |

<sup>*a*</sup> Hamette acidity function of the ILs.  $^{b}$  +++=easily miscible,+=slight miscible, -=immiscible.

these ILs were determined by Hammett method with UV-vis spectroscopy as reported.<sup>22</sup> The indicators used in the measurements were 2-nitro-aniline ( $pK_a = -0.2$ ) and 4-nitro-aniline ( $pK_a = 0.99$ ) respectively for the ILs with anions of OTf<sup>-</sup> (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) and TsO<sup>-</sup> (p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>). The obtained  $H_0$  values of the ILs are shown in Table 2. The Brønsted acidity order of the ILs can be infered from their  $H_0$  values as follows: I>II>VI>VI>VII>III>IV>VIII.

From Table 2, it can be seen that ILs **I**—**VIII** are all water-soluble. Due to double —SO<sub>3</sub>H groups contained in their cations, DAILs **I**—**IV** display poorer solubilities in organic solvents than monocationic ILs **V**—**VIII**. DAILs **I**—**IV** are almost immiscible with common organic solvents (ethyl acetate, chloroform, toluene and diethyl) except for methanol.

# Esterification catalyzed by pyrrolidine-based dicationic acidic ILs

Initially, the esterfication of methanol with benzoic acid was chosen as model reaction, and the effects of different acidic ILs on the reaction were investigated. Since there were two SO<sub>3</sub>H groups in DAILs I—IV compared to one SO<sub>3</sub>H group in ILs V—VIII, 2 mol% of ILs with respect to benzoic acid were used in the case of I—IV and 4 mol% in the case of V—VIII to allow for the comparison of their catalytic activities. The reactions were carried out at 80 °C for 8 h with the acid/alcohol/IL molar ratio of 1 : 1.5 : 0.02, and the results were presented in Table 3. Good yields were obtained in all cases. The yield of methyl benzoate increased slightly when the monocationic acidic ILs were replaced by DAILs [see *e.g.*, Entry 5 (92%), vs. Entry 1 (94%)]. While the differences in the alkanediyl chain

**Table 3** Results of esterification of methanol and benzoic acidcatalyzed by different  $ILs^a$ 

⊦ CH<sub>3</sub>OH \_\_\_\_\_

COOCH<sub>3</sub>

+ H<sub>2</sub>O

СООН

|       | $\sim$       |   |  |    |
|-------|--------------|---|--|----|
| Enter | п            | Fraction of m                             | _ Total yield of ester <sup>d</sup> /% |    |
| Ениу  | IL ·         | Upper phase/% Lower phase <sup>c</sup> /% |  |    |
| 1     | Ι            | >99.9                                     | < 0.1                                  | 94 |
| 2     | II           | 99.7                                      | 0.3                                    | 94 |
| 3     | III          | 98.2                                      | 1.8                                    | 79 |
| 4     | IV           | 96.9                                      | 3.1                                    | 78 |
| $5^b$ | $\mathbf{V}$ | 92.1                                      | 7.9                                    | 92 |
| $6^b$ | VI           | 83.3                                      | 16.7                                   | 92 |
| $7^b$ | VII          | 74.5                                      | 25.5                                   | 93 |
| $8^b$ | VIII         | 17.5                                      | 52.5                                   | 76 |

<sup>*a*</sup> Reaction conditions: 80  $^{\circ}$ C, 8 h. Acid/alcohol/IL molar ratio of 1 : 1.5 : 0.02. <sup>*b*</sup> Acid/alcohol/IL molar ratio of 1 : 1.5 : 0.04. <sup>*c*</sup> IL phase. <sup>*d*</sup> Yield of ester is based on crude isolated product. Purity of ester was tested by GC and the content of ester was no less than 95% (GC).

length between the two pyrrolidine moities or *N*-alkyl chain length of monocations almost did not influence the catalytic activities (Entries 1, 2, Entries 5—7). Significantly different catalytic activities were observed on variation of the counterions. Methyl benzoate with yield of 94% was obtained when **I** was used as catalyst, and that was 79% for **III**, which suggests that the anion plays a significant role in catalytic activity of esterification.

Upon completion of this reaction, the reaction systems were biphasic. The upper layer is the produced esters, and the lower layer is the IL phase that contains the unreacted materials, produced water and a portion of the produced esters. For comparing the separating efficiencies of ILs I-VIII from the produced ester, yields of methyl benzoate were got respectively from the upper and lower layers as shown in Table 3. The produced esters in the upper phase were isolated by decantation, and the esters dissolved in the lower phase were extracted with ethyl acetate. As seen in Table 3, the distributions of the ester between the two phases varied for different ILs. Because of their immiscibility with the ester, DAILs I-IV presented better biphasic behavior than monocationic ILs V-VIII, especially for I, in which, only less than 0.1% of methyl benzoate was dissolved (Table 3, Entry 1) and could be neglected. Therefore, in the following reactions, when I was used as catalyst, the yields of product esters were obtained directly from the upper phase, and the separation procedure was simplified in this way.

To optimize the reaction conditions, DAIL I was selected as the catalyst to investigate the effects of reaction time, temperature, catalyst dosage and alcohol/acid ratio on the esterification of methanol by benzoic acid, and the results are summarized in Table 4. The results demonstrate that chemical equilibrium can be reached in 6 h at 80  $^{\circ}$ C (Table 4, Entries 1—3). Therefore, other esterification reactions were conducted for 6 h. The ef-

 
 Table 4
 Results of esterication of methanol and benzoic acid under different conditions

| Entry <sup>a</sup> | Methanol/acid<br>molar ratio | Amount of<br>IL/mol% | <i>T</i> /℃ | Time/h | Yield <sup>b</sup> /% |
|--------------------|------------------------------|----------------------|-------------|--------|-----------------------|
| 1                  | 1.5:1                        | 2                    | 80          | 3      | 79                    |
| 2                  | 1.5:1                        | 2                    | 80          | 6      | 94                    |
| 3                  | 1.5:1                        | 2                    | 80          | 8      | 94                    |
| 4                  | 1.5:1                        | 0.5                  | 80          | 6      | 55                    |
| 5                  | 1.5:1                        | 1                    | 80          | 6      | 83                    |
| 6                  | 1.5:1                        | 3                    | 80          | 6      | 94                    |
| 7                  | 1.5:1                        | 2                    | 40          | 6      | 65                    |
| 8                  | 1.5:1                        | 2                    | 100         | 6      | 93                    |
| 9                  | 2:1                          | 2                    | 80          | 6      | 96                    |
| 10                 | 1:1                          | 2                    | 80          | 6      | 86                    |

<sup>*a*</sup> Reaction conditions: ionic liquid=IL **I**, benzoic acid (0.10 mol), methanol (0.15 mol). <sup>*b*</sup> Yield of ester is based on isolated crude product.

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fect of temperature on ester yield was examined in the temperature range 40-100 °C (Table 4, Entries 2, 7, 8) and the best reaction temperature was ca. 80 °C as shown in Table 4 (Entry 2). Increasing of the catalyst dosage had a propitious influence on the yield of methyl benzoate (Table 4, Entries 2, 4-6). When the amount of I increased from 0.5 mol% to 1 mol% (Table 4, Entries 4, 5), the yield of methyl benzoate increased rapidly from 55% to 83%, and a further increase to 2 mol% resulted in a 94% yield (Table 4, Entry 2). The data in Entries 2, 9, 10 (Table 4) indicated that the yield was enhanced while increasing the amount of methanol because the excess of one of the reactants makes the equilibrium shifting towards the products side. However, further increase of the alcohol/acid ratio to 2:1 (Entry 9) resulted in complication of separating the produced ester from ILs phase because overmuch methanol mixed with I and formed one phase at the end of the reaction. Thus, the best fit alcohol/acid ratio herein was 1.5:1 for the reaction (Entry 2).

The recycling performance of DAIL I in esterification of methanol with benzoic acid was investigated. As the foregoing results shown (Table 3), most of the methyl benzoate formed the upper layer, and only less than 0.1% of the ester was dissolved in DAIL I phase after the reaction. Thereupon, leaving out extraction procedure, I could be easily separated by decantation and regenerated by removing water in a vacuum at 110 °C for 1 h for the next reuse. This procedure was repeated for 10 cycles (See Figure 2), and even in the 10th recycle, over 88% product yield was still obtained. This indicates that I was stable enough to be recycled as the catalyst for the reaction.



Figure 2 Catalyst recycling of esterification of methanol with benzoic acid using IL I. Reaction conditions: benzoic acid (0.10 mol), methanol (0.15 mol), IL (2 mmol), 80  $^{\circ}$ C, 6 h.

Finally, the generality and scope of the esterification reaction of various acids with methanol or ethanol over DAIL I was investigated, and the results are summarized in Table 5. It was found that I was of very high activity for esterification. Both aliphatic acids and aromatic acids were smoothly transformed to esters in high yields. No by-products, such as olefins or ethers, were

detected. And all of the esters produced could be easily separated due to their immiscibility with the IL.

 Table 5
 Results of esterification for various acid and alcohol catalyzed by IL I

| Entry <sup>a</sup> | Acid                   | Alcohol           | T/℃ | Time/h | Yield <sup>b</sup> /% |
|--------------------|------------------------|-------------------|-----|--------|-----------------------|
| 1                  | Benzoic acid           | Ethanol           | 80  | 6      | 91                    |
| 2                  | Lauryl acid            | Methanol          | 80  | 10     | 98                    |
| 3                  | Stearic acid           | Methanol          | 80  | 10     | 94                    |
| 4                  | Acetic acid            | Ethanol           | 80  | 6      | 93                    |
| 5                  | <i>n</i> -Butyric acid | Methanol          | 80  | 3      | >99                   |
| 6                  | Acetic acid            | <i>n</i> -Octanol | 80  | 6      | 96                    |

<sup>*a*</sup> Reaction conditions: acid (0.10 mol), methanol (0.15 mol), n(acid) : n(methanol) : n(IL) = 1 : 1.5 : 0.02. <sup>*b*</sup> GC yield. No by-products were found.

#### Conclusion

We have prepared a series of novel dicationic acidic ionic liquids (DAILs) with strong acidities and visible hydrophilic properties, and established the potential application of these DAILs as efficient and reusable catalysts in esterification. Satisfactory yields of esters were obtained in the presence of 2 mol% of DAILs as catalysts for esterifications of methanol with aromatic or aliphatic acid, and the DAILs could be more easily separated from the produced esters than monocationic acidic ILs due to their immiscibility with organic solvents and DAIL I could be recycled and reused at least 10 times in esterification of methanol with benzoic acid. ILs with triflate anion showed better catalytic activities than those with *p*-toluene-sulfonic acid anion.

#### Experimental

#### **General remarks**

Toluene was distilled over Na. MeCN was distilled over CaH<sub>2</sub>. All other chemicals (A.R. grade) were commercially available and used without further purification. <sup>1</sup>H and <sup>13</sup>C NMR spectra: Varian INOVA 400 M spectrometer; chemical shifts ( $\delta$ ) were relative to Me<sub>4</sub>Si as an internal standard. ESI-MS: Waters ZQ 4000; in m/z (rel. %). The density and viscosity were measured by Anton Paar SVM 3000 Stabinger Viscometer at 40 and 100 °C. Thermal analysis and temperature-dependent phase behavior were examined in the circular range of -100 to 110 °C by using a NETZSCH DSC 200F3 Differential Scanning Calorimeter with scan rate of 10  $^{\circ}C/min$  under N<sub>2</sub> atmosphere. The samples for DSC measurements were tightly sealed in Al pans. The glass transition temperature  $(T_g)$  was recorded as the midpoint of the glass transition. The decomposition temperature  $(T_{\rm d})$  was recorded with 10% of mass loss by using a Pyris Diamond Perkin-Elmer TG/DTA with scan rate of 20 °C/min under  $N_2$  atmosphere. The samples for TG/DTA measurements were sealed tightly in Al<sub>2</sub>O<sub>3</sub> pans. The ion conductivity was measured by using a Mettler-FE30 digital conductivity-meter at 25  $^{\circ}$ C. Brønsted acidity: measurement of the  $H_0$  values with an Agilent 8453 UV-vis spectrophotometer and a basic indicator.

#### Preparation of SO<sub>3</sub>H-functionalized ionic liquids

Starting materials ( $\alpha, \omega$ -dipyrrolidino-alkanes and *N*-alkylpyrrolidine) were synthesized according to a similar approach as reported previously.<sup>23-25</sup>

Ionic liquids used in this article (Scheme 1 and Figure 1) were synthesized according to similar previous literatures.<sup>11-13</sup> 1,6-Dipyrrolidino-hexane (or 1,10-dipyrrolidino-decane) and 1,4-butane sultone were mixed and refluxed with a molar ratio of 1:2 in anhydrous acetonitrile for 48 h to give a white solid zwitterion salt. After washing the salt repeatedly with acetonitrile and ether to remove any unreacted starting material, the solid was dried in vacuo. Then, a twofold stoichiometric amount of CF<sub>3</sub>SO<sub>3</sub>H was added dropwise and the mixture stirred in anhydrous toluene at 80 °C for 24 h, resulting in the formation of dicationic acidic IL I or II. The IL phase was washed with toluene and ether to remove the non-ion residue and dried in vacuo. ILs III and IV could be synthesized when the zwitterion salts and  $p-CH_3C_6H_4SO_3H \cdot H_2O$  were mixed with a molar ratio of 1 : 2 in anhydrous ethanol and refluxed for 8 h. Yields of ILs **I**—**IV**: 91%—93%.

*N*-Alkylpyrrolidine reacted with 1,4-butane sultone in a molar ratio of 1 : 1 to form the white solid zwitterion. And conversion to the monocationic acidic ILs (**V**—**VIII**) was accomplished by combining equimolar quantities of the zwitterion and acid (CF<sub>3</sub>SO<sub>3</sub>H or *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H•H<sub>2</sub>O). Yields: 94%—96%.

All the above ILs are viscous liquids, and their spectral data are shown as follows.

**1,1'-(Hexane-1,6-diyl)bis**[*N*-(**4-sulfobutyl)pyrrolidine]trifluoromethanesulfonate** (**1** : **2**) (**I**) <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz)  $\delta$ : 3.36 (t, *J*=6.8 Hz, 8H), 3.16 (t, *J*= 8.0 Hz, 4H), 3.10 (t, *J*=8.0 Hz, 4H), 2.81 (t, *J*=7.2 Hz, 4H), 2.24 (t, *J*=6.8 Hz, 8H), 1.75 (t, *J*=8.0 Hz, 4H), 1.71 (t, *J*=8.0 Hz, 4H), 1.65 (t, *J*=6.8 Hz, 4H), 1.26 (t, *J*=6.8 Hz, 4H); <sup>13</sup>C NMR (D<sub>2</sub>O, 100 MHz)  $\delta$ : 119.71 (q, *J*<sub>C-F</sub>=315.2 Hz, CF<sub>3</sub>), 64.24, 64.21, 63.73, 49.89, 47.91, 21.90, 21.13. ESI-MS: *m*/*z* (+) 497.8, *m*/*z* (-) 149.0. Anal. calcd for C<sub>24</sub>H<sub>46</sub>F<sub>6</sub>N<sub>2</sub>O<sub>12</sub>S<sub>4</sub> (796.88): C 36.17, H 5.82, N 3.52; found C 36.05, H 5.91, N 3.50.

**1,1'-(Decane-1,10-diyl)** bis[*N*-(4-sulfobutyl)pyrrolidine]trifluoromethanesulfonate (**1**: **2**) (**II**) <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz)  $\delta$ : 3.33 (t, *J*=6.8 Hz, 8H), 3.14 (t, *J*= 8.0 Hz, 4H), 3.07 (t, *J*=8.0 Hz, 4H), 2.79 (t, *J*=7.2 Hz, 4H), 1.98 (t, *J*=6.8 Hz, 8H), 1.79 (t, *J*=8.0 Hz, 4H), 1.68 (t, *J*=8.0 Hz, 4H), 1.58 (t, *J*=6.8 Hz, 4H), 1.14— 1.18 (m, 12H); <sup>13</sup>C NMR (D<sub>2</sub>O, 100 MHz)  $\delta$ : 119.71 (q, *J*<sub>C-F</sub>=315.2 Hz, CF<sub>3</sub>), 62.80, 59.63, 58.75, 57.34, 49.95, 28.18, 27.97, 25.42, 22.71, 22.48, 22.35, 22.19, 21.48, 21.38, 21.14, 16.69. ESI-MS: *m*/*z* (+) 553.8, *m*/*z* (-) 149.0. Anal. calcd for C<sub>28</sub>H<sub>54</sub>F<sub>6</sub>N<sub>2</sub>O<sub>12</sub>S<sub>4</sub> (852.98): C 39.43, H 6.38, N 3.28; found C 39.35, H 6.52, N 3.21.

**1,1'-(Hexane-1,6-diyl)bis**[*N*-(**4-sulfobutyl)pyrrolidine]**-*p*-toluenesulfonate (**1**: **2**) (**III**) <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz)  $\delta$ : 7.52 (d, *J*=8.4 Hz, 4H), 7.20 (d, *J*=8.0 Hz, 4H), 3.35 (t, *J*=6.8 Hz, 8H), 3.18 (t, *J*=6.8 Hz, 4H), 2.86 (t, *J*=6.0 Hz, 4H), 2.80 (t, *J*=7.2 Hz, 4H), 2.22 (s, 6H), 2.03 (t, *J*=6.8 Hz, 8H), 1.77 (t, *J*=8.0 Hz, 4H), 1.63 (t, *J*=8.0 Hz, 4H); <sup>13</sup>C NMR (D<sub>2</sub>O, 100 MHz)  $\delta$ : 142.37, 139.39, 129.38, 125.26, 64.23, 64.21, 63.38, 57.34, 49.91, 47.90, 47.86, 21.91, 21.15, 20.39, 16.71. ESI-MS: *m*/*z* (+) 497.8, *m*/*z* (-) 171.2. Anal. calcd for C<sub>36</sub>H<sub>60</sub>N<sub>2</sub>O<sub>12</sub>S<sub>4</sub> (841.13): C 51.41, H 7.19, N 3.33; found C 51.25, H 7.27, N 3.26.

**1,1'-(Decane-1,10-diyl)bis**[*N*-(**4-sulfobutyl)pyrrolidine**]-*p*-toluenesulfonate (**1**: **2**) (**IV**) <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz)  $\delta$ : 7.50 (d, *J*=8.4 Hz, 2H), 7.19 (d, *J*=8.0 Hz, 2H), 3.31 (t, *J*=6.8 Hz, 8H), 3.07 (t, *J*=8.0 Hz, 4H), 2.78 (t, *J*=8.0 Hz, 4H), 2.22 (s, 6H), 1.97 (t, *J*= 6.8 Hz, 8H), 1.72 (t, *J*=8.0 Hz, 4H), 1.69 (t, *J*=8.0 Hz, 4H), 1.58 (t, *J*=6.8 Hz, 4H), 1.16—1.22 (m, 12H); <sup>13</sup>C NMR (D<sub>2</sub>O, 100 MHz)  $\delta$ : 141.69, 140.22, 129.21, 125.36, 59.99, 59.00, 57.83, 57.32, 49.94, 31.77, 29.24, 29.17, 28.74, 25.84, 22.43, 21.23, 20.87, 20.79, 19.19, 16.70. ESI-MS: *m*/*z* (+) 553.8, *m*/*z* (-) 171.2. Anal. calcd for C<sub>40</sub>H<sub>68</sub>N<sub>2</sub>O<sub>12</sub>S<sub>4</sub> (897.23): C 53.55, H 7.64, N 3.12; found C 53.47, H 7.69, N 3.08.

*N*-Methyl-[*N*-(4-sulfonbutyl)pyrrolidine]trifluoromethanesulfonate (V) <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz)  $\delta$ : 3.33 (t, *J*=4.8 Hz, 4H), 3.20 (t, *J*=7.6 Hz, 2H), 2.86 (s, 3H), 2.80 (t, *J*=7.2 Hz, 2H), 2.03 (t, *J*=4.8 Hz, 4H), 1.78 (t, *J*=7.6 Hz, 2H), 1.63 (t, *J*=7.6 Hz, 2H); <sup>13</sup>C NMR (D<sub>2</sub>O, 100 MHz)  $\delta$ : 119.71 (q, *J*<sub>C-F</sub>=315.2 Hz, CF<sub>3</sub>), 64.41, 63.54, 57.51, 50.06, 48.06, 22.06, 21.30, 16.86. ESI-MS: *m*/*z* (+) 222.3, *m*/*z* (-) 149.0. Anal. calcd for C<sub>10</sub>H<sub>20</sub>F<sub>3</sub>NO<sub>6</sub>S<sub>2</sub> (371.39): C 32.34, H 5.43, N 3.77; found C 32.37, H 5.59, N 3.80.

*N*-Hexyl-[*N*-(4-sulfonbutyl)pyrrolidine]trifluoromethanesulfonate (IL VI) <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz)  $\delta$ : 3.35 (t, *J*=4.8 Hz, 4H), 3.12 (t, *J*=7.6 Hz, 2H), 3.08 (t, *J*=7.6 Hz, 2H), 2.80 (t, *J*=7.2 Hz, 2H), 2.00 (t, *J*= 4.8 Hz, 4H), 1.76 (t, *J*=7.6 Hz, 2H), 1.62 (t, *J*=7.6 Hz, 2H), 1.55 (t, *J*=4.8 Hz, 4H), 1.12—1.21 (m, 6H), 0.55 (t, *J*=6.4 Hz, 3H); <sup>13</sup>C NMR (D<sub>2</sub>O, 100 MHz)  $\delta$ : 119.71 (q, *J*<sub>C-F</sub>=315.2 Hz, CF<sub>3</sub>), 62.79, 59.67, 58.78, 57.34, 49.93, 49.76, 30.35, 25.29, 22.99, 22.37, 21.66, 21.48, 21.39, 21.14, 16.70, 13.12. ESI-MS: *m*/*z* (+) 292.4, *m*/*z* (-) 149.0. Anal. calcd for C<sub>15</sub>H<sub>30</sub>F<sub>3</sub>NO<sub>6</sub>S<sub>2</sub> (441.53): C 40.80, H 6.85, N 3.17; found C 40.87, H 6.99, N 3.14.

*N*-Decyl-[*N*-(4-sulfonbutyl)pyrrolidine]trifluoromethanesulfonate (IL VII) <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz)  $\delta$ : 3.33 (t, *J*=4.8 Hz, 4H), 3.12 (t, *J*=7.6 Hz, 2H), 3.07 (t, *J*=7.6 Hz, 2H), 2.78 (t, *J*=7.2 Hz, 2H), 1.99 (t, *J*= 4.8 Hz, 4H), 1.71 (t, *J*=7.6 Hz, 2H), 1.63 (t, *J*=7.6 Hz, 2H), 1.55 (t, *J*=4.8 Hz, 4H), 1.10—1.12 (m, 12H), 1.00 (t, *J*=6.8), 0.69 (t, *J*=6.4, 3H); <sup>13</sup>C NMR (D<sub>2</sub>O, 100 MHz)  $\delta$ : 119.71 (q, *J*<sub>C-F</sub>=315.2 Hz, CF<sub>3</sub>), 62.99, 59.89, 59.34, 57.57, 50.26, 31.94, 29.54, 29.40, 29.04, 26.27, 23.06, 22.66, 21.84, 21.58, 16.94, 13.88. ESI-MS: *m/z* 

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(+) 348.5, m/z (-) 149.0. Anal. calcd for C<sub>19</sub>H<sub>38</sub>F<sub>3</sub>-NO<sub>6</sub>S<sub>2</sub> (497.63): C 45.86, H 7.70, N 2.81; found C 45.87, H 7.87, N 2.83.

*N*-Decyl-[*N*-(4-sulfonbutyl)pyrrolidine]-*p*-toluenesulfonate (IL VIII) <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz)  $\delta$ : 7.51 (d, J=8.4 Hz, 2H), 7.18 (d, J=8.0 Hz, 2H), 3.84 (t, J= 4.8 Hz, 4H), 3.31 (t, J=7.6 Hz, 2H), 3.24 (t, J=7.6 Hz, 2H), 2.79 (t, J=7.2 Hz, 2H), 2.21 (s, 3H), 1.97 (t, J= 4.8 Hz), 1.65 (t, J=7.6 Hz, 2H), 1.63 (t, J=7.6 Hz, 2H), 1.51 (t, J=4.8 Hz, 4H), 1.10—1.12 (m, 14H), 0.69 (t, J=6.8 Hz, 3H); <sup>13</sup>C NMR (D<sub>2</sub>O, 100 MHz)  $\delta$ : 142.62, 139.71, 129.62, 125.54, 62.97, 59.68, 58.87, 57.51, 50.17, 31.88, 29.43, 29.38, 29.30, 28.89, 26.08, 22.88, 22.64, 21.73, 21.65, 21.45, 20.68, 16.96, 13.95. ESI-MS: m/z (+) 348.5, m/z (-) 171.2. Anal. calcd for C<sub>25</sub>H<sub>45</sub>NO<sub>6</sub>S<sub>2</sub> (519.76): C 57.77, H 8.73, N 2.69; found C 57.65, H 8.81, N 2.67.

#### **Typical esterification procedure**

Weighed amounts of acid, alcohol, and IL were charged into a 25 mL flask equipped with a water cool condenser, then the reaction was allowed to proceed at the desired temperature for 3-10 h with vigorous stirring. Upon completion, the system became biphasic. The upper phase that contains the produced ester was isolated by decantation. The lower phase, the IL phase that contains the unreacted materials, water and a portion of the produced ester, was extracted with ethyl acetate (5 mL $\times$ 3). The combined washing layers were washed twice with 5 wt% NaHCO3 solution, then with H<sub>2</sub>O, dried over MgSO<sub>4</sub> and filtered, the filtrate was concentrated firstly by rotary evaporation then distilled under reduced pressure to get the crude product. Then the ILs could be regenerated by removing water under vacuum (1.33 Pa) at 110 °C for 1 h. The qualitative analyses were conducted with HP 6890/5793 GC-MS and the compositions of the products were analyzed by GC Agilent 6820 GC system equipped with FID detector.

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(E1003091 Pan, B.)