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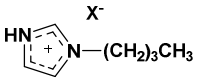
We investigated the tetraphenylporphyrin (TPP) preparation using the several acidic ionic liquids, $[HC_4im][X]$ (X^-= $CF_3SO_3^-$, ClO_4^-, Cl^-, $CF_3CO_2^-$, BF_4^-), as acid catalytic media. For such the acidic ionic liquids, the anion (X^-) of $[HC_4im][X]$ is related to the acidity of ionic liquids, and affect the porphyrin formations. This synthetic method using acidic ionic liquids can also be applied to other *meso*-substituted phenyl porphyrins and 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine, TPyP which has 4-pyridyl moieties at four *meso* positions. In $[HC_4im][CF_3CO_2]$, the TPyP could be obtained in 11% yield, and $[HC_4im][CF_3CO_2]$ could be reused at least 3 times without any loss of its catalytic activity. The TPyP synthesis methodology using the acidic ionic liquids can remove the acidic ionic liquids from TPyP only by easy filtration in contrast to traditional Alder method which need vacuum distillation or liquid-liquid extraction for removing propionic acid. Our proposed porphyrin preparation methods using the acidic ionic liquids potentially have wide applications to various useful porphyrin analogue.

Introduction

Porphyrins offer attractive features in a wide variety of catalysis, solar energy conversion, spectroscopy, and the development of organic metals. Among the porphyrins, *meso*-tetraphenylporphyrin, TPP is widely synthesized because of its easy synthetic procedure. TPP is prepared principally by two different methods, Lindsey method[1] and Adler method.[2] In the Lindsey method, condensation of benzaldehyde with pyrrole in halogenated solvent at room temperature followed by oxidation effectively provides TPP. In addition, other various porphyrin isomers, for example, *N*-confused tetraphenylporphyrin[3-5] and expanded porphyrins[6] have been produced by the modified Lindsey method. In the Adler method, refluxing propionic acid containing benzaldehyde and pyrrole open to the air followed by filtration of precipitated TPP obtained in 20% yield.[2] No other isomers than TPP such as NC-TPP are generated by the Adler method, while the advantage of this method is not required the oxidant and halogenated solvent unlike the Lindsey method. Both methods have an advantage of arranging different types of *meso*-substituted porphyrin, depending on the kind of aldehydes. Among various *meso*-substituted porphyrins, 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphyine, TPyP is considered to be one of the most important porphyrin components because TPyP can be used as a building block for multiporphyrin architectures[7] which have potential interest as zeolite like materials. In addition, TPyP is an important precursor for the water-soluble biomedical regents such as tetramethylpyridiuim porphyrin TMTPyP(4+). TPyP is formed efficiently by the Adler method. However, unlike the TPP which is formed a precipitation in propionic acid solution, TPyP is not separated from propionic acid as a precipitation due to the high solubility of TPyP. In the traditional Alder method, it is necessary for the isolation of TPyP from the reaction solution to distil the propionic acid with high boiling point (141^{o}C) or extract the propionic acid into the water phase. The distillation of reaction solution under reduced pressure has a possibility of the undesirable oligomerization of reactants or the decomposition of products. Therefore, we propose the simple methodology for the efficient synthesis of TPyP in the acidic ionic liquids using the Adler method.

Ionic liquids (ILs) could be suitable and environmentally safer replacements for the volatile, toxic, and flammable organic solvents. In fact, there are various reports about using ILs as reaction media and catalysis.[8] We have studied the utilization of ILs to prepare TPPs.[9] In the Lindsey method, we reported that hydrophobic and low viscous ILs such as

[bmim][NTf_2] and [bmim][PF_6] afforded TPPs in good yields and the advantages of the phase separated acidic IL catalyst for the Lindsey method. This method could reduce the halogenated reaction medium to 1/15 amount and could be reused ten times without any loss in catalytic activity. Recently we also reported the TPP preparation in acidic ILs using Adler method.[10] The Adler method is more green than the Lindsey method in terms of no use of harmful halogenated solvents, acid catalysts such as BF_3 and oxidant such as DDQ. Furthermore, the use of acidic ILs instead of propionic acid makes possible a more green porphyrin synthesis. In fact, the TPP was obtained in 15% yield in [HC_4im][CF_3CO_2], which was similar to the yield obtained in propionic acid (15%). In addition, [HC_4im][CF_3CO_2] could be reused at least 3 times without any loss in its catalytic activity. The use of the acidic ILs for porphyrins synthesis can afford the porphyrins without producing any acid waste. In the various acidic ILs, only the imidazolium type ILs, [HC_4im][X], could provide TPP. Herein we report the optimum acidic ILs for the porphyrin (TPP and TPyP) preparation with focus on their anion structures, and the simple and efficient green method for the synthesis of TPyP using the acidic ILs as the acid catalytic media instead of the propionic acid which is troublesome to remove from the reaction mixture.



X- = $CF_3SO_3^-$, [HC_4im][CF_3SO_3]
ClO_4^-, [HC_4im][ClO_4]
Cl^-, [HC_4im][Cl]
$CF_3CO_2^-$, [HC_4im][CF_3CO_2]
BF_4^-, [HC_4im][BF_4]

Fig. 1 The structure of Brønsted acidic ILs.

Results and discussion

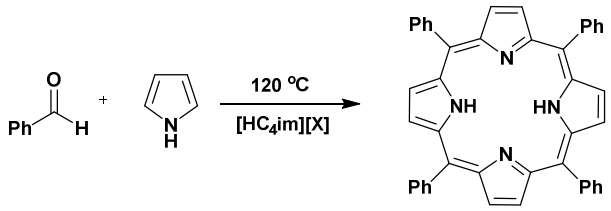
Suitable acidic ILs structure for TPP preparation

Fig. 1 shows the Brønsted acidic ILs employed in this study. These ILs are composed of the protic butylimidazolium cations and the different type of anions ([HC_4im][X]; X^-= $CF_3SO_3^-$, ClO_4^-, Cl^-, $CF_3CO_2^-$, BF_4^-). These acidic ILs are liquids at room temperature except for [HC_4im][ClO_4] and [HC_4im][CF_3CO_2]. Although [HC_4im][ClO_4] and [HC_4im][CF_3CO_2] are solid at room temperature, there were no problem in using them to pre-pare TPP and TPyP at temperatures above 100ºC.

Initially, we investigated the suitable acidic ILs structure for TPP preparation. We have previously reported that the existence of water in ILs reduced the porphyrin formation.[9b] Therefore, all the ILs were dried in vacuo (under 0.1 mbar) at 60 °C for 1 day prior to use in order to remove residual water rigorously. For example, the water content of [HC_4im][CF_3CO_2] is 0.04 wt%, while the water content of propionic acid is 0.01 wt%. Pyrrole and benzaldehyde was added to the acidic ILs at 120ºC. All the acidic ionic liquids used in this study can dissolve pyrrole and benzaldehyde completely and all the reactions were carried out under homogeneous conditions. After heating at 120ºC for 60 minutes, the solution was cooled to room temperature and diluted with distilled water. The forming porphyrin component was extracted with chloroform. After the organic phase was purified using silica gel column chromatography, the purple crystals were dried in vacuo to produce TPP, as shown in Table 1. The yield of TPP was dependent on the anion species (X^-). In ILs with the same cation, the relative acidity of ILs could be determined from the basicity of their anion (as described by its pK_a value).[11b, 12] In other words, there is a correlation between the basicity of the anions and the electolophilicity of the imidazolium cation, and the electolophilicity have an influent on the acidity of ILs. The yield of TPP for the reaction in the various ILs was compared against the pK_a values of the corresponding acid of the anion, HX in Table 1. With increasing the pK_a values of HX, the yield of TPP shows ameliorating tendency. The yield of TPP is the highest in [HC_4im][CF_3CO_2]. This finding indicated that the acidity of [HC_4im][CF_3CO_2] was most suitable for TPP preparation.

It is well known that the addition of salt such as NaCl promote the TPP formation.[13] The salt effect of ionic liquids on this TPP synthetic methods is considered. All these reaction are carried out under homogeneous conditions. TPP was not generated in the [bmim][NTf_2] without proton. When methanesulfonic acid was added to the reaction solution as an acid catalyst, TPP was generated in the [bmim][NTf_2] as well as in dichloromethane, and the reaction rate in the [bmim][NTf_2] is same level as the reaction in dichloromethane.[9b] These results suggest that the salt effect has little influence on the reactivity of the porphyrin synthesis with the acidic ionic liquids.

Table 1 TPP preparation in [HC_4im][X][a]



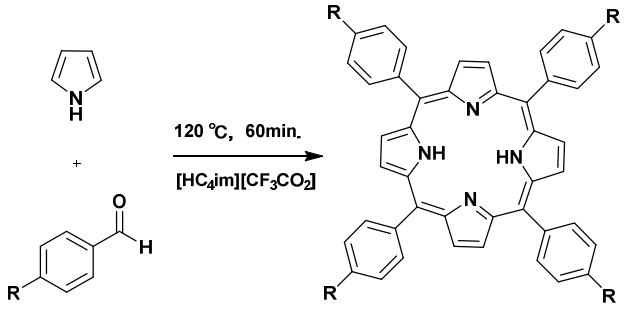
Anion of the ionic liquids, X^-	pK_a of acid of the anion, HX	Yield / %
$CF_3SO_3^-$	-14	0
ClO_4^-	-10	0
Cl^-	-8.0	4.6
$CF_3CO_2^-$	-0.25	15
BF_4^-	-0.5	9.0

[a] [pyrrole] = [aldehyde] = 280 mM, reaction time, 60 min.

Meso-phenyl substituted porphyrins preparation in $[HC_4im][CF_3CO_2]$

To examine the generality of this synthetic methodology using acidic ILs, we investigated the preparation of *meso*-substituted porphyrins in $[HC_4im][CF_3CO_2]$ (Table 2). The *meso*-substituted porphyrins were prepared by the reaction of pyrrole and corresponding 4-subtituted benzaldehyde. In $[HC_4im][CF_3CO_2]$, porphyrins were prepared in the same manner as described in the TPP preparation with only minor differences. In the preparation of *meso*-tetrakis(4-hydroxyphenyl)porphyrin (R=OH) and *meso*-tetrakis(4-methoxyphenyl)porphyrin ($R=OCH_3$) precipitates containing porphyrin components were formed when distilled water was added to the reaction mixtures containing $[HC_4im][CF_3CO_2]$ after the reaction. In these cases, unlike the preparation of TPP, porphyrins were separated from the $[HC_4im][CF_3CO_2]$ by filtration. On the other hand, *meso*-tetrakis(4-tolyl)porphyrin ($R=CH_3$) was prepared in the same manner as described in the TPP preparation. There was no significant difference in the yield between $[HC_4im][CF_3CO_2]$ and propionic acid. In $[HC_4im][CF_3CO_2]$, the porphyrin with an electron-donative substituent group can be easily generated though the porphyrin with an electron-withdrawing substituent cannot be generated. Although the yields of porphyrins were not the same, $[HC_4im][CF_3CO_2]$ has a similar tendency to propionic acid.

Table2 *Meso*-phenyl substituted porphyrins preparation in $[HC_4im][CF_3CO_2]$[a]



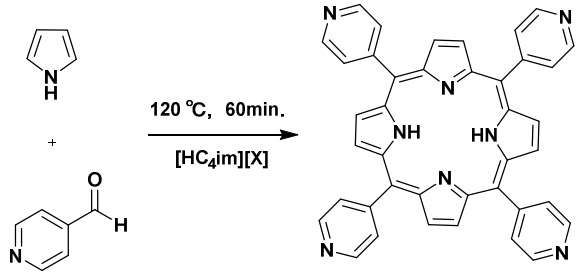
-R	Yield / %	
Solvent =	$[HC_4im][CF_3CO_2]$	propionic acid
$-CH_3$	19	21
-OH	13	7.6
$-OCH_3$	6.7	5.1
-CN	0	0

[a] [pyrrole] = [aldehyde] = 280 mM.

Tetrapyridyl-porphyrin preparation in acidic ILs

In contrast to TPP and other *meso*-substituted porphyrins preparation, TPyP is very hard to remove from the propionic acid because of the high solubility of TPyP in propionic acid. Therefore, following TPP preparation, we examined the simple and efficient green method for the synthesis of TPyP using the acidic ILs instead of propionic acid. Pyrrole and 4-pyridinecarboxaldehyde was added to the acidic ILs at 120ºC. All the acidic ionic liquids used in this study also can dissolve pyrrole and 4-pyridinecarboxaldehyde completely and all the reactions were carried out under homogeneous conditions. After heating at 120ºC for 60 min, the solution was cooled to room temperature and diluted with distilled water and a precipitate formed. The solution was filtered, and the cake on the funnel was washed with distilled water. The precipitate was diluted with chloroform and was purified using silica gel column chromatography, the purple crystals were dried in vacuo to produce TPyP, as shown in Table3. $[HC_4im][BF_4]$ showed high TPyP yield of 11%, which was similar to the yield obtained in propionic acid (14%) using the traditional Adler method. TPyP could also be obtained in other $[HC_4im][X]$. As aforementioned, the yield of TPP was dependent on their anion species (X^-). Although it did not show as clear tendency as the case of TPP synthesis, the yield of TPyP was also dependent on their anion species (X^-). It is interesting to note that the reaction in $[HC_4im][X]$ was very simple for removing the reaction solvent from the producing TPyP component as compared with the reaction in propionic acid. This TPyP synthesis methodology using $[HC_4im][X]$ could remove $[HC_4im][X]$ from TPyP only by easy filtration, while removal of propionic acid which is used in traditional Adler method requires troublesome vacuum distillation or liquid-liquid extraction.

Table3 TPyP preparation in [HC4im][X][a]



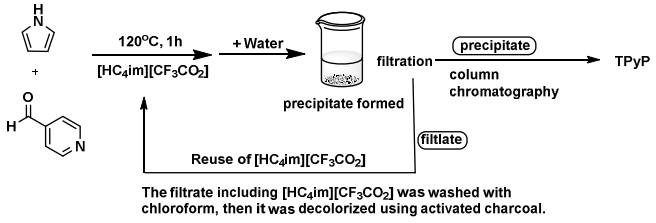
Anion of the ionic liquids, X^-	pK_a of acid of the anion, HX	Yields / %
$CF_3SO_3^-$	-14	7.4
ClO_4^-	-10	8.6
Cl^-	-8.0	6.0
$CF_3CO_2^-$	-0.25	11
BF_4^-	-0.5	9.0

[a] [pyrrole] = [4-pyridinecarboxaldehyde] = 280 mM, reaction time, 60 min.

Recycling of $[HC_4im][CF_3CO_2]$ in the preparation of Tetrapyridyl-porphyrin preparation

The most effective catalysts for the TPyP preparation, $[HC_4im][CF_3CO_2]$, was reused for the second and third cycle of the reaction, as shown in Table 4. After the first cycle, $[HC_4im][CF_3CO_2]$ was diluted with distilled water. The precipitate including TPyP was removed by filtration. The filtrate including $[HC_4im][CF_3CO_2]$ was washed with chloroform, then it was decolorized using activated charcoal. After evaporating the water, it was confirmed using ^{1}H NMR that $[HC_4im][CF_3CO_2]$ does not contain impurities. The recovery rate of $[HC_4im][CF_3CO_2]$ is 92 %. Pyrrole and 4-pyridinecarboxaldehyde were added to the recovered acidic ILs, and the reaction was carried out again. This procedure was repeated over four cycles without supplying any acid catalysts. Over the fourth cycles, the isolated yield of TPyP ranged from 11% to 10%. Continuous recycling of $[HC_4im][CF_3CO_2]$ did not affect the porphyrin yield at all. Although high reaction temperature (200 ^{o}C) is required, a solvent-free TPyP synthetic method has also been reported.[14,15] The yield of TPyP utilizing $[HC_4im][CF_3CO_2]$ is similar level to the yield by solvent-free method. Therefore, this method is an important alternative to the solvent-free method. This method using the acidic ionic liquids is greener than Lindsey and Adler methods, which the solvent can be recycled. The solvent-free method uses less solvent than these methods, however, the method using the acidic ionic liquids is not required higher reaction temperature and energy unlike the solvent-free method (reaction temperature 200 ^{o}C).

Table4 Recycling of $[HC_4im][CF_3CO_2]$ in the preparation of TPyP[a]



Cycle	1	2	3	4
Yield / %	11	10	10	10

[a] [pyrrole] = [4-Pyridinecarboxaldehyde] = 280 mM, reaction time 60 min, reaction temperature 120 ºC.

Experimental

Materials

All reagents were reagent grade and were used as received from Aldrich without further purification. All acidic ionic liquids ($[HC_4im][X]$; X^-= $CF_3SO_3^-$, ClO_4^-, Cl^-, $CF_3CO_2^-$, BF_4^-) were prepared according to published procedures.[11] All the ILs were dried *in vacuo* (under 0.1 mbar) at 60 ^{o}C for 1 days prior to use. TLC analyses was performed on 0.25 mm Silica gel Merck 60 F254 plates. NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts (δ ppm) in $CDCl_3$ were reported downfield from TMS (0 ppm) for ^{1}H NMR.

General Procedure for *meso*-tetraphenylporphyrin, TPP (1) in Acidic Ionic Liquids

TPP was prepared in the 5 spices of acidic ionic liquids ($[HC_4im][X]$; X^-= $CF_3SO_3^-$, ClO_4^-, Cl^-, $CF_3CO_2^-$, BF_4^-). In the case of $[HC_4im][CF_3CO_2]$, pyrrole (0.19 mL, 2.8 mmol) and benzaldehyde (0.285 mL, 2.8 mmol) were added to 10 mL of the $[HC_4im][CF_3CO_2]$ at 120ºC. After heating at 120ºC for 60 minutes, the solution was cooled to room temperature and diluted with distilled water (50 mL). The forming porphyrin component was extracted with chloroform (50 mL). The organic layer was washed with brine (50 mL) and dried over anhydrous sodium sulphate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel ($CHCl_3$) to give the 65mg of TPP (**1**) (0.11 mmol, 15 %) as purple crystals. ^{1}H NMR (400 MHz, $CDCl_3$-TMS): δ = 8.84 (s, 8H, β-pyrrole), 8.21 (d, 8H, phenyl-ortho), 7.79-7.71 (m, 12H, phenyl-meta, para), 2.77 (s, 2H, NH).

Procedure for *meso*-tetrakis(4-tolyl)porphyrin, (2) in $[HC_4im][CF_3CO_2]$

Pyrrole (0.155 mL, 2.2 mmol) and 4-tolualdehyde (0.264 mL, 2.2 mmol) were added to 8.0 mL of the $[HC_4im][CF_3CO_2]$ at 120ºC. After heating at 120ºC for 60 min, the solution was cooled to room temperature and diluted with distilled water (50 mL). The forming porphyrin component was extracted with chloroform (50 mL). The organic layer was washed with brine (50 mL) and dried over anhydrous sodium sulphate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel ($CHCl_3$), to give 70 mg of (**2**) (0.10 mmol, 19 %) as purple crystals. ^{1}H NMR (400 MHz, $CDCl_3$-TMS): δ = 8.85 (s, 8H, β-pyrrole), 8.09 (d, 8H, tolyl-ortho), 7.55 (d, 8H, tolyl-meta), 2.70 (s, 12H, CH_3), 2.77 (s, 2H, NH).

Procedure for *meso*-tetrakis(4-hydroxyphenyl)porphyrin, (3) in $[HC_4im][CF_3CO_2]$

Pyrrole (0.155 mL, 2.2 mmol) and 4-hydroxybenzaldehyde (0.27 g, 2.2 mmol) were added to 8.0 mL of the $[HC_4im][CF_3CO_2]$ at 120ºC. After heating at 120ºC for 60 min, the solution was cooled to room temperature and diluted with distilled water (50 mL) and a precipitate formed. The solution was filtered, and the cake on the funnel was washed with distilled water. The precipitate was diluted with a minimum amount of acetone and purified by column chromatography on silica gel (hexane / acetone). The eluate was evaporated to dryness and the residue was recrystallized from MeOH / $CHCl_3$ to give 50 mg of (**3**) (0.074 mmol, 13 %) as purple crystals. ^{1}H NMR (400 MHz, $CDCl_3$-TMS):δ = 9.97 (s, 4H, OH), 8.87 (s, 8H,

β-pyrrole), 8.00 (d, 8H, phenol-ortho), 7.21 (d, 8H, phenol-meta), 2.88 (s, 2H, NH).

Procedure for *meso*-tetrakis(4-methoxyphenyl)porphyrin, (4) in [HC_4im][CF_3CO_2]

Pyrrole (0.155 mL, 2.2 mmol) and 4-anisaldehyde (0.273 mL, 2.2 mmol) were added to 8.0 mL of the [HC_4im][CF_3CO_2] at 120ºC. After heating at 120ºC for 60 min, the solution was cooled to room temperature and diluted with distilled water (50 mL) and a precipitate formed. The solution was filtered, and the cake on the funnel was washed with distilled water. The precipitate was diluted with a minimum amount of chloroform and purified by column chromatography on silica gel (10% acetone / chloroform). The eluate was evaporated to dryness and the residue was recrystallized from MeOH / $CHCl_3$ to give 28 mg of (**4**) (0.037 mmol, 6.7 %) as purple crystal. ^{1}H NMR (400 MHz, $CDCl_3$-TMS): δ = 8.86 (s, 8H, *β*-pyrrole), 8.12 (d, 8H, methoxyphenyl-ortho), 7.29 (d, 8H, methoxyphenyl-meta), 4.10 (s, 12H, CH_3), 2.70 (s, 12H, CH_3), 2.77 (s, 2H, NH).

Procedure for *meso*-tetrakis(4-cyanophenyl)porphyrin, (5) in [HC_4im][CF_3CO_2]

Pyrrole (0.155 mL, 2.2 mmol) and 4-cyanobenzaldehyde (0.29 g, 2.2 mmol) were added to 8.0 mL of the [HC_4im][CF_3CO_2] at 120ºC. After heating at 120ºC for 60 min, the solution was cooled to room temperature and diluted with distilled water (50 mL) and a precipitate formed. The solution was filtered, and the cake on the funnel was washed with distilled water. However, further purification procedures were not carried out because only a trace of porphyrin formation was observed by TLC.

General Procedure for porphyrins, (2), (3), (4), (5) in propionic acid

These compounds were prepared in almost same procedure with only minor differences. In the case of (2), Pyrrole (0.155 mL, 2.2 mmol) and 4-tolualdehyde (0.264 mL, 2.2 mmol) were added to the propionic acid (8.0 mL) and refluxed for 60 min, the solution was cooled to room temperature and diluted with distilled water (50 mL) and a precipitate formed. The solution was filtered, and the cake on the funnel was washed with hot distilled water. The precipitate was dried *in vacuo* to produce 77.8 mg of TPP (0.116 mmol, 21 %).

General Procedure for 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphyine, TPyP, (6) in Acidic Ionic Liquids

TPyP was prepared in the 5 spices of acidic ionic liquids ([HC_4im][X]; X^-= $CF_3SO_3^-$, ClO_4^-, Cl^-, $CF_3CO_2^-$, BF_4^-). In the case of [HC_4im][CF_3CO_2], pyrrole (0.19 mL, 2.8 mmol) and 4-pyridinecarboxaldehyde (0.263 mL, 2.8 mmol) were added to [HC_4im][CF_3CO_2] (10 mL) at 120ºC. After heating at 120ºC for 60 minutes, the solution was cooled to room temperature and diluted with distilled water (50 mL) and a precipitate formed. The solution was filtered, and the cake on the funnel was washed with distilled water. The precipitate was diluted with a minimum amount of chloroform and purified by column chromatography on silica gel (MeOH / $CHCl_3$). The purple crystals were dried *in vacuo* to produce 48 mg of TPyP (**6**) (0.077 mmol, 11 %). ^{1}H NMR (400 MHz, $CDCl_3$-TMS): δ = 9.07 (d, 8H, pyridyl-meta), 8.87 (s, 8H, β-pyrrole), 8.16 (d, 8H, pyridyl-ortho), 2.92 (s, 2H, NH).

Procedure for 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphyine, TPyP, (6) in propionic acid

Pyrrole (0.19 mL, 2.8 mmol) and 4-pyridinecarboxaldehyde (0.263 mL, 2.8 mmol) were added to propionic acid (10 mL) and refluxed for 60 minutes, the solution was cooled to room temperature. After the oligomer component was filtered off, propionic acid was removed by distillation under reduced pressure to give a dark residue. The residue was purified by column chromatography on silica gel (MeOH / $CHCl_3$). The purple crystals were dried *in vacuo* to produce 61 mg of TPyP **(6)** (0.098 mmol, 14 %).

Conclusions

We have shown that the relationship between the anion structure of [HC_4im][X] and its acidity plays an important role in Adler porphyrin preparation method. The general TPyP preparation in propionic acid need troublesome removing process, whereas the reaction in [HC_4im][CF_3CO_2] produced TPyP in 11% yield and TPyP can separate from the ILs only by filtration. In other words, this findings suggest that the using of [HC_4im][X] ILs can purified TPyP easier than the traditional Adler method using propionic acid. In addition, [HC_4im][CF_3CO_2] could be reused at least 3 times without any loss of the catalytic activity.

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Notes and references

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16 The abbreviations and full name of the used IL are shown below:
$[HC_4im][CF_3SO_3]$, 1-butylimidazolium trifluoromethanesulfonate
$[HC_4im][ClO_4]$, 1-butylimidazolium perchlorate
$[HC_4im][Cl]$, 1-butylimidazolium chloride
$[HC_4im][CF_3CO_2]$, 1-butylimidazolium trifluoroacetate
$[HC_4im][BF_4]$, 1-butylimidazolium tetrafluoroborate

