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A simple method for efficient synthesis of tetrapyridyl-porphyrin using Adler method in acidic ionic liquids

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

Introduction

Porphyrins offer attractive features in a wide variety of applications including 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, the Lindsey method[1] and the Adler method.[2] In the Lindsey method, condensation of benzaldehyde with pyrrole in a halogenated solvent at room temperature is followed by oxidation to effectively provide 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. By means of the Adler method, TPP was prepared by refluxing in propionic acid containing benzaldehyde and pyrrole open to the air. After filtration, TPP was 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 that the use of an oxidant and halogenated solvent is not required unlike in the Lindsey method. Both methods have an advantage of preparing different types of *meso*-substituted porphyrins, depending on the kind of aldehydes used. Among the various *meso*-substituted porphyrins, 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-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 5,10,15,20-tetrakis(1-methyl-4-pyridino)porphyrin TMPyP(4+). TPyP is formed efficiently by the Adler method. However, unlike TPP, which is formed as a precipitate in the propionic acid solution, TPyP is not separated from propionic acid as a precipitate 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 °C) or extract the propionic acid into the water phase. The distillation of the reaction solution under reduced pressure has a possibility of the undesirable oligomerization of reactants or the decomposition of products. Therefore, we propose a simple methodology for the efficient synthesis of TPyP in 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 on using ILs as reaction media and catalysts.[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 yield 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 the amount and could be reused ten times without any loss in catalytic activity. Recently we also reported TPP preparation in acidic ILs using the Adler method.[10] The Adler method is

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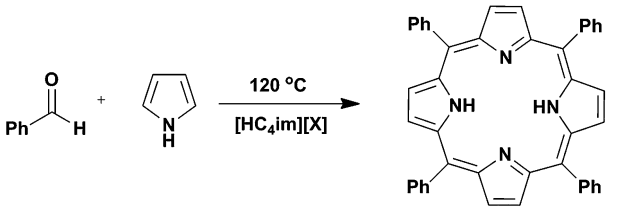
more green than the Lindsey method because harmful halogenated solvents, acid catalysts (such as BF_3) and oxidants (such as DDQ) are not required. Furthermore, the use of acidic ILs instead of propionic acid makes a more green porphyrin synthesis possible. In fact, TPP was obtained in 15% yield in $[HC_4im][CF_3CO_2]$, 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 acidic ILs for porphyrins synthesis can afford the porphyrins without producing any acid waste. In the various acidic ILs investigated, only the imidazolium type ILs, $[HC_4im][X]$, could provide TPP. Herein, we report the optimum acidic ILs for the preparation of porphyrins (TPP and TPyP) with a 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.

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 minutes.

Results and discussion

Suitable acidic IL structures for the preparation of TPP

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^-, $CF_3CO_2^-$, and 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 prepare TPP and TPyP at temperatures above 100 °C.

Initially, we investigated the suitable acidic ILs structures for TPP preparation. We have previously reported that the existence of water in ILs reduced porphyrin formation.[9b] Therefore, all 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 120 °C. 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 120 °C 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.

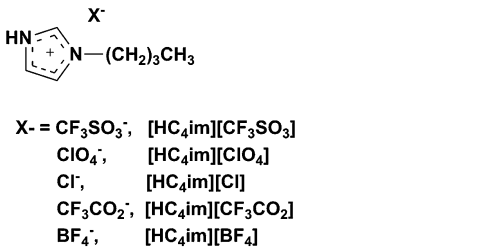


Fig. 1 The structure of the Brønsted acidic ILs.

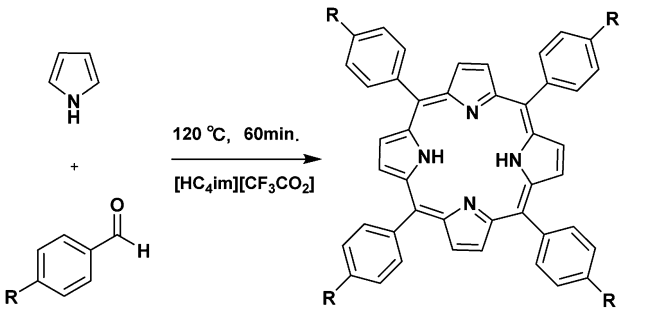
The yield of TPP was dependent on the anion species (X^-). In ILs with the same cation, the relative acidity of ILs could be determined from the basicity of their anion (as described by its pK_a value).[11b,12] In other words, there is a correlation between the basicity of the anions and the electrophilicity of the imidazolium cation, and the electrophilicity has an influence 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) shown in Table 1. With increasing 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 the preparation of TPP.

It is well known that the addition of a salt such as NaCl promotes the formation of TPP.[13] The salt effect of ionic liquids on this TPP synthetic method was considered. All these reactions are carried out under homogeneous conditions. TPP was not generated in the $[bmim][NTf_2]$ without protons. 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 $[bmim][NTf_2]$ was the 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.

Preparation of *meso*-phenyl substituted porphyrins 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 4-substituted benzaldehyde. In $[HC_4im][CF_3CO_2]$, porphyrins were prepared in the same manner as described in the preparation of TPP with only minor differences. In the preparation of *meso*-tetrakis(4-hydroxyphenyl)porphyrin (R = OH) and *meso*-

Table 2 *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

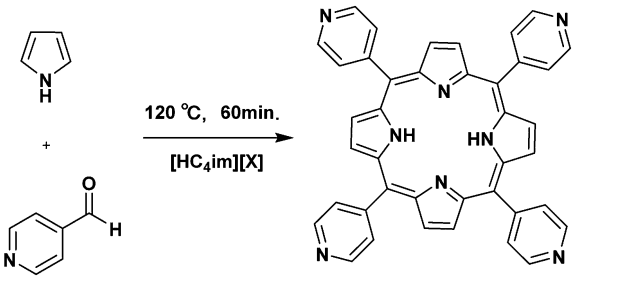
[a] [Pyrrole] = [aldehyde] = 280 mM.

tetrakis(4-methoxyphenyl)porphyrin (R = OCH_3) precipitates, containing the porphyrin components were formed when distilled water was added to the reaction mixture 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. In contrast, *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-donating 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.

Tetrapyridyl-porphyrin preparation in acidic ILs

In contrast to the preparation of TPP and other *meso*-substituted porphyrins, TPyP is very difficult to remove from the propionic acid because of its high solubility. Therefore, following the preparation of TPP, 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 120 °C. All the acidic ionic liquids used in this study can also dissolve pyrrole and 4-pyridinecarboxaldehyde completely, and all the reactions were carried out under homogeneous conditions. After heating at 120 °C for 60 minutes, the solution was cooled to room temperature, diluted with distilled water and a precipitate was 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

Table 3 TPyP preparation in $[HC_4im][X]$[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

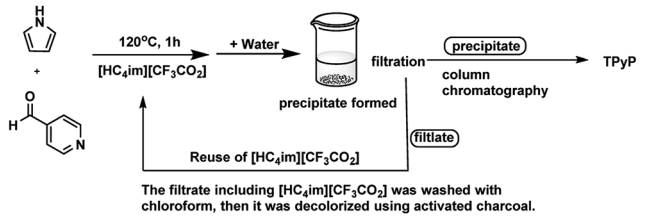
[a] [Pyrrole] = [4-pyridinecarboxaldehyde] = 280 mM, reaction time, 60 minutes.

produce TPyP, as shown in Table 3. $[HC_4im][BF_4]$ showed a 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 $[HC_4im][X]$ ILs. As aforementioned, the yield of TPP was dependent on the anion species (X^-). Although it did not show a clear tendency as in 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 TPyP component produced when compared with the reaction in propionic acid. The TPyP synthesis methodology using $[HC_4im][X]$ could remove $[HC_4im][X]$ from TPyP by easy filtration, while the removal of propionic acid, which is used in traditional Adler method requires troublesome vacuum distillation or liquid–liquid extraction.

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

The most effective catalyst 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, and then decolorized using activated charcoal. After evaporating the water, it was confirmed using ^1H NMR that $[HC_4im][CF_3CO_2]$ does not contain any impurities. The recovery rate of $[HC_4im][CF_3CO_2]$ was 92%. Pyrrole and 4-pyridinecarboxaldehyde were added to the recovered acidic IL, and the reaction was repeated. This procedure was repeated over four cycles without supplying any acid catalysts. Over the four 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 a high reaction temperature (200 °C) was required, a solvent-free

Table 4 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 minutes, reaction temperature 120 °C.

TPyP synthetic method has also been reported.[14,15] The yield of TPyP utilizing $[HC_4im][CF_3CO_2]$ is similar to the yield obtained by the 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 the Lindsey and Adler methods, in which the solvent can be recycled. The solvent-free method uses less solvent than these methods, however, the method using the acidic ionic liquids does not require higher reaction temperatures and energy unlike the solvent-free method (reaction temperature 200 °C).

Experimental

Materials

All reagents were of 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^-, $CF_3CO_2^-$, and BF_4^-) were prepared according to published procedures.[11] All ILs were dried *in vacuo* (under 0.1 mbar) at 60 °C for 1 day prior to use. TLC analysis 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 ^1H NMR.

General procedure for *meso*-tetraphenylporphyrin, TPP (1) in acidic ionic liquids

TPP was prepared in the 5 species of acidic ionic liquids ($[HC_4im][X]$; $X^- = CF_3SO_3^-$, ClO_4^-, Cl^-, $CF_3CO_2^-$, and 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 $[HC_4im][CF_3CO_2]$ at 120 °C. After heating at 120 °C for 60 minutes, the solution was cooled to room temperature and diluted with distilled water (50 mL). The porphyrin component formed 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 65 mg of TPP (**1**) (0.11 mmol, 15%) as purple crystals. ^1H 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 $[HC_4im][CF_3CO_2]$ at 120 °C. After heating at 120 °C for 60 minutes, the solution was cooled to room temperature and diluted with distilled water (50 mL). The porphyrin component formed was extracted with chloroform (50 mL). The organic layer was washed with brine (50 mL) and dried over anhydrous sodium sulphate. After the 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. ^1H 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 $[HC_4im][CF_3CO_2]$ at 120 °C. After heating at 120 °C for 60 minutes, the solution was cooled to room temperature, diluted with distilled water (50 mL) and a precipitate was 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). In addition, 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. ^1H 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 $[HC_4im][CF_3CO_2]$ at 120 °C. After heating at 120 °C for 60 minutes, the solution was cooled to room temperature, diluted with distilled water (50 mL) and a precipitate was formed. The solution was filtered, and the cake on the filter 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 crystals. ^1H 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 $[HC_4im][CF_3CO_2]$ at 120 °C.

After heating at 120 °C for 60 minutes, the solution was cooled to room temperature, diluted with distilled water (50 mL) and a precipitate was 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 using almost the 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 minutes, the solution was cooled to room temperature, diluted with distilled water (50 mL) and a precipitate was formed. The solution was filtered, and the cake on the funnel was washed with hot distilled water. Further, 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)-21*H*,23*H*-porphyine, TPyP, (6) in acidic ionic liquids

TPyP was prepared in the 5 species of acidic ionic liquids ([HC_4im][X]; X = $CF_3SO_3^-$, ClO_4^-, Cl^-, $CF_3CO_2^-$, and 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 120 °C. After heating at 120 °C for 60 minutes, the solution was cooled to room temperature, diluted with distilled water (50 mL) and a precipitate formed. The solution was filtered, and the cake on the filter 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)-21*H*,23*H*-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 porphyrin preparation using the Adler method. The general TPyP preparation in propionic acid needs a troublesome solvent removal process, whereas the reaction in [HC_4im][CF_3CO_2] produced TPyP in 11% yield, and TPyP can be separated from IL only by filtration. In other words, this finding suggests that using [HC_4im][X] ILs can purify TPyP easier than with 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 catalytic activity.

Abbreviations

[HC_4im]	1-Butylimidazolium
[CF_3SO_3]	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

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Notes and references

1 J. S. Lindsey, I. Schreiman, H. Hsu, P. Kearney and A. Marguerettaz, *J. Org. Chem.*, 1987, **52**, 827.
2 (*a*) A. Adler, F. Longo and W. Shergalis, *J. Am. Chem. Soc.*, 1964, **86**, 3145; (*b*) A. Adler, F. Longo, J. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476.
3 H. Furuta, T. Asano and T. Ogawa, *J. Am. Chem. Soc.*, 1994, **116**, 767.
4 P. Chmielewski, L. Latos-Grazynski, K. Rachlewicz and T. Glowiak, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 779.
5 (*a*) G. Geier III, D. Haynes and J. S. Lindsey, *Org. Lett.*, 1999, **9**, 1455; (*b*) G. Geier III and J. S. Lindsey, *J. Org. Chem.*, 1999, **64**, 1596; (*c*) G. Geier III, Y. Ciringh, F. Li, M. Haynes and J. S. Lindsey, *Org. Lett.*, 2000, **2**, 1745.
6 (*a*) J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi and A. Osuka, *J. Am. Chem. Soc.*, 2001, **123**, 7190; (*b*) S. Saito and A. Osuka, *Angew. Chem., Int. Ed.*, 2011, **50**, 4342.
7 (*a*) M. Kondo, Y. Kimura, K. Wada, T. Mizutani, Y. Ito and S. Kitagawa, *Chem. Lett.*, 2000, 818; (*b*) I. Goldberg, *Chem. – Eur. J.*, 2000, **6**, 3863; (*c*) L. Carlucci, G. Ciani, D. M. Proserpio and F. Porta, *Angew. Chem.*, 2003, **115**, 331; (*d*) C. M. Drain, A. Varotto and I. Radivojevic, *Chem. Rev.*, 2009, **109**, 1630; (*e*) I. Beletskaya, V. S. Tyurin, A. Y. Tsivadze, R. Guilard and C. Stern, *Chem. Rev.*, 2009, **109**, 1659.
8 (*a*) T. Welton, *Chem. Rev.*, 1999, **99**, 2071; (*b*) P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772; (*c*) R. Sheldon, *Chem. Commun.*, 2001, 2399; (*d*) J. Dupont, R. F. de Souza and P. A. Z. Suqrez, *Chem. Rev.*, 2002, **102**, 3667.

9 (*a*) S. Kitaoka, K. Nobuoka and Y. Ishikawa, *Chem. Commun.*, 2004, 1902; (*b*) S. Kitaoka, K. Nobuoka and Y. Ishikawa, *Tetrahedron*, 2005, **61**, 7678.
10 S. Kitaoka, K. Nobuoka, R. Hirakawa, K. Ihara and Y. Ishikawa, *Chem. Lett.*, 2013, **42**, 1397.
11 (*a*) H. P. Zhu, F. Yang, J. Tang and M. Y. He, *Green Chem.*, 2003, **5**, 38; (*b*) S. S. Palimkar, S. A. Siddiqui, T. Daniel, R. J. Lahoti and K. V. Srinivasan, *J. Org. Chem.*, 2003, **68**, 9371; (*c*) H. P. Zhu, F. Yang, P. Cui, J. Tang and M. Y. He, *Tetrahedron Lett.*, 2004, **45**, 4963; (*d*) G. Zhao, T. Jiang, H. Gao, J. Huang and D. Sun, *Green Chem.*, 2004, **6**, 75; (*e*) A. R. Gholap, K. Venkatesan, T. Daniel, R. J. Lahoti and K. V. Srinivasan, *Green Chem.*, 2004, **6**, 147.
12 (*a*) S. A. Siddiqui, T. M. Potewar, R. J. Lahoti and K. V. Srinivasan, *Synthesis*, 2006, **17**, 2849; (*b*) T. L. Greaves and C. J. Drummond, *Chem. Rev.*, 2008, **108**, 206.
13 F. Li, K. Yang, J. S. Tytonas, K. A. MacCrum and J. S. Lindsey, *Tetrahedron*, 1997, **53**, 12339.
14 C. M. Drain and X. Gong, *Chem. Commun.*, 1997, 2117.
15 S. Nia, X. Gong, C. M. Drain, M. Jurow, W. Rizvi and M. Qureshy, *J. Porphyrins Phthalocyanines*, 2014, **14**, 621.