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**Full Paper**

# Design and Synthesis of Piperazine-Based Task-Specific Ionic Liquids for Liquid–Liquid Extraction of $Cu^{II}$, $Ni^{II}$, and $Co^{II}$ from Water

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The novel synthesis of task-specific ionic liquids (TSILs) introducing piperazine substructures was described. Piperazine functional groups were easily grafted onto an imidazolium cationic derivative via a simple four-step process starting from available materials such as imidazole, ethylene glycol, and 1-butylamine or 3-dimethylaminopropylamine. Effects of pH, temperature, and structure of functional groups on the performance of liquid–liquid extraction of $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$ from water were investigated. It was found that TSILs were efficient for removal of these metal ions in mild acid solutions. The TSIL with an extra nitrogen atom showed a higher capability to separate metal ions, especially for $Cu^{2+}$. This may be ascribed to the intrinsic structure of the functional groups – the more coordination sites, the higher the affinity for the metal ions. Furthermore, the thermodynamics indicated that the extraction process was exothermic and spontaneous in nature.

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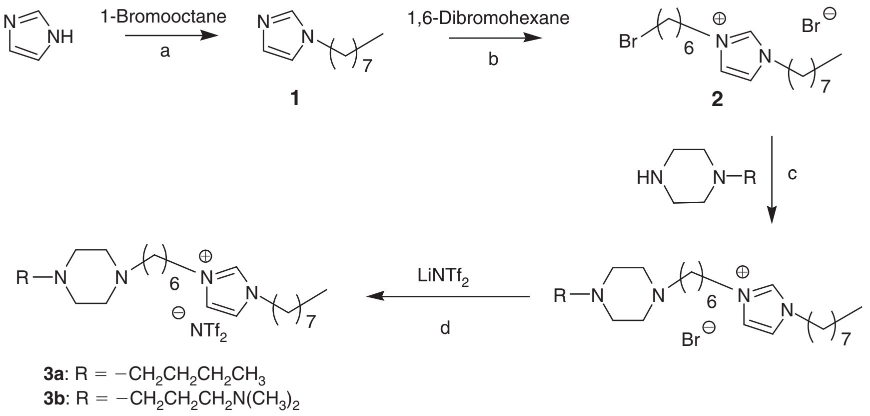
## Introduction

Heavy metals as persistent environment contaminants in rivers and streams have become one of the most critical public problems of the century.[1] Insufficient pre-treatment of wastewater would bring negative effects, generating serious toxicological threats to living organisms and accumulation of the toxic metal compounds in the food chain.[2,3] Copper, nickel, and cobalt are the most general metallic pollutants detected in industrial effluents and they are toxic to the flora, fauna, and even the humans.[4–7] Therefore, techniques for heavy metals removal from wastewater are of particular importance. At present, the usage of ionic liquids (ILs) to extract heavy metal ions is an attractive option.

ILs have been proposed to be promising solvents to displace conventional volatile solvents in the extraction of a variety of substances owing to their negligible vapour pressure, high thermal stability, and high ionic conductivity.[8–10] Many researchers have investigated ILs for the extraction and separation of metal cations.[11–16] Furthermore, efficient extraction processes by adding complex chelatants in ILs as extracting agents, such as β-diketone,[17–19] phosphates,[20] quinoline derivatives,[21] crown ethers,[22] and calixarene,[23] to remove metals have been studied. Some recent reports have involved task-specific ionic liquid (TSILs) that have potential applications in metal extraction.[24–35] TSILs appended with some functional groups that could impart particular reactivity, thereby enhancing their capacity for interaction with metal ions are an interesting option. This approach that does not require the addition of extra extracting agent would effectively solve the problem of miscibility between the extracting agent and solvent. TSILs bearing ethylene glycol[33,34] or thioether, thiourea, or urea[24] groups appeared to be efficient to extract metal ions such as mercury and cadmium. Americium ion was effectively removed from water by TSILs bearing functional groups of 2-hydroxybenzylamine entities, and more than 99 % of americium was successfully regenerated into the receiving phase with 1M perchloric acid.[27] Prausnitz et al. synthesized four new TSILs and found that those featuring disulfide functional groups were efficient for $Hg^{2+}$ and $Cu^{2+}$, whereas those featuring nitrile functional groups were efficient for $Ag^{+}$ and $Pd^{2+}$.[12] Dupont et al. reported TSILs containing a betaine derivative cation and a dicyanamide anion for the removal of heavy metals from water and suggested that the extraction mechanism was a mixed process of ion-pairing and cation exchange.[32] New bifunctional fluoroionphore-ionic liquid hybrid was reported by Jin et al. – the sensing system could detect $Hg^{2+}$ in a low detection limit of 800 pM, and be simply recovered using an ethylenediaminetetraacetic acid (EDTA) treatment.[35]

In this work, piperazine-based hydrophobic TSILs were designed and synthesized using available ethylene glycol, 1-butylamine or 3-dimethylaminopropylamine, and imidazole as starting materials. The synthetic TSILs are generated by



**Scheme 1.** Synthetic procedure of TSILs. Reaction conditions: (a) NaH, THF, room temperature (rt), 24 h; (b) MeCN, reflux under $N_2$ atmosphere, 24 h; (c) $K_2CO_3$, MeCN, 90°C, 72 h; and (d) $LiNTf_2$, $H_2O$, rt, 12 h.

association of an imidazolium cationic derivative with piperazine functional groups and a bis(trifluoromethanesulfonyl) imide anion ($NTf_2^-$) (Scheme 1). Imidazolium cation is commonly used to prepare TSILs that can be easily derivatized by functional groups through a simple synthetic route. And the chelating ability of piperazine units for metal ions is well known.[36,37] Subsequently, the investigation on removal of $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$ from water was conducted. To further understand the extraction behaviour of these TSILs, the extraction thermodynamics as well as acid concentration variations were studied.

## Results and Discussion

### Synthesis of the Task-Specific Ionic Liquids 3a and 3b

Here, two piperazine units were prepared, one contained a common alkyl chain and the other contained an alkyl chain employing a nitrogen atom. They were acquired easily by hydrolysis of N-heteroalkyl-N′-tosylpiperazines which were synthesized through one-step cyclization using available ethylene glycol and 1-butylamine or 3-dimethylaminopropylamine as starting materials according to the literature.[38]

The piperazine functional groups were successfully grafted onto imidazolium derivative via a simple four-step process starting from imidazole. First, the ionic compound **2** was obtained through a two-step alkylated reaction using 1-bromooctane and 1, 6-dibromohexane. Then, piperazine units were introduced into compound **2**; the resulting task-specific ionic liquids **3a** and **3b** were finally generated by anion exchange using lithium bis(trifluoromethanesulfonyl)imide.

### Liquid–Liquid Extraction Studies

#### Effects of pH

The pH is an important parameter influencing the liquid–liquid extraction process of metal ions. TSILs **3a** and **3b** are pH sensitive owing to their functionalization by tertiary amine groups. A systematic research was carried out to study the effects of pH on extraction of $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$ ions using the TSILs. The percentage extraction ($E$ %) was calculated using Eqn 1:

$$E\,\% = \frac{C^{M}_{\mathrm{Init}} - C^{M}_{\mathrm{Final}}}{C^{M}_{\mathrm{Init}}} \times 100\,\% \qquad (1)$$

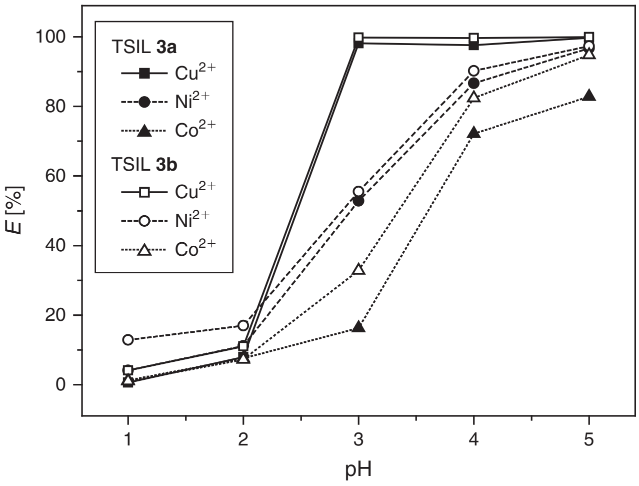


**Fig. 1.** Effect of pH on the removal of $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$ ions by TSILs (initial metal ion concentration: 200 mg $L^{-1}$; TSILs diluted in [Bmim][$NTf_2$] concentration: 175 mmol $L^{-1}$; contact time: 1 h; 30°C).

where $M$ stands for metal ion, $C$ is the concentration of the metal ion, and subscripts Init and Final stand for the values obtained before and after the extraction experiment, respectively.

As shown in Fig. 1, high extraction percentages were observed at the higher pH value for the three metal ions $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$. It may be ascribed to the protonation of the functional groups in a strong acidic medium and the competition between $H^+$ and metal ions to interact with TSILs. For $Cu^{2+}$ ion, the percentage extraction was 98 % at pH 3, whereas the percentage extraction was only 16 % for $Co^{2+}$ ion when employing TSIL **3a**. This result indicated that TSIL **3a** may have potential selectivity toward $Cu^{2+}$ and $Co^{2+}$ ions. Using TSIL **3b**, this selectivity was obviously decreased. This may be attributed to TSIL **3b** having higher capabilities for metal ions extraction. For $Ni^{2+}$ ion, the percentage extraction increased more smoothly.

#### Effect of Functionalization

Then, the effect of TSILs on the percentage of extraction and distribution coefficient of metal ions $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$ (metal ion concentration 200 mg $L^{-1}$) was investigated at pH 5.0

**Table 1. Effect of ILs on the percentage of extraction (*E*) and distribution coefficient (*D*) of $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$**

| Metal ion$^{A}$ | *E* [%] | | | *D* | | |
|---|---|---|---|---|---|---|
| | [Bmim][$NTf_2$] | TSIL **3a**$^{B}$ | TSIL **3b**$^{B}$ | [Bmim][$NTf_2$] | TSIL **3a**$^{B}$ | TSIL **3b**$^{B}$ |
| $Cu^{2+}$ | 11 | >99 | >99 | 1 | 3990 | 19990 |
| $Ni^{2+}$ | 10 | 97 | 977 | 1 | 297 | 369 |
| $Co^{2+}$ | 9 | 83 | 95 | 1 | 48 | 184 |

$^{A}$Metal ion concentration: $200\,mg\,L^{-1}$; pH 5.0; 30°C.
$^{B}$TSILs diluted in [Bmim][$NTf_2$].

and 30°C. The distribution coefficient (*D*) was calculated using Eqn 2:

$$D = \frac{C^{M}_{\text{Init}} - C^{M}_{\text{Final}}}{C^{M}_{\text{Final}}}\frac{V_{W}}{V_{IL}} \qquad (2)$$

where *M* stands for metal ion, *C* is the concentration of the metal ion, subscripts Init and Final stand for the values obtained before and after the extraction experiment, respectively, $V_W$ and $V_{IL}$ are the volumes of the aqueous phase and ionic liquid, respectively.

The results are shown in Table 1. As observed, when employing [Bmim][$NTf_2$] (1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide) as extracting agent alone, the percentages of extraction of $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$ metal ions were very low under our operating conditions i.e. only 11 %, 10 %, and 9 %, respectively. However, TSILs **3a** and **3b** bearing piperazine functionality both showed high capabilities for these metal ions extraction. This may be attributed to the piperazine units that could effectively interact with metal ions via their nitrogen atoms. In addition, for $Co^{2+}$, $Ni^{2+}$, and $Cu^{2+}$, the percentage of extraction and distribution coefficient of the two TSILs both displayed an increasing tendency. Comparison between TSILs **3a** and **3b** revealed that **3b** was obviously superior to **3a** to remove the three metal ions. Particularly, TSIL **3b** presented a very high removal ability for $Cu^{2+}$; the distribution coefficient was high, reaching 19990, which may be ascribed to the extra nitrogen atom in the alkyl chain of piperazine, and higher affinity for the metal ions could be obtained.

### *Determination of Thermodynamic Parameters*

The effect of temperature on distribution coefficient has been studied at varying temperatures from 303 to 333 K. The thermodynamic parameters, such as enthalpy ($\Delta H$), entropy ($\Delta S$), and Gibbs free energy ($\Delta G$), could be calculated by the following equations:[23]

$$\log D = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \qquad (3)$$

$$\Delta G = \Delta H - T\Delta S \qquad (4)$$

Straight lines were obtained by plotting log *D* against 1000/*T*, as shown in Fig. 2. In this figure, we found that the distribution coefficients increased with decreasing temperatures, suggesting that the extraction process was exothermic. The enthalpy changes could be calculated from the slopes of the straight lines and the corresponding entropy changes could be extracted from the intercepts according to Eqn 3. The results are shown in Table 2. The negative enthalpy changes and the entropy changes also showed that the process was exothermic. Compared with **3a**, the enthalpy changes for **3b** were more negative, indicating there was a relatively stronger interaction between **3b** and the metal ions. Under the conditions, for all metal ions, the Gibbs free energy changes were negative, thereby revealing the spontaneous nature of the extraction process. The Gibbs free energy changes for the extraction of $Cu^{2+}$ were more negative than that for $Ni^{2+}$ and $Co^{2+}$, indicating that the interaction of synthetic TSILs with $Cu^{2+}$ was thermodynamically more favourable than the interactions with other metal ions.

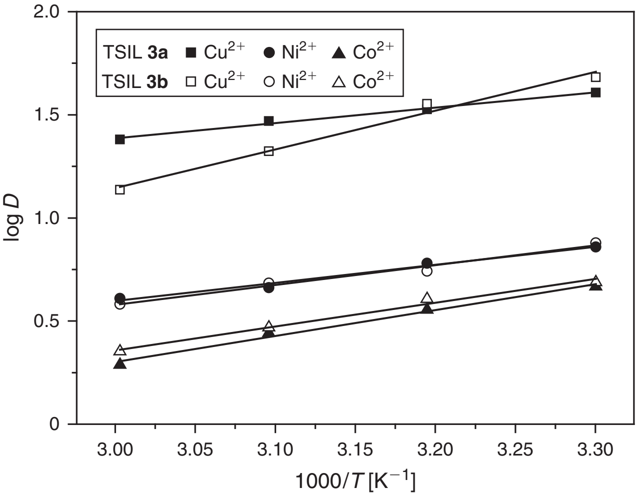


**Fig. 2.** Dependence of $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$ extraction on temperature (initial metal ions concentration: $200\,mg\,L^{-1}$; TSILs diluted in [Bmim][$NTf_2$] concentration: $175\,mmol\,L^{-1}$; contact time: 1 h).

**Table 2. Thermodynamic parameters for the extraction process of $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$ using the synthetic TSILs**

| Metal ion | $\Delta G^{A}$ [$kJ\,mol^{-1}$] | | $\Delta H$ [$kJ\,mol^{-1}$] | | $\Delta S$ [$J\,K^{-1}\,mol^{-1}$] | |
|---|---|---|---|---|---|---|
| | TSIL **3a** | TSIL **3b** | TSIL **3a** | TSIL **3b** | TSIL **3a** | TSIL **3b** |
| $Cu^{2+}$ | −9.37 | −10.37 | −14.2 | −36.0 | −16.2 | −86.0 |
| $Ni^{2+}$ | −5.21 | −5.26 | −16.8 | −18.4 | −38.9 | −44.1 |
| $Co^{2+}$ | −4.28 | −4.40 | −24.1 | −22.1 | −66.5 | −59.4 |

$^{A}T = 298$ K.

## Conclusion

Two novel task-specific ionic liquids bearing piperazine substructures were successfully synthesized through a simple four-step process starting from available materials imidazole, ethylene glycol, and 1-butylamine or 3-dimethylaminopropylamine.

Then, the synthetic TSILs were tested for liquid–liquid extraction of $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$ from water. TSILs **3a** and **3b** both showed high extraction efficiency for the three metal ions. $Cu^{2+}$ showed higher distribution coefficient relative to $Ni^{2+}$ and $Co^{2+}$ – the distribution coefficient could reach up to 19990 when using TSIL **3b**. TSIL **3b** presented superior capability to **3a** under the conditions employed to extract the three metal ions, and may be ascribed to the extra nitrogen atom in the alkyl chain of piperazine, and thus higher affinity to the metal ions was obtained. The synthetic TSILs were pH sensitive; higher percentage extraction was observed at higher pH values for $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$ under our operating conditions. And the thermodynamic parameters indicated that the extraction process was exothermic and spontaneous in nature. The results of the experiments suggest that the synthetic TSILs can be used as potential extracting solvents for copper, nickel, and cobalt.

## Experimental

### Materials

Chemicals were of reagent grade and used without further purification unless otherwise stated. The $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded with a Bruker DPX 400 using $CDCl_3$ as solvent and TMS as internal standard at room temperature. High-resolution mass spectrometry (HRMS) and electrospray ionization mass spectrometry (ESI–MS) were conducted using the ESI-mode. Silica gel (300–400 mesh) was used for flash chromatography. The metal ion concentrations were measured by a PGENERAL TAS-990 atomic absorption spectrophotometer fitted with copper, cobalt, and nickel hollow cathode lamps. The instrument was set at 324.7 nm for copper, 240.7 nm for cobalt, and 320.0 nm for nickel. A centrifuge (SORVALL fresco) was used to separate ionic liquid and aqueous phase.

### Synthesis of Task-Specific Ionic Liquids

#### 1-Octylimidazole (*1*)

Imidazole (3.41 g, 50 mmol) and NaH (1.34 g, 54 mmol) were dissolved in THF (10 mL) under $N_2$ in an ice bath for 45 min, followed by addition of 1-bromooctane (9.65 g, 50 mmol). The solution was stirred for 24 h at room temperature and then concentrated under reduced pressure after filtration. The residue was purified by flash chromatography ($SiO_2$; petroleum ether/ethyl acetate = 5 : 1 as eluent) to give **1** as a light yellow oil (5.97 g, 60 %). $\delta_H$ ($CDCl_3$, 400 MHz) 7.42 (1H, s), 7.01 (1H, s), 6.87 (1H, s), 3.89 (2H, t, *J* 8.0), 1.76–1.73 (2H, m), 1.31–1.25 (10H, m), 0.87 (3H, t, *J* 7.2). $\delta_C$ ($CDCl_3$, 100 MHz) 136.2, 128.4, 118.1, 46.4, 31.2, 30.6, 28.6, 28.5, 26.0, 22.1, 13.6. *m/z* (ESI) 181 ($[M + H]^+$). *m/z* 181.1708. HRMS (ESI) Anal. Calc. for $C_{11}H_{21}N_2$ ($[M + H]^+$) 181.1705.

#### 3-(6-Bromohexyl)-1-octyl-imidazolium Bromide (*2*)

1,6-Dibromohexane (10.00 g, 42 mmol) was dissolved in anhydrous acetonitrile (10 mL) and introduced into a three-neck round-bottom flask. After the solution was heated gently to reflux, a solution of **1** (0.50 g, 2.80 mmol) in anhydrous acetonitrile (5 mL) was added dropwise under $N_2$ atmosphere. The reaction mixture was stirred for 24 h at reflux and then cooled to room temperature. The solvent was removed to give a residue, which was purified by washing with anhydrous diethyl ether (3 × 5 mL), and concentrated under reduced pressure. The residue was dried under vacuum to afford **2** as a puce oil (1.01 g, 85 %). $\delta_H$ ($CDCl_3$, 400 MHz) 10.32 (1H, s), 7.62 (1H, s), 7.50 (1H, s), 4.40 (2H, t, *J* 7.2), 4.34 (2H, t, *J* 7.6), 3.43–3.40 (4H, m), 2.03–1.84 (6H, m), 1.51–1.23 (12H, m), 0.87 (3H, t, *J* 6.8). $\delta_C$ ($CDCl_3$, 100 MHz) 136.3, 122.1, 121.8, 49.9, 49.6, 33.7, 32.3, 32.1, 31.5, 30.1, 30.0, 28.9, 27.2, 26.1, 25.1, 22.4, 14.0. *m/z* (ESI) 345 ($[M]^+$). *m/z* 345.1733. HRMS (ESI) Anal. Calc. for $C_{17}H_{32}BrN_2$ ($[M]^+$) 345.1728.

#### Task-Specific Ionic Liquids (*3*)

Compound **2** (0.14 g, 0.35 mmol), mono-substituted piperazine (0.44 mmol; for the synthesis of mono-substituted piperazine, see Supplementary Material), anhydrous acetonitrile (8 mL), and potassium carbonate (0.30 g, 2.2 mmol) were added in a 100-mL round-bottom flask. Then, the reaction mixture was refluxed under $N_2$ atmosphere for 72 h. The mixture was then cooled to room temperature and filtered. The filtrate was concentrated and the residue was purified by washing with anhydrous diethyl ether (3 × 5 mL), and dried under vacuum to give functionalized ionic liquids as a light yellow oil. Functionalized ionic liquids (1.11 mmol), lithium bis(trifluoromethanesulfonyl)imide (0.32 g, 1.11 mmol), and Milli-Q water (18.2 MΩ cm; 10 mL) were stirred at room temperature for 12 h to exchange the anions. Dichloromethane (15 mL) was then added to extract the product, and washed with Milli-Q water (3 × 10 mL). The organic layer was dried with anhydrous $Na_2SO_4$. The solvent was removed by rotary evaporation to give final TSILs **3**.

TSIL **3a**. Light yellow oil (0.211 g, 88 %). $\delta_H$ ($CDCl_3$, 400 MHz) 8.56 (1H, s), 7.32–7.26 (2H, m), 4.17–4.13 (4H, m), 3.46–3.41 (2H, m), 2.33–2.23 (6H, m), 1.87–1.71 (6H, m), 1.50–1.42 (4H, m), 1.33–1.25 (18H, m), 0.93–0.85 (6H, m). $\delta_C$ ($CDCl_3$, 100 MHz) 134.8, 122.1, 122.1, 120.2 (q, $J_{C-F}$ 310), 58.5, 58.3, 53.1, 50.1, 50.0, 46.5, 31.6, 30.0, 29.9, 29.0, 28.9, 28.8, 27.3, 26.8, 26.6, 26.1, 26.0, 22.6, 20.8, 14.1. *m/z* (ESI) 405 ($[M]^+$). *m/z* 405.3953. HRMS (ESI) Anal. Calc. for $C_{25}H_{49}N_4$ ($[M]^+$) 405.3952.

TSIL **3b**. Light yellow oil (0.225 g, 90 %). $\delta_H$ ($CDCl_3$, 400 MHz) 8.59 (1H, s), 7.31 (1H, s), 7.28 (1H, s), 4.16 (6H, t, *J* 7.6), 2.99 (2H, m), 2.65 (2H, m), 2.45–2.27 (8H, m), 2.21 (6H, s), 1.86 (6H, m), 1.68–1.64 (2H, m), 1.37–1.22 (14H, m), 0.88–0.85 (3H, m). $\delta_C$ ($CDCl_3$, 100 MHz)135.3, 122.5, 122.5, 120.6 (q, $J_{C-F}$ 301), 58.6, 58.3, 57.0, 53.5, 53.4, 50.5, 50.3, 45.7, 32.0, 30.3, 30.2, 29.4, 29.2, 27.2, 26.9, 26.5, 26.4, 25.3, 23.0, 14.5. *m/z* (ESI) 434 ($[M]^+$). *m/z* 434.4197. HRMS (ESI) Anal. Calc. for $C_{26}H_{52}N_5$ ($[M]^+$) 434.4217.

### Liquid–Liquid Extraction of Metal Ions

Liquid–liquid extraction of metal ions was carried out starting from aqueous solutions containing $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$. The initial pH was adjusted with hydrochloric acid from 1 to 5. Product **3a** or **3b** was dissolved in [Bmim][$NTf_2$] to achieve a concentration of 175 mmol $L^{-1}$. Then, 20 μL of TSIL/IL was mixed with 200 μL of the above mentioned metal ion solutions (initial concentration of 200 mg $L^{-1}$) of various pH values, and stirred for 1 h while keeping the temperature at 30°C. Then, the mixture was centrifuged at 2000 *g* for 5 min and the residual concentration of the metal ions was determined.

Uptake experiments examining the effect of temperature were performed by adding 200 μL metal ion solution (200 mg $L^{-1}$) of which the pH was 3.0 into tubes containing 20 μL TSIL/IL, and incubated at 30, 40, 50, or 60°C with constant stirring for 1 h.

After incubation, the mixtures were centrifuged at 2000 *g* for 5 min to separate the aqueous solution from the ionic liquid, and a TAS-990 atomic absorption spectrophotometer was used to determine the residual concentration of metal ions.

## Supplementary Material

A description of the synthesis of piperazine functional groups as well as $^1$H NMR, $^{13}$C NMR, and HRMS spectra of compounds **1**, **2**, **3a**, and **3b** are available on the Journal's website.

## Acknowledgements

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