Electronic Supplementary Information

Induction of lignin solubility for a series of polar ionic liquids by the addition of small amount of water

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Synthesis of ILs

$[C_2mim]^+$ salts, $[Pip_{14}]^+$ salts, and $[Pyr_{14}]^+$ salts

$[C_2mim]Br$ (Tokyo Chemical Industry Co., Ltd.) was converted into $[C_2mim]OH$ aquaous solution using anion exchange resin; Amberlite IRN78 (SUPELCO). Then, small excess molar of corresponding acid was added for neutralisation. The solution was evaporated and dried *in vacuo* to yield colorless liquid. IL was individually dissolved in dichloromethane and passed through a column filled with active alumina. The dichloromethane was removed by evaporation and the resulting liquid was dried *in vacuo* at 80 °C for 10 hrs. Water content of ILs was confirmed to be less than 0.2 wt% by Karl Fischer titration. The same method was performed to synthesize $[Pip_{14}]^+$ salts and $[Pyr_{14}]^+$ salts. Structure of these ILs was confirmed by ^{1}H-NMR spectra (JEOL ECX-α500).

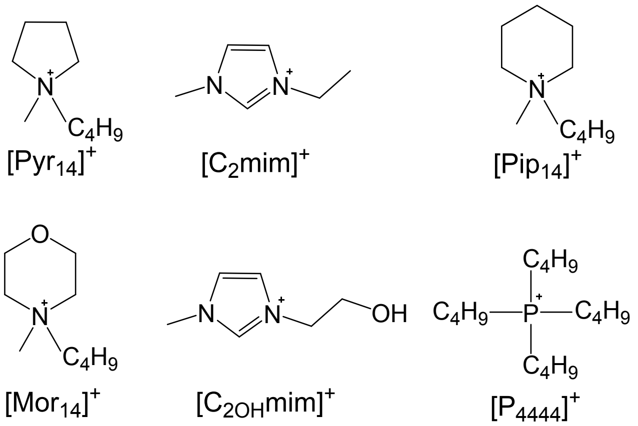


Fig. S1 Structure of cations to prepare ILs used in this study.

$[P_{4444}]CH_3O(H)PO_2$

Dimethyl phosphite (Tokyo Chemical Industry Co., Ltd.) was added to $[P_{4444}]OH$ aqueous solution (Hokko Chemical Industry Co., Ltd.). This solution was stirred for 5 hrs. and concentrated by evaporation. The residual liquid was repeatedly washed with anhydrous diethyl ether. The resulting liquid was dissolved in dichloromethane and then passed through a column filled with active alumina. The dichloromethane was removed by evaporation and the resulting liquid was dried *in vacuo* at 80 °C for 10 hrs, yielding tetrabutylphosphonium methylphosphonate as a colorless liquid.

$[P_{4444}]N(CN)_2$

$NaN(CN)_2$ (Tokyo Chemical Industry Co., Ltd.) was mixed with equimolar $AgNO_3$ aqueous solution. The mixture was stirred overnight and filtrated to yield $AgN(CN)_2$. The solid was dried *in vacuo* and mixed with equimolar

$[P_{4444}]Br$ (Tokyo Chemical Industry Co., Ltd.) in dried acetone. The solution was stirred overnight and filtrated to yield $[P_{4444}]N(CN)_2$. Acetone was removed by evaporation and the IL was dried *in vacuo* at 80 °C for 10 hrs.

$[P_{4444}]CF_3CO_2$

$[P_{4444}]OH$ aqueous solution (Hokko Chemical Industry Co., Ltd.) was neutralized with small excess amount of trifluoroacetic acid (Tokyo Chemical Industry Co., Ltd.). Water was removed by evaporation and the resulting liquid was dried *in vacuo* to yield $[P_{4444}]CF_3CO_2$. The salt was dissolved in dichloromethane and then passed through a column filled with active alumina. The dichloromethane was removed by evaporation and the resulting liquid was dried *in vacuo* at 80 °C for 10 hrs.

$[Mor_{14}]CF_3CO_2$

1-Bromobutane (Tokyo Chemical Industry Co., Ltd.) was added to 4-methylmorpholine (Tokyo Chemical Industry Co., Ltd.) dissolved in acetonitrile. The mixture was stirred for 72 hrs. at 80 °C to yield 1-butyl-1-methylmorpholinium bromide ($[Mor_{14}]Br$). The salt was recrystallized in acetonitrile/ethylacetate mixture, and dried *in vacuo* for 10 hrs. at 80 °C. Bromide anion of $[Mor_{14}]Br$ was converted into hydroxide anion by anion exchange resin; Amberlite IRN78 (SUPELCO) to prepare $[Mor_{14}]OH$ aquaous solution. Then, small excess amount of trifluoroacetic acid was added to the hydroxide aqueous solution to neutralize. The solution was evaporated and dried *in vacuo*. The salt was dissolved in dichloromethane and then passed through a column filled with active alumina. The dichloromethane was removed by evaporation and the resulting liquid was dried *in vacuo* at 80 °C for 10 hrs.

$[C_{2OH}mim]N(CF_3SO_3)_2$

2-Bromoethanol (Tokyo Chemical Industry Co., Ltd.) was added to 1-methylimidazole (Tokyo Chemical Industry Co., Ltd.) dissolved in THF. The mixture was stirred for 72 hrs. at 80 °C. THF was removed by evaporation to yield 1-(2-hydroxyethyl)-3-methylimidazolium bromide ($[C_{2OH}mim]Br$). The salt was recrystallised in mixture of methanol and ethylacetate and dried *in vacuo* for 10 hrs. at 80 °C. $[C_{2OH}mim]Br$ was then mixed with $Li[N(CF_3SO_3)_2]$ (Tokyo Chemical Industry Co., Ltd.) in dichloromethane. Then the mixture was washed with Milli-Q® water three times. The dichloromethane was removed by evaporation and the resulting liquid was dried *in vacuo* at 80 °C for 10 hrs.

^{1}H-NMR data of ILs

$[C_2mim]CH_3O(H)PO_2$

^{1}H-NMR (500 MHz, DMSO-D6, 25 °C, Me_4Si) $\delta_H = 1.41$ (t, $J = 14.32$ Hz, 3H, NCH_2CH_3) , 3.22 (d, $J = 17.76$ Hz, 3H, $POCH_3$), 3.86 (s, 3H, NCH_3), 4.20 (q, $J = 21.77$ Hz, 2H, NCH_2CH_3), 5.93-7.04 (d, $J = 556.7$ Hz, 1H, PH), 7.73-7.82 (d, $J = 45.82$ Hz, 2H, $NCHCHN$), 9.35 (1H, s, $NCHN$).

$[C_2mim]CH_3CO_2$

^{1}H-NMR (500 MHz, DMSO-D6, 25 °C, Me_4Si) δ_H =1.39-1.43 (m, $J = 21.05$ Hz, 3H, NCH_2CH_3), 1.56 (s, 3H, CO_2CH_3), 3.88 (s, 3H, NCH_3), 4.22 (q, $J = 21.77$ Hz, 2H, NCH_2CH_3), 7.76-7.86 (d, $J = 45.82$ Hz, 2H, $NCHCHN$), 9.94 (s, 1H, $\mathrm{NC}\mathit{H}\mathrm{N}$).

$\mathrm{[C_2mim]CF_3CO_2}$

$^1\mathrm{H}$-NMR (500 MHz, DMSO-D6, 25 °C, $\mathrm{Me_4Si}$) δ_H =1.42 (m, *J* = 14.89 Hz, 3H, $\mathrm{NCH_2C}\mathit{H_3}$), 3.88 (s, 3H, $\mathrm{NC}\mathit{H_3}$), 4.22 (m, *J* = 22.34 Hz, 2H, $\mathrm{NC}\mathit{H_2}\mathrm{CH_3}$), 7.76-7.85 (d, *J* = 45.82 Hz, 2H, $\mathrm{NC}\mathit{H}\mathrm{C}\mathit{H}\mathrm{N}$), 9.31 (s, 1H, $\mathrm{NC}\mathit{H}\mathrm{N}$).

$\mathrm{[C_2mim]CH_3SO_3}$

$^1\mathrm{H}$-NMR (500 MHz, DMSO-D6, 25 °C, $\mathrm{Me_4Si}$) δ_H = 1.42 (t, *J* = 14.89 Hz, 3H, $\mathrm{NCH_2C}\mathit{H_3}$) , 2.37 (s, 3H, $\mathrm{SO_3C}\mathit{H_3}$), 3.91 (s, 3H, $\mathrm{NC}\mathit{H_3}$), 4.23 (q, *J* = 21.77 Hz, 2H, $\mathrm{NC}\mathit{H_2}\mathrm{CH_3}$), 7.76-7.85 (d, *J* = 48.11 Hz, 2H, $\mathrm{NC}\mathit{H}\mathrm{C}\mathit{H}\mathrm{N}$), 9.31 (s, 1H, $\mathrm{NC}\mathit{H}\mathrm{N}$).

$\mathrm{[C_2mim]CF_3SO_3}$

$^1\mathrm{H}$-NMR (500 MHz, DMSO-D6, 25 °C, $\mathrm{Me_4Si}$) δ_H = 1.44 (t, *J* = 14.32 Hz, 3H, $\mathrm{NCH_2C}\mathit{H_3}$), 3.87 (s, 3H, $\mathrm{NC}\mathit{H_3}$), 4.21 (m, *J* = 22.34 Hz, 2H, $\mathrm{NC}\mathit{H_2}\mathrm{CH_3}$), 7.69-7.78 (d, *J* = 43.53 Hz, 2H, $\mathrm{NC}\mathit{H}\mathrm{C}\mathit{H}\mathrm{N}$), 9.10 (s, 1H, $\mathrm{NC}\mathit{H}\mathrm{N}$).

$\mathrm{[C_2mim]N(CN)_2}$

$^1\mathrm{H}$-NMR (500 MHz, DMSO-D6, 25 °C, $\mathrm{Me_4Si}$) δ_H = 1.45 (t, *J* = 14.89 Hz, 3H, $\mathrm{NCH_2C}\mathit{H_3}$), 3.89 (s, 3H, $\mathrm{NC}\mathit{H_3}$) , 4.24 (q, *J* = 22.34 Hz, 2H, $\mathrm{NC}\mathit{H_2}\mathrm{CH_3}$), 7.69-7.77 (d, *J* = 42.96 Hz, 2H, $\mathrm{NC}\mathit{H}\mathrm{C}\mathit{H}\mathrm{N}$) , 9.13 (s, 1H, $\mathrm{NC}\mathit{H}\mathrm{N}$).

$\mathrm{[C_2mim]BF_4}$

$^1\mathrm{H}$-NMR (500 MHz, DMSO-D6, 25 °C, $\mathrm{Me_4Si}$) δ_H = 1.41 (t, *J* = 14.89 Hz, 3H, $\mathrm{NCH_2C}\mathit{H_3}$), 3.86 (s, 3H, $\mathrm{NC}\mathit{H_3}$), 4.21 (q, *J* = 21.77 Hz, 2H, $\mathrm{NC}\mathit{H_2}\mathrm{CH_3}$), 7.37-7.65 (d, *J* = 42.96 Hz, 2H, $\mathrm{NC}\mathit{H}\mathrm{C}\mathit{H}\mathrm{N}$), 9.02 (s, 1H, $\mathrm{NC}\mathit{H}\mathrm{N}$).

$\mathrm{[C_2mim]N(CF_3SO_3)_2}$

$^1\mathrm{H}$-NMR (500 MHz, DMSO-D6, 25 °C, $\mathrm{Me_4Si}$) δ_H = 1.45 (t, *J* = 14.89 Hz, 3H, $\mathrm{NCH_2C}\mathit{H_3}$), 3.87 (s, 3H, $\mathrm{NC}\mathit{H_3}$), 4.22 (q, *J* = 21.77 Hz, 2H, $\mathrm{NC}\mathit{H_2}\mathrm{CH_3}$), 7.67-7.74 (d, *J* = 39.52 Hz, 1H, $\mathrm{NC}\mathit{H}\mathrm{C}\mathit{H}\mathrm{N}$), 9.11 (s, 1H, $\mathrm{NC}\mathit{H}\mathrm{N}$).

$\mathrm{[Pyr_{14}]CF_3CO_2}$

$^1\mathrm{H}$-NMR (500 MHz, DMSO-D6, 25 °C, $\mathrm{Me_4Si}$) δ_H = 0.93 (t, *J* = 14.32 Hz, 3H, $\mathrm{NCH_2CH_2CH_2C}\mathit{H_3}$), 1.32 (m, *J* = 37.23 Hz, 2H, $\mathrm{NCH_2CH_2C}\mathit{H_2}\mathrm{CH_3}$), 1.68 (m, *J* = 32.08 Hz, 2H, $\mathrm{NCH_2C}\mathit{H_2}\mathrm{CH_2CH_3}$), 2.10 (d, *J* = 19.47 Hz, 4H, $\mathrm{NCH_2C}\mathit{H_2}\mathrm{C}\mathit{H_2}\mathrm{CH_2N}$), 2.99 (s, 3H, $\mathrm{NC}\mathit{H_3}$), 3.31 (m, *J* = 16.61 Hz, 2H, $\mathrm{NC}\mathit{H_2}\mathrm{CH_2CH_2CH_3}$), 3.42-3.51 (m, *J* = 49.26 Hz, 4H, $\mathrm{NC}\mathit{H_2}\mathrm{CH_2CH_2C}\mathit{H_2}\mathrm{N}$).

$\mathrm{[Mor_{14}]CF_3CO_2}$

$^1\mathrm{H}$-NMR (500 MHz, DMSO-D6, 25 °C, $\mathrm{Me_4Si}$) δ_H = 0.94 (t, *J* = 14.89 Hz, 3H, $\mathrm{NCH_2CH_2CH_2C}\mathit{H_3}$), 1.32 (m, *J* = 36.66 Hz, 2H, $\mathrm{NCH_2CH_2C}\mathit{H_2}\mathrm{CH_3}$), 1.65 (m, *J* = 32.08 Hz, 2H, $\mathrm{NCH_2C}\mathit{H_2}\mathrm{CH_2CH_3}$), 3.11 (s, 3H, $\mathrm{NC}\mathit{H_3}$), 3.37-3.43 (m, *J* = 33.79 Hz, 6H, $\mathrm{NC}\mathit{H_2}\mathrm{CH_2OCH_2C}\mathit{H_2}\mathrm{NC}\mathit{H_2}\mathrm{CH_2CH_2CH_3}$), 3.91 (s, 4H, $\mathrm{NCH_2C}\mathit{H_2}\mathrm{OC}\mathit{H_2}\mathrm{CH_2N}$).

$[\mathrm{Pip_{14}}]\mathrm{CF_3CO_2}$

^{1}H-NMR (500 MHz, DMSO-D6) δ_H = 0.94 (t, *J* = 14.89 Hz, 3H, $\mathrm{NCH_2CH_2CH_2C}\mathit{H_3}$), 1.32 (m, *J* = 36.66 Hz, 2H, $\mathrm{NCH_2CH_2C}\mathit{H_2}\mathrm{CH_3}$), 1.53 (m, *J* = 45.25 Hz, 2H, $\mathrm{NCH_2CH_2C}\mathit{H_2}\mathrm{CH_2CH_2N}$), 1.61-1.67 (m, *J* = 31.50 Hz, 2H, $\mathrm{NCH_2C}\mathit{H_2}\mathrm{CH_2CH_3}$), 1.78 (s, 4H, $\mathrm{NCH_2C}\mathit{H_2}\mathrm{CH_2C}\mathit{H_2}\mathrm{CH_2N}$), 2.98 (s, 3H, $\mathrm{NC}\mathit{H_3}$), 3.29 (m, *J* = 36.66 Hz, 6H, $\mathrm{N(C}\mathit{H_2}\mathrm{CH_2CH_2CH_2C}\mathit{H_2}\mathrm{)N(C}\mathit{H_2}\mathrm{CH_2CH_2CH_3))}$.

$[\mathrm{P_{4444}}]\mathrm{CF_3CO_2}$

^{1}H-NMR (500 MHz, DMSO-D6, 25 °C, $\mathrm{Me_4Si}$) δ_H = 0.92 (t, *J* = 14.32 Hz, 12H, $\mathrm{PCH_2CH_2CH_2C}\mathit{H_3}$), 1.37-1.50 (m, *J* = 67.01 Hz, 16H, $\mathrm{PCH_2C}\mathit{H_2}\mathrm{C}\mathit{H_2}\mathrm{CH_3}$), 2.16-2.22 (m, *J* = 30.36 Hz, 8H, $\mathrm{PC}\mathit{H_2}\mathrm{CH_2CH_2CH_3}$).

$[\mathrm{P_{4444}}]\mathrm{CH_3O(H)PO_2}$

^{1}H-NMR (500 MHz, DMSO-D6, 25 °C, $\mathrm{Me_4Si}$) δ_H = 0.92 (m, *J* = 29.78 Hz, 12H, $\mathrm{PCH_2CH_2CH_2C}\mathit{H_3}$), 1.44 (m, *J* = 67.01 Hz, 16H, $\mathrm{PCH_2C}\mathit{H_2}\mathrm{C}\mathit{H_2}\mathrm{CH_3}$), 2.21 (m, *J* = 29.78 Hz, 8H, $\mathrm{PC}\mathit{H_2}\mathrm{CH_2CH_2CH_3}$), 3.22 (m, *J* = 14.89 Hz, 3H, $\mathrm{POC}\mathit{H_3}$), 5.91-7.02 (d, *J* = 555.59 Hz, 1H, $\mathrm{P}\mathit{H}$).

$[\mathrm{P_{4444}}]\mathrm{N(CN)_2}$

^{1}H-NMR (500 MHz, DMSO-D6, 25 °C, $\mathrm{Me_4Si}$) δ_H = 0.92 (t, *J* = 23.81 Hz, 12H, $\mathrm{PCH_2CH_2CH_2C}\mathit{H_3}$), 1.38-1.49 (m, *J* = 59.53 Hz, 16H, $\mathrm{PCH_2C}\mathit{H_2}\mathrm{C}\mathit{H_2}\mathrm{CH_3}$), 2.17-2.23 (m, *J* = 29.77 Hz, 8H, $\mathrm{PC}\mathit{H_2}\mathrm{CH_2CH_2CH_3}$).

$[\mathrm{C_{2OH}mim}]\mathrm{N(CF_3SO_3)_2}$

^{1}H-NMR (500 MHz, DMSO-D6, 25 °C, $\mathrm{Me_4Si}$) δ_H = 3.75 (m, *J* = 15.11 Hz, 2H, $\mathrm{NCH_2C}\mathit{H_2}\mathrm{OH}$), 3.88 (s, *J* = 12.82 Hz, 3H, $\mathrm{NC}\mathit{H_3}$), 4.23 (q, *J* = 10.07 Hz, 2H, $\mathrm{NC}\mathit{H_2}\mathrm{CH_2OH}$), 5.18 (t, *J* = 10.53 Hz, 1H, $\mathrm{NCH_2CH_2O}\mathit{H}$), 7.67 (d, *J* = 16.49 Hz, 2H, $\mathrm{NC}\mathit{H}\mathrm{C}\mathit{H}\mathrm{N}$), 9.08 (s, 1H, $\mathrm{NC}\mathit{H}\mathrm{N}$).

Evaluation of polarity of ILs

Polarity of ILs was evaluated based on Kamlet-Taft parameters.[1] Solvatochromic dyes (Reichardt's dye, 4-nitroaniline, and *N, N*-diethyl-4-nitroaniline) individually dissolved in dry methanol were mixed with ILs. The mixture was dried *in vacuo* to remove methanol. For evaluation of IL/water mixtures, weighed methanol solution containing solvatochromic dyes was treated *in vacuo* beforehand to expel methanol and mixed with IL/water mixtures. UV-Vis spectra of the mixtures were recorded by Shimadzu UV-PC2450. Hydrogen bond donating ability (α value), hydrogen bond accepting ability (β value), and polarizability (π*value) were calculated based on the equations below.

$$\nu_{Dye} = 1/(\lambda_{max} \times 10^{-4})$$

$$E_T(30) = 0.9986\left(2.86\nu_{Reichardt's\ dye}\right) - 8.6878$$

$$\pi^* = 8.641 - 0.314\nu_{N,N-diethyl-4-nitroaniline}$$

$$\beta = \left[1.315\nu_{N,N-diethyl-4-nitroaniline} - \nu_{4-nitroaniline} + 2.64\right]/2.80$$

$$\alpha = 0.0649E_T(30) - 0.72\pi^* - 2.03$$

Experimental errors of α and β are less than 0.02 and 0.01, respectively when spectral error of 1 nm in λ_{max}.

Evaluation of lignin extraction degree from cedar powder

To ILs or their mixture with water, 5 wt% of ceder powder was added and stirred at 60 °C for 10 hrs. The mixture was centrifuged at 15,000 rpm. for 10 min to separate insoluble residue and liquid phase. Concentration of dissolved lignin (C_{lignin} in wt%), in the liquid phase was evaluated using UV-Vis spectroscopy, because phenolic group in AL has the maximum absorption at 280 nm. The baseline was recorded using ILs or IL/water mixture stirred at 60 °C for 10 hrs. In order to obtain C_{lignin}, a standard line was depicted by plotting the absorbance of $[C_2mim]CH_3O(H)PO_2$ containing defined amount of AL and the added weight of AL. The AL dissolution was conducted at 60 °C. C_{ligin} was calculated by the measured absorbance using the linear equation seen in Fig. S2.

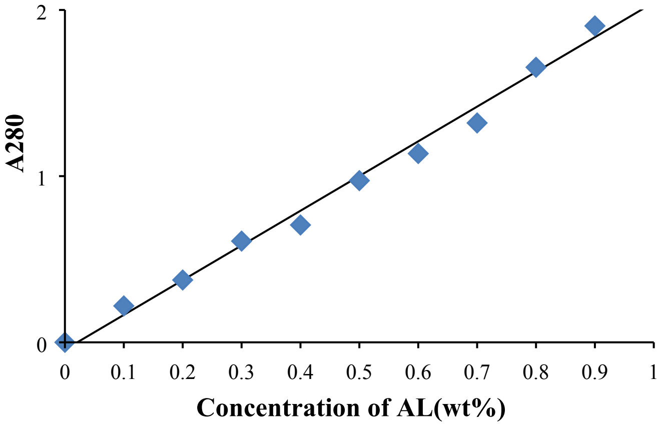


Fig. S2. Absorbance at 280 nm of AL dissolved in $[C_2mim]CH_3O(H)PO_2$.

Amount of extracted lignin (W_{lignin}) was then calculated form Eq.S1, where W_{CP} is a weight of added cedar powder and W_{solvent} is a weight of solvent.

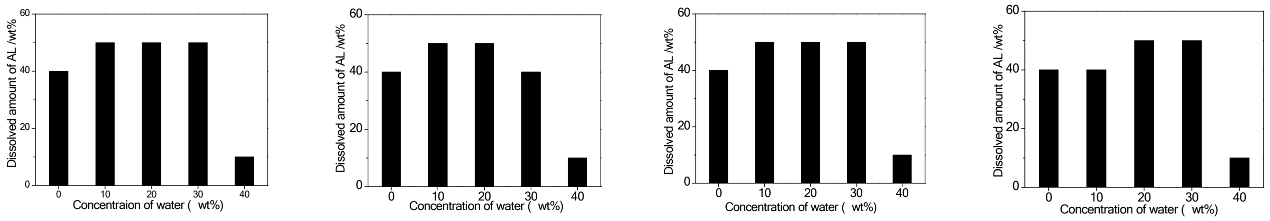
$$W_{\text{lignin}} = (W_{\text{CP}} + W_{\text{solvent}}) \times C_{\text{lignin}} / 100 \cdots \text{Eq.S1}$$

The W_{lignin} out of the quantity of lignin contained in the added cedar powder was defined as the extracted degree of lignin ($\%E_{\text{lignin}}$) as shown in Eq.S2. The weight of lignin in the cedar powder was estimated as when lignin content is 32.6 % according to Klason method.[2]

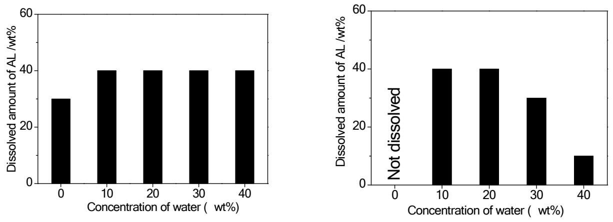
$$\%E_{\text{lignin}} = W_{\text{lignin}} / (W_{\text{CP}} \times 0.326) \cdots \text{Eq.S2}$$

AL solubility in IL/water mixtures

AL solubility in IL/water mixtures was determined as described in the experimental procedure. The effect of the amount of the added water on the dissolution of AL in several ILs are shown in Figs. S3 and S4.

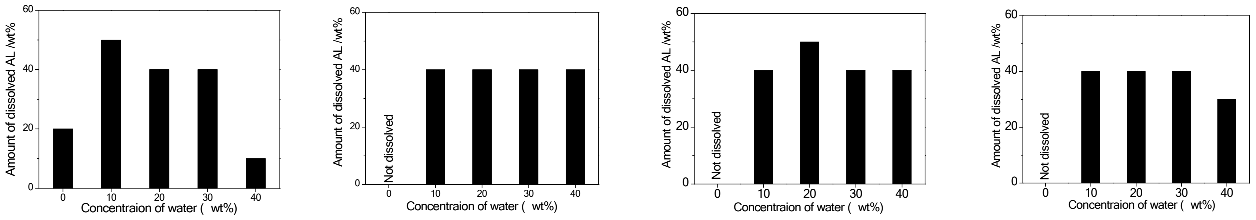


[C_2mim]CH_3CO_2 [C_2mim]CF_3CO_2 [C_2mim]$CH_3O(H)PO_2$ [C_2mim]CH_3SO_3



[C_2mim]$N(CN)_2$ [C_2mim]CF_3SO_3

Fig. S3 Effect of water addition on the AL solubility in [C_2mim] salts.



[Pyr_{14}]CF_3CO_2 [P_{4444}]CF_3CO_2 [Mor_{14}]CF_3CO_2 [Pip_{14}]CF_3CO_2

Fig. S4 Effect of water addition on the AL solubility in CF_3CO_2 salts.

Water concentration of ILs

In the present work, the unit of water concentration is based on weight% for convenient procedure. However, water content based on mol% is preferable for discussion at molecular level. We therefore have also taken number of water molecules per one ion pair (mol/mol) into account in the Tables S1 and S2.

Table S1. Water concentration of $[C_2mim]^+$ salts (weight% and mol/mol).

Water (wt%)	H$_2$O/IL (mol/mol)					
	CH_3CO_2	$CH_3O(H)PO_2$	CF_3CO_2	CH_3SO_3	$N(CN)_2$	CF_3SO_3
10	1.05	1.27	1.38	1.27	1.09	1.60
20	2.36	2.86	3.11	2.86	2.46	3.61
30	4.05	4.90	5.33	4.91	4.21	6.19
40	6.30	7.63	8.29	7.63	6.56	9.63

Table S2. Water concentration of CF_3CO_2 salts (weight% and mol/mol).

Water content (wt%)	H$_2$O/IL (mol/mol)			
	cation			
	$[Pyr_{14}]$	$[P_{4444}]$	$[Mor_{14}]$	$[Pip_{14}]$
10	1.57	2.30	1.67	1.66
20	3.54	5.17	3.76	3.74
30	6.07	8.86	6.45	6.40
40	9.44	13.78	10.04	9.96

References

1 C. Reichardt, *Green Chem.*, 2005, **7**, 339-351.

2 N. Phaiboonsilpa, K. Yamauchi, X. Lu and S. Saka, *J. Wood Sci.*, 2010, **56**, 331-338.