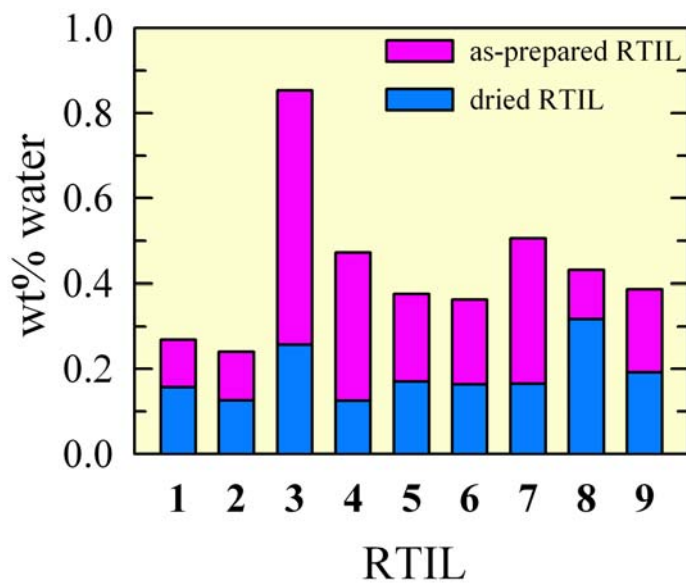


## Supplementary Information

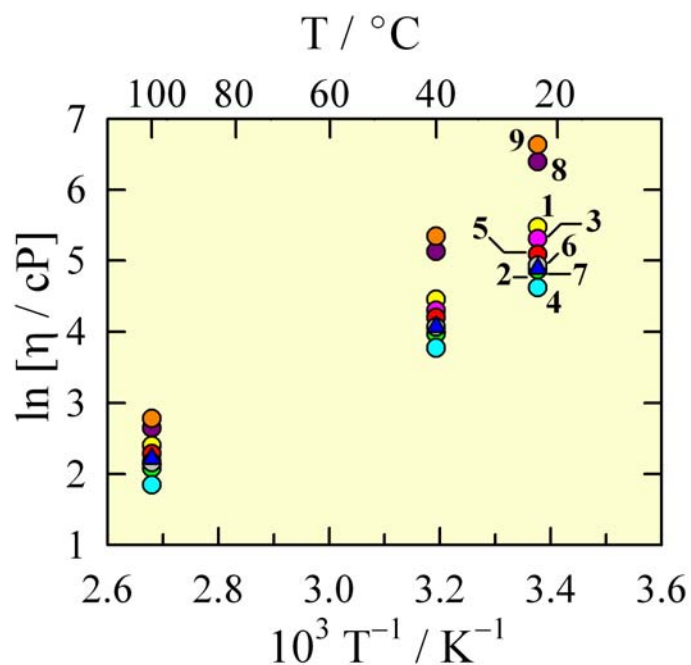
### Brønsted acidic room temperature ionic liquids derived from *N,N*-dimethylformamide and similar protophilic amides

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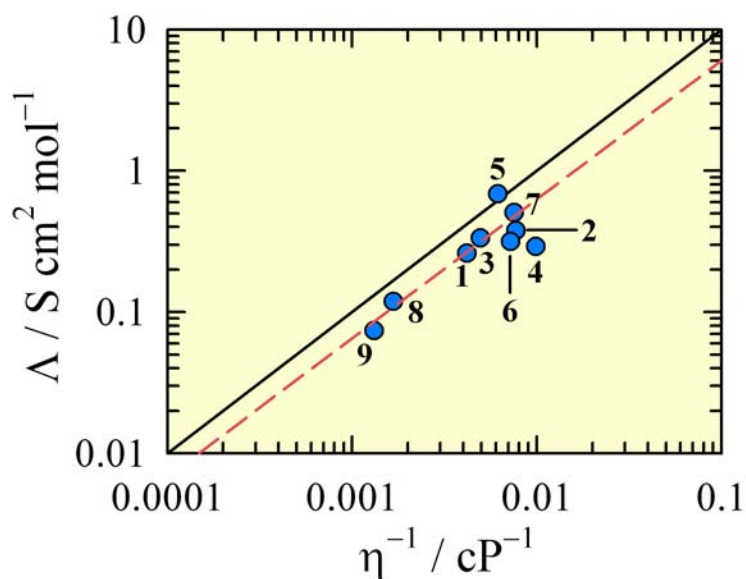
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**Fig. S1** Water contents of amide-based RTILs 1–9 measured before and after drying (under vacuum, 60 °C, overnight) based on Karl–Fischer water analysis (Mettler Toledo DL39 Coulometric KF Titrator).



**Fig. S2** Arrhenius plot of the viscosities of RTILs 1–9. At room temperature, the order in  $\eta$  is  $4 < 2 \approx 7 \approx 6 < 5 < 3 < 1 \ll 8 < 9$ .



**Fig. S3** Walden plot showing marginally *subionic* behavior for RTILs 1–9. The position of “ideal” Walden behavior, denoted by the solid line, was fixed using data for dilute aqueous KCl solutions known to be completely dissociated and to have ions of equal mobility. Note that RTIL 5 with behavior approaching the ideal Walden line gave the highest room temperature ionic conductivity ( $2.81 \text{ mS cm}^{-1}$ ).

**Table 1** Summary of physicochemical properties for RTIL **1-9**<sup>a</sup>

RTIL	density / gm <sup>-3</sup> (23 °C)	$\eta$ / cP (25 °C)	$T_g$ / °C <sup>b</sup>	$T_m$ / °C <sup>b</sup>	$T_d$ / °C <sup>b</sup>	$T_d$ / °C (HR) <sup>c</sup>	$\sigma_{25}$ / mScm <sup>-1</sup> (25 °C) <sup>d</sup>	$\sigma_{50}$ / mScm <sup>-1</sup> (50 °C) <sup>d</sup>	$\sigma_{100}$ / mScm <sup>-1</sup> (100 °C) <sup>d</sup>
1	1.553	239	-80.4	8.6	189	155	1.14	3.01	10.61
2	1.428	130	-87.5	-	194	158	1.41	2.74	6.88
3	1.334	202	-74.5	6.2	189	165	1.09	2.89	9.71
4	1.162	101	-94.2	-	189	164	0.77	2.04	6.46
5	1.507	162	-86.2	7.3	232	194	2.81	7.24	21.24
6	1.417	138	-87.2	-7.2	213	184	1.13	2.97	5.17
7	1.468	133	-92.3	-	236	185	1.94	4.48	11.84
8	1.411	599	-62.5	-	217	190	0.39	1.31	3.95
9	1.496	760	-76.4	-	216	180	0.28	0.86	3.44

<sup>a</sup> Equimolar (1:1) salts (amide: Tf<sub>2</sub>N<sup>-</sup>) prepared. <sup>b</sup>  $T_g$  = glass-transition temperature determined by differential scanning calorimeter (DSC);  $T_m$  = melting temperature determined by DSC;  $T_d$  = decomposition temperature (temperature of 10% overall weight loss) determined by TGA (heating rate = 10°C/min). <sup>c</sup> Decomposition temperature determined by TGA (heating rate = 5°C/min, hold when overall weight loss was higher than 0.5%, and re-ramped with a heating rate of 5 °C /min when the overall weight loss was less than 0.5%). <sup>d</sup>  $\sigma_T$  = conductivity measured at temperature of T ( °C).