

## SUPPLEMENTARY INFORMATION

### Hydrogen bonds in protic ionic liquids and their correlation with physicochemical properties

Muhammed Shah Miran,<sup>‡</sup> Hiroshi Kinoshita, Tomohiro Yasuda, Md. Abu Bin Hasan Susan<sup>‡</sup> and Masayoshi Watanabe\*

*Department of Chemistry and Biotechnology, Yokohama National University,  
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan*

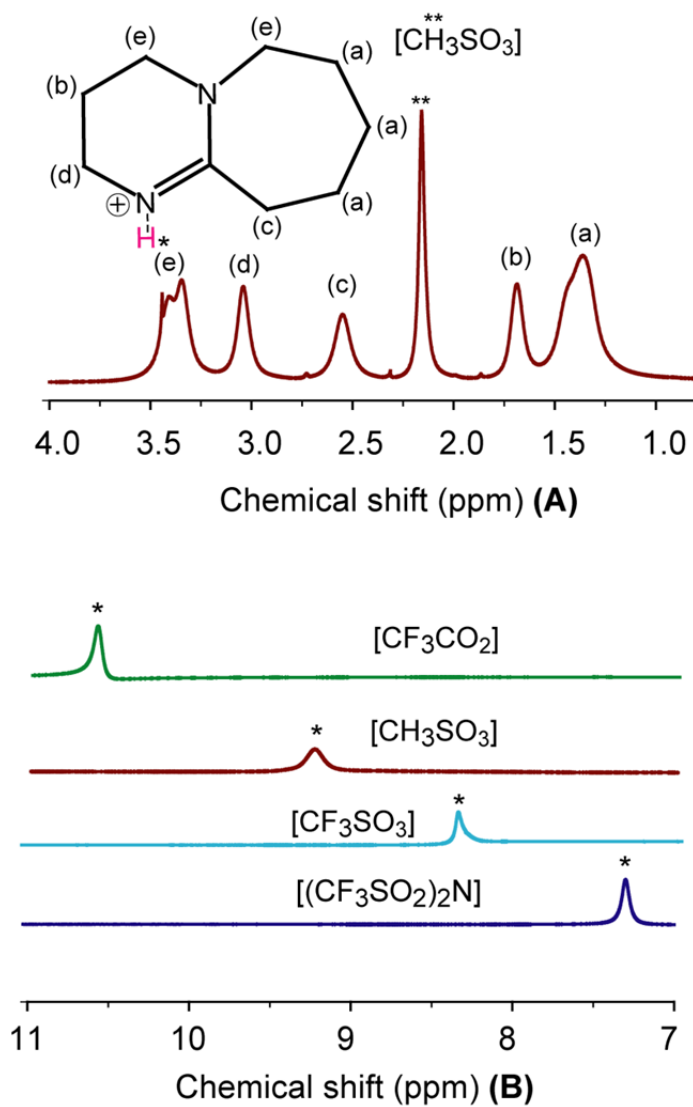
*<sup>‡</sup>Permanent address: Department of Chemistry, University of Dhaka, Dhaka 1000,  
Bangladesh*

\*E-mail: mwatanab@ynu.ac.jp

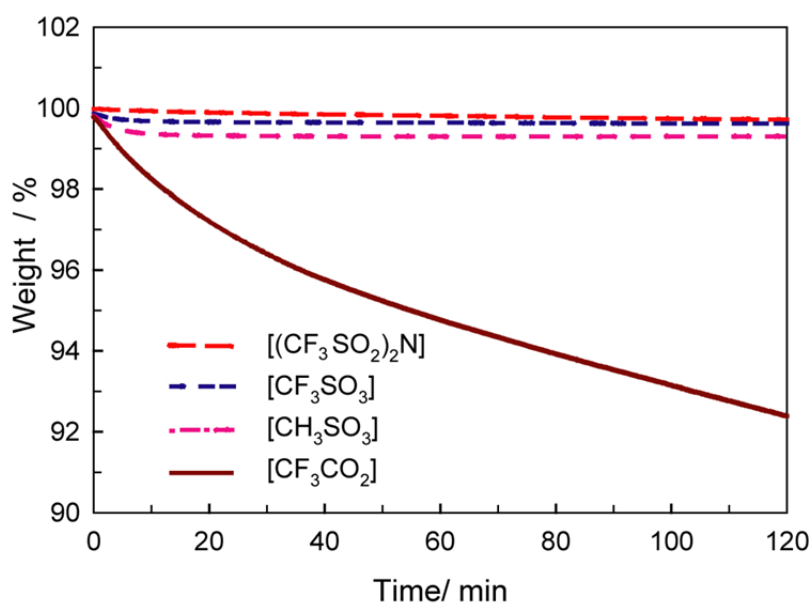
**Table S1.** Thermal behaviors of [DBU]-based PILs

Protic ionic liquids	$\Delta pK_a$	$T_m / (^\circ\text{C})^a$	$T_g / (^\circ\text{C})^a$	$T_d / (^\circ\text{C})^b$
[DBU][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	23.4	25	--	451
[DBU][CF <sub>3</sub> SO <sub>3</sub> ]	20.4	23	- 62	431
[DBU][CH <sub>3</sub> SO <sub>3</sub> ]	15.4	--	- 42	288
[DBU][CF <sub>3</sub> CO <sub>2</sub> ]	13.0	--	- 56	183

<sup>a</sup> $T_m$  and  $T_g$  are melting point and glass transition temperature respectively, measured by differential scanning calorimetry. <sup>b</sup>Onset temperature of mass loss ( $T_d$ ) determined by thermogravimetric analysis.



**Figure S1.**  $^1\text{H}$  NMR spectra of [DBU] based PILs containing [CH<sub>3</sub>SO<sub>3</sub>] (A) and other anions (B) for N-H proton at 30 °C. All spectra were recorded using a double tube; sample was taken in the inner tube and, deuterated DMSO containing TMS was taken in the outer tube as the standard.



**Figure S2.** Time-dependent isothermal TG for [DBU]-based PILs at 130 °C for 2 h under an N<sub>2</sub> atmosphere.

**Table S2.** Self-diffusion coefficient determined by PGSE-NMR<sup>†</sup> for [DBU]-based PILs at different temperature.

Temperature / °C	[DBU][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]		[DBU][CF <sub>3</sub> SO <sub>3</sub> ]		[DBU][CF <sub>3</sub> CO <sub>2</sub> ]	
	Self-diffusion coefficient, $D / 10^{-8} \text{ cm}^2 \text{ s}^{-1}$					
	Cation	Anion	Cation	Anion	Cation	Anion
50	21.8	18.4	8.07	5.87	7.10	3.99
70	43.8	38.0	15.5	15.0	16.0	14.4
90	83.7	72.9	36.9	33.1	39.3	39.0
110	130.0	142.0	71.0	64.9	80.4	80.2

<sup>†</sup> The PGSE-NMR measurements were done by utilizing a JEOL JNM-AL 400 spectrometer with a 9.4 T narrow bore superconducting magnet equipped with a JEOL pulse field gradient probe and a current amplifier. The self-diffusion coefficients were measured using the simple Hahn spin-echo sequence, incorporating a sine gradient pulses,  $\Delta$ , which was set at 30-50 ms, and the duration of the field gradient,  $\delta$ , was varied.

**Table S3.** VFT equation parameters for molar conductivity data

$A_{\text{imp}} = A_o \exp[-B/(T-T_o)]$			
	$A_o/10^{-1} \text{ Scm}^2\text{mol}^{-1}$	$B/10^2 \text{ K}$	$T_o/\text{K}$
$[(\text{CF}_3\text{SO}_2)_2\text{N}]$	1.9 ± 0.2	7.21 ± 0.30	190.0 ± 4
$[\text{CF}_3\text{SO}_3]$	2.7 ± 0.2	9.41 ± 0.26	189.0 ± 3
$[\text{CF}_3\text{CO}_2]$	0.7 ± 0.2	5.54 ± 0.89	232.0 ± 11

**Experimental conditions:**

Molar conductivity has been calculated from the ionic conductivity and molar concentration at the same temperature. Ionic conductivities were determined by measurement of the complex impedance spectra between 10 MHz and 0.01 Hz on a potentiostat (Autolab, PGSTAT30). The temperature was controlled at 20 °C intervals in the range of 30-150 °C using a constant temperature oven DKN 611.