Preparation procedure and physical properties of porous glasses used in this study.

The matrices used in this study were treated as follows; the Controlled-Pore Glasses (CPGs) purchased from Sigma Aldrich Co. Ltd. (80-120 mesh powder) were washed in nitric acid and rinsed by deionized water for several times, and then dried at 423 K for one hour. The surface-modified CPG (CPG-CH_3) was prepared by the similar silylation procedure.[S1] The Vycor glass (Corning, Vycor 7930) was washed and dried as previously described in detail.[S2] The physical properties of the matrices were listed in Table S1.

Table S1. Physical Properties of Matrices Used in this Study

matrix	mean pore diameter / nm	pore distribution /%	surface area / m^2 g^{-1}
CPG 7.5 [a]	7.5	±6.0	140
CPG 11.5 [a]	11.5	±7.3	119.5
CPG 22.6 [a]	22.6	±6.2	94
CPG 50.0 [b]	(50.0)	-	-
Vycor [c]	7.0	±7.0	103

[a] Provided from Sigma Aldrich Co. Ltd. [b] Estimated. [c] Cited from ref.[S3]

Preparation procedure of ionic liquids used in this study.

The ionic liquids [BMIM]X was prepared in our laboratory as previously described.[S4] First, the precursor 1-butyl-3-methylimidazolium chloride, [BMIM]Cl, was obtained by heating and stirring equimolar amounts of 1-methylimidazole (Wako, 98% or Sigma-Aldrich, 99%) and 1-chlorobutane (Tokyo Kasei, 98%) at 343 K for 72 h. The resulting viscous yellow liquid was cooled to room temperature and washed with ethyl acetate several times. The remaining ethyl acetate was roughly evaporated, and then completely removed by heating at 343 K for 12 h under vacuum. An aqueous solution of HPF_6 (Aldrich), CF_3SO_3H (Wako), or $Li(CF_3SO_2)_2N$ (Kanto) was deliberately added to a [BMIM]Cl aqueous or dichloromethane solution in an ice-bath for 12 h. The upper aqueous layer was decanted, and the lower ionic liquid was washed with water and saturated $NaHCO_3$ aqueous solutions several times until the aqueous phase was no longer acidic and did not generate AgCl precipitate by $AgNO_3$ test. After dichloromethane was removed at 343 K with an evaporator for a few hours, the ionic liquid was stirred with activated charcoal at room temperature to remove traces of colored impurities. Then, the charcoal was removed by filtration through neutral alumina column. The obtained colorless liquid was dried under vacuum at 343 K for 30 h to remove any excess water.

A dichloromethane solution of commercial [EMIM][PF_6] (Tokyo Kasei, 98%) was washed with water several times. It was confirmed that the aqueous phase was not acidic and did not generate AgCl precipitate by $AgNO_3$ test. The dichloromethane solution was stirred with activated charcoal at room temperature. Then, the charcoal was removed by filtration through neutral alumina column. The obtained colorless liquid was dried under vacuum at 343 K for 30 h to remove any excess water.

The water contents of ILs prepared in the similar manner were determined by Karl-Fischer titration as shown in Table S2. The densities and viscosities of ILs in our lab, which were recently reported,[S5] also guarantees high purity of the samples.

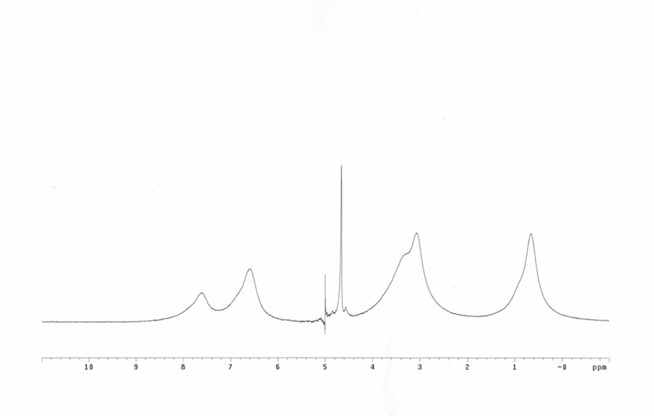
Table S2. Water Contents of ILs Used in this Study

IL	water content / w/w-ppm
[BMIM][PF_6]	33 ± 8
[BMIM][$(CF_3SO_2)_2N$]	19 ± 3
[BMIM][CF_3SO_3]	< 400
[EMIM][PF_6]	not determined

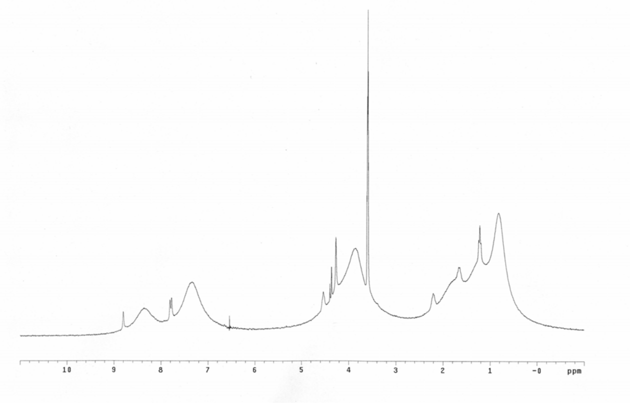
^{1}H NMR spectra of ionic liquids confined in Vycor.

^{1}H NMR spectra of [EMIM][PF$_6$] and [BMIM][PF$_6$] confined in Vycor at 288 and 293 K are given as follows.

^{1}H NMR of [EMIM][PF$_6$] confined in Vycor at 288 K



^{1}H NMR of [BMIM][PF$_6$] confined in Vycor at 293 K



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