Supporting information for

4,5-Dihaloimidazolium-based ionic liquids: Effects of halogen-bonding on crystal structures and ionic conductivity

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Measurement

We measured ^{1}H NMR spectra on a JEOL JNM-ECA 500 in DMSO-d_6 or $CDCl_3$ at room temperature. The chemical shifts of the ^{1}H signals were obtained relative to tetramethylsilane (δ = 0.00) as the internal standard. Elemental analyses were carried out using a Perkin-Elmer 2400 and CE instruments EA1110 apparatus.

We studied phase transition behaviour on a RIGAKU Thermoplus EVO DSC 8230 and a RIGAKU Thermoplus 2 TG 8120. The heating and cooling rates were 10 °C min^{-1}. The melting point was taken at the peak-top of exothermic peak. The onset of the change in heat capacity was taken as the glass transition temperature. The onset of the change in weight was taken as the thermal decomposition temperature. The density and viscosity measurement was carried out on an Anton paar DMA 4500 and Anton paar AMVn, respectively. Ionic conductivity was measured by the complex impedance method over a frequency range running from 10 Hz to 1 MHz, using a HIOKI 3532-80 chemical impedance meter. A measuring cell constant was calibrated with 0.01M KCl aqueous solution.

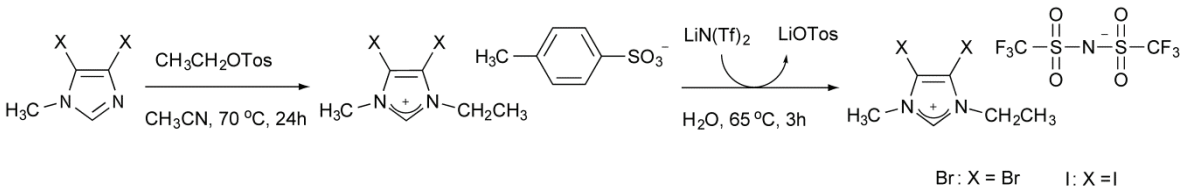
We performed single-crystal X-ray analysis on a Bruker APEX II. The single crystals of **Br** and **I** were obtained from aqueous solutions. The single crystal was mounted in a wire loop with a minimal amount of paratone-N (Hampton Research), and was cooled to −100 °C with a stream of nitrogen gas. We collected diffraction data for the crystals using a Bruker APEX II CCD area detector using MoK_α-radiation (λ = 0.71073 Å). The crystal structures were refined with SHELXL-97. Non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and included in the calculation using the riding atom model.

Materials

We purchased ionic liquid **H** from Kanto Kagaku. The ionic liquid was dried under 17.5 Pa at 100 °C for 24h before used.

Synthetic procedure

The synthetic procedures of **Br** and **I** are shown in scheme S1. 4,5-dibromo-1-methylimidazole[1] and 4,5-diiodo-1-methylimidazole[2] were prepared according to a previously reported procedure. We purchased all reagents and solvents from Wako or TCI, and used as received. The quaternization reactions were carried out under an argon atmosphere.



Tos: p-toluenesulfonyl group, Tf: trifluoromethanesulfonyl group

Scheme S1 Synthetic procedure of **Br** and **I**

Synthesis of 4,5-dibromo-1-ethyl-3-methylimidazolium p-toluenesulfonate

Ethyl *p*-toluenesulfonate (11.0 g, 55.0 mmol) was added to a solution of 4,5-dibromo-1-methylimidazole (12.0 g, 50.0 mmol) in acetonitrile (30 mL). The mixture was refluxed for 24h at 70 °C. After the solution was cooled to room temperature, diethyl ether (100 mL) was added to the solution. The precipitation was collected by suction filtration, and purified by performing recrystallization from a mixed acetonitrile-ethyl acetate (2:1) solution. After drying in *vacuo* at 50 °C for 3 days, we obtained 4,5-dibromo-1-ethyl-3- methylimidazolium *p*-toluenesulfonate as a white powder in 84.1 % yield. ^{1}H NMR (DMSO-d_6, 500MHz, 25 °C): δ = 1.32 (t, CH_2–CH_3, 3H), 2.22 (s, C–CH_3, 3H), 3.74 (s, N–CH_3, 3H), 4.10 (q, N–CH_2, 2H), 7.05 (d, C–H, 2H), 7.41 (s, C–H, 2H), 9.50 (s, C–H, 1H). Elemental analysis: calcd. for $C_{13}H_{16}Br_2N_2O_3S_1$: C, 35.47; H, 3.66; N, 6.36. Found: C, 35.47, H, 3.53, N, 6.29.

Synthesis of 4,5-dibromo-1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonly)imide, **Br**

An aqueous solution of lithium bis(trifluoromethanesulfonyl)imide (7.2 g, 25.0 mmol) was added dropwise to a stirring solution of 4,5-dibromo-1-ethyl-3-methylimidazolim *p*-toluenesufonate (10 g, 22.7 mmol) in water (30 mL) at 65 °C over 3h. After the biphasic

solution was cooled to room temperature, the lower ionic liquid layer was collected *via* a separating funnel, dissolved in ethylacetate (100 mL) and washed with water (20 mL) three times. The organic layer was collected, and the solvent removed by rotary evaporator. The residual liquid was dissolved in dichloromethane (100 mL) and washed with water (20 mL) for three times. The organic layer was collected, dried over anhydrous $MgSO_4$, filtered and the solvent removed in *vacuo* to yield the desired salt as a colourless liquid. The liquid crystallized slowly at room temperature. The residual white powder was recrystallized from a mixed dichloromethane/hexane (2:1) solution. After drying in *vacuo* at 50 °C for 3 days, we obtained the salt **Br** as colourless crystals in 80.0 % yield. ^{1}H NMR ($CDCl_3$, 500MHz, 25 °C): δ = 1.35 (t, CH_2–C*H*$_3$, 3H), 3.77 (s, N–CH_3, 3H), 4.15 (q, N–CH_2–, 2H), 9.43 (s, C–H, 1H). Elemental analysis: calcd. for $C_8H_9Br_2F_6N_3O_4S_2$: C, 17.50; H, 1.65; N, 7.65. Found: C, 17.47, H, 1.44, N, 7.31.

Synthesis of 4,5-diiodo-3-ethyl-1-methylimidazolium p-toluene sulfonate

Ethyl *p*-toluenesulfonate (7.92 g, 39.5 mmol) was added to a solution of 4,5-diiodo-1-methylimidazole (12.0 g, 35.9 mmol) in acetonitrile (50 mL). The mixture was refluxed at 70 °C for 24h. After the reaction, the desired salt was precipitated as white powder. The precipitation was collected by suction filtration, and purified by performing recrystallization from a mixed ethanol-etylacetate (3:1) solution. After drying in *vacuo* at 50 °C for 3 days, we obtained 1-butyl-4,5-diiodo-3-methylimidazolium *p*-toluenesulfonate as a white powder in 57.7 % yield. ^{1}H NMR (DMSO-d_6, 500MHz, 25 °C): δ = 1.32 (t, CH_2–C*H*$_3$, 3H), 2.23 (s, C–CH_3, 3H), 3.77 (s, N–CH_3, 3H), 4.12 (q, N–CH_2, 2H), 7.05 (d, C–H, 2H), 7.41 (s, C–H, 2H), 9.44 (s, C–H, 1H). Elemental analysis: calcd. for $C_{13}H_{16}I_2N_2O_3S_1$: C, 29.23; H, 3.02; N, 5.24. Found: C, 29.15, H, 2.58, N, 5.18.

Synthesis of 4,5-diiodo-3-ethyl-1-methylimidazolium bis(trifluoromethansulfonyl)imide, **I**

An aqueous solution of lithium bis(trifluoromethanesulfonyl)imide (5.9 g, 20.6 mmol) was added dropwise to a stirring solution of 4,5-diiodo-1-ethyl-3-methylimidazolim *p*-toluenesufonate (10 g, 18.7 mmol) in water (30 mL) at 65 °C over 3h. After the biphasic solution was cooled to room temperature, the lower ionic liquid layer was collected *via* a separating funnel, dissolved in ethylacetate (100 mL) and washed with distilled water (20 mL) for three times. The organic layer was collected, and the solvent removed by rotary evaporator. The residual liquid was dissolved in dichloromethane (100 mL) and washed with distilled water (20 mL) for three times. The organic layer was collected, dried over anhydrous $MgSO_4$, filtered

and the solvent removed in *vacuo* to yield the desired salt as a colourless liquid. The liquid slowly crystallized at room temperature. The residual white powder was recrystallized from a mixed dichloromethane/hexane (3:1) solution. After drying in *vacuo* at 50 °C for 3 days, we obtained the salt **I** as colourless crystals in 90.0 % yield. ^{1}H NMR (DMSO-d_6, 500MHz, 25 °C): δ = 1.322 (t, CH_2–CH_3, 3H), 3.769 (s, N–CH_3, 3H), 4.122 (q, N–CH_2–, 2H), 9.426 (s, C–H, 1H). Elemental analysis: calcd. for $C_8H_9F_6I_2N_3O_4S_2$: C, 14.94; H, 1.41; N, 6.53. Found: C, 14.88, H, 1.24, N, 6.20.

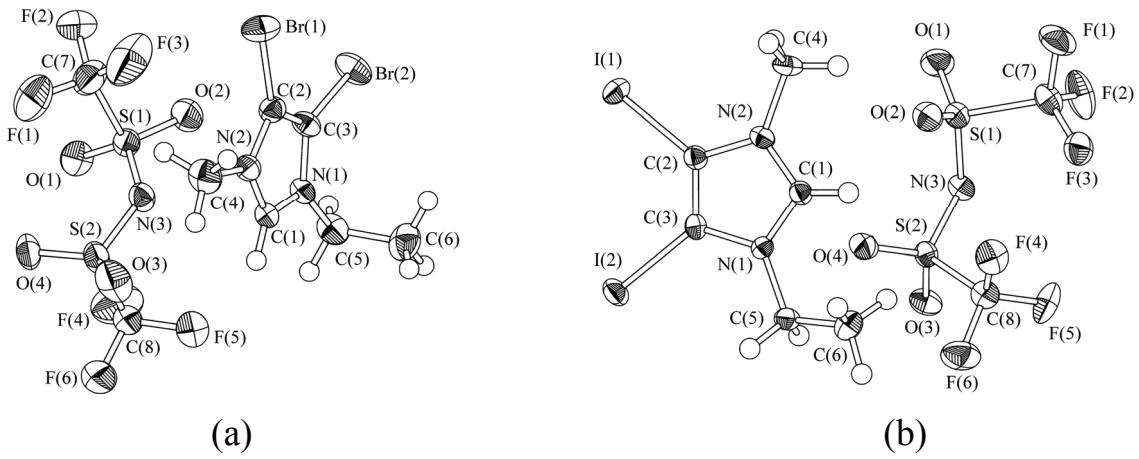
[References]

1. J. F. O'Connell, J. Parquette,W. E. Yelle, W.Wang and H. Rapoport, *Synthesis*, 1988, 767.
2. T. Mukai and K. Nishikawa, *Solid State Sci*., 2010, **12**, 783.

Table S1 Crystal and refinement data

	Br	**I**
Chemical formula	$C_8H_9Br_2F_6N_3O_4S_2$	$C_8H_9F_6I_2N_3O_4S_2$
Formula weight	549.12	643.10
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	P_{bca}
a / Å	9.6737(5)	8.2841(4)
b / Å	13.8295(8)	16.1160(8)
c / Å	13.7694(8)	26.3361(14)
β / °	106.9790(10)	
V / Å^3	1761.81(17)	3516.0(3)
Z	4	8
D_c / g cm^{-3}	2.070	2.430
Absorption coefficient / mm^{-1}	4.918	3.895
F(000)	1064	2416
T / K	173	173
$\theta_{min,\ max}$ / °	2.14, 27.26	1.55, 28.56
Reflections collected	9676	18783
Independent reflections, R_{int}	3921, 0.0330	4197, 0.0385
Max. and min. transmission	0.6391 and 0.5258	0.8291 and 0.5927
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3921 / 0 / 228	4197 / 0 / 228
Goodness-of-fit on F^2	0.967	1.024
R_1	0.0374 (0.0635)*	0.0307 (0.0466)*
wR_2	0.0785 (0.0853)*	0.0654 (0.0704)*
Largest diff. peak and hole / e.Å^{-3}	0.385 and −0.587	0.429 and −1.117
CCDC	942517	763036

*Number in parentheses is for all data.



(a) (b)

Fig. S1 Asymmetric units of **Br** (a) and **I** (b) with 50% provability.

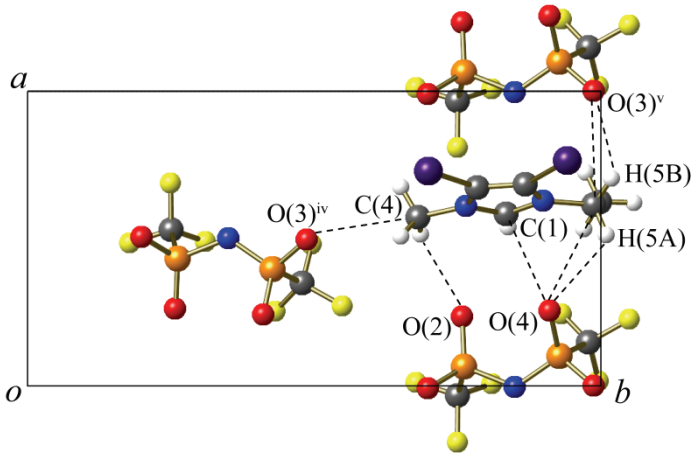


Fig. S2 Interactions in the ion domain of the **I** crystal viewed along the *c* axis. The colours represent the following: C, grey; H, white; O, red; N, blue; F, yellow; S, orange, and I, purple.

Table S2 Weak hydrogen-bonding in the ion domain of the **I** crystal.

C-H···O	$d_{H\cdots O}$ / Å	$d_{H\cdots O}$ − vdw / Å	$d_{C\cdots O}$ / Å	$d_{C\cdots O}$ − vdw / Å	$\angle_{C\text{-}H\cdots O}$ / °
C(4)–H(4C)···O(3)^{iv}	2.66	−0.06	3.206(4)	−0.014	117
C(5)–H(5B)···O(3)^{v}	2.52	−0.20	3.192(4)	−0.028	125
C(4)–H(4A)···O(2)	2.64	−0.08	3.337(5)	+0.117	129
C(5)–H(5A)···O(4)	2.67	−0.05	3.230(4)	+0.01	116

Symmetry codes: (iv) 1/2 − *x*, −1/2 + *y*, *z*; (v) 1 + *x*, *y*, *z*

Table S3 Interactions in the fluoro/hydrocarbon domain of the **Br** and **I** crystal.

Comp.	C–H/F···F	$d_{H/F\cdots F}$ / Å	$d_{H/F\cdots F}$ − vdw / Å	$d_{C\cdots F}$ / Å	$d_{C\cdots F}$ − vdw / Å	$\angle_{C\text{-}H/F\cdots F}$ / °
Br	C(5)–H(5B)···F(5)	2.65	−0.02	3.506(5)	+0.336	145
	C(6)–H(6B)···F(6)^{iii}	2.64	−0.03	3.416(5)	+0.246	136
I	C(6)–H(6A)···F(4)	2.64	−0.03	3.593(4)	+0.423	165
	C(6)–H(6C)···F(5)^{v}	2.62	−0.05	3.495(5)	+0.325	149
	C(7)–F(2)···F(3)^{vi}	2.868(3)	−0.072			145.6(3)
	C(7)–F(3)···F(2)^{iii}	2.868(3)	−0.072			101.3(2)

Symmetry codes: **Br**: (iii) −*x*, −*y*, −*z*; **I**: (vi) −1/2 + *x*, *y*, 1/2 − *z*.

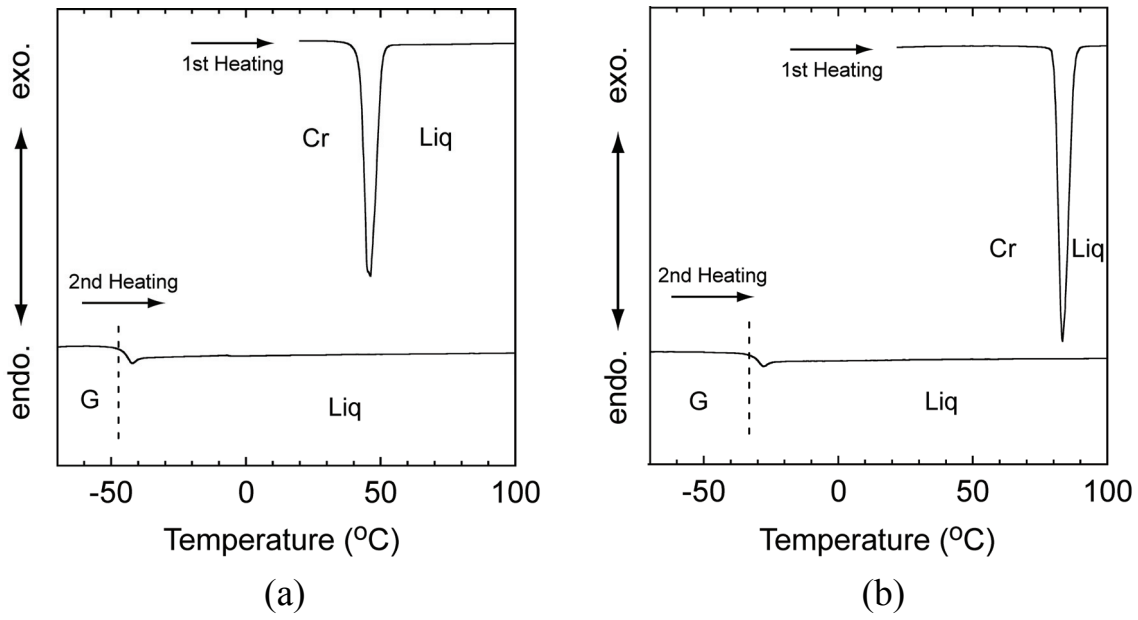


Fig. S3 DSC curves of (a) **Br** and (b) **I** of the first and second heating.
Cr: Crystal, Liq: isotropic liquid and G: Glass

Table S4 Viscosity and density of **H**, **Br** and **I**.

t / °C	**H**		**Br**		**I**	
	η / cP	ρ / g cm^{-3}	η / cP	ρ / g cm^{-3}	η / cP	ρ / g cm^{-3}
10	60.8	1.534	-[a]	1.922	-[b]	-[b]
15	48.8	1.529	1258	1.917	-[b]	-[b]
20	39.9	1.524	783	1.911	-[b]	-[b]
25	33.1	1.519	508	1.904	-[b]	-[b]
30	27.9	1.514	344	1.898	-[b]	-[b]
35	23.8	1.509	240	1.892	-[b]	-[b]
40	20.4	1.504	173	1.886	-[b]	-[b]
45	17.8	1.499	129	1.880	-[b]	-[b]
50	15.5	1.494	99.6	1.874	-[b]	-[b]
55	13.7	1.489	78.0	1.868	-[b]	-[b]
60	12.1	1.484	62.1	1.862	-[b]	-[b]
65	10.8	1.479	50.5	1.856	-[b]	2.080
70	9.67	1.474	41.3	1.850	-[b]	2.074
75	8.70	1.469	34.6	1.844	-[b]	2.068
80	7.89	1.465	29.0	1.838	-[b]	2.062
85	7.16	1.460	24.8	1.832	-[b]	2.056
90	6.54	1.455	21.4	1.826	47.9	2.049

[a] Over 2000 cP, [b] Crystallized in the measuring cell

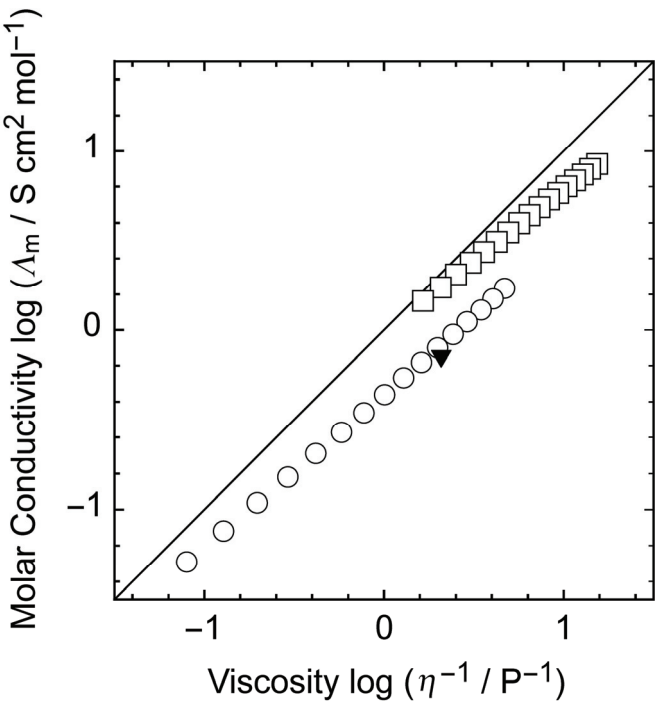


Fig. S4 Walden plot of the molar conductivity and viscosity data in the present study, **H** (□), **Br** (○), and **I** (▼). The solid line represents the ideal 1:1 Walden line.