Electronic Supplementary Information

Mixing states of imidazolium-based ionic liquid, [C_4mim][TFSI], with cycloethers studied by SANS, IR, NMR, and MD simulations

Masahiro Kawano[a], Koichiro Sadakane[b], Hiroki Iwase[c], Masaru Matsugami[d], Bogdan A. Marekha[e], Abdenacer Idrissi[f], and Toshiyuki Takamuku[g,*]

[a]*Department of Chemistry and Applied Chemistry, Graduate School of Science and Engineering, Saga University, Honjo-machi, Saga 840-8502, Japan*

[b]*Faculty of Life and Medical Sciences, Doshisha University, 1-3 Tatara Miyakodani, Kyotanabe, Kyoto 610-0394, Japan*

[c]*Comprehensive Research Organization for Science and Society (CROSS), 162-1 Shirakata, Tokai, Ibaraki 319-1106, Japan*

[d]*Faculty of Liberal Studies, National Institute of Technology, Kumamoto College, 2659-2 Suya, Koshi, Kumatomo 861-1102, Japan*

[e]*Molecular Spectroscopy Department, Max Planck Institute for Polymer Research, 10 Ackermannweg, 55128 Mainz, Germany*

[f]*University of Lille, CNRS, UMR 8516-LASIR-Laboratoire de Spectrochimie Infrarouge et Raman, F-59000 Lille, France*

[g]*Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi, Saga 840-8502, Japan*

*Corresponding Author
Toshiyuki Takamuku
E-mail: takamut@cc.saga-u.ac.jp

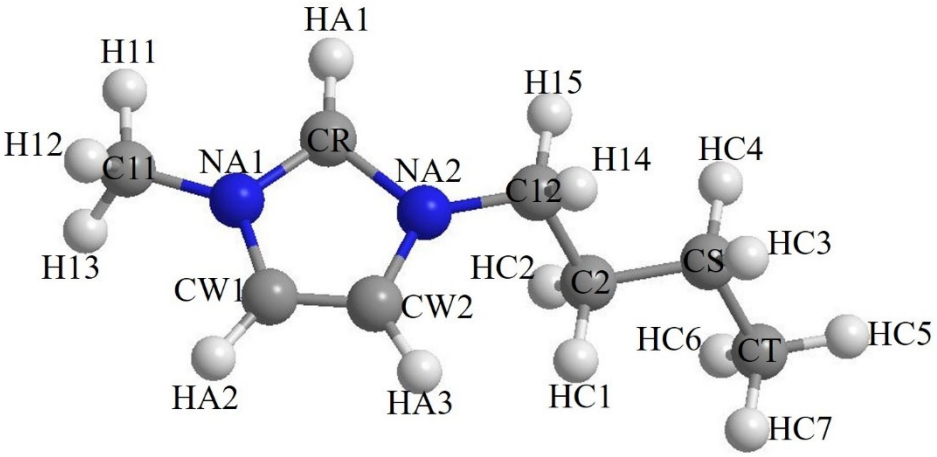

Fig. S1 Structure of $[C_4mim]^+$.

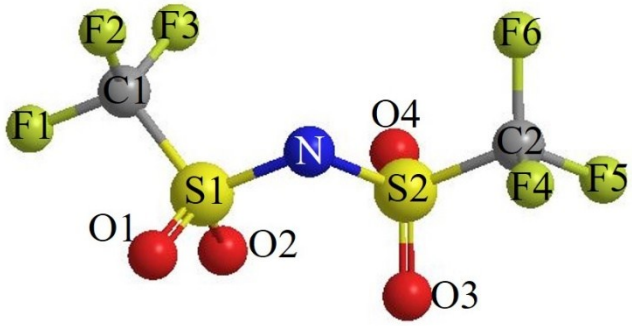

Fig. S2 Structure of $[TFSI]^-$.

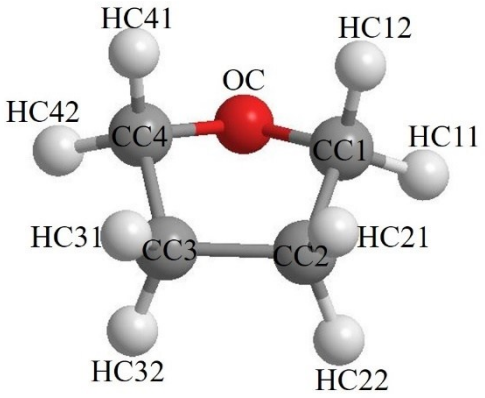

Fig. S3 Structure of THF.

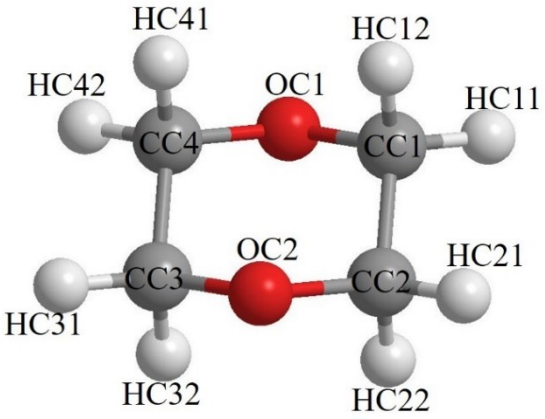

Fig. S4 Structure of 1,4-DIO.

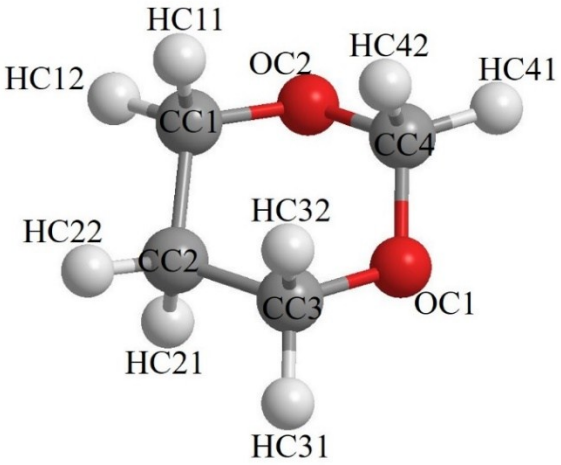

Fig. S5 Structure of 1,3-DIO.

Table S1. Atomic parameters for [C_4mim][TFSI] and cycloethers.

	Atom	Charge / *e*	Mass / amu	σ / Å	ε / kcal mol^{-1}
[C_4mim]$^+$	NA1	0.150	14.007	3.250	0.170
	CR	-0.110	12.011	3.550	0.070
	NA2	0.150	14.007	3.250	0.170
	CW1	-0.130	12.011	3.550	0.070
	C11	-0.170	12.011	3.500	0.066
	CW2	-0.130	12.011	3.550	0.070
	C12	-0.170	12.011	3.500	0.066
	C2	0.010	12.011	3.500	0.066
	CS	-0.120	12.011	3.500	0.066
	CT	-0.180	12.011	3.500	0.066
	HA1	0.210	1.008	2.420	0.030
	HA2	0.210	1.008	2.420	0.030
	H11	0.130	1.008	2.500	0.030
	H12	0.130	1.008	2.500	0.030
	H13	0.130	1.008	2.500	0.030
	HA3	0.210	1.008	2.420	0.030
	H14	0.130	1.008	2.500	0.030
	H15	0.130	1.008	2.500	0.030
	HC1	0.060	1.008	2.500	0.030
	HC2	0.060	1.008	2.500	0.030
	HC3	0.060	1.008	2.500	0.030
	HC4	0.060	1.008	2.500	0.030
	HC5	0.060	1.008	2.500	0.030
	HC6	0.060	1.008	2.500	0.030
	HC7	0.060	1.008	2.500	0.030
[TFSI]$^-$	N	-0.660	14.007	3.250	0.170
	S1	1.020	32.064	3.550	0.250
	S2	1.020	32.064	3.550	0.250
	C1	0.350	12.011	3.500	0.066
	C2	0.350	12.011	3.500	0.066
	O1	-0.530	15.999	2.960	0.210
	O2	-0.530	15.999	2.960	0.210
	O3	-0.530	15.999	2.960	0.210

Cont.	O4	-0.530	15.999	2.960	0.210
	F1	-0.160	18.998	2.950	0.053
	F2	-0.160	18.998	2.950	0.053
	F3	-0.160	18.998	2.950	0.053
	F4	-0.160	18.998	2.950	0.053
	F5	-0.160	18.998	2.950	0.053
	F6	-0.160	18.998	2.950	0.053
THF	CC1	0.140	12.011	3.500	0.066
	HC11	0.030	1.008	2.500	0.030
	HC12	0.030	1.008	2.500	0.030
	CC2	-0.120	12.011	3.500	0.066
	HC21	0.060	1.008	2.500	0.030
	HC22	0.060	1.008	2.500	0.030
	CC3	-0.120	12.011	3.500	0.066
	HC31	0.060	1.008	2.500	0.030
	HC32	0.060	1.008	2.500	0.030
	CC4	0.140	12.011	3.500	0.066
	HC41	0.030	1.008	2.500	0.030
	HC42	0.030	1.008	2.500	0.030
	OC	-0.400	15.9994	2.900	0.140
1,4-DIO	CC1	0.140	12.011	3.500	0.066
	OC1	-0.400	15.9994	2.900	0.140
	HC11	0.030	1.008	2.500	0.030
	HC12	0.030	1.008	2.500	0.030
	CC2	0.140	12.011	3.500	0.066
	OC2	-0.400	15.9994	2.900	0.140
	HC21	0.030	1.008	2.500	0.030
	HC22	0.030	1.008	2.500	0.030
	CC3	0.140	12.011	3.500	0.066
	HC31	0.030	1.008	2.500	0.030
	HC32	0.030	1.008	2.500	0.030
	CC4	0.140	12.011	3.500	0.066
	HC41	0.030	1.008	2.500	0.030
	HC42	0.030	1.008	2.500	0.030

Cont.

1,3-DIO	CC1	0.140	12.011	3.500	0.066
	HC12	0.030	1.008	2.500	0.030
	HC11	0.030	1.008	2.500	0.030
	CC2	-0.120	12.011	3.500	0.066
	HC21	0.060	1.008	2.500	0.030
	HC22	0.060	1.008	2.500	0.030
	CC3	0.140	12.011	3.500	0.066
	HC31	0.030	1.008	2.500	0.030
	HC32	0.030	1.008	2.500	0.030
	OC1	-0.400	15.9994	2.900	0.140
	CC4	0.200	12.011	3.500	0.066
	HC41	0.100	1.008	2.500	0.030
	HC42	0.100	1.008	2.500	0.030
	OC2	-0.400	15.9994	2.900	0.140

Table S2. Bond stretching parameters for [C_4mim][TFSI] and cycloethers.

	Bond	r / Å
$[C_4mim]^+$	NA1-CR	1.315
	NA1-CW1	1.378
	NA1-C11	1.466
	CR-NA2	1.315
	CR-HA1	1.080
	NA2-CW2	1.378
	NA2-C12	1.466
	CW1-CW2	1.341
	CW1-HA2	1.080
	C11-H11	1.090
	C11-H12	1.090
	C11-H13	1.090
	CW2-HA3	1.080
	C12-C2	1.529
	C12-H14	1.090
	C12-H15	1.090
	C2-CS	1.529
	C2-HC1	1.090
	C2-HC2	1.090
	CS-CT	1.529
	CS-HC3	1.090
	CS-HC4	1.090
	CT-HC5	1.090
	CT-HC6	1.090
	CT-HC7	1.090
$[TFSI]^-$	N-S1	1.570
	N-S2	1.570
	S1-C1	1.818
	S1-O1	1.437
	S1-O2	1.437
	S2-C2	1.818
	S2-O3	1.437
	S2-O4	1.437

Cont.	C1-F1	1.323
	C1-F2	1.323
	C1-F3	1.323
	C2-F4	1.323
	C2-F5	1.323
	C2-F6	1.323
THF	CC1-HC11	1.090
	CC1-HC12	1.090
	CC1-CC2	1.529
	CC1-OC	1.410
	CC2-HC21	1.090
	CC2-HC22	1.090
	CC2-CC3	1.529
	CC3-HC31	1.090
	CC3-HC32	1.090
	CC3-CC4	1.529
	CC4-HC41	1.090
	CC4-HC42	1.090
	CC4-OC	1.410
1,4-DIO	CC1-OC1	1.410
	CC1-CC2	1.529
	CC1-HC11	1.090
	CC1-HC12	1.090
	CC2-OC2	1.410
	CC2-HC21	1.090
	CC2-HC22	1.090
	CC3-OC2	1.410
	CC3-CC4	1.529
	CC3-HC31	1.090
	CC3-HC32	1.090
	CC4-OC1	1.410
	CC4-HC41	1.090
	CC4-HC42	1.090
1,3-DIO	CC2-HC21	1.090

Cont.	CC1-HC12	1.090
	CC1-CC2	1.529
	CC1-OC2	1.410
	CC1-HC11	1.090
	CC2-HC22	1.090
	CC2-CC3	1.529
	CC4-OC2	1.380
	CC3-HC31	1.090
	CC3-OC1	1.410
	CC4-OC1	1.380
	CC3-HC32	1.090
	CC4-HC41	1.090
	CC4-HC42	1.090

Table S3. Angle bending parameters for [C_4mim][TFSI] and cycloethers.

	Angle	K / kcal mol^{-1} rad^{-2}	θ / degree
[C_4mim]$^+$	NA1-CR-NA2	70.00	109.8
	NA1-CR-HA1	35.00	125.1
	NA1-CW1-CW2	70.00	107.1
	NA1-CW1-HA2	35.00	122.0
	NA1-C11-H11	37.50	110.7
	NA1-C11-H12	37.50	110.7
	NA1-C11-H13	37.50	110.7
	CR-NA1-CW1	70.00	108.0
	CR-NA1-C11	70.00	126.4
	CR-NA2-CW2	70.00	108.0
	CR-NA2-C12	70.00	126.4
	NA2-CR-HA1	35.00	125.1
	NA2-CW2-CW1	70.00	107.1
	NA2-CW2-HA3	35.00	122.0
	NA2-C12-C2	58.30	112.7
	NA2-C12-H14	37.50	110.7
	NA2-C12-H15	37.50	110.7
	CW1-NA1-C11	70.00	125.6
	CW1-CW2-HA3	35.00	130.9
	CW2-NA2-C12	70.00	125.6
	CW2-CW1-HA2	35.00	130.9
	C12-C2-CS	58.30	112.7
	C12-C2-HC1	37.50	110.7
	C12-C2-HC2	37.50	110.7
	C2-C12-H14	37.50	110.7
	C2-C12-H15	37.50	110.7
	C2-CS-CT	58.30	112.7
	C2-CS-HC3	37.50	110.7
	C2-CS-HC4	37.50	110.7
	CS-C2-HC1	37.50	110.7
	CS-C2-HC2	37.50	110.7
	CS-CT-HC5	37.50	110.7
	CS-CT-HC6	37.50	110.7
	CS-CT-HC7	37.50	110.7

Cont.	CT-CS-HC3	37.50	110.7
	CT-CS-HC4	37.50	110.7
	H11-C11-H12	33.00	107.8
	H11-C11-H13	33.00	107.8
	H12-C11-H13	33.00	107.8
	H14-C12-H15	33.00	107.8
	HC1-C2-HC2	33.00	107.8
	HC3-CS-HC4	33.00	107.8
	HC4-CT-HC6	33.00	107.8
	HC5-CT-HC7	33.00	107.8
	HC6-CT-HC7	33.00	107.8
$[TFSI]^-$	N-S1-C1	91.30	103.5
	N-S1-O1	94.20	113.6
	N-S1-O2	94.20	113.6
	N-S2-C2	91.30	103.5
	N-S2-O3	94.20	113.6
	N-S2-O4	94.20	113.6
	S1-N-S3	80.10	125.6
	S1-C1-F1	82.90	111.7
	S1-C1-F2	82.90	111.7
	S1-C1-F3	82.90	111.7
	S2-C2-F4	82.90	111.7
	S2-C2-F5	82.90	111.7
	S2-C2-F6	82.90	111.7
	C1-S1-O1	103.90	102.6
	C1-S1-O2	103.90	102.6
	C2-S2-O3	103.90	102.6
	C2-S2-O4	103.90	102.6
	O1-S1-O2	115.70	118.5
	O3-S2-O4	115.70	118.5
	F1-C1-F2	93.30	107.1
	F1-C1-F3	93.30	107.1
	F2-C1-F3	93.30	107.1
	F4-C2-F5	93.30	107.1
	F4-C2-F6	93.30	107.1
	F5-C2-F6	93.30	107.1

Cont.

THF	HC11-CC1-HC12	33.00	107.8
	CC2-CC1-HC11	37.50	110.7
	HC11-CC1-OC	35.00	109.5
	CC2-CC1-HC12	37.50	110.7
	HC12-CC1-OC	35.00	109.5
	CC2-CC1-OC	50.00	109.5
	CC1-CC2-HC21	37.50	110.7
	CC1-CC2-HC22	37.50	110.7
	CC1-CC2-CC3	58.35	112.7
	HC21-CC2-HC22	33.00	107.8
	CC3-CC2-HC21	37.50	110.7
	CC3-CC2-HC22	37.50	110.7
	CC2-CC3-HC31	37.50	110.7
	CC2-CC3-HC32	37.50	110.7
	CC2-CC3-CC4	58.35	112.7
	HC31-CC3-HC32	33.00	107.8
	CC4-CC3-HC31	37.50	110.7
	CC4-CC3-HC32	37.50	110.7
	CC3-CC4-HC41	37.50	110.7
	CC3-CC4-HC42	37.50	110.7
	CC3-CC4-OC	50.00	109.5
	HC41-CC4-HC42	33.00	107.8
	HC41-CC4-OC	35.00	109.5
	HC42-CC4-OC	35.00	109.5
	CC1-OC-CC4	60.00	109.5
1,4-DIO	HC11-CC1-OC1	35.00	109.5
	HC12-CC1-OC1	35.00	109.5
	CC2-CC1-OC1	50.00	109.5
	CC2-CC1-HC11	37.50	110.7
	CC2-CC1-HC12	37.50	110.7
	HC11-CC1-HC12	33.00	107.8
	CC1-CC2-OC2	50.00	109.5
	CC1-CC2-HC21	37.50	110.7
	CC1-CC2-HC22	37.50	110.7
	HC21-CC2-OC2	35.00	109.5

Cont.	HC22-CC2-OC2	35.00	109.5
	HC21-CC2-HC22	33.00	107.8
	CC2-OC2-CC3	60.00	109.5
	CC4-CC3-OC2	50.00	109.5
	HC31-CC3-OC2	35.00	109.5
	HC32-CC3-OC2	35.00	109.5
	CC4-CC3-HC31	37.50	110.7
	CC4-CC3-HC32	37.50	110.7
	HC31-CC3-HC32	33.00	107.8
	CC3-CC4-OC1	50.00	109.5
	CC3-CC4-HC41	37.50	110.7
	CC3-CC4-HC42	37.50	110.7
	HC41-CC4-OC1	35.00	109.5
	HC42-CC4-OC1	35.00	109.5
	HC41-CC4-HC42	33.00	107.8
	CC1-OC1-CC4	60.00	109.5
1,3-DIO	CC1-CC2-HC21	37.50	110.7
	HC21-CC2-HC22	33.00	107.8
	CC3-CC2-HC21	37.50	110.7
	CC2-CC1-HC12	37.50	110.7
	HC12-CC1-OC2	35.00	109.5
	HC12-CC1-HC11	33.00	107.8
	CC2-CC1-OC2	50.00	109.5
	CC2-CC1-HC11	37.50	110.7
	CC1-CC2-HC22	37.50	110.7
	CC1-CC2-CC3	58.35	112.7
	HC11-CC1-OC2	35.00	109.5
	CC1-OC2-CC4	60.00	109.5
	CC3-CC2-HC22	37.50	110.7
	CC2-CC3-HC31	37.50	110.7
	CC2-CC3-OC1	50.00	109.5
	CC2-CC3-HC32	37.50	110.7
	OC2-CC4-OC1	92.60	111.55
	HC41-CC4-OC2	35.00	109.5
	HC42-CC4-OC2	35.00	109.5
	HC31-CC3-OC1	35.00	109.5

Cont.	HC31-CC3-HC32	33.00	107.8
	CC4-OC1-CC3	60.00	109.5
	HC32-CC3-OC1	35.00	109.5
	HC41-CC4-OC1	35.00	109.5
	HC42-CC4-OC1	35.00	109.5
	HC42-CC4-HC41	33.00	109.5

Table S4. Dihedral parameters for [C_4mim][TFSI] and cycloethers.

	Dihedral	V_1 / kcal mol^{-1}	V_2 / kcal mol^{-1}	V_3 / kcal mol^{-1}	V_4 / kcal mol^{-1}
[C_4mim]$^+$	NA1-CR-NA2-CW2	0.000	4.650	0.000	0.000
	NA1-CR-NA2-C12	0.000	4.650	0.000	0.000
	NA1-CW1-CW2-NA2	0.000	10.750	0.000	0.000
	NA1-CW1-CW2-HA3	0.000	10.750	0.000	0.000
	CR-NA1-CW1-CW2	0.000	3.000	0.000	0.000
	CR-NA1-CW1-HA2	0.000	3.000	0.000	0.000
	CR-NA1-C11-H11	0.000	0.000	0.000	0.000
	CR-NA1-C11-H12	0.000	0.000	0.000	0.000
	CR-NA1-C11-H13	0.000	0.000	0.000	0.000
	CR-NA2-CW2-CW1	0.000	3.000	0.000	0.000
	CR-NA2-CW2-HA3	0.000	3.000	0.000	0.000
	CR-NA2-C12-C2	-1.259	0.000	0.000	0.000
	CR-NA2-C12-H14	0.000	0.000	0.000	0.000
	CR-NA2-C12-H15	0.000	0.000	0.000	0.000
	NA2-CR-NA1-CW1	0.000	4.650	0.000	0.000
	NA2-CR-NA1-C11	0.000	4.650	0.000	0.000
	NA2-CW2-CW1-HA2	0.000	10.750	0.000	0.000
	NA2-C12-C2-CS	-1.787	0.756	-0.287	0.000
	NA2-C12-C2-HC1	0.000	0.000	0.088	0.000
	NA2-C12-C2-HC2	0.000	0.000	0.088	0.000
	CW1-NA1-CR-HA1	0.000	4.650	0.000	0.000
	CW1-NA1-C11-H11	0.000	0.000	0.124	0.000
	CW1-NA1-C11-H12	0.000	0.000	0.124	0.000
	CW1-NA1-C11-H13	0.000	0.000	0.124	0.000
	CW1-CW2-NA2-C12	0.000	3.000	0.000	0.000
	C11-NA1-CR-HA1	0.000	4.650	0.000	0.000
	CW2-CW1-NA1-C11	0.000	3.000	0.000	0.000
	C11-NA1-CW1-HA2	0.000	3.000	0.000	0.000
	CW2-NA2-CR-HA1	0.000	4.650	0.000	0.000
	CW2-NA2-C12-C2	-1.709	1.459	0.190	0.000
	CW2-NA2-C12-H14	0.000	0.000	0.124	0.000
	CW2-NA2-C12-H15	0.000	0.000	0.124	0.000
	C12-NA2-CR-HA1	0.000	4.650	0.000	0.000

Cont.	C12-NA2-CW2-HA3	0.000	3.000	0.000	0.000
	C12-C2-CS-CT	1.739	-0.157	0.279	0.000
	C12-C2-CS-HC3	0.000	0.000	0.366	0.000
	C12-C2-CS-HC4	0.000	0.000	0.366	0.000
	C2-CS-CT-HC5	0.000	0.000	0.366	0.000
	C2-CS-CT-HC6	0.000	0.000	0.366	0.000
	C2-CS-CT-HC7	0.000	0.000	0.366	0.000
	CS-C2-C12-H14	0.000	0.000	0.366	0.000
	CS-C2-C12-H15	0.000	0.000	0.366	0.000
	CT-CS-C2-HC1	0.000	0.000	0.366	0.000
	CT-CS-C2-HC2	0.000	0.000	0.366	0.000
	HA2-CW1-CW2-HA3	0.000	10.750	0.000	0.000
	H14-C12-C2-HC1	0.000	0.000	0.318	0.000
	H14-C12-C2-HC2	0.000	0.000	0.318	0.000
	H15-C12-C2-HC1	0.000	0.000	0.318	0.000
	H15-C12-C2-HC2	0.000	0.000	0.318	0.000
	HC1-C2-CS-HC3	0.000	0.000	0.318	0.000
	HC1-C2-CS-HC4	0.000	0.000	0.318	0.000
	HC2-C2-CS-HC3	0.000	0.000	0.318	0.000
	HC2-C2-CS-HC4	0.000	0.000	0.318	0.000
	HC3-CS-CT-CH5	0.000	0.000	0.318	0.000
	HC3-CS-CT-CH6	0.000	0.000	0.318	0.000
	HC3-CS-CT-CH7	0.000	0.000	0.318	0.000
	HC4-CS-CT-CH5	0.000	0.000	0.318	0.000
	HC4-CS-CT-CH6	0.000	0.000	0.318	0.000
	HC4-CS-CT-CH7	0.000	0.000	0.318	0.000
$[TFSI]^-$	N-S1-C1-F1	0.000	0.000	0.316	0.000
	N-S1-C1-F2	0.000	0.000	0.316	0.000
	N-S1-C1-F3	0.000	0.000	0.316	0.000
	N-S2-C2-F4	0.000	0.000	0.316	0.000
	N-S2-C2-F5	0.000	0.000	0.316	0.000
	N-S2-C2-F6	0.000	0.000	0.316	0.000
	S1-N-S2-C2	7.829	-2.489	-0.763	0.000
	S1-N-S2-O3	0.000	0.000	-0.003	0.000
	S1-N-S2-O4	0.000	0.000	-0.003	0.000
	S2-N-S1-C1	7.829	-2.489	-0.763	0.000

Cont.	S2-N-S1-O1	0.000	0.000	-0.003	0.000
	S2-N-S1-O2	0.000	0.000	-0.003	0.000
	O1-S1-C1-F1	0.000	0.000	0.347	0.000
	O1-S1-C1-F2	0.000	0.000	0.347	0.000
	O1-S1-C1-F3	0.000	0.000	0.347	0.000
	O2-S1-C1-F1	0.000	0.000	0.347	0.000
	O2-S1-C1-F2	0.000	0.000	0.347	0.000
	O2-S1-C1-F3	0.000	0.000	0.347	0.000
	O3-S2-C2-F4	0.000	0.000	0.347	0.000
	O3-S2-C2-F5	0.000	0.000	0.347	0.000
	O3-S2-C2-F6	0.000	0.000	0.347	0.000
	O4-S2-C2-F4	0.000	0.000	0.347	0.000
	O4-S2-C2-F5	0.000	0.000	0.347	0.000
	O4-S2-C2-F6	0.000	0.000	0.347	0.000
THF	HC11-CC1-CC2-HC21	0.000	0.000	0.300	0.000
	HC11-CC1-CC2-HC22	0.000	0.000	0.300	0.000
	CC3-CC2-CC1-HC11	0.000	0.000	0.300	0.000
	HC12-CC1-CC2-HC21	0.000	0.000	0.300	0.000
	HC12-CC1-CC2-HC22	0.000	0.000	0.300	0.000
	CC3-CC2-CC1-HC12	0.000	0.000	0.300	0.000
	HC21-CC2-CC1-OC	0.000	0.000	0.468	0.000
	HC22-CC2-CC1-OC	0.000	0.000	0.468	0.000
	CC3-CC2-CC1-OC	1.711	-0.500	0.663	0.000
	CC4-OC-CC1-HC11	0.000	0.000	0.760	0.000
	CC4-OC-CC1-HC12	0.000	0.000	0.760	0.000
	CC2-CC1-OC-CC4	0.650	-0.250	0.670	0.000
	CC1-CC2-CC3-HC31	0.000	0.000	0.300	0.000
	CC1-CC2-CC3-HC32	0.000	0.000	0.300	0.000
	CC1-CC2-CC3-CC4	1.300	-0.050	0.200	0.000
	HC21-CC2-CC3-HC31	0.000	0.000	0.300	0.000
	HC21-CC2-CC3-HC32	0.000	0.000	0.300	0.000
	CC4-CC3-CC2-HC21	0.000	0.000	0.300	0.000
	HC22-CC2-CC3-HC31	0.000	0.000	0.300	0.000
	HC22-CC2-CC3-HC32	0.000	0.000	0.300	0.000
	CC4-CC3-CC2-HC22	0.000	0.000	0.300	0.000
	CC2-CC3-CC4-HC41	0.000	0.000	0.300	0.000

Cont.	CC2-CC3-CC4-HC42	0.000	0.000	0.300	0.000
	CC2-CC3-CC4-OC	1.711	-0.500	0.663	0.000
	HC31-CC3-CC4-HC41	0.000	0.000	0.300	0.000
	HC31-CC3-CC4-HC42	0.000	0.000	0.300	0.000
	HC31-CC3-CC4-OC	0.000	0.000	0.468	0.000
	HC32-CC3-CC4-HC41	0.000	0.000	0.300	0.000
	HC32-CC3-CC4-HC42	0.000	0.000	0.300	0.000
	HC32-CC3-CC4-OC	0.000	0.000	0.468	0.000
	CC3-CC4-OC-CC1	0.650	-0.250	0.670	0.000
	CC1-OC-CC4-HC41	0.000	0.000	0.760	0.000
	CC1-OC-CC4-HC42	0.000	0.000	0.760	0.000
1,4-DIO	CC2-CC1-OC1-CC4	0.650	-0.250	0.670	0.000
	CC4-OC1-CC1-HC11	0.000	0.000	0.760	0.000
	CC4-OC1-CC1-HC12	0.000	0.000	0.760	0.000
	OC1-CC1-CC2-OC2	-0.550	0.000	0.000	0.000
	HC21-CC2-CC1-OC1	0.000	0.000	0.468	0.000
	HC22-CC2-CC1-OC1	0.000	0.000	0.468	0.000
	HC11-CC1-CC2-OC2	0.000	0.000	0.468	0.000
	HC11-CC1-CC2-HC21	0.000	0.000	0.300	0.000
	HC11-CC1-CC2-HC22	0.000	0.000	0.300	0.000
	HC12-CC1-CC2-OC2	0.000	0.000	0.468	0.000
	HC12-CC1-CC2-HC21	0.000	0.000	0.300	0.000
	HC12-CC1-CC2-HC22	0.000	0.000	0.300	0.000
	CC1-CC2-OC2-CC3	0.650	-0.250	0.670	0.000
	CC3-OC2-CC2-HC21	0.000	0.000	0.760	0.000
	CC3-OC2-CC2-HC22	0.000	0.000	0.760	0.000
	CC4-CC3-OC2-CC2	0.650	-0.250	0.670	0.000
	CC2-OC2-CC3-HC31	0.000	0.000	0.760	0.000
	CC2-OC2-CC3-HC32	0.000	0.000	0.760	0.000
	OC2-CC3-CC4-OC1	-0.550	0.000	0.000	0.000
	HC41-CC4-CC3-OC2	0.000	0.000	0.468	0.000
	HC42-CC4-CC3-OC2	0.000	0.000	0.468	0.000
	HC31-CC3-CC4-OC1	0.000	0.000	0.468	0.000
	HC31-CC3-CC4-HC41	0.000	0.000	0.300	0.000
	HC31-CC3-CC4-HC42	0.000	0.000	0.300	0.000
	HC32-CC3-CC4-OC1	0.000	0.000	0.468	0.000

Cont.	HC32-CC3-CC4-HC41	0.000	0.000	0.300	0.000
	HC32-CC3-CC4-HC42	0.000	0.000	0.300	0.000
	CC3-CC4-OC1-CC1	0.650	-0.250	0.670	0.000
	CC1-OC1-CC4-HC41	0.000	0.000	0.760	0.000
	CC1-OC1-CC4-HC42	0.000	0.000	0.760	0.000
1,3-DIO	HC12-CC1-CC2-HC21	0.000	0.000	0.300	0.000
	HC12-CC1-CC2-HC22	0.000	0.000	0.300	0.000
	CC3-CC2-CC1-HC12	0.000	0.000	0.300	0.000
	HC21-CC2-CC1-OC2	0.000	0.000	0.468	0.000
	HC22-CC2-CC1-OC2	0.000	0.000	0.468	0.000
	CC3-CC2-CC1-OC2	1.711	-0.500	0.663	0.000
	HC11-CC1-CC2-HC21	0.000	0.000	0.300	0.000
	HC11-CC1-CC2-HC22	0.000	0.000	0.300	0.000
	CC3-CC2-CC1-HC11	0.000	0.000	0.300	0.000
	CC4-OC2-CC1-HC12	0.000	0.000	0.760	0.000
	CC4-OC2-CC1-CC2	0.650	-0.250	0.670	0.000
	CC4-OC2-CC1-HC11	0.000	0.000	0.760	0.000
	HC21-CC2-CC3-HC31	0.000	0.000	0.300	0.000
	HC21-CC2-CC3-OC1	0.000	0.000	0.468	0.000
	HC21-CC2-CC3-HC32	0.000	0.000	0.300	0.000
	CC1-CC2-CC3-HC32	0.000	0.000	0.300	0.000
	CC1-CC2-CC3-OC1	1.711	-0.500	0.663	0.000
	CC1-CC2-CC3-HC32	0.000	0.000	0.300	0.000
	HC22-CC2-CC3-HC31	0.000	0.000	0.300	0.000
	HC22-CC2-CC3-OC1	0.000	0.000	0.468	0.000
	HC22-CC2-CC3-HC32	0.000	0.000	0.300	0.000
	CC1-OC2-CC4-OC1	-0.375	-1.358	0.004	0.000
	CC1-OC2-CC4-HC41	0.000	0.000	0.760	0.000
	CC1-OC2-CC4-HC42	0.000	0.000	0.760	0.000
	CC4-OC1-CC3-CC2	0.650	-0.250	0.670	0.000
	CC4-OC1-CC3-HC31	0.000	0.000	0.760	0.000
	CC4-OC1-CC3-HC32	0.000	0.000	0.760	0.000
	CC3-OC1-CC4-OC2	-0.375	-1.358	0.004	0.000
	CC3-OC1-CC4-HC41	0.000	0.000	0.760	0.000
	CC3-OC1-CC4-HC42	0.000	0.000	0.760	0.000

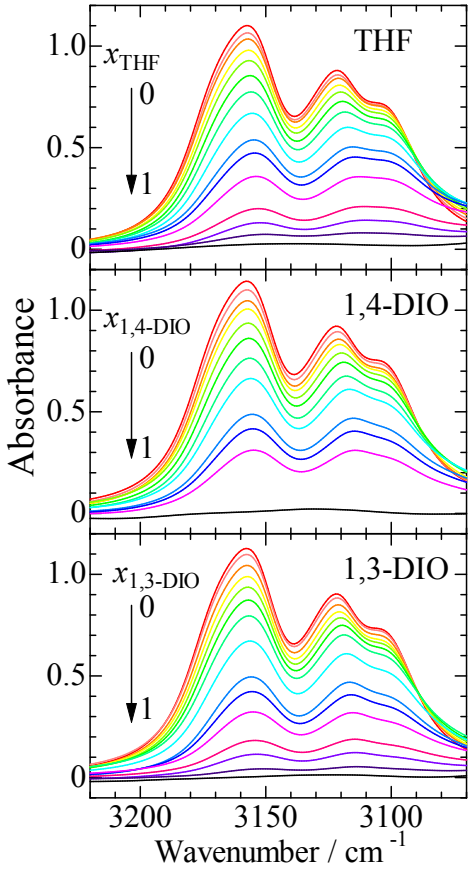

Fig. S6 IR spectra of the C-H stretching vibrations of the imidazolium ring within $[C_4mim]^+$ in $[C_4mim][TFSI]$–ML solutions at various x_{ML}.

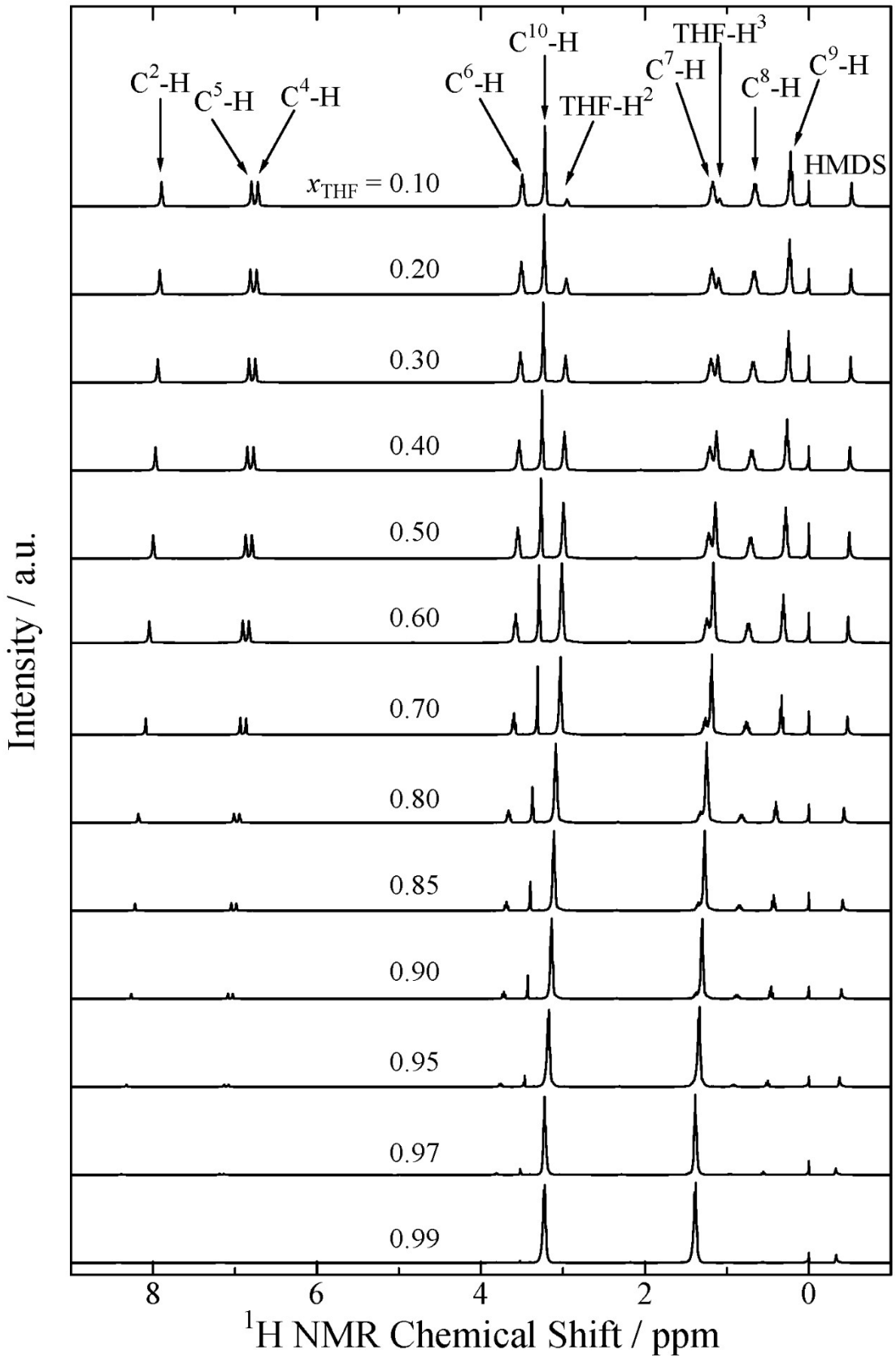

Fig. S7 ^{1}H NMR spectra of [C_4mim][TFSI]–THF solutions as a function of x_{THF}.

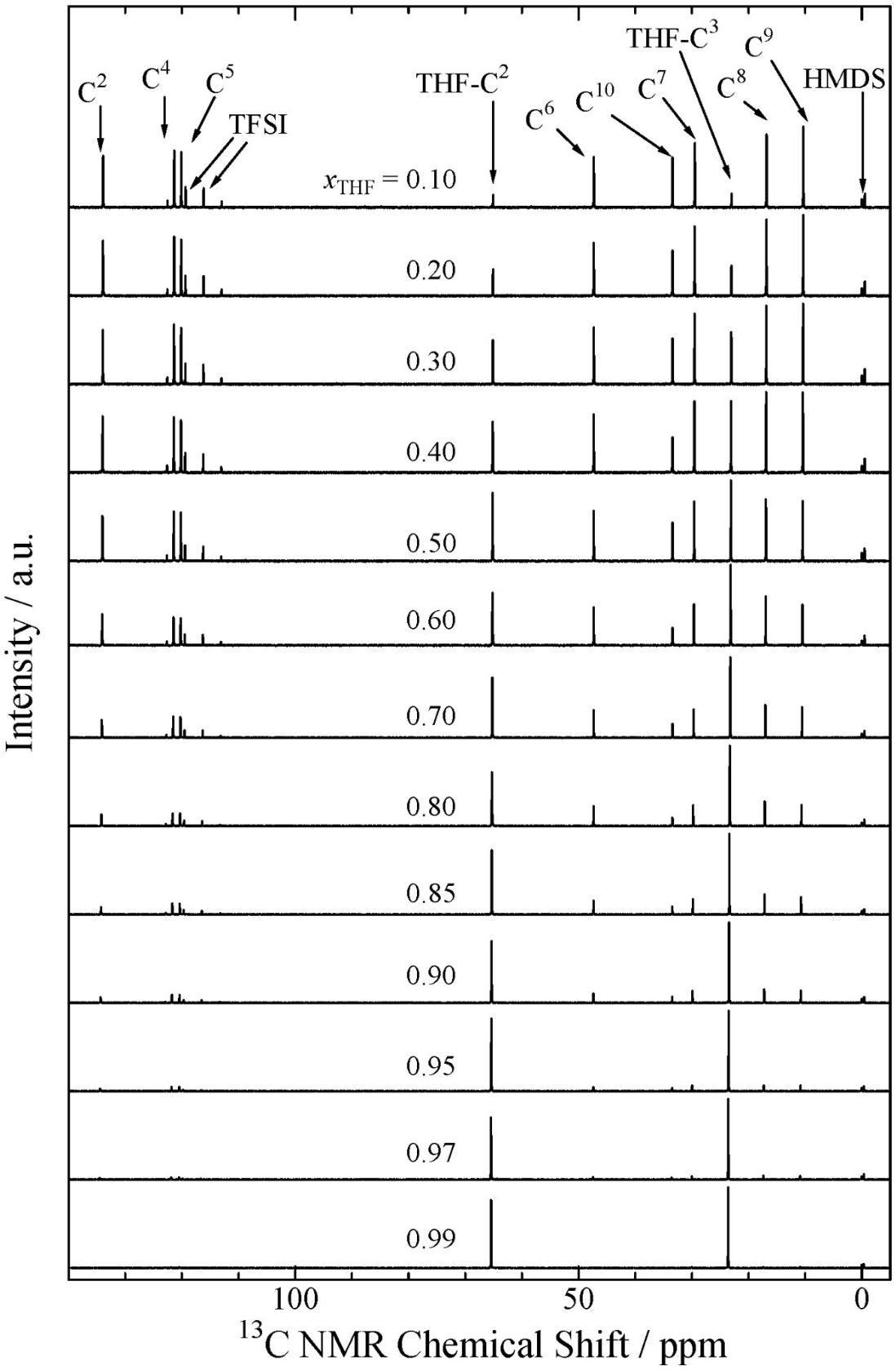

Fig. S8 ^{13}C NMR spectra of [C_4mim][TFSI]–THF solutions as a function of x_{THF}.

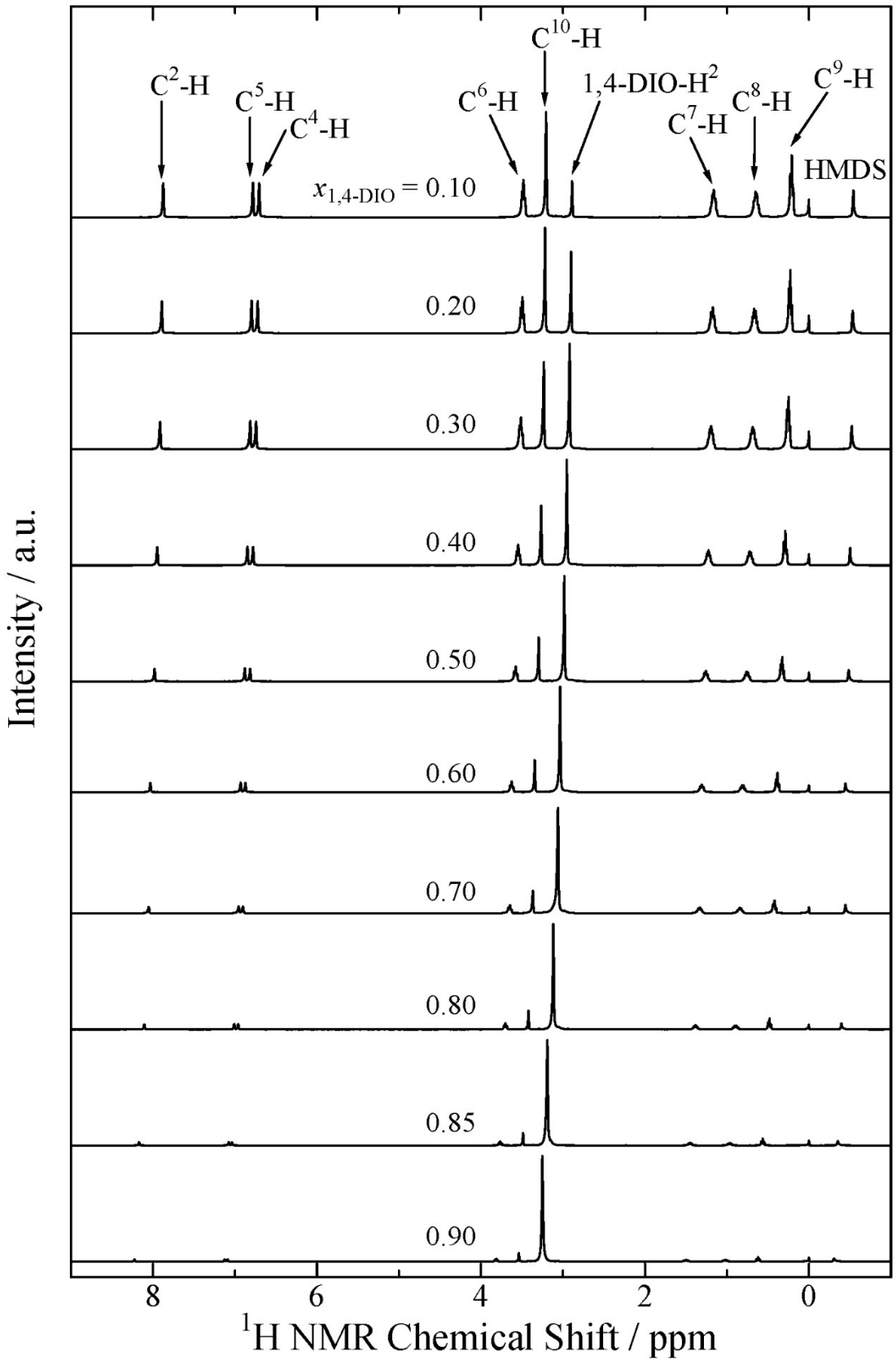

Fig. S9 ^{1}H NMR spectra of [C_4mim][TFSI]−1,4-DIO solutions as a function of $x_{1,4\text{-DIO}}$.

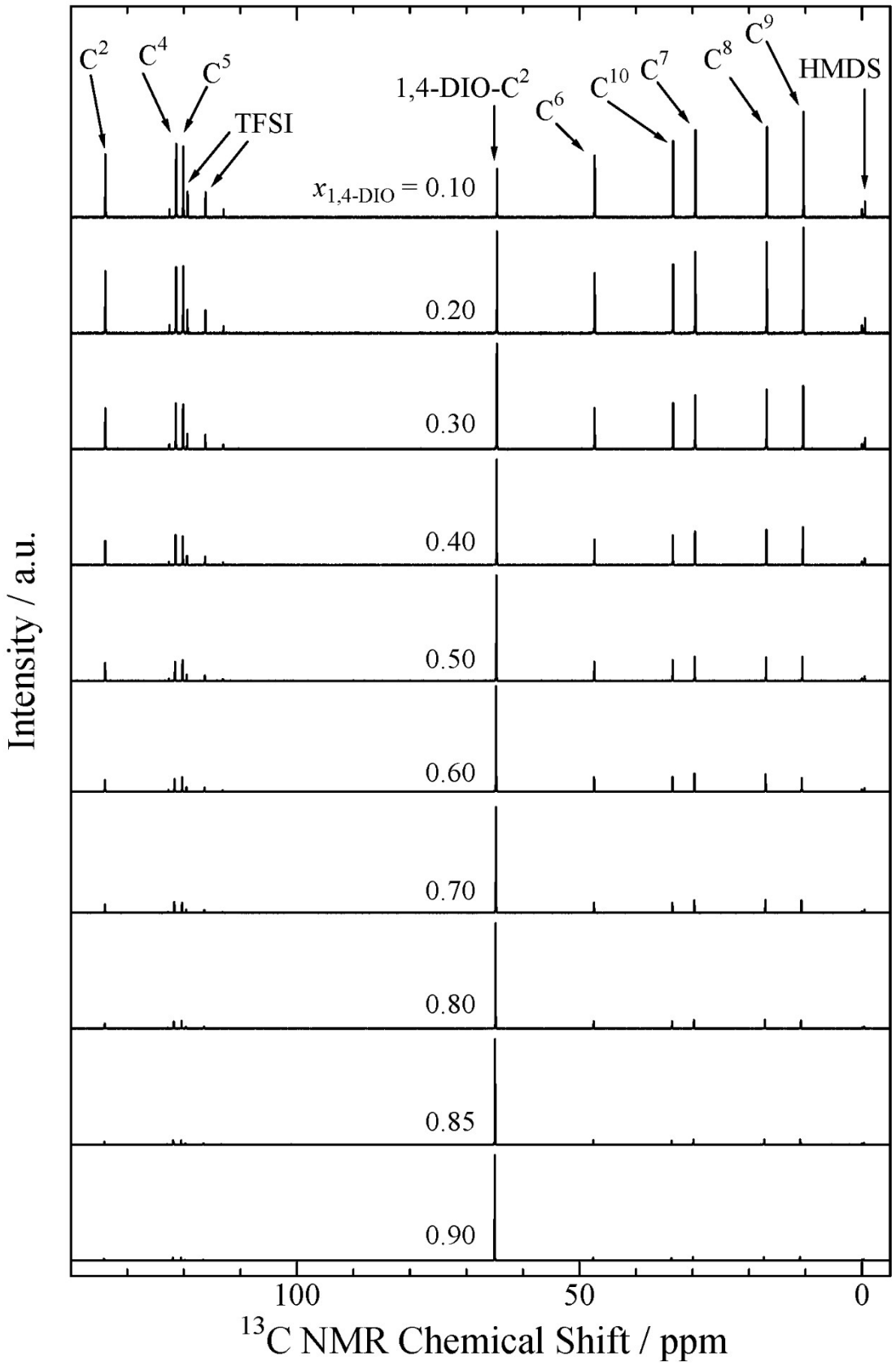

Fig. S10 ^{13}C NMR spectra of [C_4mim][TFSI]−1,4-DIO solutions as a function of $x_{1,4\text{-DIO}}$.

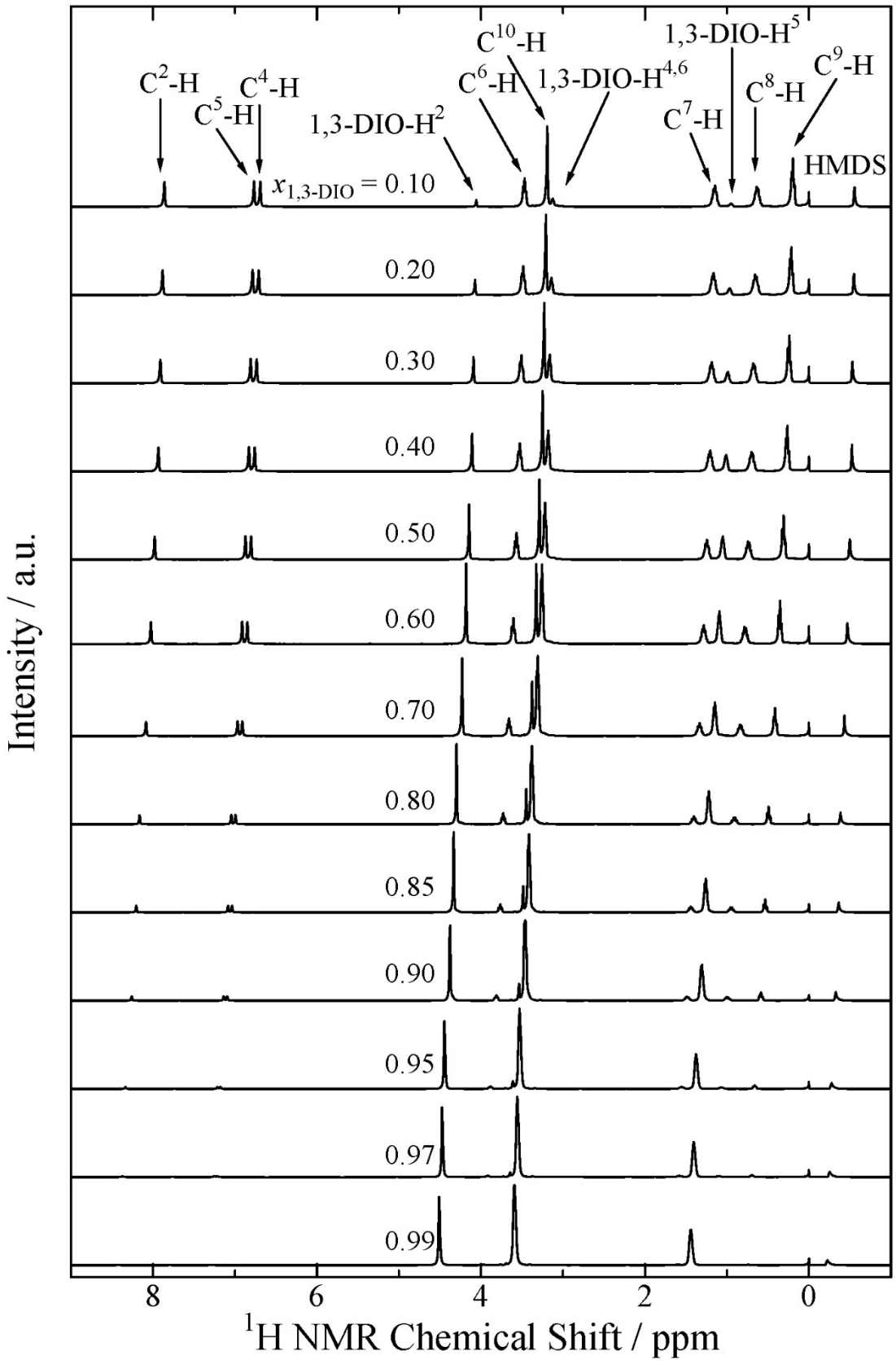

Fig. S11 ^{1}H NMR spectra of [C_4mim][TFSI]−1,3-DIO solutions as a function of $x_{1,3\text{-DIO}}$.

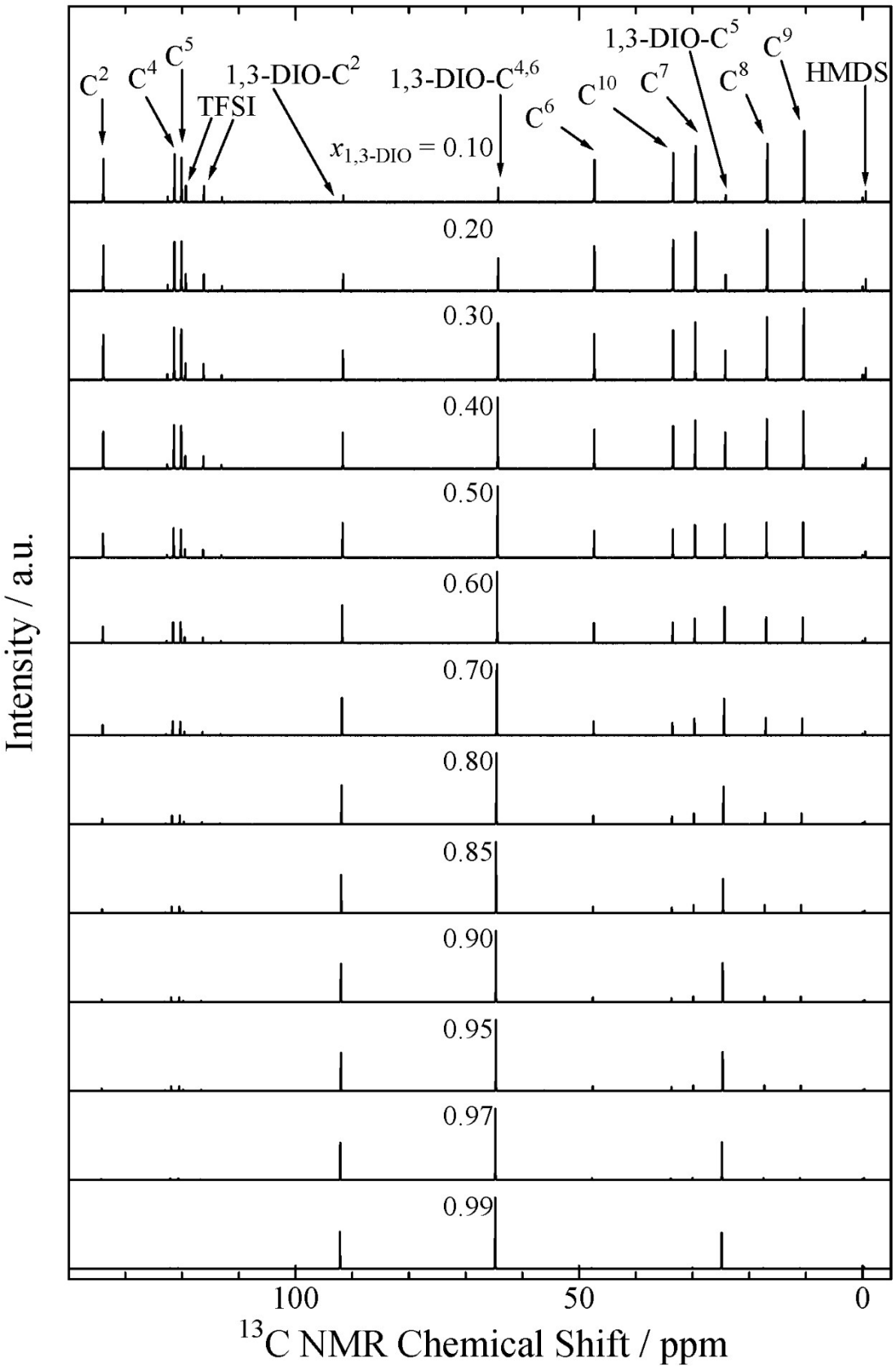

Fig. S12 ^{13}C NMR spectra of [C_4mim][TFSI]−1,3-DIO solutions as a function of $x_{1,3\text{-DIO}}$.

Table S5. The potential energy of the C^2-H–O_{ML} interaction and $[C_4mim]^+$–ML interaction for $[C_4mim][TFSI]$–ML solutions. E_{El} and E_{LJ} represent the short-range electrostatic interaction energies for the C^2-H–O_{ML} interaction and the short-range Lennard–Jones energies for the $[C_4mim]^+$–ML interaction, respectively. E_{El} of the 1,4-DIO and 1,3-DIO O atoms were estimated for one of the two O atoms within the cycloether molecules to fairly compare that of THF.

	E_{El} / kJ mol^{-1}			E_{LJ} / kJ mol^{-1}		
x_{ML}	THF	1,4-DIO	1,3-DIO	THF	1,4-DIO	1,3-DIO
0.1	-246	-118	-266	-1000	-1151	-1136
0.3	-795	-743	-887	-3068	-3567	-3712
0.5	-1452	-1232	-1459	-5375	-6034	-6043
0.7	-1809	-1653	-1984	-6478	-7889	-8063
0.9	-1307	-1010	-1529	-4510	-4974	-5992
0.99	-191	-118	-216	-634	-641	-823

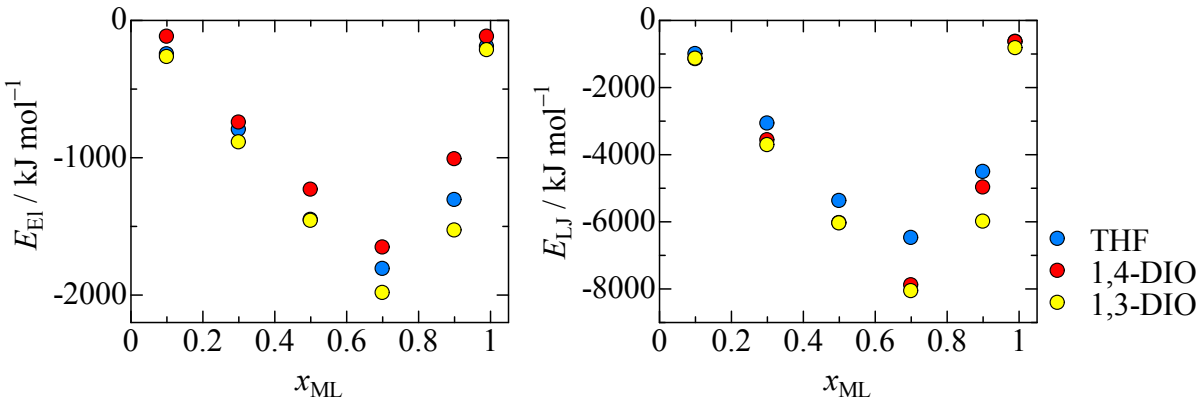

Fig. S13 ML mole fraction dependence of the electrostatic interaction energies E_{El} between the imidazolium C^2-H atom and the cycloether O atoms and the Lennard–Jones energies E_{LJ} between $[C_4mim]^+$ and cycloether molecules for $[C_4mim][TFSI]$–ML solutions.

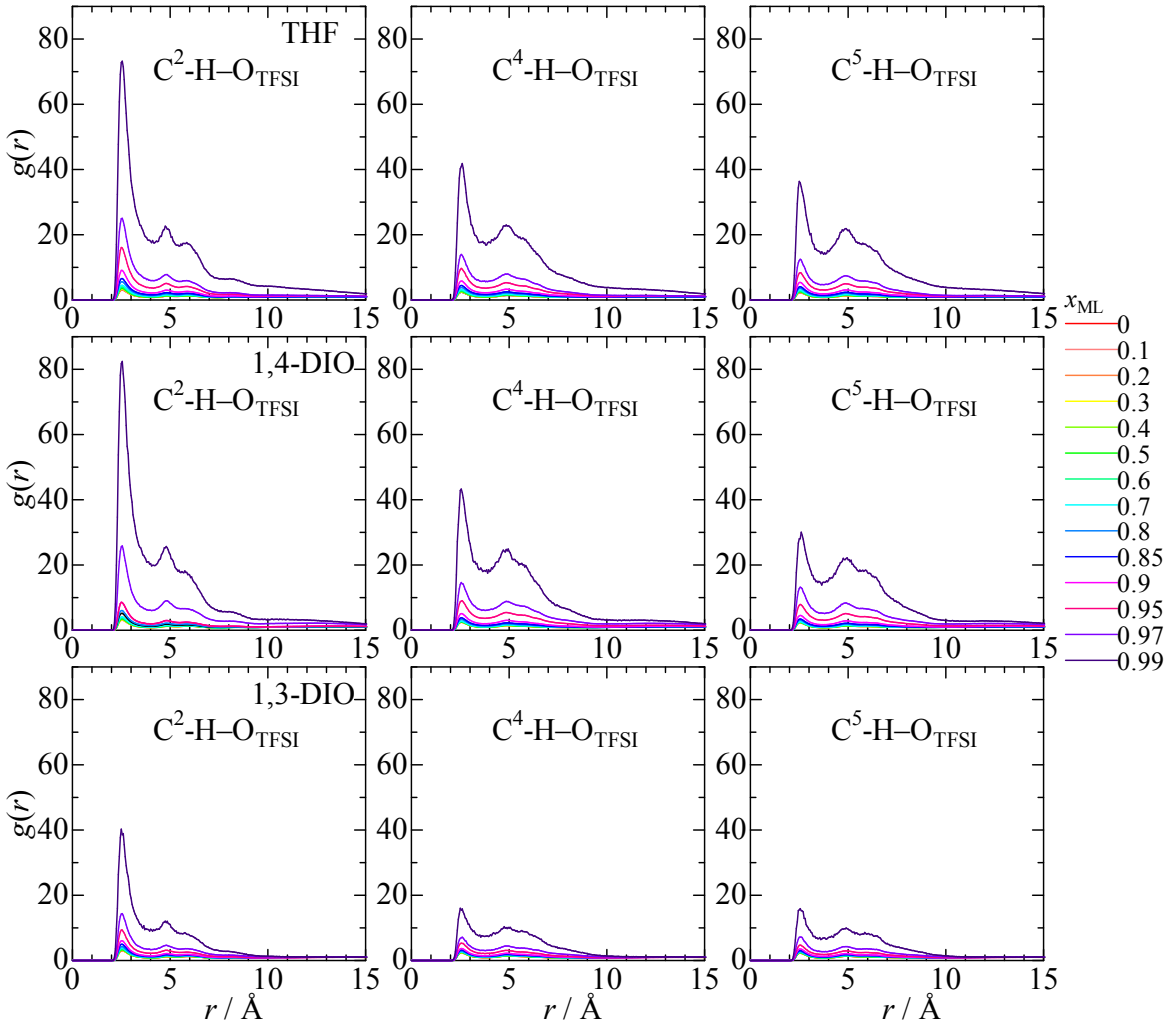

Fig. S14 Concentration dependence of pair correlation functions, $g(r)$s, for the $C^{2,4,5}$-H–O_{TFSI} interaction in [C_4mim][TFSI]–THF (upper), –1,4-DIO (middle), and –1,3-DIO (bottom) systems.

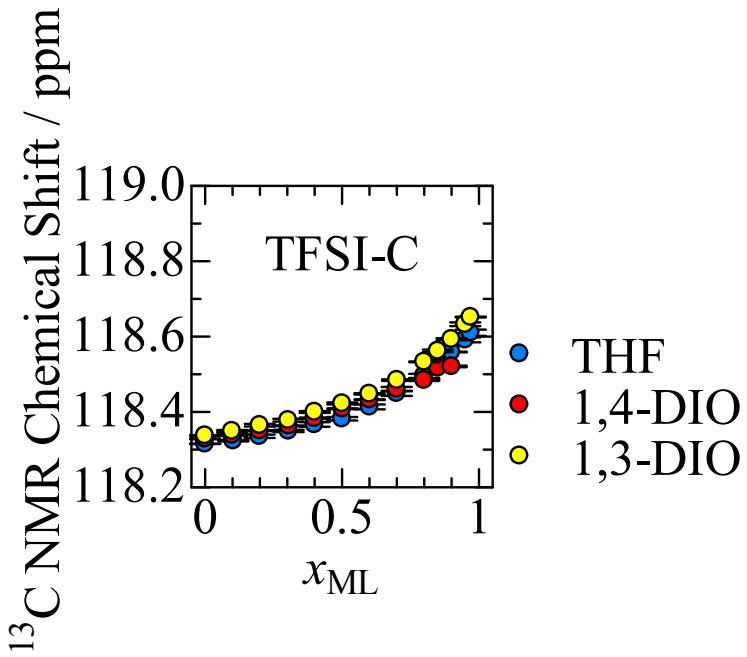

Fig. S15 ^{13}C NMR chemical shifts of $[TFSI]^-$ in $[C_4mim][TFSI]$–ML solutions as a function of x_{ML}. The standard deviations σ are given by error bars.