Supporting Information

Low-Frequency Spectra of 1-Methyl-3-octylimidazolium Tetrafluoroborate Mixtures with Methanol, Acetonitrile, and Dimethyl Sulfoxide: A Combined Study of Femtosecond Raman-Induced Kerr Effect Spectroscopy and Molecular Dynamics Simulations

Masatoshi Ando,[†] Masahiro Kawano,[‡] Atsuya Tashiro,[‡] Toshiyuki Takamuku,[*,#] Hideaki Shirota[*,†]

[†]*Department of Chemistry, Graduate School of Science, Chiba University, 1-33 Yayoi, Inage-ku, Chiba 263-8522, Japan*

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

[#]*Faculty of Science and Engineering, Saga University, Honjo-machi, Saga 840-8502, Japan*

Email: takamut@cc.saga-u.ac.jp and shirota@faculty.chiba-u.jp

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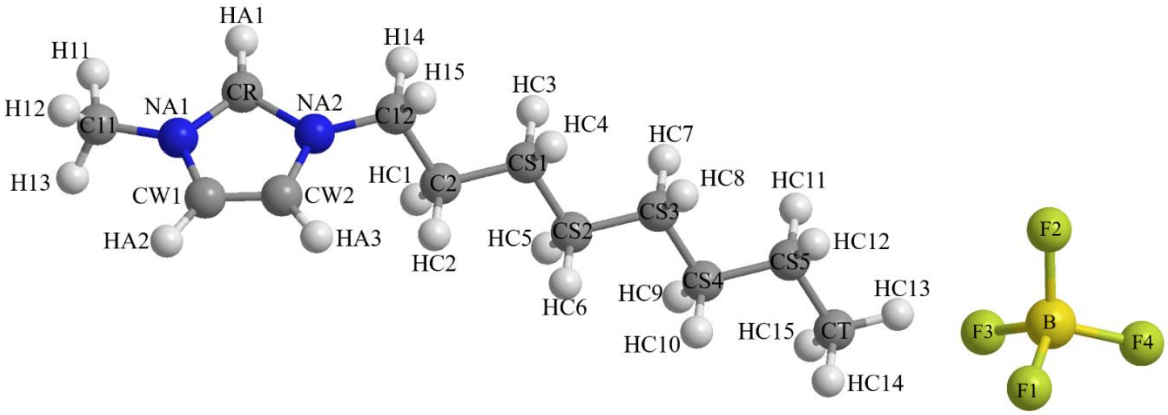

Figure S1. Structure of [MOIm][BF_4].

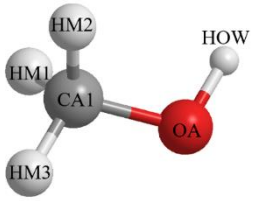

Figure S2. Structure of MeOH.

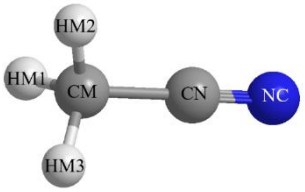

Figure S3. Structure of MeCN.

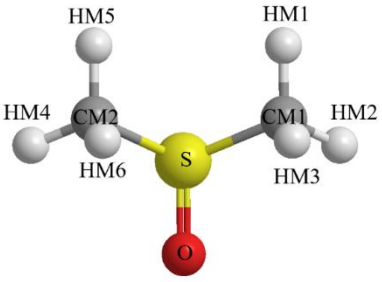

Figure S4. Structure of DMSO.

Table S1. Force Field Parameters Used for $[MOIm]^+$,[1,2] $[BF_4]^-$,[3] MeOH,[4] MeCN,[5] and DMSO.[6,7] The Notation of the Atoms within the Molecules is Depicted in Figures S1–S4.

Point Charges and van der Waals Parameters.

	Atom	Charge (e)	σ (Å)	ε (kcal mol^{-1})
$[MOIm]^+$	NA1	0.150	3.250	0.170
	NA2	0.150	3.250	0.170
	CR	-0.110	3.550	0.070
	HA1	0.210	2.420	0.030
	CW1	-0.130	3.550	0.070
	HA2	0.210	2.420	0.030
	CW2	-0.130	3.550	0.070
	HA3	0.210	2.420	0.030
	C11	-0.170	3.500	0.066
	H11	0.130	2.500	0.030
	H12	0.130	2.500	0.030
	H13	0.130	2.500	0.030
	C12	-0.170	3.500	0.066
	H14	0.130	2.500	0.030
	H15	0.130	2.500	0.030
	C2	0.010	3.500	0.066
	HC1	0.060	2.500	0.030
	HC2	0.060	2.500	0.030
	CS1	-0.120	3.500	0.066
	HC3	0.060	2.500	0.030
	HC4	0.060	2.500	0.030
	CS2	-0.120	3.500	0.066
	HC5	0.060	2.500	0.030
	HC6	0.060	2.500	0.030
	CS3	-0.120	3.500	0.066
	HC7	0.060	2.500	0.030
	HC8	0.060	2.500	0.030
	CS4	-0.120	3.500	0.066
	HC9	0.060	2.500	0.030
	HC10	0.060	2.500	0.030
	CS5	-0.120	3.500	0.066
	HC11	0.060	2.500	0.030
	HC12	0.060	2.500	0.030

	CT	-0.180	3.500	0.066
	HC13	0.060	2.500	0.030
	HC14	0.060	2.500	0.030
	HC15	0.060	2.500	0.030
$[BF_4]^-$	F1	-0.490	3.120	0.061
	B	0.960	3.580	0.095
	F2	-0.490	3.120	0.061
	F3	-0.490	3.120	0.061
	F4	-0.490	3.120	0.061
MeOH	CA1	0.145	3.500	0.066
	HM1	0.040	2.500	0.030
	HM2	0.040	2.500	0.030
	HM3	0.040	2.500	0.030
	OA	-0.683	3.120	0.170
	HOW	0.418	0.000	0.000
MeCN	NC	-0.560	3.200	0.170
	CN	0.460	3.300	0.066
	CM	-0.080	3.300	0.066
	HM1	0.060	2.500	0.015
	HM2	0.060	2.500	0.015
	HM3	0.060	2.500	0.015
DMSO	CM1	-0.020	3.500	0.066
	HM1	0.060	2.500	0.030
	HM2	0.060	2.500	0.030
	HM3	0.060	2.500	0.030
	S	0.139	3.560	0.395
	CM2	-0.020	3.500	0.066
	HM4	0.060	2.500	0.030
	HM5	0.060	2.500	0.030
	HM6	0.060	2.500	0.030
	O	-0.459	2.930	0.280

Intramolecular Atom-Atom Bond Lengths.

	Bond	*r* (Å)
$[MOIm]^+$	CR-NA1	1.315
	CR-NA2	1.315
	C11-H11	1.090
	C11-H12	1.090
	C11-H13	1.090
	NA2-C11	1.466
	CR-HA1	1.080
	CW2-NA2	1.378
	CW1-NA1	1.378
	CW2-CW1	1.341
	CW2-HA3	1.080
	CW1-HA2	1.080
	NA1-C12	1.466
	C12-H14	1.090
	C12-H15	1.090
	C12-C2	1.529
	C2-HC1	1.090
	C2-HC2	1.090
	C2-CS1	1.529
	CS1-HC3	1.090
	CS1-HC4	1.090
	CS1-CS2	1.529
	CS2-HC5	1.090
	CS2-HC6	1.090
	CS2-CS3	1.529
	CS3-HC7	1.090
	CS3-HC8	1.090
	CS3-CS4	1.529
	CS4-HC9	1.090
	CS4-HC10	1.090
	CS4-CS5	1.529
	CS5-HC11	1.090
	CS5-HC12	1.090
	CS5-CT	1.529
	CT-HC13	1.090
	CT-HC14	1.090

	CT-HC15	1.090
$[BF_4]^-$	B-F1	1.394
	B-F2	1.394
	B-F3	1.394
	B-F4	1.394
MeOH	CA1-OA	1.410
	CA1-HM1	1.090
	CA1-HM2	1.090
	CA1-HM3	1.090
	OA-HOW	0.945
MeCN	CN-NC	1.157
	CT-CN	1.470
	CT-HM1	1.090
	CT-HM2	1.090
	CT-HM3	1.090
DMSO	CM1-S	1.810
	CM2-S	1.810
	S-O	1.530
	CM2-HM4	1.090
	CM2-HM5	1.090
	CM2-HM6	1.090
	CM1-HM1	1.090
	CM1-HM2	1.090
	CM1-HM3	1.090

Bond Angle Potentials.

	Angle	K (kcal mol^{-1} rad^{-2})	θ (degree)
[MOIm]$^{+}$	H11-C11-H12	33.00	107.8
	H11-C11-H13	33.00	107.8
	H12-C11-H13	33.00	107.8
	NA2-C11-H11	37.50	110.7
	NA2-C11-H12	37.50	110.7
	NA2-C11-H13	37.50	110.7
	CR-NA2-C11	70.00	126.4
	CW2-NA2-C11	70.00	125.6
	NA2-CR-HA1	35.00	125.1
	NA1-CR-HA1	35.00	125.1
	NA2-CR-NA1	70.00	109.8
	CR-NA2-CW2	70.00	108.0
	CR-NA1-CW1	70.00	108.0
	NA2-CW2-CW1	70.00	107.1
	NA1-CW1-CW2	70.00	107.1
	NA1-CW2-HA3	35.00	122.0
	NA1-CW1-HA2	35.00	122.0
	CW2-CW1-HA2	35.00	130.9
	CW1-CW2-HA3	35.00	130.9
	CW2-NA1-C12	70.00	125.6
	CR-NA1-C12	70.00	126.4
	NA1-C12-H14	37.50	110.7
	NA1-C12-H15	37.50	110.7
	NA1-C12-C2	58.30	112.7
	C2-C12-H14	37.50	110.7
	C2-C12-H15	37.50	110.7
	H14-C12-H15	33.00	107.8
	C12-C2-HC1	37.50	110.7
	C12-C2-HC2	37.50	110.7
	C12-C2-CS1	58.30	112.7
	CT-CS5-HC11	37.50	110.7
	CT-CS5-HC12	37.50	110.7
	CS1-C2-HC1	37.50	110.7
	CS1-C2-HC2	37.50	110.7
	C2-CS1-HC3	37.50	110.7

	C2-CS1-HC4	37.50	110.7
	CS2-CS1-HC3	37.50	110.7
	CS2-CS1-HC4	37.50	110.7
	CS3-CS2-HC5	37.50	110.7
	CS3-CS2-HC6	37.50	110.7
	CS3-CS2-HC5	37.50	110.7
	CS3-CS2-HC6	37.50	110.7
	CS2-CS3-HC7	37.50	110.7
	CS2-CS3-HC8	37.50	110.7
	CS4-CS3-HC7	37.50	110.7
	CS4-CS3-HC8	37.50	110.7
	CS3-CS4-HC9	37.50	110.7
	CS3-CS4-HC10	37.50	110.7
	CS5-CS4-HC9	37.50	110.7
	CS5-CS4-HC10	37.50	110.7
	CS4-CS5-HC11	37.50	110.7
	CS4-CS5-HC12	37.50	110.7
	HC1-C2-HC2	33.00	107.8
	HC3-CS1-HC4	33.00	107.8
	HC5-CS2-HC6	33.00	107.8
	HC7-CS3-HC8	33.00	107.8
	HC9-CS4-HC10	33.00	107.8
	HC11-CS5-HC12	33.00	107.8
	CS4-CS5-CT	58.30	112.7
	C2-CS1-CS2	58.30	112.7
	CS1-CS2-CS3	58.30	112.7
	CS2-CS3-CS4	58.30	112.7
	CS3-CS4-CS5	58.30	112.7
	CS5-CT-HC13	37.50	110.7
	CS5-CT-HC14	37.50	110.7
	CS5-CT-HC15	37.50	110.7
	HC13-CT-HC14	33.00	107.8
	HC13-CT-HC15	33.00	107.8
	HC14-CT-HC15	33.00	107.8
$[BF_4]^-$	F2-B-F1	80.01	109.5
	F3-B-F1	80.01	109.5
	F4-B-F1	80.01	109.5

	F3-B-F2	80.01	109.5
	F4-B-F2	80.01	109.5
	F4-B-F3	80.01	109.5
MeOH	HM1-CA1-OA	35.00	109.5
	HM2-CA1-OA	35.00	109.5
	HM3-CA1-OA	35.00	109.5
	CA1-OA-HOW	55.00	108.5
	HM2-CA1-HM1	33.00	107.8
	HM3-CA1-HM1	33.00	107.8
	HM3-CA1-HM2	33.00	107.8
MeCN	CM-CN-NC	150.00	180.0
	HM1-CM-CN	35.00	108.5
	HM2-CM-CN	35.00	108.5
	HM3-CM-CN	35.00	108.5
	HM2-CM-HM1	33.00	107.8
	HM3-CM-HM1	33.00	107.8
	HM3-CM-HM2	33.00	107.8
DMSO	HM1-CM1-S	35.00	109.5
	HM2-CM1-S	35.00	109.5
	HM3-CM1-S	35.00	109.5
	CM1-S-CM2	62.00	98.9
	CM1-S-O	47.80	107.0
	O-S-CM2	47.80	107.0
	S-CM2-HM4	35.00	109.5
	S-CM2-HM5	35.00	109.5
	S-CM2-HM6	35.00	109.5
	HM4-CM2-HM5	33.00	107.8
	HM6-CM2-HM4	33.00	107.8
	HM6-CM2-HM5	33.00	107.8
	HM1-CM1-HM2	33.00	107.8
	HM3-CM1-HM1	33.00	107.8
	HM3-CM1-HM2	33.00	107.8

Torsion Potentials

	Dihedral	V_1 (kcal mol^{-1})	V_2 (kcal mol^{-1})	V_3 (kcal mol^{-1})	V_4 (kcal mol^{-1})
$[MOIm]^+$	CR-NA2-C11-H11	0.000	0.000	0.000	0.000
	CR-NA2-C11-H12	0.000	0.000	0.000	0.000
	CR-NA2-C11-H13	0.000	0.000	0.000	0.000
	CW2-NA2-C11-H11	0.000	0.000	0.124	0.000
	CW2-NA2-C11-H12	0.000	0.000	0.124	0.000
	CW2-NA2-C11-H13	0.000	0.000	0.124	0.000
	C11-NA2-CR-HA1	0.000	4.650	0.000	0.000
	NA1-CR-NA2-C11	0.000	4.650	0.000	0.000
	CW1-CW2-NA-C11	0.000	3.000	0.000	0.000
	C11-NA2-CW2-HA3	0.000	3.000	0.000	0.000
	NA1-CR-NA2-C11	0.000	4.650	0.000	0.000
	NA2-CW2-CW1-HA2	0.000	10.750	0.000	0.000
	NA1-CW1-CW2-HA3	0.000	10.750	0.000	0.000
	NA2-CW2-CW1-NA1	0.000	10.750	0.000	0.000
	CW2-NA2-CR-HA1	0.000	4.650	0.000	0.000
	CW1-NA1-CR-HA1	0.000	4.650	0.000	0.000
	CR-NA2-CW2-HA3	0.000	3.000	0.000	0.000
	CR-NA1-CW1-HA2	0.000	3.000	0.000	0.000
	CR-NA1-CW1-CW2	0.000	3.000	0.000	0.000
	CR-NA2-CW2-CW1	0.000	3.000	0.000	0.000
	C12-NA1-CR-HA1	0.000	4.650	0.000	0.000
	C12-NA1-CW1-HA2	0.000	3.000	0.000	0.000
	C12-NA1-CW1-CW2	0.000	3.000	0.000	0.000
	CR-NA1-C12-H14	0.000	0.000	0.000	0.000
	CR-NA1-C12-H15	0.000	0.000	0.000	0.000
	C12-C2-CS1-HC3	0.000	0.000	0.366	0.000
	C12-C2-CS1-HC4	0.000	0.000	0.366	0.000
	HC1-C2-CS1-HC3	0.000	0.000	0.318	0.000
	HC1-C2-CS1-HC4	0.000	0.000	0.318	0.000
	HC2-C2-CS1-HC3	0.000	0.000	0.318	0.000
	HC2-C2-CS1-HC4	0.000	0.000	0.318	0.000
	HC3-CS1-CS2-HC5	0.000	0.000	0.318	0.000
	HC3-CS1-CS2-HC6	0.000	0.000	0.318	0.000

HC4-CS1-CS2-HC5	0.000	0.000	0.318	0.000
HC4-CS1-CS2-HC6	0.000	0.000	0.318	0.000
HC5-CS2-CS3-HC7	0.000	0.000	0.318	0.000
HC5-CS2-CS3-HC8	0.000	0.000	0.318	0.000
HC6-CS2-CS3-HC7	0.000	0.000	0.318	0.000
HC6-CS2-CS3-HC8	0.000	0.000	0.318	0.000
HC7-CS3-CS4-HC9	0.000	0.000	0.318	0.000
HC7-CS3-CS4-HC10	0.000	0.000	0.318	0.000
HC8-CS3-CS4-HC9	0.000	0.000	0.318	0.000
HC8-CS3-CS4-HC10	0.000	0.000	0.318	0.000
HC9-CS4-CS5-HC11	0.000	0.000	0.318	0.000
HC9-CS4-CS5-HC12	0.000	0.000	0.318	0.000
HC10-CS4-CS5-HC11	0.000	0.000	0.318	0.000
HC10-CS4-CS5-HC12	0.000	0.000	0.318	0.000
HC11-CS5-CT-HC13	0.000	0.000	0.318	0.000
HC11-CS5-CT-HC14	0.000	0.000	0.318	0.000
HC11-CS5-CT-HC15	0.000	0.000	0.318	0.000
HC12-CS5-CT-HC13	0.000	0.000	0.318	0.000
HC12-CS5-CT-HC14	0.000	0.000	0.318	0.000
HC12-CS5-CT-HC15	0.000	0.000	0.318	0.000
HC9-CS4-CS5-CT	0.000	0.000	0.366	0.000
HC10-CS4-CS5-CT	0.000	0.000	0.366	0.000
C12-C2-CS1-CS2	1.739	-0.157	0.279	0.000
C2-CS1-CS2-CS3	1.739	-0.157	0.279	0.000
CS1-CS2-CS3-CS4	1.739	-0.157	0.279	0.000
CS2-CS3-CS4-CS5	1.739	-0.157	0.279	0.000
CS3-CS4-CS5-CT	1.739	-0.157	0.279	0.000
CS3-CS4-CS5-HC11	0.000	0.000	0.366	0.000
CS3-CS4-CS5-HC12	0.000	0.000	0.366	0.000
CS2-CS3-CS4-HC9	0.000	0.000	0.366	0.000
CS2-CS3-CS4-HC10	0.000	0.000	0.366	0.000
CS1-CS2-CS3-HC7	0.000	0.000	0.366	0.000
CS1-CS2-CS3-HC8	0.000	0.000	0.366	0.000
C2-CS1-CS2-HC5	0.000	0.000	0.366	0.000
C2-CS1-CS2-HC6	0.000	0.000	0.366	0.000
CS2-CS1-C2-HC1	0.000	0.000	0.366	0.000
CS2-CS1-C2-HC2	0.000	0.000	0.366	0.000
CS3-CS2-CS1-HC3	0.000	0.000	0.366	0.000

	CS3-CS2-CS1-HC4	0.000	0.000	0.366	0.000
	CS4-CS3-CS2-HC5	0.000	0.000	0.366	0.000
	CS4-CS3-CS2-HC6	0.000	0.000	0.366	0.000
	CS5-CS4-CS3-HC7	0.000	0.000	0.366	0.000
	CS5-CS4-CS3-HC8	0.000	0.000	0.366	0.000
	CS4-CS5-CT-HC13	0.000	0.000	0.366	0.000
	CS4-CS5-CT-HC14	0.000	0.000	0.366	0.000
	CS4-CS5-CT-HC15	0.000	0.000	0.366	0.000
	HA3-CW2-CW1-HA2	0.000	10.750	0.000	0.000
	CW1-NA1-C12-H14	0.000	0.000	0.124	0.000
	CW1-NA1-C12-H15	0.000	0.000	0.124	0.000
	CW1-NA1-C12-C2	-1.709	1.459	0.190	0.000
	CR-NA1-C12-C2	-1.259	0.000	0.000	0.000
	NA1-C12-C2-CS1	-1.787	0.756	-0.287	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
	NA1-C12-C2-HC1	0.000	0.000	0.088	0.000
	NA1-C12-C2-HC2	0.000	0.000	0.088	0.000
	CS1-C2-C12-HC14	0.000	0.000	0.366	0.000
	CS1-C2-C12-HC15	0.000	0.000	0.366	0.000
	NA1-CR-NA2-CW2	0.000	4.650	0.000	0.000
	NA2-CR-NA1-CW1	0.000	4.650	0.000	0.000
MeOH	HM1-CA1-OA-HOW	0.000	0.000	0.450	0.000
	HM2-CA1-OA-HOW	0.000	0.000	0.450	0.000
	HM3-CA1-OA-HOW	0.000	0.000	0.450	0.000
MeCN	HM1-CM-CN-NC	0.000	0.000	0.000	0.000
	HM2-CM-CN-NC	0.000	0.000	0.000	0.000
	HM3-CM-CN-NC	0.000	0.000	0.000	0.000
DMSO	HM1-CM1-S-CM2	0.000	0.000	0.647	0.000
	HM1-CM1-S-O	0.000	0.000	0.647	0.000
	HM2-CM1-S-CM2	0.000	0.000	0.647	0.000
	HM2-CM1-S-O	0.000	0.000	0.647	0.000
	HM3-CM1-S-CM2	0.000	0.000	0.647	0.000
	HM3-CM1-S-O	0.000	0.000	0.647	0.000

CM1-S-CM2-HM4	0.000	0.000	0.647	0.000
CM1-S-CM2-HM5	0.000	0.000	0.647	0.000
CM1-S-CM2-HM6	0.000	0.000	0.647	0.000
O-S-CM2-HM4	0.000	0.000	0.647	0.000
O-S-CM2-HM5	0.000	0.000	0.647	0.000
O-S-CM2-HM6	0.000	0.000	0.647	0.000

(1) Canongia Lopes, J. N.; Deschamps, J.; Padua, A. A. H. Modeling Ionic Liquids Using a Systematic All-Atom Force Field. *J. Phys. Chem. B,* **2004,** *108*, 2038–2047.

(2) Canongia Lopes, J. N.; Deschamps, J.; Padua, A. A. H. Modeling Ionic Liquids Using a Systematic All-Atom Force Field (Corrections). *J. Phys. Chem. B,* **2004,** *108*, 11250–11250.

(3) Canongia Lopes, J. N.; Padua, A. A. H. Molecular Force Field for Ionic Liquids III: Imidazolium, Pyridinium, and Phosphonium Cations; Chloride, Bromide, and Dicyanamide Anions. *J. Phys. Chem. B* **2006,** *110*, 19586–19592.

(4) Kaminski, G.; Jorgensen, W. L. Performance of the AMBER94, MMFF94, and OPLS-AA Force Fields for Modeling Organic Liquids. *J. Phys. Chem.* **1996,** *100*, 18010–18013.

(5) Price, M. L. P.; Ostrovsky, D.; Jorgensen, W. L. Gas-Phase and Liquid-State Properties of Esters, Nitriles, and Nitro Compounds with the OPLS-AA Force Field. *J. Comput. Chem.* **2001,** *22*, 1340–1352.

(6) Zheng, Y.-J.; Ornstein, R. L. A Molecular Dynamics and Quantum Mechanics Analysis of the Effect of DMSO on Enzyme Structure and Dynamics: Subtilisin. *J. Am. Chem. Soc.* **1996,** *118*, 4175–4180.

(7) Vasudevan, V.; Mushrif, S. H. Insights into the Solvation of Glucose in Water, Dimethyl Sulfoxide (DMSO), Tetrahydrofuran (THF) and *N*,*N*-Dimethylformamide (DMF) and Its Possible Implications on the Conversion of Glucose to Platform Chemicals. *RSC Adv.* **2015,** *5*, 20756–20763.

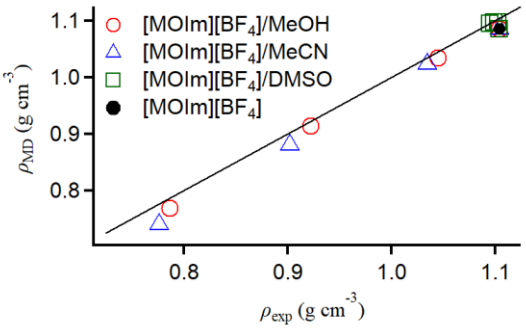

Figure S5. Plots of MD Simulation Densities ρ_{MD} vs. Experimental Densities ρ_{exp} of Neat [MOIm][BF_4] and [MOIm][BF_4] Mixtures with MeOH, MeCN, and DMSO with X_{ML} = 0.6 and 0.9 at 298.2 K. Solid Line Indicates the Ideal Relationship Between Both Densities.

Table S2. Atom Coordination Parameters of the Optimized $[MOIm]^+$, $[BF_4]^-$, MeOH, MeCN, and DMSO Calculated by the B3LYP/6-311++G(d,p) Level of Theory.

$[MOIm]^+$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.411096	-1.178369	-0.714072
2	6	0	4.617674	-0.624064	-1.013559
3	6	0	3.709623	0.551722	0.616044
4	7	0	2.859182	-0.431414	0.308456
5	1	0	2.909485	-2.033214	-1.134459
6	1	0	5.360702	-0.906971	-1.739816
7	1	0	3.554832	1.297525	1.378033
8	6	0	1.526098	-0.648845	0.922523
9	1	0	1.449867	-1.715286	1.142780
10	1	0	1.528323	-0.116034	1.874884
11	7	0	4.787085	0.458302	-0.171440
12	6	0	5.958610	1.346605	-0.140111
13	1	0	6.082242	1.818089	-1.114505
14	1	0	5.800556	2.113757	0.615155
15	1	0	6.847158	0.768236	0.111273
16	6	0	0.380367	-0.177558	0.024712
17	1	0	0.423306	-0.709041	-0.932251
18	1	0	0.511134	0.887267	-0.197685
19	6	0	-0.985245	-0.410821	0.684985
20	1	0	-1.101473	-1.476737	0.915938
21	1	0	-1.021643	0.118680	1.644965
22	6	0	-2.155932	0.049227	-0.192915
23	1	0	-2.118330	-0.480389	-1.152989
24	1	0	-2.037431	1.114889	-0.425309
25	6	0	-3.524637	-0.178833	0.459086
26	1	0	-3.641698	-1.244719	0.692151
27	1	0	-3.560669	0.349641	1.420148
28	6	0	-4.697504	0.279912	-0.414820
29	1	0	-4.661824	-0.248066	-1.376467
30	1	0	-4.580856	1.346056	-0.648430
31	6	0	-6.068040	0.053243	0.233886
32	1	0	-6.103891	0.580735	1.194689
33	1	0	-6.184892	-1.011970	0.466894
34	6	0	-7.234032	0.514138	-0.644913
35	1	0	-8.194495	0.338573	-0.154011
36	1	0	-7.165592	1.583797	-0.865836
37	1	0	-7.247135	-0.021164	-1.599330
Rotational constants (GHz):			2.8861246	0.1410664	0.1404856

$[BF_4]^-$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	9	0	0.818148	0.818148	0.818148
2	9	0	-0.818148	-0.818148	0.818148
3	9	0	0.818148	-0.818148	-0.818148
4	9	0	-0.818148	0.818148	-0.818148
5	5	0	0.000000	0.000000	0.000000
Rotational constants (GHz):			4.9675917	4.9675917	4.9675917

MeOH.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.667672	-0.020306	0.000000
2	1	0	1.083940	0.987432	-0.000001
3	1	0	1.028567	-0.544973	-0.893244
4	1	0	1.028567	-0.544971	0.893245
5	8	0	-0.749784	0.122117	0.000000
6	1	0	-1.148834	-0.752592	0.000000
Rotational constants (GHz):			128.0433562	24.6414553	23.794049

MeCN.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	-1.176150
2	1	0	0.000000	1.024910	-1.552841
3	1	0	-0.887598	-0.512455	-1.552841
4	1	0	0.887598	-0.512455	-1.552841
5	6	0	0.000000	0.000000	0.280499
6	7	0	0.000000	0.000000	1.433204
Rotational constants (GHz):			159.1253204	9.2451372	9.2451372

DMSO.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000001	0.234317	-0.444120
2	8	0	0.000017	1.500306	0.386766
3	6	0	-1.369676	-0.813548	0.184843
4	1	0	-2.295689	-0.294642	-0.060786
5	1	0	-1.343964	-1.786577	-0.309424
6	1	0	-1.274322	-0.913131	1.267048
7	6	0	1.369661	-0.813573	0.184842
8	1	0	1.274307	-0.913140	1.267048
9	1	0	1.343927	-1.786607	-0.309414
10	1	0	2.295683 -	0.294688	-0.060796
Rotational constants (GHz):			6.7929108	6.6990013	4.0730769

Table S3. Liquid Properties, Density ρ, Surface Tension γ, Viscosity η, Electrical Conductivity σ, and Molar Electrical Conductivity Λ of [MOIm][BF_4] Mixtures with MeOH, MeCN, and DMSO at 293.0 K.

X_{ML}	ρ [a] (g cm^{-3})	γ [b] (mN m^{-1})	η [c] (cP)	σ [c] (mS cm^{-1})	Λ (S cm^2 mol^{-1})
			[MOIm][BF_4]/MeOH		
0 (IL)	1.108	33.4	459	0.771	0.20
0.2	1.096	33.0	158	1.19	0.25
0.4	1.078	31.8	56.1	2.20	0.37
0.6	1.049	29.8	17.6	6.13	0.77
0.7	1.026	28.4	10.3	9.94	1.04
0.8	0.990	26.8	4.62	17.6	1.46
0.9	0.928	25.2	1.82	23.5	1.45
0.95	0.875	24.1	1.18	21.9	1.12
0.97	0.847	23.8	0.918	18.0	0.84
0.99	0.812	23.0	0.734	9.90	0.42
1 (MeOH)	0.792	22.7	0.645	–	–
			[MOIm][BF_4]/MeCN		
0.2	1.092	32.9	137	2.38	0.51
0.4	1.072	32.7	40.7	2.82	0.49
0.6	1.047	32.9	12.5	8.21	1.08
0.7	1.027	32.8	6.47	12.5	1.38
0.8	1.006	32.7	3.00	15.3	1.36
0.9	0.940	32.7	1.07	33.4	2.32
0.95	0.873	31.3	0.753	39.7	2.42
0.97	0.834	30.1	0.533	32.9	1.90
0.99	0.803	29.8	0.419	17.6	0.95
1 (MeCN)	0.782	29.2	0.374	–	–
			[MOIm][BF_4]/DMSO		
0.2	1.108	33.8	221	1.40	0.20
0.4	1.107	34.9	93.3	1.44	0.31
0.6	1.106	36.0	35.2	3.09	0.26
0.7	1.106	36.9	19.2	3.93	0.45
0.8	1.104	38.4	9.82	7.82	0.50
0.9	1.104	40.3	4.76	9.79	0.84
0.95	1.103	41.7	3.17	8.07	0.87
0.97	1.102	42.4	2.70	7.39	0.65
0.99	1.101	43.0	2.30	3.07	0.57
1 (DMSO)	1.101	43.3	2.13	–	–

[a] ±0.1%. [b] ±2%. [c] ±5%.

Table S4. Biexponential Fit Parameters for Kerr Transients of [MOIm][BF_4]/MeOH, [MOIm][BF_4]/MeCN, and [MOIm][BF_4]/DMSO at 293.0 K.

Mole Fraction X	a_0	a_1	τ_1 (ps)	a_2	τ_2 (ps)
[MOIm][BF_4]/MeOH					
0 ([MOIm][BF_4])	0.00018	0.00375	1.45	0.00133	9.79
0.20	0.00034	0.00455	1.42	0.00154	9.70
0.40	0.00050	0.00523	1.39	0.00182	9.13
0.60	0.00102	0.00588	1.27	0.00238	6.30
0.70	0.00118	0.00782	1.04	0.00286	5.40
0.80	0.00152	0.00941	0.78	0.00412	4.26
0.90	0.00153	0.02018	0.65	0.00473	4.01
0.95	0.00121	0.03140	0.55	0.00469	3.68
0.97	0.00093	0.03285	0.47	0.00430	3.34
0.99	0.00045	0.06082	0.46	0.00311	2.96
1 (MeOH)	0 (Fixed)	0.09552	0.40	0.00247	2.55
[MOIm][BF_4]/MeCN					
0 ([MOIm][BF_4])	0.00015	0.00389	1.44	0.00145	9.78
0.20	0.00035	0.00522	1.45	0.00155	9.77
0.40	0.00055	0.00610	1.51	0.00218	9.51
0.60	0.00082	0.00924	1.53	0.00357	9.42
0.70	0.00096	0.01110	1.65	0.00514	8.98
0.80	0.00071	0.01751	1.67	0.00775	8.94
0.90	0.00055	0.03321	1.78	0.01084	7.21
0.95	0.00037	0.05466	1.64	0.01240	5.46
0.97	0.00029	0.06927	1.63	0.01076	5.01
0.99	0 (Fixed)	0.09429	1.54	0.00840	4.04
1 (MeCN)	0 (Fixed)	0.10434	1.53	0.00829	2.31
[MOIm][BF_4]/DMSO					
0 ([MOIm][BF_4])	0.00021	0.00414	1.45	0.00137	9.99
0.20	0.00029	0.00509	1.36	0.00149	9.41
0.40	0.00029	0.00547	1.35	0.00159	8.50
0.60	0.00036	0.00629	1.26	0.00180	7.79
0.70	0.00047	0.00627	1.23	0.00187	7.42
0.80	0.00041	0.00763	1.16	0.00221	7.00
0.90	0.00037	0.00845	1.13	0.00238	6.59
0.95	0.00018	0.00848	1.07	0.00276	6.37
0.97	0.00014	0.00958	1.04	0.00278	6.36
0.99	0.00002	0.00986	1.04	0.00309	6.20
1 (DMSO)	0 (Fixed)	0.01072	1.01	0.00315	6.04

Table S5. Fit Parameters for Fourier Transform Kerr Spectra of [MOIm][BF_4]/MeOH, [MOIm][BF_4]/MeCN, and [MOIm][BF_4]/DMSO.
Intermolecular (mainly).

ML Mole Fraction, X_{ML}	M_1 (cm^{-1})	$a_{O,1}$	$\omega_{O,1}$ (cm^{-1})	$a_{O,2}$	$\omega_{O,2}$ (cm^{-1})	$a_{G,1}$	$\omega_{G,1}$ (cm^{-1})	$\Delta\omega_{G,1}$ (cm^{-1})	$a_{G,2}$	$\omega_{G,2}$ (cm^{-1})	$\Delta\omega_{G,2}$ (cm^{-1})	$a_{G,3}$	$\omega_{G,3}$ (cm^{-1})	$\Delta\omega_{G,3}$ (cm^{-1})
[MOIm][BF_4]/MeOH														
0 ([MOIm][BF_4])	69.2	0.028	3.3	0.033	14.3	0.219	44.6	65.2	0.221	98.4	65.1	–	–	–
0.20	68.7	0.035	3.3	0.033	14.0	0.211	43.2	64.8	0.216	97.1	66.2	–	–	–
0.40	68.3	0.039	3.3	0.034	14.0	0.170	41.2	57.8	0.230	92.3	69.6	–	–	–
0.60	67.9	0.037	3.7	0.032	13.9	0.178	40.0	61.7	0.211	93.1	70.4	–	–	–
0.70	68.4	0.029	4.2	0.028	14.0	0.157	36.3	63.4	0.198	90.9	74.5	–	–	–
0.80	70.5	0.040	8.6	–	–	0.153	17.5	53.1	0.245	72.3	96.2	0.012	175	34.4
0.90	72.7	0.035	8.5	–	–	0.088	23.2	44.4	0.332	38.8	127	0.019	216	85.1
0.95	74.0	0.029	8.9	–	–	0.088	23.8	48.9	0.249	44.3	129	0.019	219	95.4
0.97	75.8	0.024	9.8	–	–	0.074	29.3	48.2	0.216	46.8	132	0.018	221	93.3
0.99	78.3	0.021	9.1	–	–	0.089	26.9	53.1	0.153	60.3	132	0.017	226	92.7
1 (MeOH)	79.3	0.017	9.6	–	–	0.084	30.9	52.5	0.122	75.3	124	0.020	229	98.7
[MOIm][BF_4]/MeCN														
0 ([MOIm][BF_4])	69.1	0.028	3.3	0.032	14.3	0.231	48.0	69.5	0.186	101.8	62.4	–	–	–
0.20	68.8	0.039	3.0	0.037	12.4	0.282	39.2	72.7	0.215	98.7	65.9	–	–	–
0.40	67.9	0.052	3.1	0.042	11.8	0.300	38.0	67.0	0.259	94.9	68.0	–	–	–
0.60	67.5	0.088	3.0	0.054	11.7	0.370	41.0	63.2	0.301	95.6	67.0	0.012	155	33.8
0.70	66.6	0.126	2.9	0.066	11.1	0.443	40.6	64.4	0.317	95.7	66.7	0.017	161	41.4
0.80	65.6	0.256	2.4	0.105	9.4	0.559	29.8	67.1	0.420	87.8	74.8	0.019	174	51.0
0.90	64.9	0.484	2.6	0.157	9.6	0.785	36.2	72.9	0.179	82.0	131	0.217	96.0	59.2
0.95	62.4	0.691	2.8	0.204	10.0	0.956	40.5	74.1	0.189	90.8	124	0.179	100	57.2
0.97	61.2	0.883	2.8	0.241	10.0	1.073	41.4	74.3	0.195	94.6	124	0.175	101	56.5
0.99	59.5	1.084	3.1	0.259	10.9	1.591	29.5	93.7	0.263	84.6	123	–	–	–
1 (MeCN)	58.3	1.200	3.1	0.291	10.7	1.693	29.5	92.3	0.267	85.3	121	–	–	–

[MOIm][BF_4]/DMSO														
0 ([MOIm][BF_4])	69.0	0.029	3.3	0.033	14.9	0.213	47.0	62.9	0.196	100	62.3	–	–	–
0.20	68.9	0.031	3.3	0.030	15.2	0.207	48.8	62.9	0.166	103	59.7	–	–	–
0.40	68.2	0.035	3.4	0.028	15.4	0.207	51.2	64.2	0.137	104	59.0	–	–	–
0.60	67.3	0.034	3.6	0.025	15.1	0.197	51.1	65.0	0.117	105	58.5	–	–	–
0.70	66.5	0.035	3.6	0.023	14.7	0.195	51.1	66.8	0.057	110	52.8	–	–	–
0.80	65.3	0.028	4.4	0.019	15.5	0.199	54.9	79.9	0.012	112	36.8	–	–	–
0.90	64.9	0.034	4.4	0.016	17.0	0.186	58.5	92.6	–	–	–	–	–	–
0.95	63.8	0.040	4.6	0.014	24.0	0.133	71.4	82.2	–	–	–	–	–	–
0.97	62.7	0.040	4.6	0.014	22.7	0.136	69.0	82.0	–	–	–	–	–	–
0.99	62.1	0.041	4.6	0.014	21.9	0.140	67.2	81.9	–	–	–	–	–	–
1 (DMSO)	61.6	0.041	4.5	0.013	21.3	0.140	66.7	81.0	–	–	–	–	–	–

Intramolecular.

ML Mole Fraction, X_{ML}	$a_{L,1}$	$\omega_{L,1}$ (cm^{-1})	$\Delta\omega_{L,1}$ (cm^{-1})	$a_{L,2}$	$\omega_{L,2}$ (cm^{-1})	$\Delta\omega_{L,2}$ (cm^{-1})
[MOIm][BF_4]/MeOH						
0 ([MOIm][BF_4])	29.2	172	30.4	14.1	217	27.4
0.20	27.9	171	30.6	9.02	217	24.4
0.40	32.1	171	32.6	8.88	217	24.3
0.60	29.9	171	32.2	12.7	217	28.3
0.70	27.6	172	32.0	19.7	217	31.4
0.80	–	–	–	17.3	216	30.2
0.90	–	–	–	–	–	–
0.95	–	–	–	–	–	–
0.97	–	–	–	–	–	–
0.99	–	–	–	–	–	–
1 (MeOH)	–	–	–	–	–	–

[MOIm][BF_4]/MeCN						
0 ([MOIm][BF_4])	29.1	171	31.2	6.47	217	21.9
0.20	24.9	171	29.0	10.4	216	25.5
0.40	27.5	172	30.1	5.96	215	22.6
0.60	15.0	175	23.8	21.8	214	32.3
0.70	24.5	177	32.8	12.2	215	27.0
0.80	24.2	171	35.3	10.5	219	25.2
0.90	–	–	–	–	–	–
0.95	–	–	–	–	–	–
0.97	–	–	–	–	–	–
0.99	–	–	–	–	–	–
1 (MeCN)	–	–	–	–	–	–
[MOIm][BF_4]/DMSO						
0 ([MOIm][BF_4])	43.4	172	34.6	4.57	215	17.2
0.20	37.8	172	33.5	4.47	215	17.1
0.40	36.7	171	34.8	2.83	216	15.2
0.60	24.3	171[a]	32.5	2.42	216[a]	13.6
0.70	24.8	171[a]	34.8	1.59	216[a]	14.6
0.80	13.5	171[a]	33.0	–	–	–
0.90	4.32	171[a]	39.1	–	–	–
0.95	–	–	–	–	–	–
0.97	–	–	–	–	–	–
0.99	–	–	–	–	–	–
1 (DMSO)	–	–	–	–	–	–

[a] Fixed.

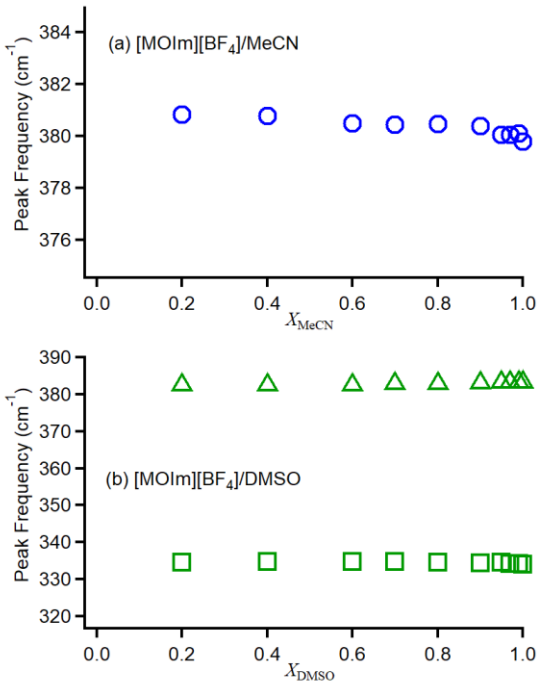

Figure S6. X_{ML} dependence of the peak frequencies of intramolecular vibrational bands of solvents in the Kerr spectra. (a) [MOIm][BF_4]/MeCN and (b) [MOIm][BF_4]/DMSO.

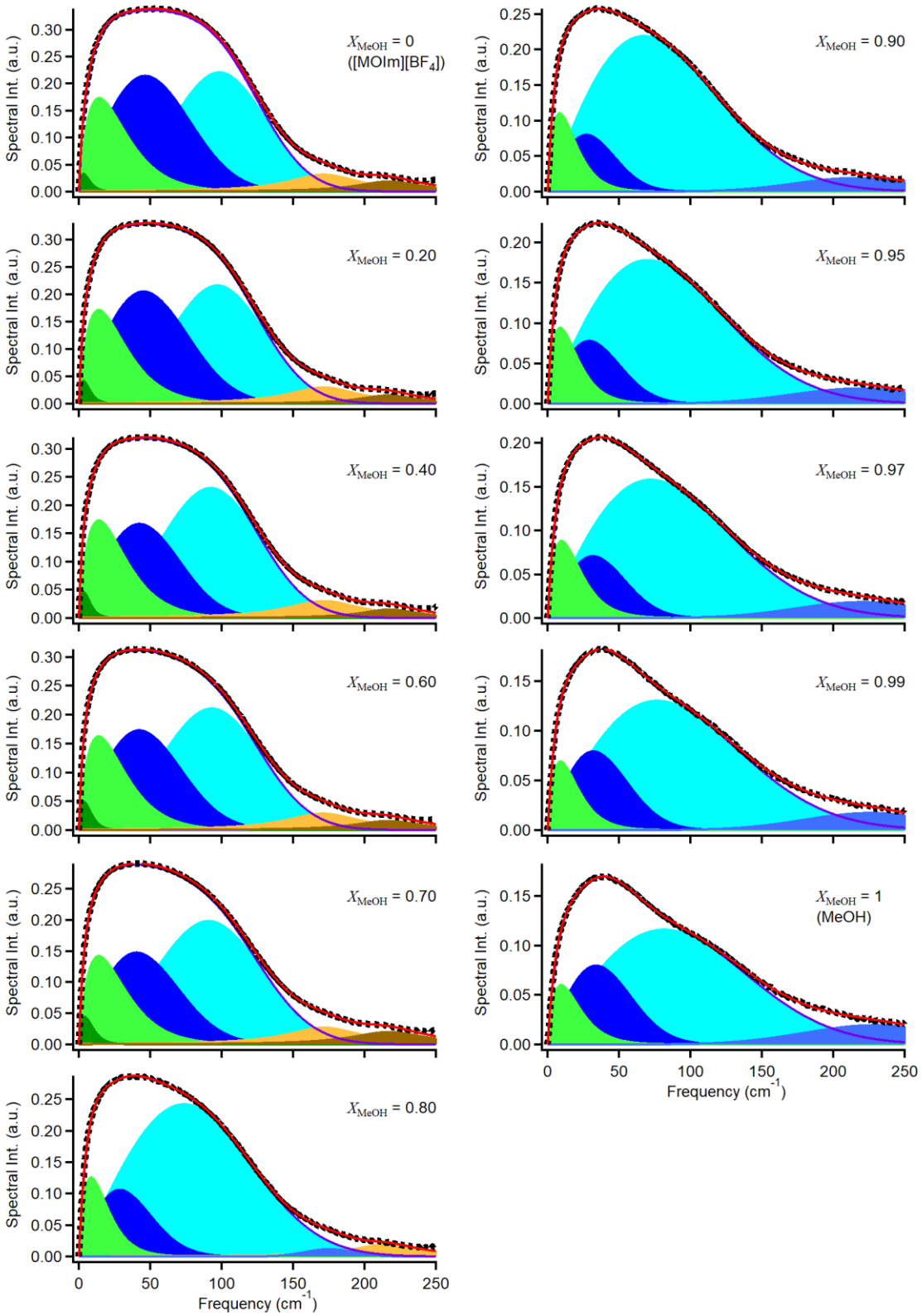

Figure S7. Line-Shape Analysis Results for Low-Frequency Spectra of [MOIm][BF_4] Mixtures with MeOH.

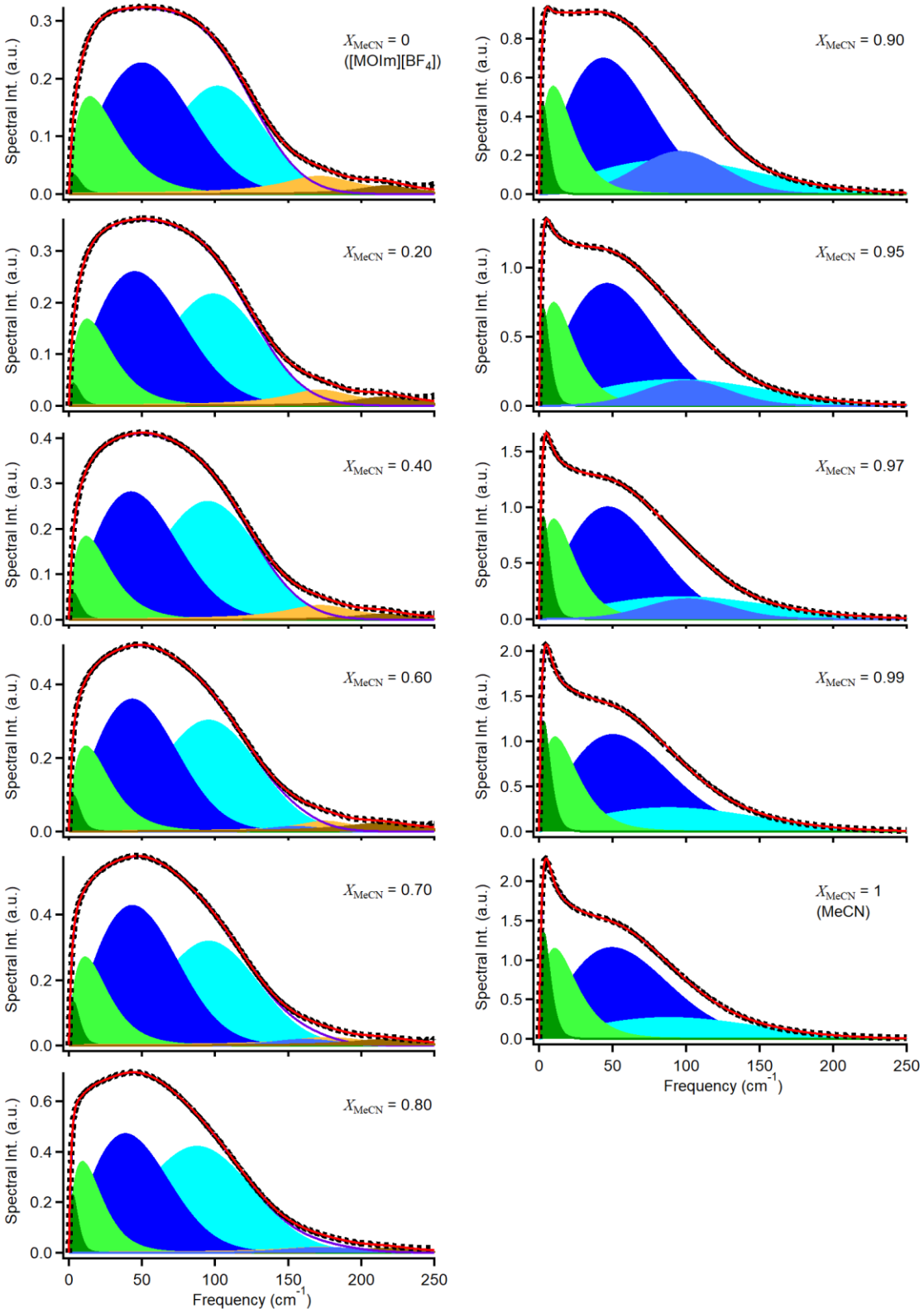

Figure S8. Line-Shape Analysis Results for Low-Frequency Spectra of [MOIm][BF$_4$] Mixtures with MeCN.

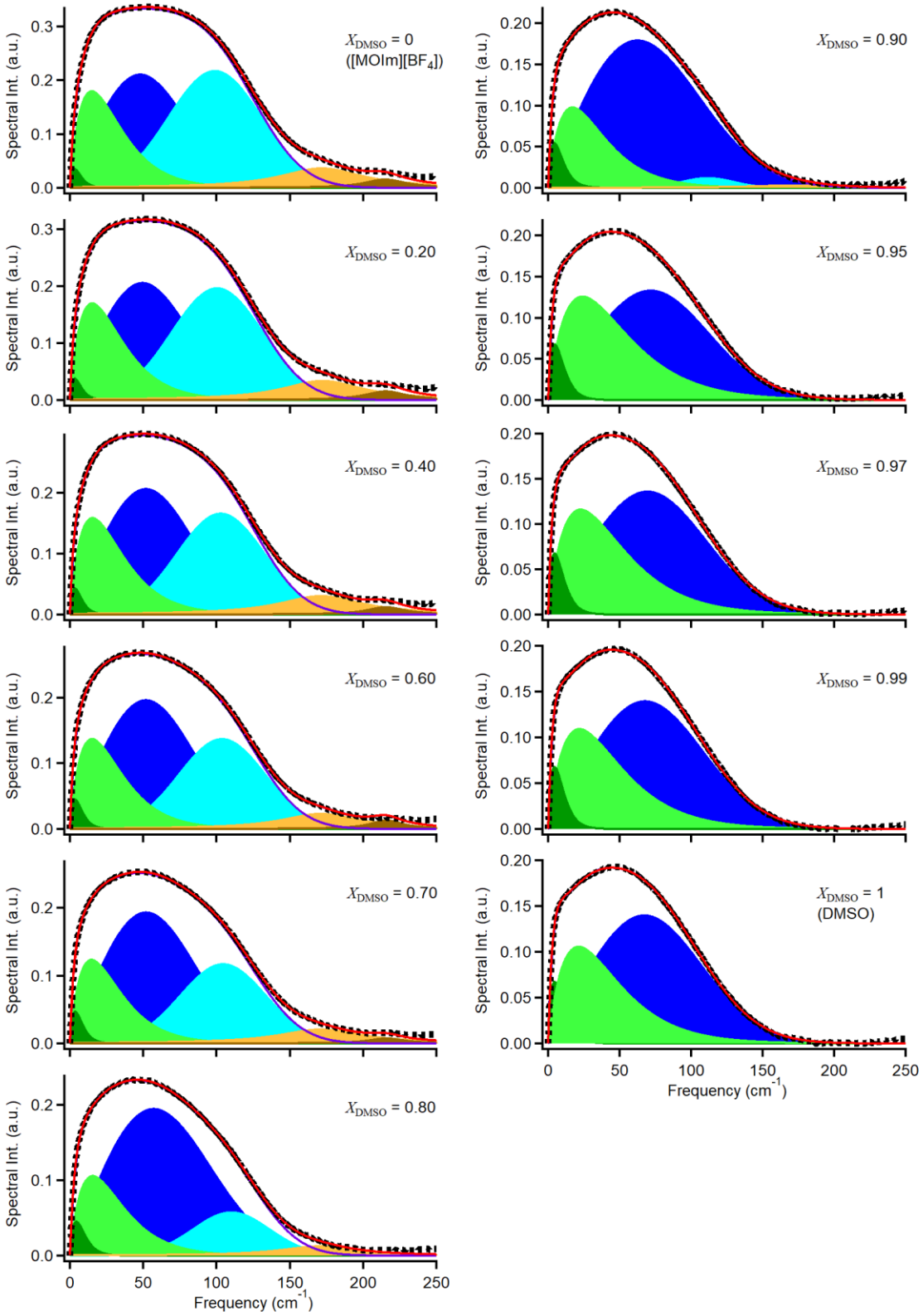

Figure S9. Line-Shape Analysis Results for Low-Frequency Spectra of [MOIm][BF_4] Mixtures with DMSO.