

Supplementary Information

Dynamics of fluorinated imide-based ionic liquids using Nuclear Magnetic Resonance techniques

Tawhid Pranto^{a,b}, Carla C. Fraenza^{c,*1}, Frederik Philippi^d, Daniel Rauber^e, Christopher W. M. Kay^{e,f}, Tom Welton^d, Steven G. Greenbaum^{a,c}, Sophia Suarez^{a,b,*}

^aDepartment of Physics, The Graduate Center of CUNY, New York, NY, USA.

^bDepartment of Physics, Brooklyn College of CUNY, New York, NY, USA.

^cDepartment of Physics & Astronomy, Hunter College of CUNY, New York, NY, USA.

^dDepartment of Chemistry, Molecular Sciences Research Hub, Imperial College London, London, UK.

^eDepartment of Chemistry, Saarland University, Saarbrücken, Germany.

^fLondon Centre for Nanotechnology, University College London, London, UK.

*Corresponding authors

E-mail: carla.cecilia.fraenza@unc.edu.ar (Carla C. Fraenza),

snsuarez@brooklyn.cuny.edu (Sophia Suarez).

¹Present address: IFEG-CONICET and National University of Cordoba, Cordoba, Argentina.

1. Self-diffusion coefficients measured by PFG-NMR

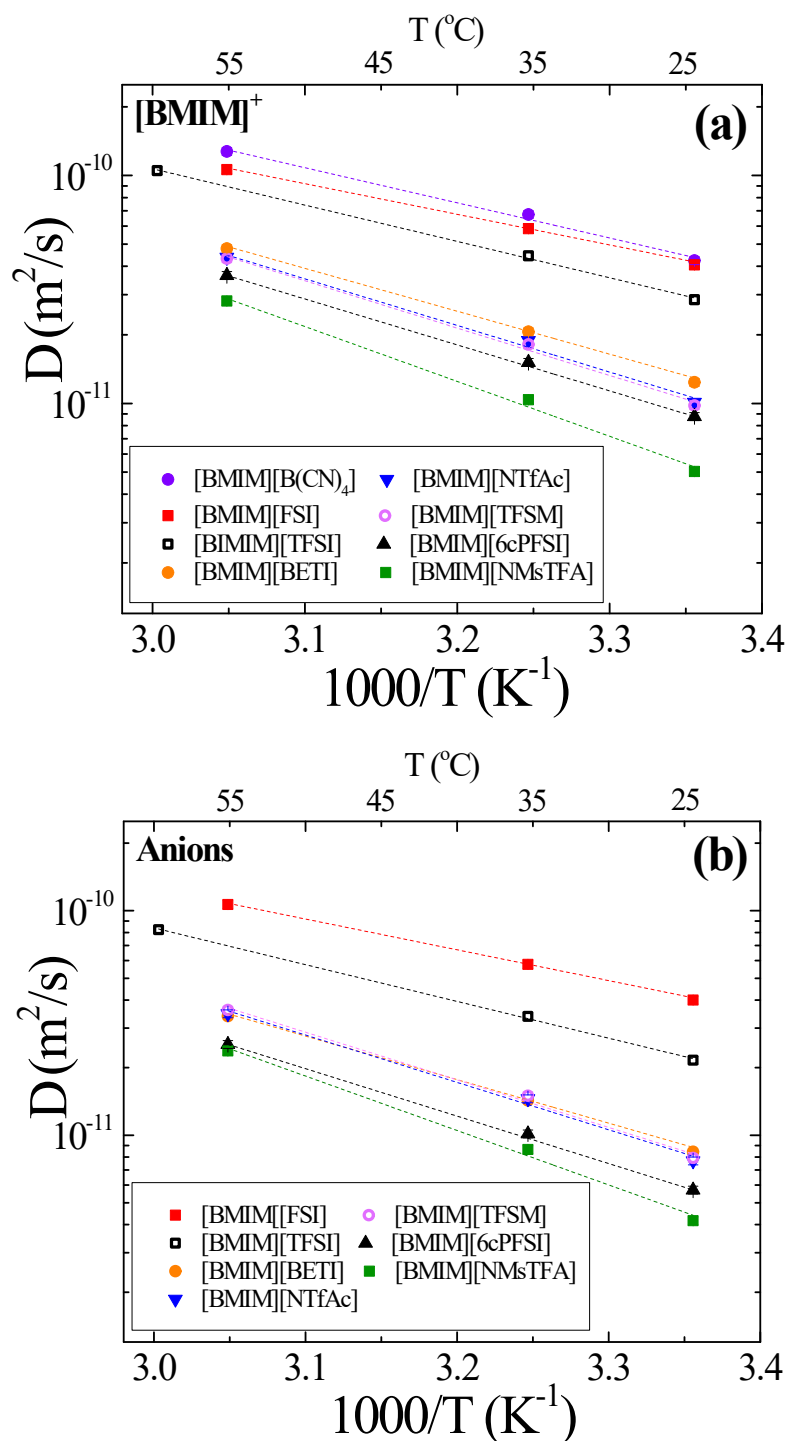


Figure S1. Temperature dependence of self-diffusion coefficients of **(a)** the [BMIM]⁺ cation and **(b)** the anions ([FSI]⁻, [BETI]⁻, [NTfAc]⁻, [TFSM]⁻, [6cPFSI]⁻ and [NM_sTFA]⁻) in the ILs. Self-diffusion coefficients for [BMIM]⁺ and [TFSI]⁻ in [BMIM][TFSI] are included for comparison purposes and the values at 60°C are taken with permission from reference (20). Lines represent the linear fittings of the data using an Arrhenius equation.

Table S1. Self-diffusion coefficients (D) for [BMIM]⁺ (¹H) and the anions (¹⁹F) in all studied ILs, at 25, 35 and 55°C.

Temperature (°C)	$D \text{ [m}^2\text{/s]} \times 10^{-12}$														
	[BMIM] [TFSM]		[BMIM] [NMsTFA]		[BMIM] [NTfAc]		[BMIM] [6cPFSI]		[BMIM] [BETI]		[BMIM] [FSI]		[BMIM] [B(CN) ₄]	[BMIM] [TFSI]	
	¹ H	¹⁹ F	¹ H	¹⁹ F	¹ H	¹⁹ F	¹ H	¹⁹ F	¹ H	¹⁹ F	¹ H	¹⁹ F	¹ H	¹ H	¹⁹ F
25	9.8 ±0.4	7.9 ±0.3	5.0 ±0.2	4.1 ±0.2	10.1± 0.4	7.7 ±0.3	8.8 ±0.3	5.7 ±0.2	12.4 ±0.5	8.5 ±0.2	40.5 ±1	40 ±2	42 ±1	28.5 ±1	21.6 ±0.9
35	18.0 ±0.7	15.0 ±0.6	10.4 ±0.4	8.6 ±0.3	18.9 ±0.7	14.5 ±0.6	15.2 ±0.6	10.1 ±0.4	20.6 ±0.8	14.3 ±0.6	58.5 ±2	57.7 ±2	67.4 ±2	44.4 ±2	33.8 ±1
55	43 ±1	36 ±1	28.1 ±1	23.7 ±0.9	43.8 ±1	34.8 ±1	36.4 ±1	25.4 ±1	47.8 ±2	34 ±1	106 ±4	106.5 ±4	128 ±5	-----	-----

2. Dispersions of the longitudinal relaxation rate

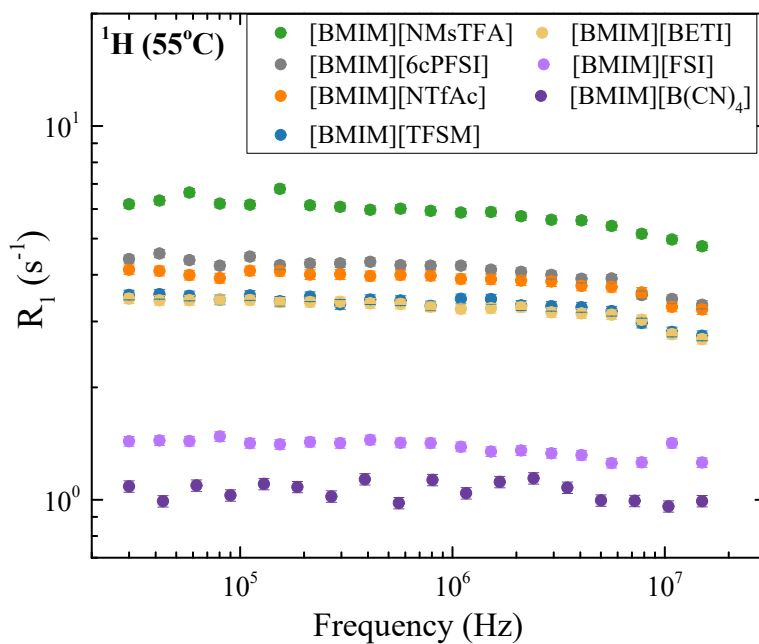


Figure S2. ¹H relaxation rate dispersions for [BMIM][NMstFA], [BMIM][6cPFSI], [BMIM][NTfAc], [BMIM][TFSM], [BMIM][BETI], [BMIM][FSI], and [BMIM][B(CN)₄], recorded at 55°C. Frequencies are ¹H Larmor frequencies.

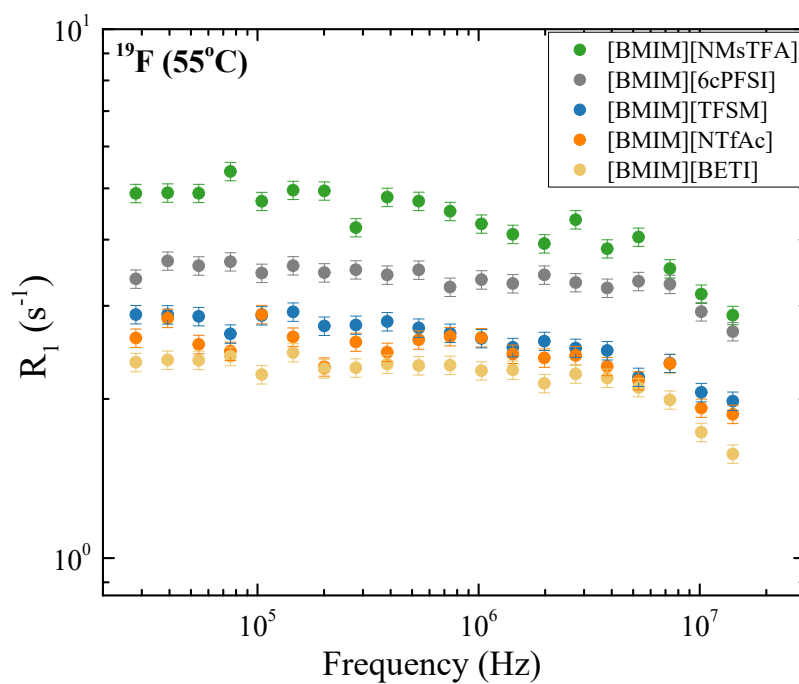


Figure S3. ^{19}F relaxation rate dispersions for [BMIM][NMsTFA], [BMIM][6cPFSI], [BMIM][TFSM], [BMIM][NTfAc], and [BMIM][BETI], recorded at 55°C. Due to the low signal-to-noise ratio, collecting anion dispersion data was impossible for [BMIM][FSI]. Frequencies are ^{19}F Larmor frequencies.

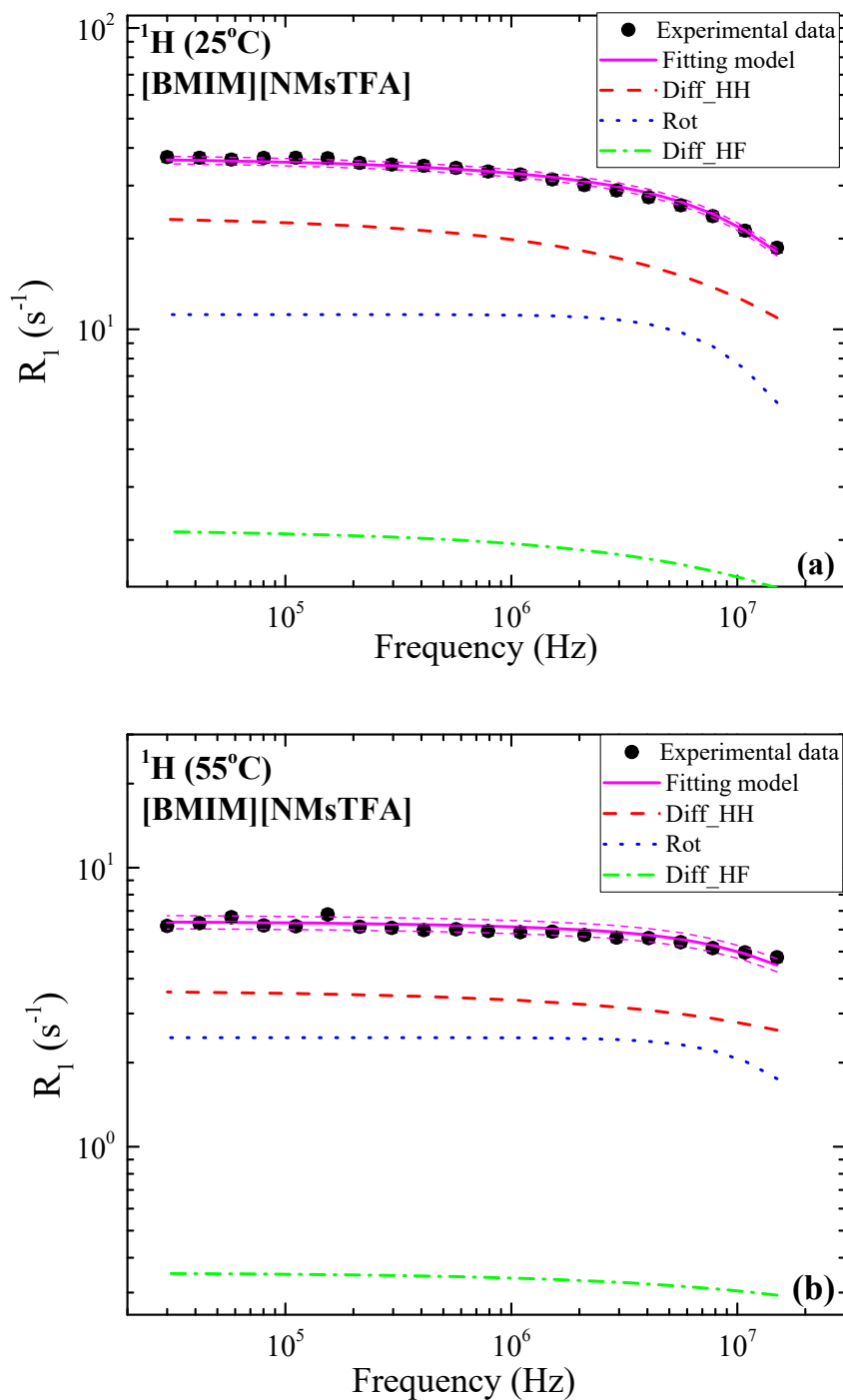


Figure S4. ^1H relaxation rate dispersions for [BMIM][NMSTFA] and their corresponding fittings using the model given by Eq. (7), recorded at 25°C **(a)** and 55°C **(b)**. Additionally, rotational contribution (Rot), and homonuclear (Diff_HH), and heteronuclear (Diff_HF) translational contributions are shown. Magenta dashed lines represent the fitting error. Frequencies are ^1H Larmor frequencies.

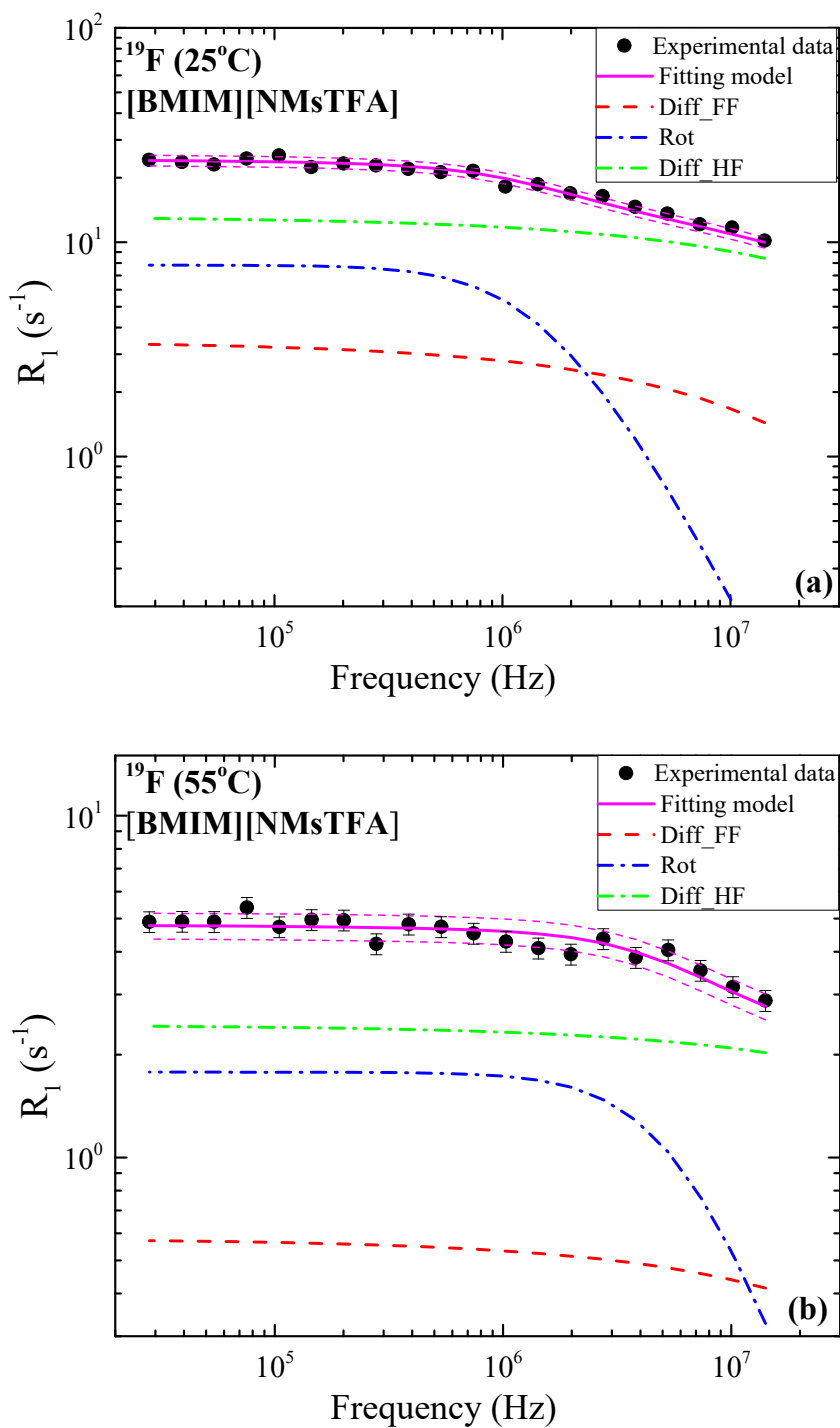


Figure S5. ^{19}F relaxation rate dispersions for [BMIM][NMsTFA] and their corresponding fittings using the model given by Eq. (7), recorded at 25°C (a) and 55°C (b). Additionally, rotational contribution (Rot), homonuclear (Diff_FF), and heteronuclear (Diff_HF) translational contributions are shown. Magenta dashed lines represent the fitting error. Frequencies are ^{19}F Larmor frequencies.

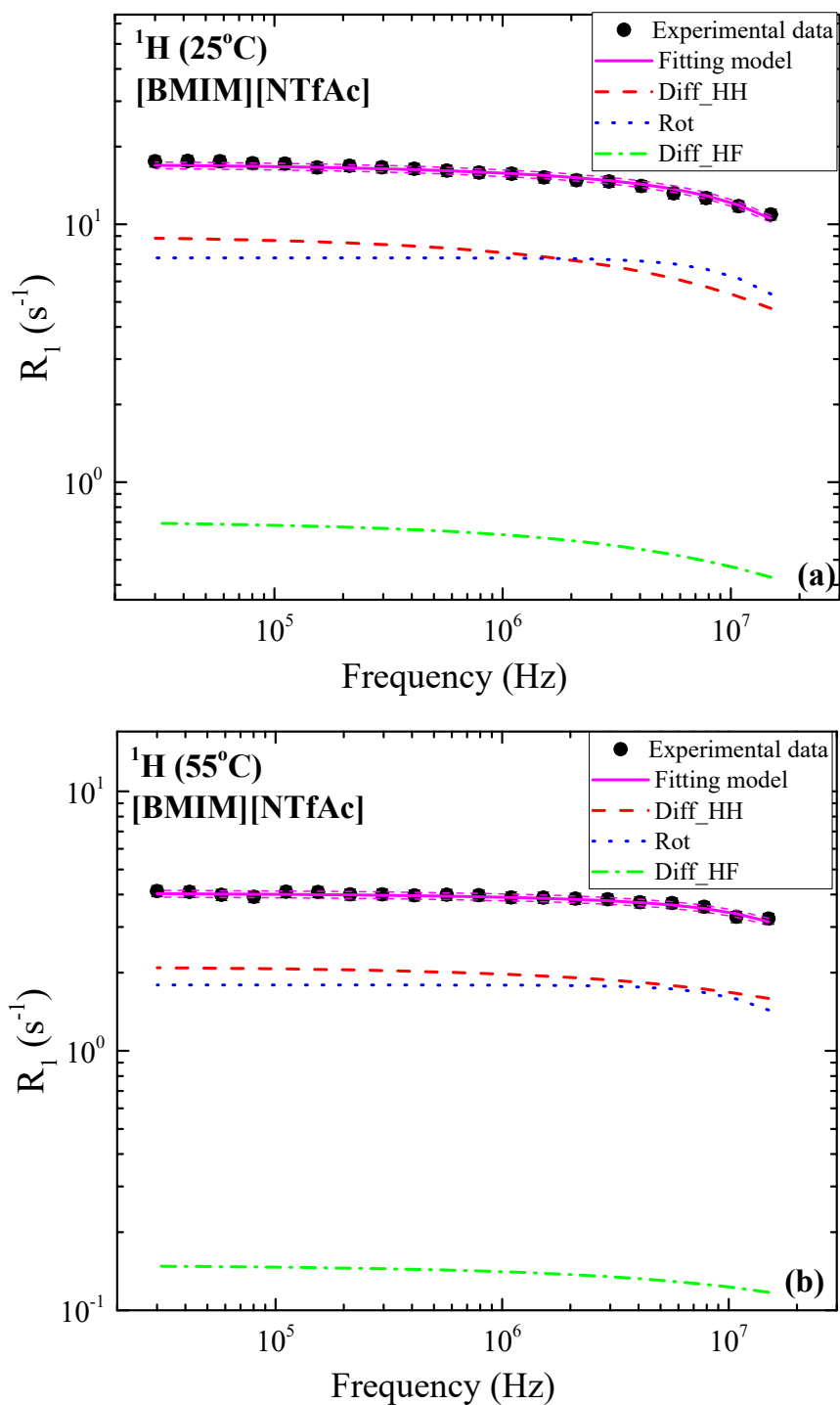


Figure S6. ^1H relaxation rate dispersions for [BMIM][NTfAc] and their corresponding fittings using the model given by Eq. (7), recorded at 25°C (a) and 55°C (b). Additionally, rotational contribution (Rot), homonuclear (Diff_HH), and heteronuclear (Diff_HF) translational contributions are shown. Magenta dashed lines represent the fitting error. Frequencies are ^1H Larmor frequencies.

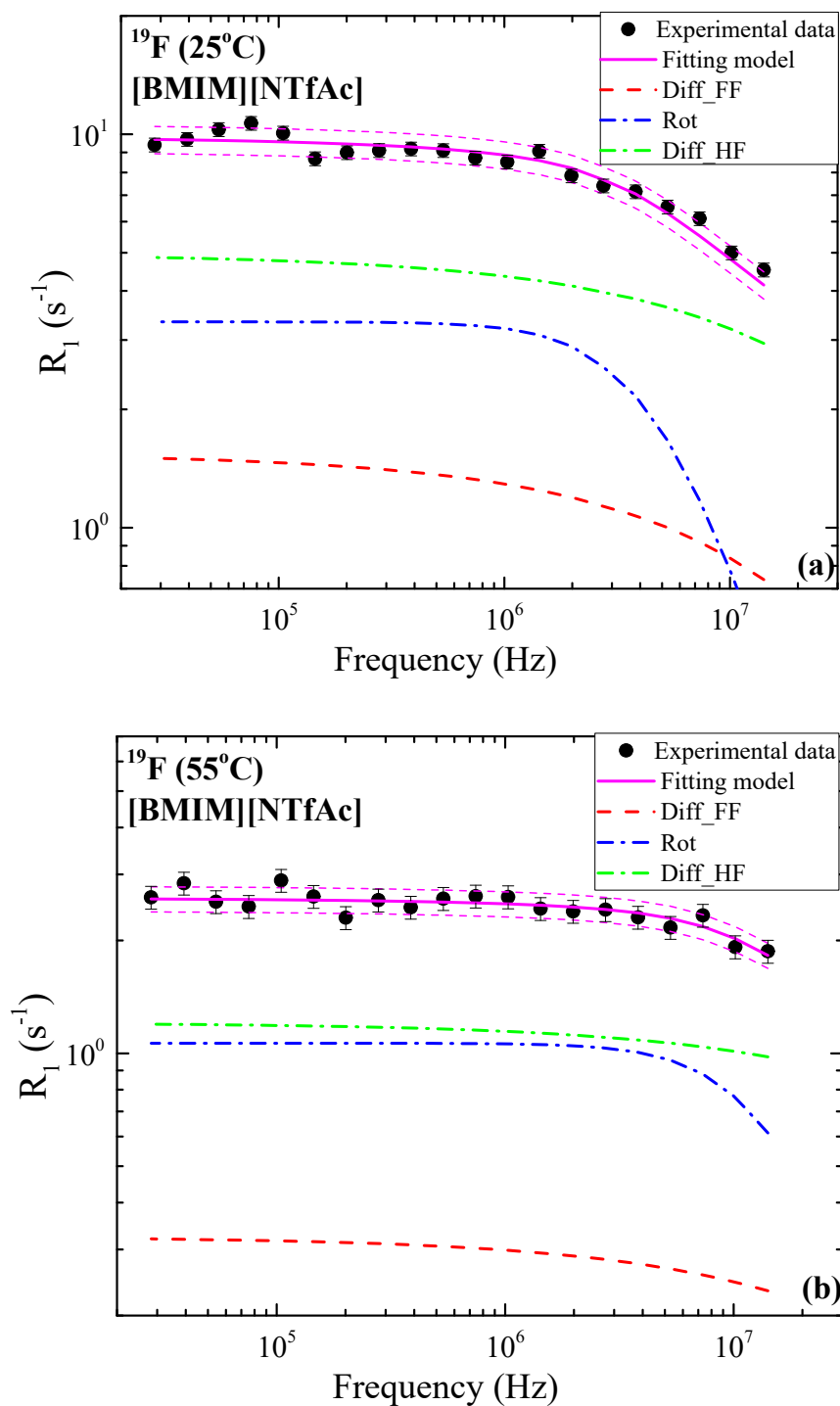


Figure S7. ^{19}F relaxation rate dispersions for [BMIM][NTfAc] and their corresponding fittings using the model given by Eq. (7), recorded at 25°C (a) and 55°C (b). Additionally, rotational contribution (Rot), homonuclear (Diff_HH), and heteronuclear (Diff_HF) translational contributions are shown. Magenta dashed lines represent the fitting error. Frequencies are ^{19}F Larmor frequencies.

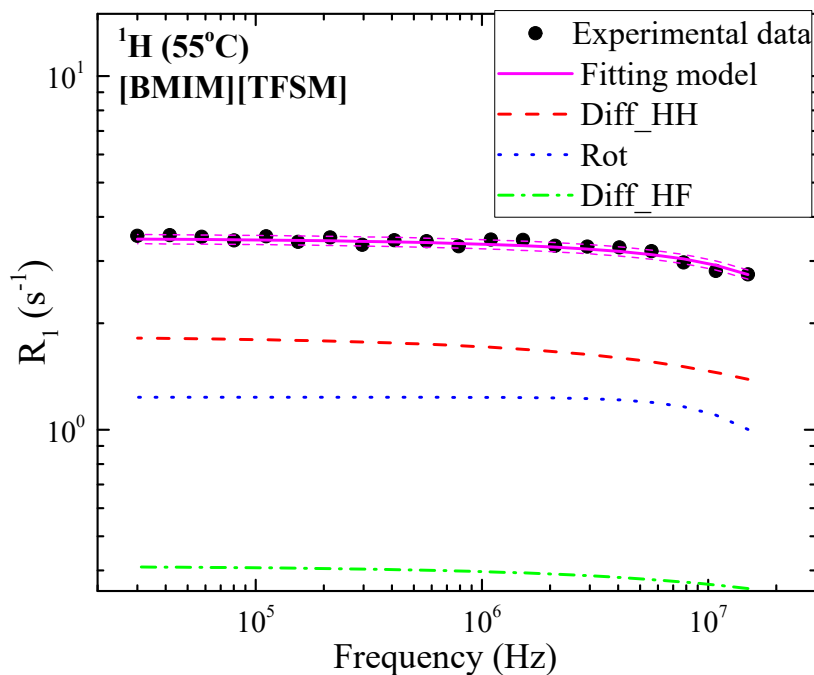


Figure S8. ^1H relaxation rate dispersion for [BMIM][TFSM] and its corresponding fitting using the model given by Eq. (7), recorded at 55°C. Additionally, rotational contribution (Rot), homonuclear (Diff_HH), and heteronuclear (Diff_HF) translational contributions are shown. Magenta dashed lines represent the fitting error. Frequencies are ^1H Larmor frequencies.

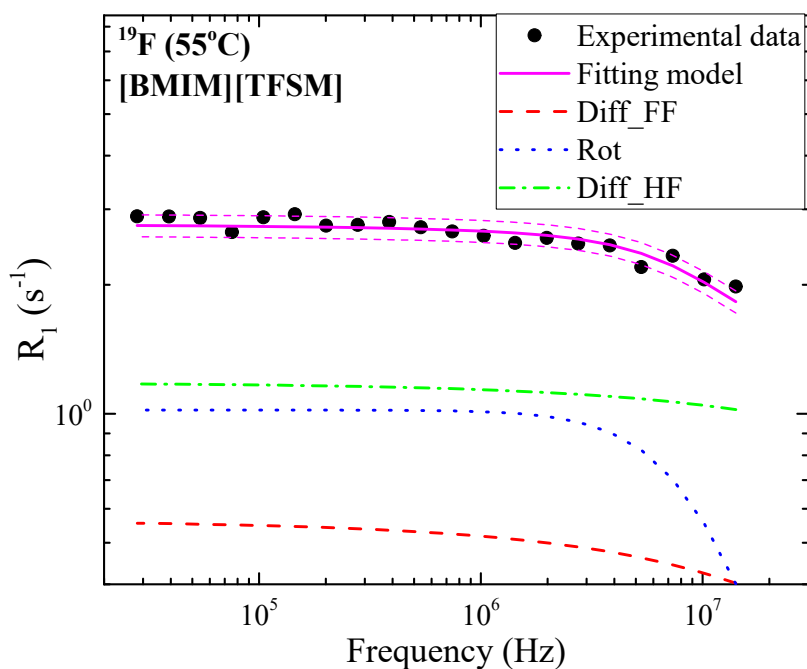


Figure S9. ^{19}F relaxation rate dispersion for [BMIM][TFSM] and its corresponding fitting using the model given by Eq. (7), recorded 55°C. Additionally, rotational contribution (Rot),

homonuclear (Diff_HH), and heteronuclear (Diff_HF) translational contributions are shown. Magenta dashed lines represent the fitting error. Frequencies are ^{19}F Larmor frequencies.

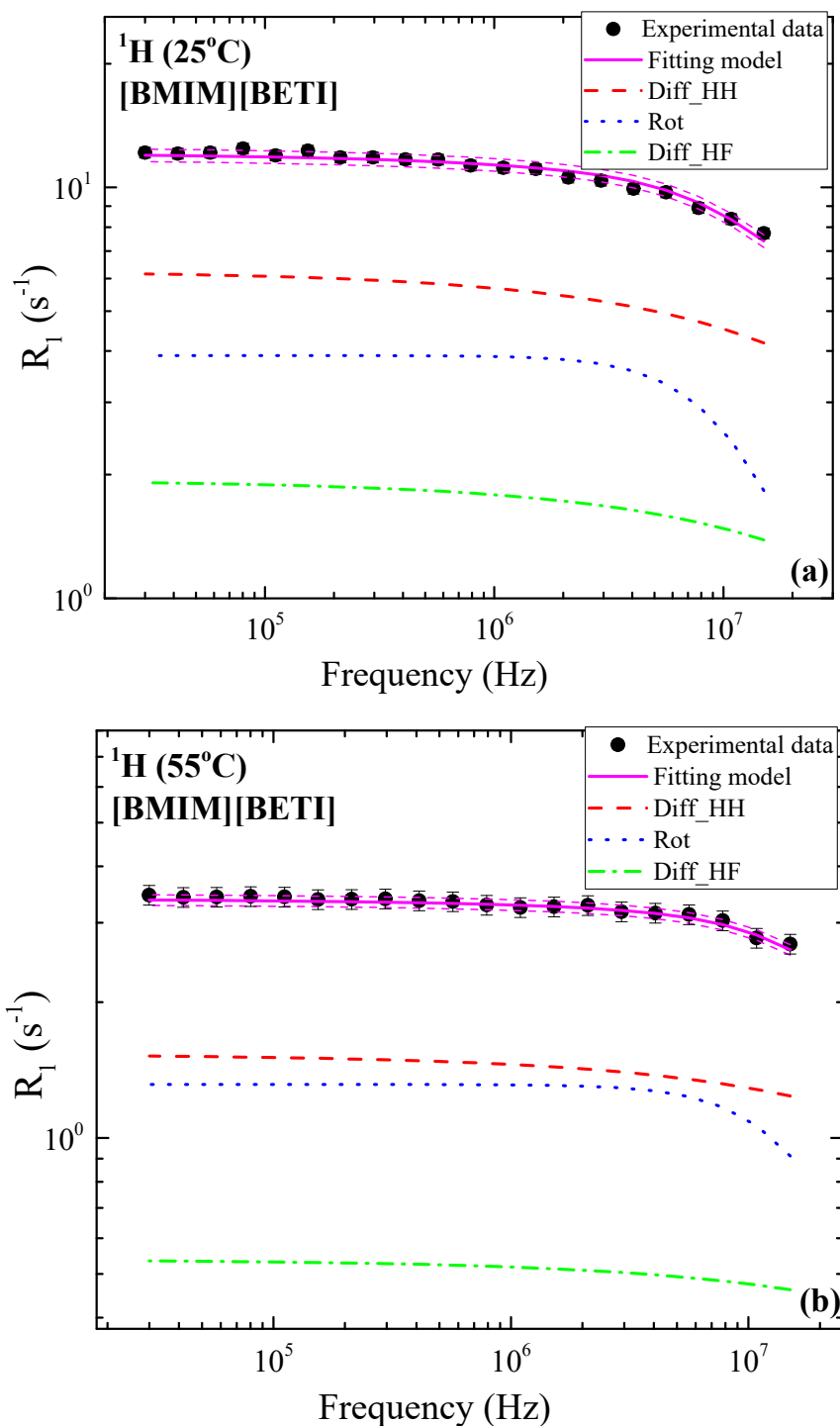


Figure S10. ^1H relaxation rate dispersions for [BMIM][BETI] and their corresponding fittings using the model given by Eq. (7), recorded at 25°C (a) and 55°C (b). Additionally, rotational contribution (Rot), homonuclear (Diff_HH), and heteronuclear (Diff_HF) translational

contributions are shown. Magenta dashed lines represent the fitting error. Frequencies are ^1H Larmor frequencies.

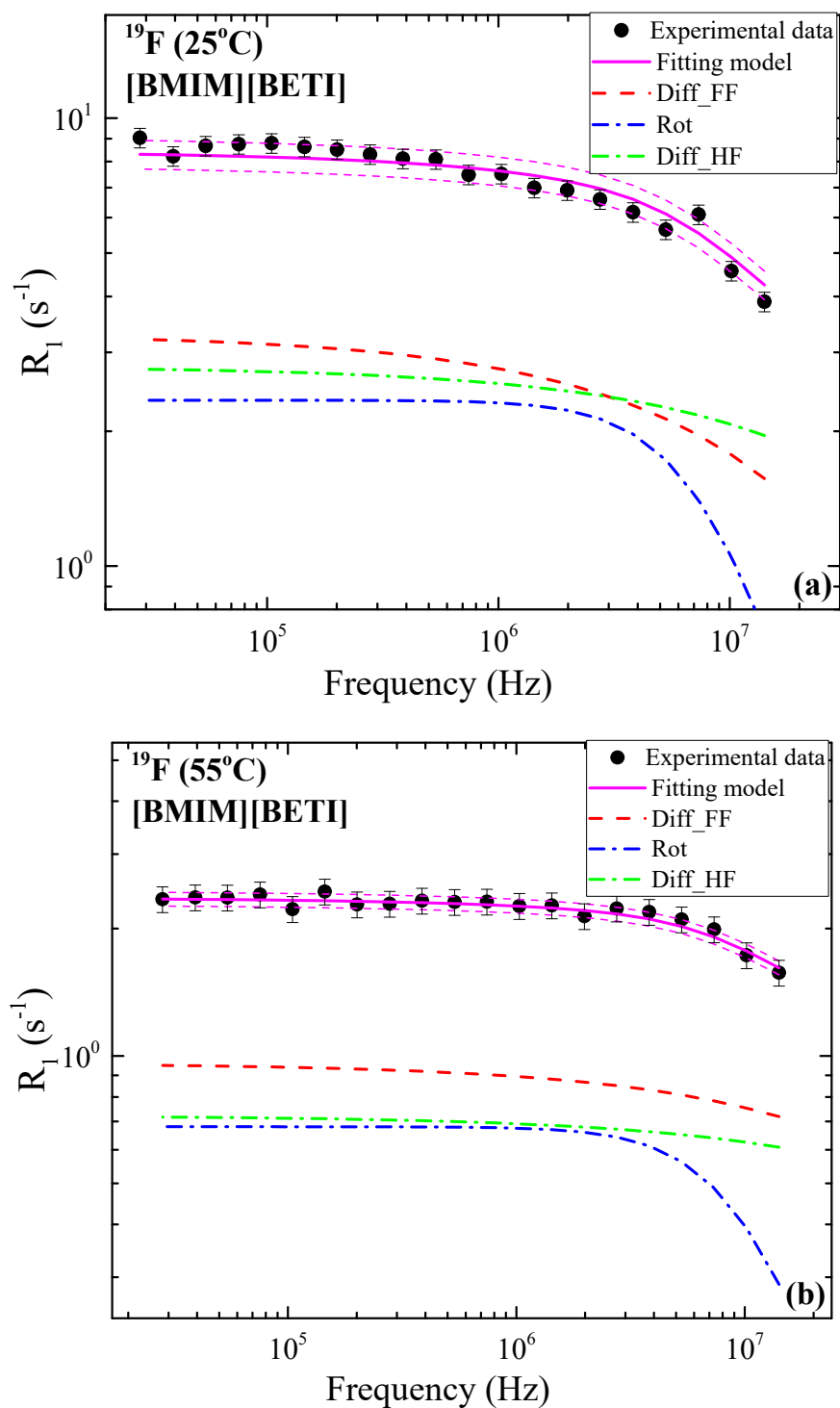


Figure S11. ^{19}F relaxation rate dispersions for [BMIM][BETI] and their corresponding fittings using the model given by Eq. (7), recorded at 25°C (a) and 55°C (b). Additionally, rotational contribution (Rot), homonuclear (Diff_HH), and heteronuclear (Diff_HF)

translational contributions are shown. Magenta dashed lines represent the fitting error. Frequencies are ^{19}F Larmor frequencies.

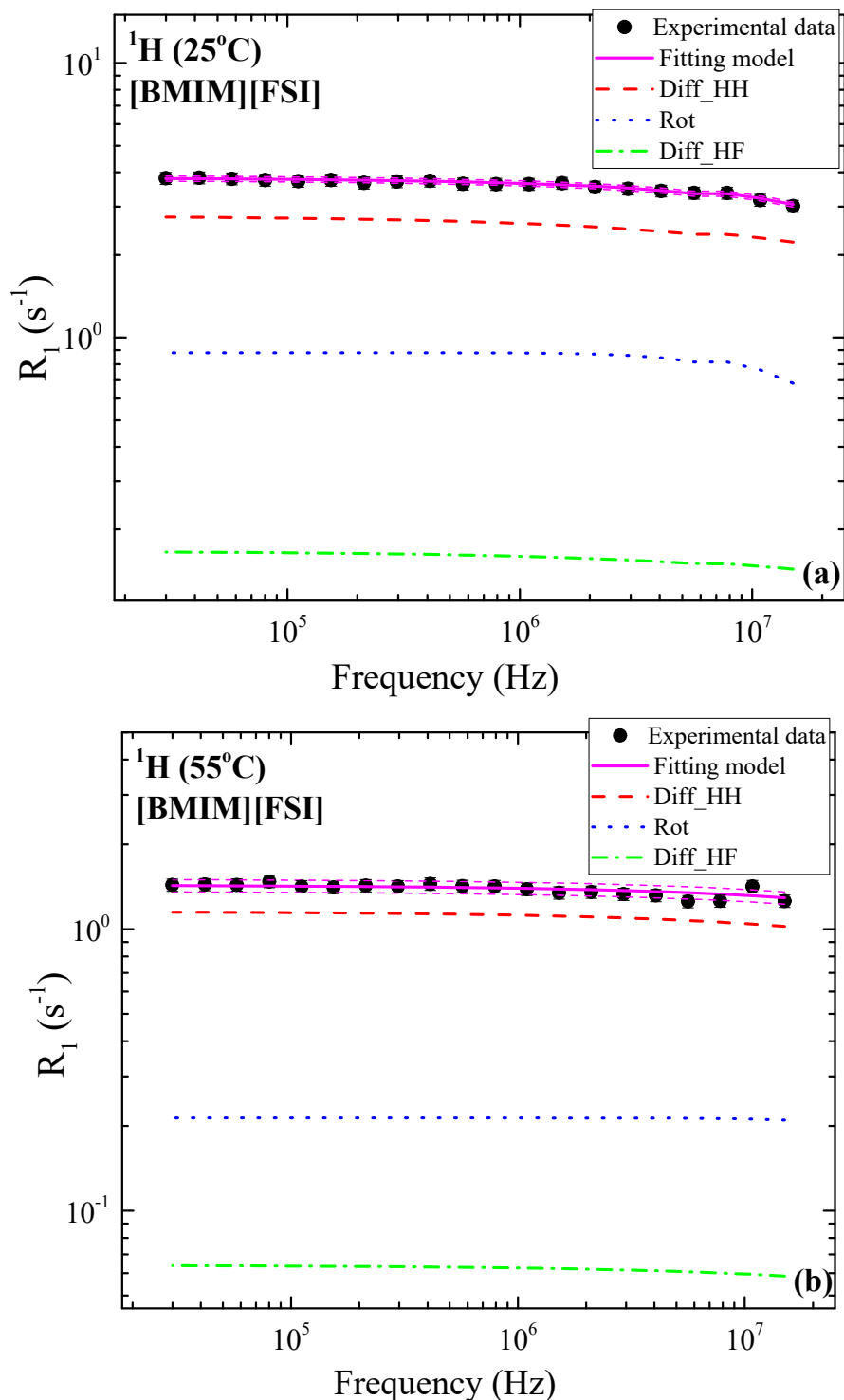


Figure S12. ^1H relaxation rate dispersions for $[\text{BMIM}][\text{FSI}]$ and their corresponding fittings using the model given by Eq. (7), recorded at 25°C (a) and 55°C (b). Additionally, rotational contribution (Rot), homonuclear (Diff_HH), and heteronuclear (Diff_HF) translational

contributions are shown. Magenta dashed lines represent the fitting error. Frequencies are ^1H Larmor frequencies.

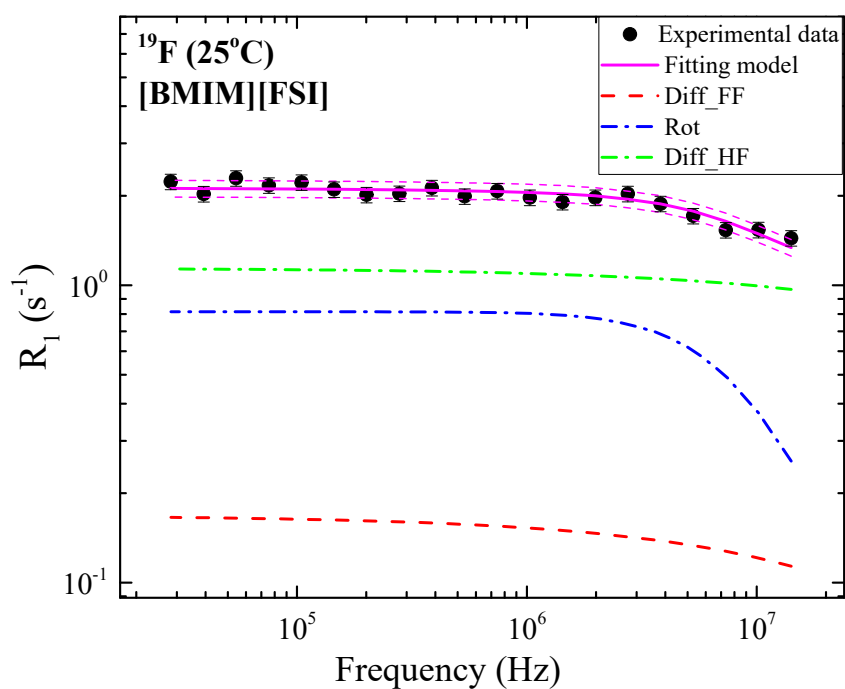


Figure S13. ^{19}F relaxation rate dispersions for [BMIM][FSI] and their corresponding fittings using the model given by Eq. (7), recorded at 25°C. Additionally, rotational contribution (Rot), homonuclear (Diff_HH), and heteronuclear (Diff_HF) translational contributions are shown. Due to the low signal-to-noise ratio, collecting anion dispersion data was impossible at 55°C. Magenta dashed lines represent the fitting error. Frequencies are ^{19}F Larmor frequencies.

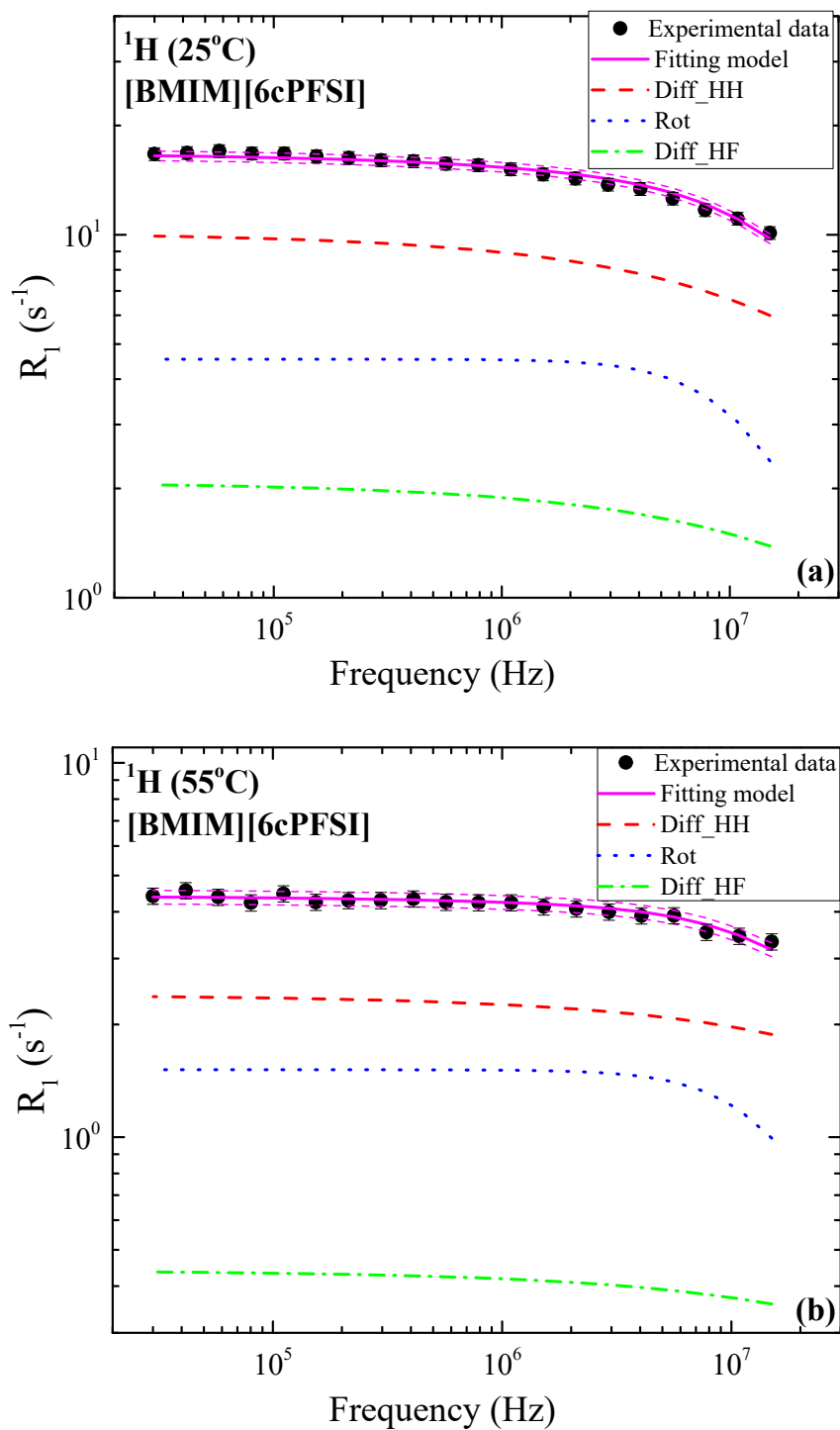


Figure S14. ^1H relaxation rate dispersions for [BMIM][6cPFSI] and their corresponding fittings using the model given by Eq. (7), recorded at 25°C (a) and 55°C (b). Additionally, rotational contribution (Rot), homonuclear (Diff_HH), and heteronuclear (Diff_HF) translational contributions are shown. Magenta dashed lines represent the fitting error. Frequencies are ^1H Larmor frequencies.

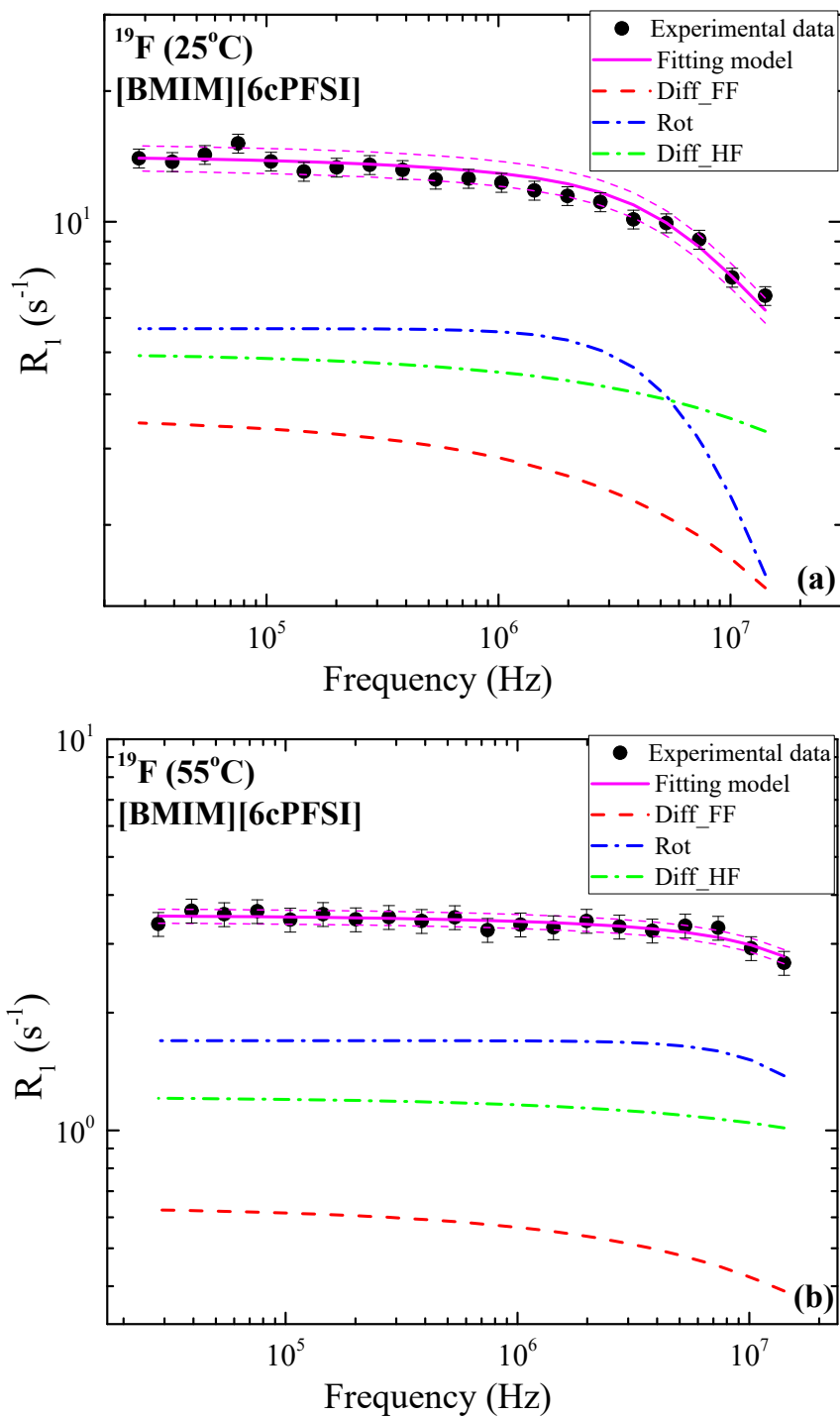


Figure S15. ¹⁹F relaxation rate dispersions for [BMIM][6cPFSI] and their corresponding fittings using the model given by Eq. (7), recorded at 25°C **(a)** and 55°C **(b)**. Additionally, rotational contribution (Rot), homonuclear (Diff_HH), and heteronuclear (Diff_HF) translational contributions are shown. Magenta dashed lines represent the fitting error. Frequencies are ¹⁹F Larmor frequencies.

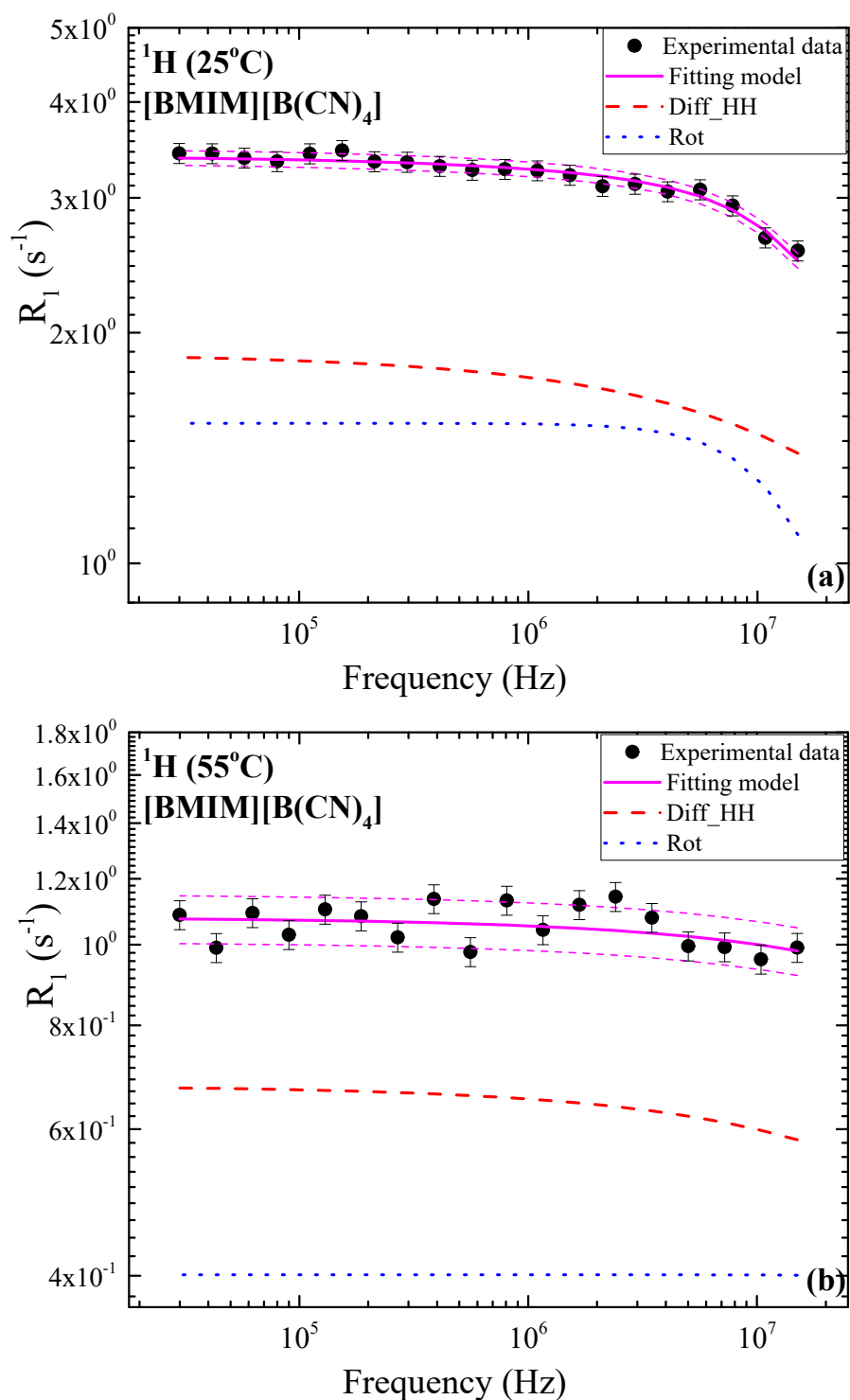


Figure S16. ^1H relaxation rate dispersions for $[\text{BMIM}][\text{B}(\text{CN})_4]$ and their corresponding fittings using the model given by Eq. (7), recorded at 25°C (a) and 55°C (b). Rotational contribution (Rot), and homonuclear (Diff_HH) translational contribution are also shown. Magenta dashed lines represent the fitting error. Frequencies are ^1H Larmor frequencies.

3. Fitting parameters for the relaxation dispersions

Table S2. Parameters obtained using the model given by Eq. (7) to describe the longitudinal relaxation rate profiles for [BMIM]⁺ (¹H) and the anions (¹⁹F) of all studied ILs, at 25°C.

Parameters	[BMIM] [TFSM]		[BMIM] [NMsTFA]		[BMIM] [NTfAc]		[BMIM] [6cPFSI]		[BMIM] [BETI]		[BMIM] [FSI]		[BMIM] [B(CN) ₄]
	¹ H	¹⁹ F	¹ H	¹⁹ F	¹ H	¹⁹ F	¹ H	¹⁹ F	¹ H	¹⁹ F	¹ H	¹⁹ F	¹ H
d_{HH} [m] $\times 10^{-10}$	3.4 ± 0.2	-----	3.0 ± 0.1	-----	3.7 ± 0.2	-----	2.8 ± 0.1	-----	2.7 ± 0.1	-----	2.7 ± 0.1	----- -	3.6 ± 0.1
d_{FF} [m] $\times 10^{-10}$	-----	3.6 ± 0.1	-----	3.1 ± 0.2	-----	3.7 ± 0.2	-----	3.8 ± 0.2	-----	3.9 ± 0.2	----- -	4.7 ± 0.2	-----
d_{HF} [m] $\times 10^{-10}$	2.4 ± 0.1	2.0 ± 0.2	2.0 ± 0.1	2.0 ± 0.1	3.1 ± 0.2	3.1 ± 0.1	2.3 ± 0.1	2.4 ± 0.1	2.4 ± 0.1	2.5 ± 0.1	2.1 ± 0.1	2.3 ± 0.1	-----
D_H [m ² /s] $\times 10^{-12}$	9.9 ± 0.1	9.7 ± 0.3	5.0 ± 0.1	4.9 ± 0.2	10.1 ± 0.3	7.7 ± 0.8	8.8 ± 0.1	8.8 ± 0.2	12.8 ± 0.2	12.7 ± 0.2	41 ± 2	40 ± 1	42 ± 1
D_F [m ² /s] $\times 10^{-12}$	7.9 ± 0.3	8.0 ± 0.2	4.1 ± 0.1	4.1 ± 0.1	7.6 ± 0.3	7.7 ± 0.2	5.7 ± 0.2	5.7 ± 0.1	8.8 ± 0.2	8.5 ± 0.3	40 ± 1	40 ± 3	-----
A_R [1/s ²] $\times 10^8$	2.0 ± 0.1	0.5 ± 0.1	3.8 ± 0.2	0.3 ± 0.1	4.1 ± 0.1	0.40 ± 0.05	1.6 ± 0.1	1.0 ± 0.1	1.20 ± 0.08	0.50 ± 0.03	0.60 ± 0.04	0.20 ± 0.04	0.80 ± 0.05
τ_R [s] $\times 10^{-9}$	5.1 ± 0.2	17 ± 1	5.9 ± 0.3	59 ± 3	3.6 ± 0.2	17 ± 1	5.7 ± 0.3	10.9 ± 0.7	6.4 ± 0.3	10.0 ± 0.5	3.2 ± 0.1	9.8 ± 0.5	3.7 ± 0.2

Table S3. Parameters obtained using the model given by Eq. (7) to describe the longitudinal relaxation rate profiles for [BMIM]⁺ (¹H) and the anions (¹⁹F) of all studied ILs, at 55°C.

Parameters	[BMIM] [TFSM]		[BMIM] [NMsTFA]		[BMIM] [NTfAc]		[BMIM] [6cPFSI]		[BMIM] [BETI]		[BMIM] [FSI]	[BMIM] [B(CN) ₄]
	¹ H	¹⁹ F	¹ H	¹⁹ F	¹ H	¹⁹ F	¹ H	¹⁹ F	¹ H	¹⁹ F	¹ H	¹ H
d_{HH} [m] $\times 10^{-10}$	3.4 ± 0.1	-----	3.2 ± 0.1	-----	3.5 ± 0.1	-----	2.8 ± 0.1	-----	2.8 ± 0.1	-----	2.5 ± 0.1	3.3 ± 0.1
d_{FF} [m] $\times 10^{-10}$	-----	3.7 ± 0.2	-----	3.1 ± 0.2	-----	3.8 ± 0.2	-----	4.6 ± 0.3	-----	3.3 ± 0.1	-----	-----
d_{HF} [m] $\times 10^{-10}$	2.1 ± 0.1	2.0 ± 0.1	2.1 ± 0.1	2.0 ± 0.1	3.3 ± 0.2	2.7 ± 0.2	2.5 ± 0.1	2.6 ± 0.1	2.2 ± 0.1	2.4 ± 0.1	2.1 ± 0.1	-----
D_H [m ² /s] $\times 10^{-12}$	43 ± 1	43 ± 1	28 ± 3	23 ± 3	44 ± 2	35 ± 3	37 ± 1	37 ± 2	48 ± 1	48 ± 1	106 ± 3	127 ± 2
D_F [m ² /s] $\times 10^{-12}$	36 ± 1	36 ± 2	24 ± 2	24 ± 1	34 ± 3	35 ± 1	25 ± 1	25 ± 2	34 ± 1	34 ± 1	106 ± 4	-----
A_R [1/s ²] $\times 10^8$	8.8 ± 0.2	0.30 ± 0.05	1.30 ± 0.05	0.25 ± 0.02	1.2 ± 0.1	0.39 ± 0.07	0.7 ± 0.1	1 ± 0.1	0.7 ± 0.1	0.18 ± 0.02	0.56 ± 0.08	3.8 ± 0.2
τ_R [s] $\times 10^{-9}$	2.8 ± 0.2	7.6 ± 0.4	3.7 ± 0.2	14 ± 1	2.9 ± 0.1	5.4 ± 0.3	4.3 ± 0.2	3.8 ± 0.2	3.9 ± 0.2	7.6 ± 0.3	0.8 ± 0.2	0.20 ± 0.01