

Supporting Information

NMR Relaxometry and Diffusometry Analysis of Dynamics in Ionic Liquids and Ionogels for Use in Lithium Ion Batteries

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Ionogel characterization

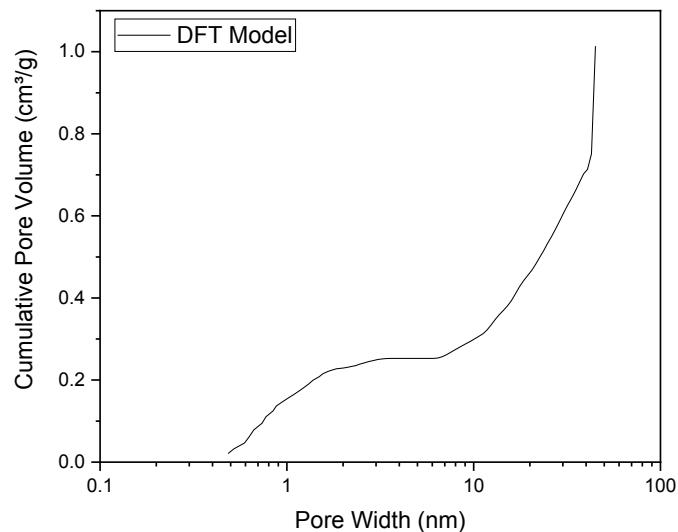


Figure S1. N₂ adsorption isotherm obtained using the Micromeritics Tarazona DFT model for cylindrical-pore oxides.

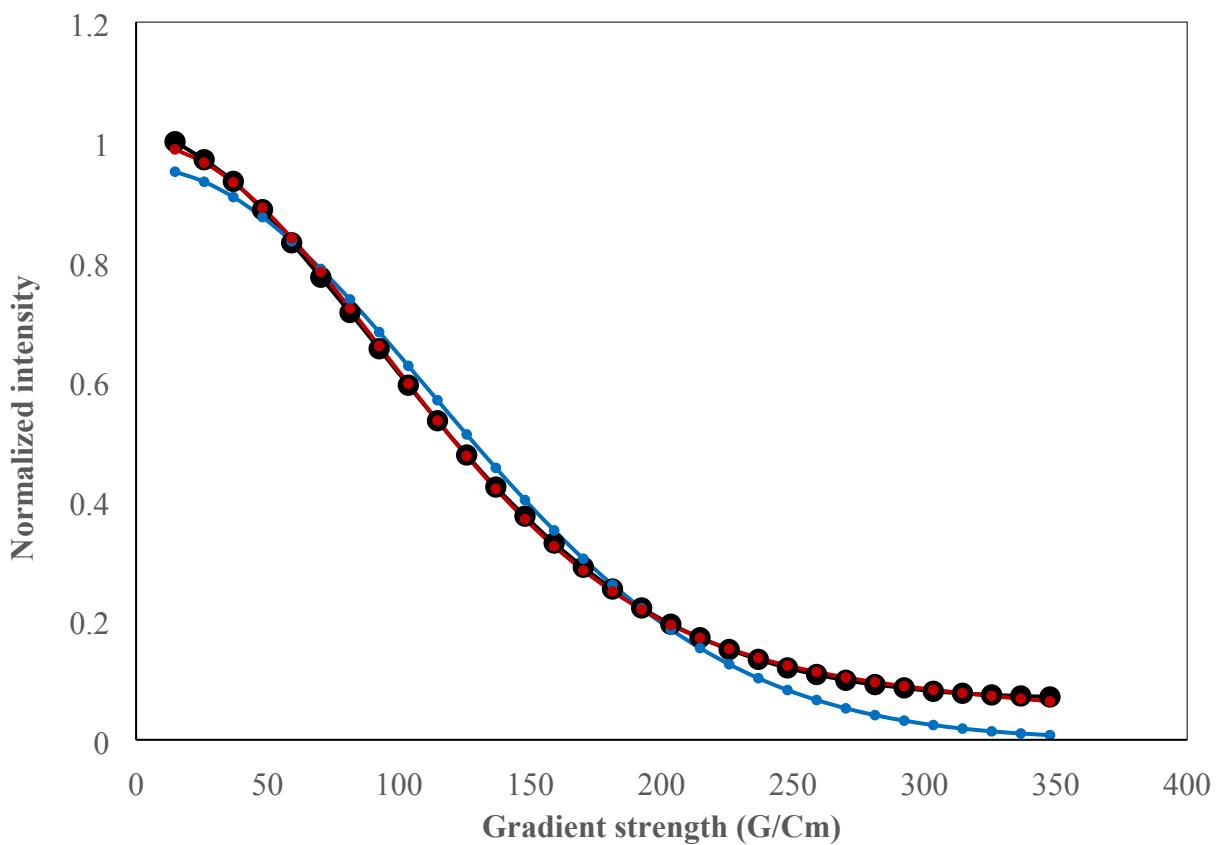


Figure S2: ^1H diffusion for IG with 0.5M LiTFSI at 40°C . Black symbols are experimental data, blue curve is best single-value fit, red curve is two-value fit.

Self-diffusion coefficients

Temperature	Samples (0M LiTFSI)	$D_{F1}(\text{m}^2\text{s}^{-1})$	$D_{H1}(\text{m}^2\text{s}^{-1})$	$D_{H2}(\text{m}^2\text{s}^{-1})$	$D_{HAvg}(\text{m}^2\text{s}^{-1})$
20°C	IL	1.45×10^{-11}	2.16×10^{-11} (93%)	4.53×10^{-12} (7%)	2.04×10^{-11}
	IG	9.25×10^{-12}	1.41×10^{-11} (90%)	2.11×10^{-12} (10%)	-
60°C	IL	8.23×10^{-11}	1.05×10^{-10}	-	-
	IG	5.16×10^{-11}	6.79×10^{-11}	-	-
100°C	IL	2.27×10^{-10}	2.85×10^{-10}	-	-
	IG	1.54×10^{-10}	1.89×10^{-10}	-	-

Table S1. Self-diffusion coefficients (D) of TFSI⁻ (F) and BMIM⁺ (H) in ionic liquids (ILs) and ionogels (IGs) with 0M LiTFSI, at different temperatures. For ILs, the percentage values within parenthesis are the weighting factors A and B and they represent different aggregates; D_{HAvg} is the weighted average of D_{H1} and D_{H2} . For IGs, these weighting factors correspond to W_{bulk} (larger value) and W_{surf} (smaller value) (see Eq. (20) in the main manuscript for more details) and D_{H2} is D_{surf} for BMIM⁺.

Temperature	Samples (0.5M LiTFSI)	$D_{Li1}(\text{m}^2\text{s}^{-1})$	$D_{F1}(\text{m}^2\text{s}^{-1})$	$D_{F2}(\text{m}^2\text{s}^{-1})$	$D_{FAvg}(\text{m}^2\text{s}^{-1})$	$D_{H1}(\text{m}^2\text{s}^{-1})$	$D_{H2}(\text{m}^2\text{s}^{-1})$	$D_{HAvg}(\text{m}^2\text{s}^{-1})$
20°C	IL	6.09×10^{-12}	8.93×10^{-12} (79%)	2.84×10^{-12} (21%)	7.65×10^{-12}	1.78×10^{-11} (62%)	4.82×10^{-12} (38%)	1.29×10^{-11}
	IG	2.75×10^{-12}	4.52×10^{-12} (75%)	1.31×10^{-12} (25%)	-	7.96×10^{-12} (73%)	5.75×10^{-13} (27%)	-
40°C	IL	1.72×10^{-11}	2.56×10^{-11}	-	-	4.02×10^{-11}	-	-
	IG	6.72×10^{-12}	9.88×10^{-12}	-	-	2.06×10^{-11} (84%)	2.75×10^{-12} (16%)	-
60°C	IL	3.62×10^{-11}	5.42×10^{-11}	-	-	8.19×10^{-11}	-	-
	IG	1.63×10^{-11}	2.46×10^{-11}	-	-	5.18×10^{-11} (78%)	1.36×10^{-11} (22%)	-
80°C	IL	7.15×10^{-11}	1.00×10^{-10}	-	-	1.52×10^{-10}	-	-
	IG	3.23×10^{-11}	4.81×10^{-11}	-	-	8.24×10^{-11} (92%)	9.65×10^{-12} (8%)	-
100°C	IL	1.17×10^{-10}	1.64×10^{-10}	-	-	2.42×10^{-10}	-	-
	IG	5.60×10^{-11}	8.27×10^{-11}	-	-	1.37×10^{-10} (93%)	2.75×10^{-11} (7%)	-

Table S2. Self-diffusion coefficients (D) of Li⁺, TFSI⁻ (F) and BMIM⁺ (H) in ionic liquids (ILs) and ionogels (IGs) with 0.5M LiTFSI, at different temperatures. For ILs, the percentage values within parenthesis are the weighting factors A and B that represent different aggregates; D_{iAvg} is the weighted average of D_{i1} and D_{i2} , where i stands for F or H. For IGs, these weighting factors correspond to W_{bulk} (larger value) and W_{surf} (smaller value) (see Eq. (20) in the main manuscript for more details) and D_{i2} is D_{surf} , where i stands for F or H.

Temperature	Samples (1M LiTFSI)	D_{Li1} (m^2s^{-1})	D_{Li2} (m^2s^{-1})	D_{F1} (m^2s^{-1})	D_{F2} (m^2s^{-1})	D_{FAvg} (m^2s^{-1})	D_{H1} (m^2s^{-1})	D_{H2} (m^2s^{-1})	D_{HAvg} (m^2s^{-1})
	IL	1.62×10^{-12}	-	2.46×10^{-12} (90%)	6.53×10^{-13} (10%)	2.28×10^{-12}	6.28×10^{-12} (64%)	2.96×10^{-12} (36%)	5.08×10^{-12}

20°C	IG	1.03 x 10 ⁻¹² (76%)	2.65 x 10 ⁻¹³ (22%)	1.04 x 10 ⁻¹² (85%)	2.90 x 10 ⁻¹⁴ (15%)	-	3.24 x 10 ⁻¹² (69%)	3.39 x 10 ⁻¹³ (31%)	-
	IL	2.24 x 10 ⁻¹²	-	3.36 x 10 ⁻¹² (90%)	1.15 x 10 ⁻¹² (10%)	3.14 x 10 ⁻¹²	7.78 x 10 ⁻¹² (82%)	2.69 x 10 ⁻¹² (18%)	6.86 x 10 ⁻¹²
25°C	IG	1.26 x 10 ⁻¹² (85%)	3.45 x 10 ⁻¹³ (15%)	1.41 x 10 ⁻¹² (89%)	1.57 x 10 ⁻¹⁴ (11%)	-	4.63 x 10 ⁻¹² (69%)	4.55 x 10 ⁻¹³ (31%)	-
	IL	5.84 x 10 ⁻¹²	-	8.65 x 10 ⁻¹² (90%)	2.78 x 10 ⁻¹² (10%)	8.06 x 10 ⁻¹²	1.74 x 10 ⁻¹¹ (93%)	3.50 x 10 ⁻¹² (7%)	1.64 x 10 ⁻¹¹
40°C	IG	3.47 x 10 ⁻¹² (89%)	5.81 x 10 ⁻¹³ (11%)	3.83 x 10 ⁻¹² (92%)	1.00 x 10 ⁻¹³ (8%)	-	9.27 x 10 ⁻¹² (85%)	5.38 x 10 ⁻¹³ (15%)	-
	IL	1.85 x 10 ⁻¹¹	-	2.93 x 10 ⁻¹¹	-	-	4.45 x 10 ⁻¹¹ (95%)	7.22 x 10 ⁻¹² (5%)	4.26 x 10 ⁻¹¹
60°C	IG	9.75 x 10 ⁻¹² (91%)	1.23 x 10 ⁻¹² (9%)	1.07 x 10 ⁻¹¹ (94%)	5.91 x 10 ⁻¹³ (6%)	-	2.31 x 10 ⁻¹¹ (92%)	5.46 x 10 ⁻¹³ (8%)	-

Table S3. Self-diffusion coefficients (D) of Li⁺, TFSI⁻ (F) and BMIM⁺ (H) in ionic liquids (IL) and ionogels (IG) with 1M LiTFSI, at different temperatures. For ILs, the percentage values within parenthesis are the weighting factors A and B that represent different aggregates; D_{iAvg} is the weighted average of D_{i1} and D_{i2} , where i stands for F or H. For IGs, these weighting factors correspond to W_{bulk} (larger value) and W_{surf} (smaller value) (see Eq. (20) in the main manuscript for more details) and D_{i2} is D_{surf} , where i stands for Li, F or H.

Sample		Transference number					
		20°C	25°C	40°C	60°C	80°C	100°C
0.5M LITFSI	IL	0.034	-	0.039	0.039	0.042	0.043
	IG	0.033	-	0.033	0.032	0.037	0.038
1M LITFSI	IL	0.059	0.063	0.070	0.076	-	-
	IG	0.12	0.067	0.082	0.088	-	-

Table S4. Effective Li-transference numbers at different concentrations of LiTFSI and temperatures.

Dispersions of the spin-lattice relaxation rate

a) Analysis of hydrogen and fluorine relaxation profiles

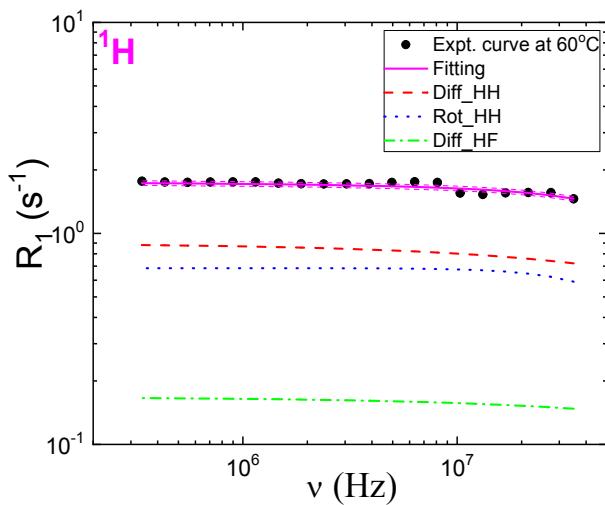


Figure S3. ^1H relaxation rate dispersion for [BMIM] TFSI ionic liquid with 0M LiTFSI and its corresponding fitting using the model given by Eq. (7), recorded at 60°C.

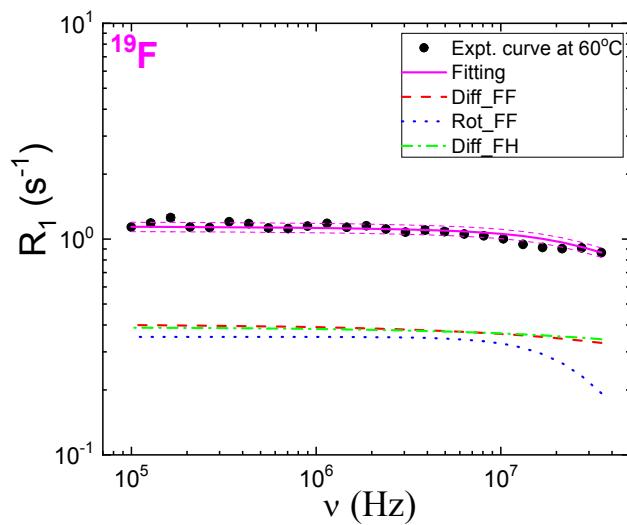


Figure S4. ^{19}F relaxation rate dispersion for [BMIM] TFSI ionic liquid with 0M LiTFSI and its corresponding fitting using the model given by Eq. (7), recorded at 60°C.

Parameters	[BMIM] TFSI + 0M LiTFSI			
	IL_1H 30 °C	IL_1H 60 °C	IL_19F 30 °C	IL_19F 60 °C
d_{HH} [m] $\times 10^{-10}$	2.9±0.1	2.7±0.2	-----	-----
d_{FF} [m] $\times 10^{-10}$	-----	-----	2.5±0.2	2.3±0.2
d_{HF} [m] $\times 10^{-10}$	2.4±0.2	2.3±0.2	2.4±0.1	2.4±0.2
D_H [m ² /s] $\times 10^{-11}$	3.3±0.3	10±1	3.3±0.2	10.4±0.5
D_F [m ² /s] $\times 10^{-11}$	2.3±0.1	8.2±0.2	2.3±0.2	8.2±0.3
A_R [1/s ²] $\times 10^8$	1.7±0.2	1.4±0.2	0.11±0.01	0.28±0.2
τ_R [s] $\times 10^{-9}$	1.8±0.2	1.0±0.1	11±1	2.5±0.2

Table S5. Parameters obtained using the model given by Eq. (7) to describe the measured ¹H and ¹⁹F spin-lattice relaxation rate profiles of ionic liquids (IL) with 0M LiTFSI, at different temperatures.

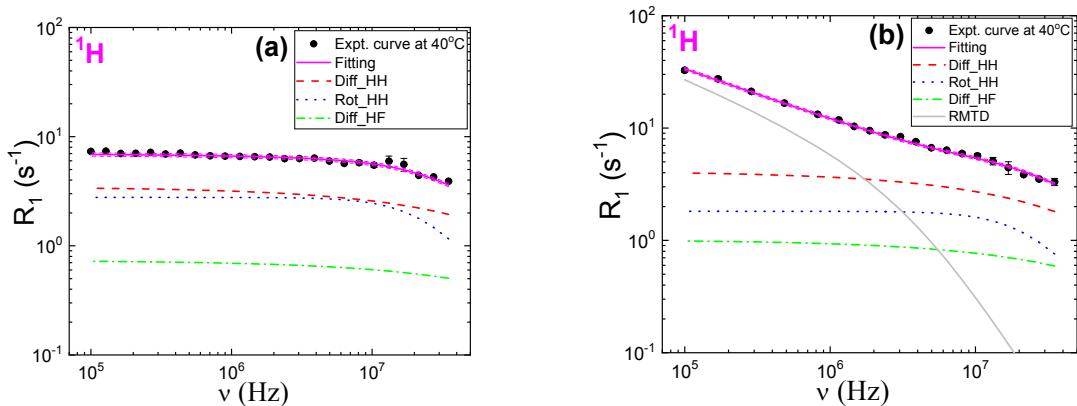


Figure S5. ¹H relaxation rate dispersions for (a) IL and (b) IG with 1M LiTFSI and their corresponding fittings using the models given by Eq. (7) and (8), recorded at 40°C.

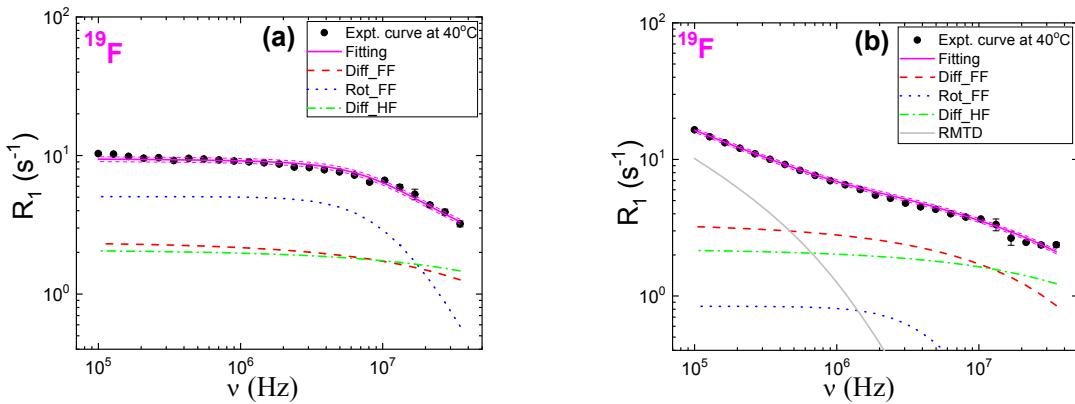


Figure S6. ^{19}F relaxation rate dispersions for **(a)** IL and **(b)** IG with 1M LiTFSI and their corresponding fittings using the models given by Eq. (7) and (8), recorded at 40°C.

Parameters	[BMIM] TFSI + 1M LiTFSI											
	IL_1H 30 °C	IL_1H 40 °C	IL_1H 60 °C	IG_1H 30 °C	IG_1H 40 °C	IG_1H 60 °C	IL_19F 30 °C	IL_19F 40 °C	IL_19F 60 °C	IG_19F 30 °C	IG_19F 40 °C	IG_19F 60 °C
d_{HH} [m] $\times 10^{-10}$	2.8±0.2	2.7±0.1	2.7±0.2	2.7±0.1	3.0±0.2	2.8±0.2	-----	-----	-----	-----	-----	-----
d_{FF} [m] $\times 10^{-10}$	-----	-----	-----	-----	-----	-----	2.4±0.3	2.2±0.2	2.3±0.2	3.1±0.1	3.0±0.2	3.0±0.1
d_{HF} [m] $\times 10^{-10}$	2.3±0.1	2.3±0.2	2.3±0.1	2.4±0.2	2.4±0.1	2.3±0.2	2.2±0.1	2.0±0.2	2.6±0.2	2.7±0.2	2.8±0.3	2.7±0.1
D_H [m ² /s] $\times 10^{-12}$	7.7±0.6	16±2	43±3	5.6±0.3	10.0±0.6	23±2	7.6±0.5	14±1	40±4	5.8±0.3	11.2±0.7	25±3
D_F [m ² /s] $\times 10^{-12}$	4.6±0.2	8.7±0.5	29±2	2.1±0.2	4.0±0.3	11±1	4.5±0.2	8.5±0.4	29±3	2.4±0.3	4.1±0.4	12±2
D_{surf} [m ² /s] $\times 10^{-13}$	-----	-----	-----	4.9±0.3	5.5±0.2	5.6±0.3	-----	-----	-----	0.29±0.01	0.96±0.05	6.3±0.5
A_{RMTD} [s ^{-3/2}] $\times 10^4$	-----	-----	-----	1.0±0.1	1.7±0.2	2.3±0.2	-----	-----	-----	1.5±0.2	1.4±0.1	1.1±0.1
l_{min} [m] $\times 10^{-10}$	-----	-----	-----	1.6±0.1	2.1±0.2	2.1±0.2	-----	-----	-----	1.5±0.1	1.7±0.2	4.0±0.3
l_{max} [m] $\times 10^{-9}$	-----	-----	-----	30±2	55±3	71±5	-----	-----	-----	5±1	25±2	57±4
A_R [1/s ²] $\times 10^8$	2.5±0.2	1.8±0.1	1.7±0.1	1.5±0.1	1.4±0.1	1.9±0.2	1.4±0.2	1.3±0.1	1.5±0.2	0.11±0.02	0.11±0.01	0.18±0.02
τ_R [s] $\times 10^{-9}$	4.2±0.2	3.1±0.1	1.1±0.1	4.3±0.3	3.1±0.2	1.3±0.1	14±1	7.8±0.5	2.8±0.2	51±2	17±1	8.4±0.4

Table S6. Parameters obtained using the models given by Eq. (7) and (8) to describe the measured ^1H and ^{19}F spin–lattice relaxation rate profiles of ionic liquids (IL) and ionogels (IG) with 1M LiTFSI, at different temperatures.

b) Analysis of lithium relaxation profiles

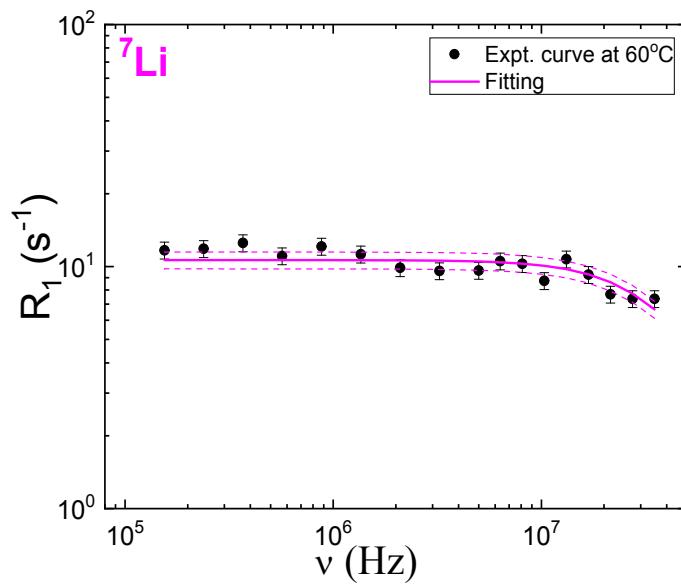


Figure S7. ${}^7\text{Li}$ relaxation rate dispersion for IL with 1M LiTFSI and its corresponding fitting using the models given by Eq. (14) and (16), recorded 60°C.

Parameters	[BMIM] TFSI + 1M LITFSI				
	IL- ${}^7\text{Li}$ 30 °C	IL- ${}^7\text{Li}$ 40 °C	IL- ${}^7\text{Li}$ 60 °C	IG- ${}^7\text{Li}$ 30 °C	IG- ${}^7\text{Li}$ 40 °C
$A_Q [1/\text{s}^2] \times 10^9$	3.1±0.2	2.3±0.3	1.1±0.2	1.0±0.1	0.70±0.08
$\tau_{jump} [\text{s}] \times 10^{-9}$	3.3±0.2	2.5±0.1	2.0±0.2	4.7±0.2	2.7±0.2
$A_{RMTD_power} [1/\text{s}^{-(p+1)}] \times 10^7$	-----	-----	-----	2.0±0.2	1.9±0.3
p	-----	-----	-----	0.70±0.05	0.7±0.1

Table S7. Parameters obtained using the models given by Eq. (14) and (16) to describe the measured ${}^7\text{Li}$ spin-lattice relaxation rate profiles of ionic liquids (IL) and ionogels (IG) with 1M LiTFSI, at different temperatures.