

## Supplementary Information

Probing Translational and Rotational Dynamics in Hydrophilic/Hydrophobic Anions based Imidazolium Ionic  
Liquid-water mixtures

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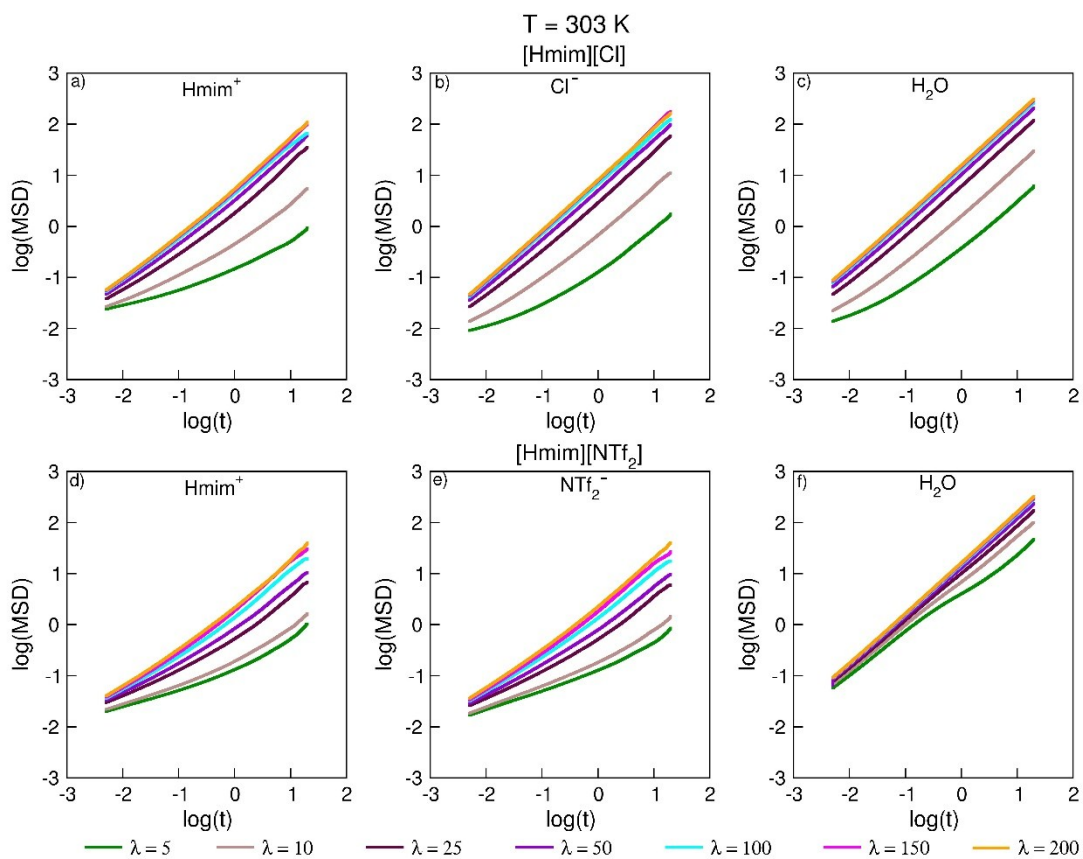
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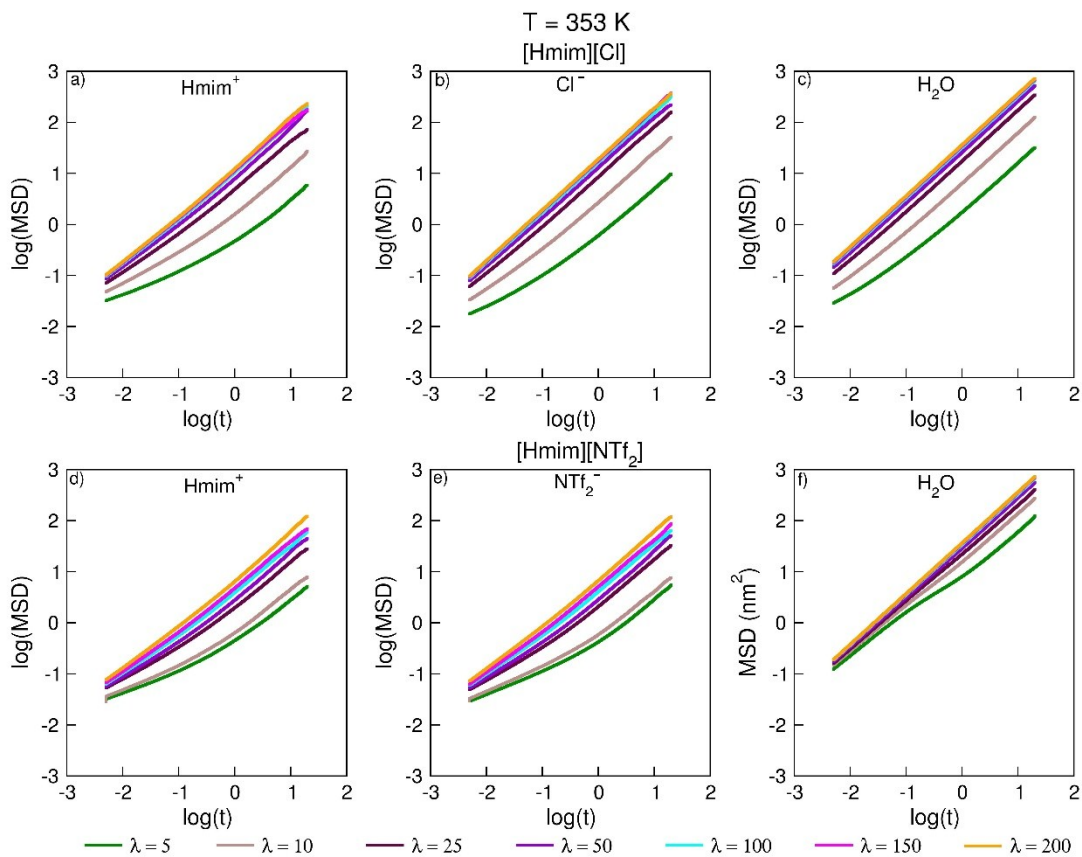
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**Table S1:** System size, density of neat and hydrated [Hmim][Cl] and [Hmim][NTf<sub>2</sub>] IL

$\lambda$	Number of ion pairs	Number of water molecules	[Hmim][Cl]				[Hmim][NTf <sub>2</sub> ]			
			Total number of atoms	H <sub>2</sub> O (wt %)	$\rho$ (g cm <sup>-3</sup> ) (303 K)	$\rho$ (g cm <sup>-3</sup> ) (353 K)	Total number of atoms	H <sub>2</sub> O (wt %)	$\rho$ (g cm <sup>-3</sup> ) (303 K)	$\rho$ (g cm <sup>-3</sup> ) (353 K)
Neat	500	-	16000	-	1.010	0.983	23000	-	1.428	1.377
0.25	500	125	16375	2.17	1.015	0.990	23375	1.00	1.421	1.371
0.5	500	250	16750	4.25	1.023	0.995	23750	1.97	1.416	1.365
1	500	500	17500	8.15	1.032	1.006	24500	3.87	1.405	1.354
2	500	1000	19000	15.08	1.046	1.015	26000	7.45	1.387	1.333
5	125	625	5875	30.74	1.056	1.018	7625	16.74	1.302	1.256
10	125	1250	7750	47.02	1.049	1.009	9500	28.69	1.245	1.199
25	125	3125	13375	68.94	1.033	0.992	15125	50.14	1.156	1.114
50	125	6250	22750	81.61	1.017	0.978	24500	66.79	1.095	1.055
100	125	12500	41500	89.87	1.005	0.968	43250	80.01	1.051	1.012
150	125	18750	60250	93.01	1.001	0.964	62000	85.78	1.037	0.999
200	125	25000	79000	94.67	0.998	0.962	80750	88.94	0.989	0.979



**Figure S1:**  $\log(\text{MSD})$  vs.  $\log(t)$  plot for cations, anions and water molecules in low, intermediate and high water concentration of [Hmim][Cl] (a,b,c) and [Hmim][NTf<sub>2</sub>] IL (d, e, f) at **T = 303 K**

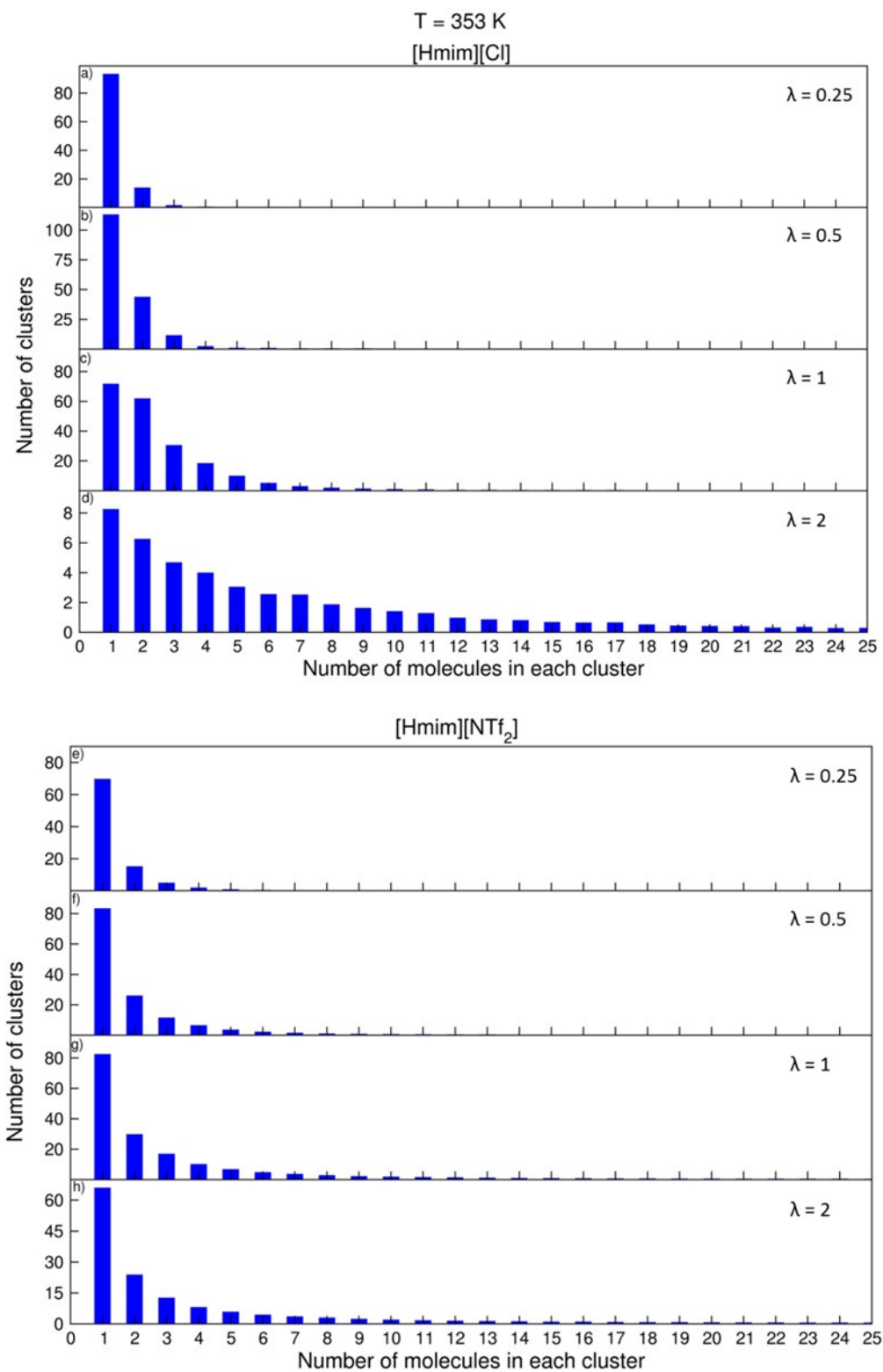


**Figure S2:**  $\log(\text{MSD})$  vs.  $\log(t)$  plot for cations, anions and water molecules in low, intermediate and high water concentration of [Hmim][Cl] (a,b,c) and [Hmim][NTf<sub>2</sub>] IL (d, e, f) at **T = 353 K**

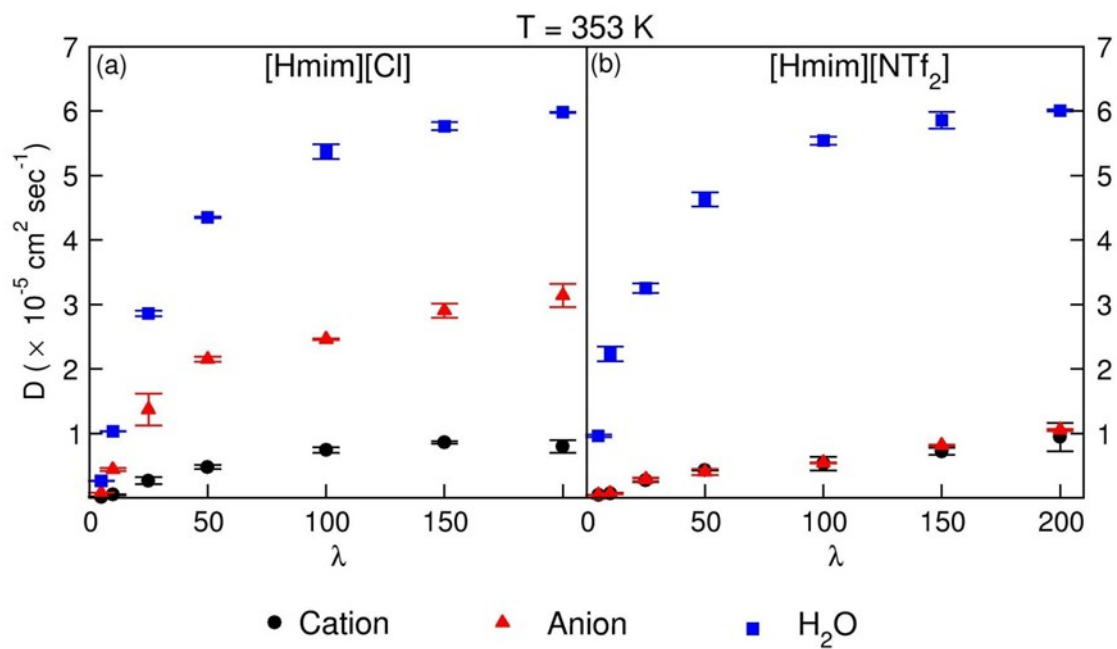
**Table S2:** Fraction of bridging water molecules at ultra-low water concentration of [Hmim][Cl] and [Hmim][NTf<sub>2</sub>] IL

**T = 353 K**

$\lambda$	[Hmim][Cl]	[Hmim][NTf <sub>2</sub> ]
0.25	0.495	0.054
0.5	0.500	0.051
1	0.470	0.047
2	0.200	0.039

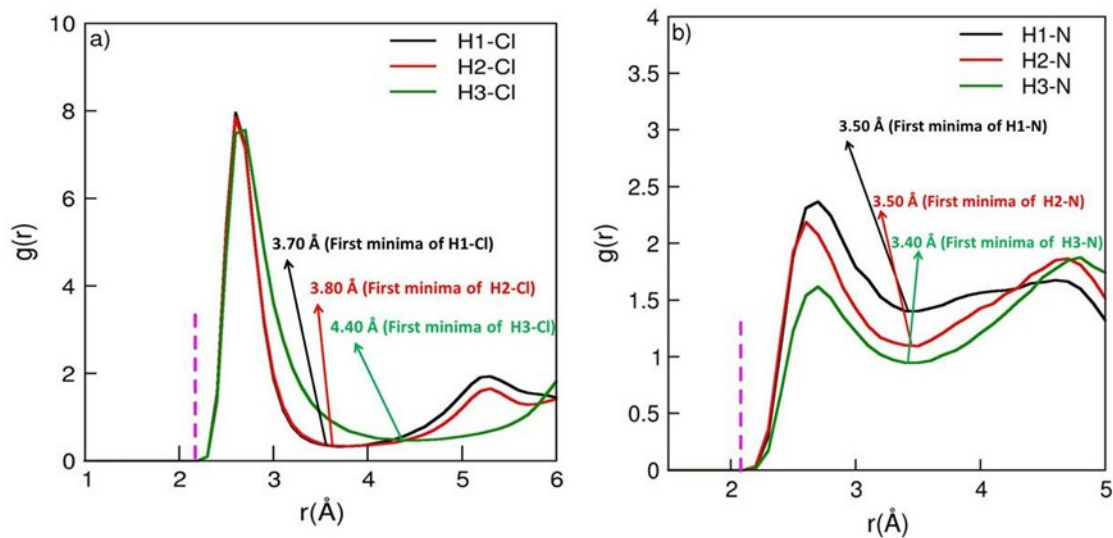


**Figure S3:** Water cluster distribution at ultra-low water concentration in [Hmim][Cl] IL and [Hmim][NTf<sub>2</sub>] IL at T = 353



**Figure S4:** Diffusion coefficients of  $\text{Hmim}^+$  cations, anions and water molecules in hydrated  $[\text{Hmim}][\text{Cl}]$  and  $[\text{Hmim}][\text{NTf}_2]$  ILs at  $T = 353 \text{ K}$

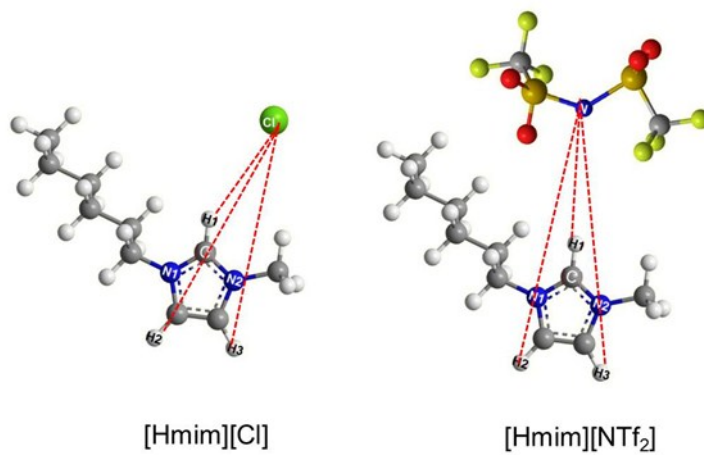


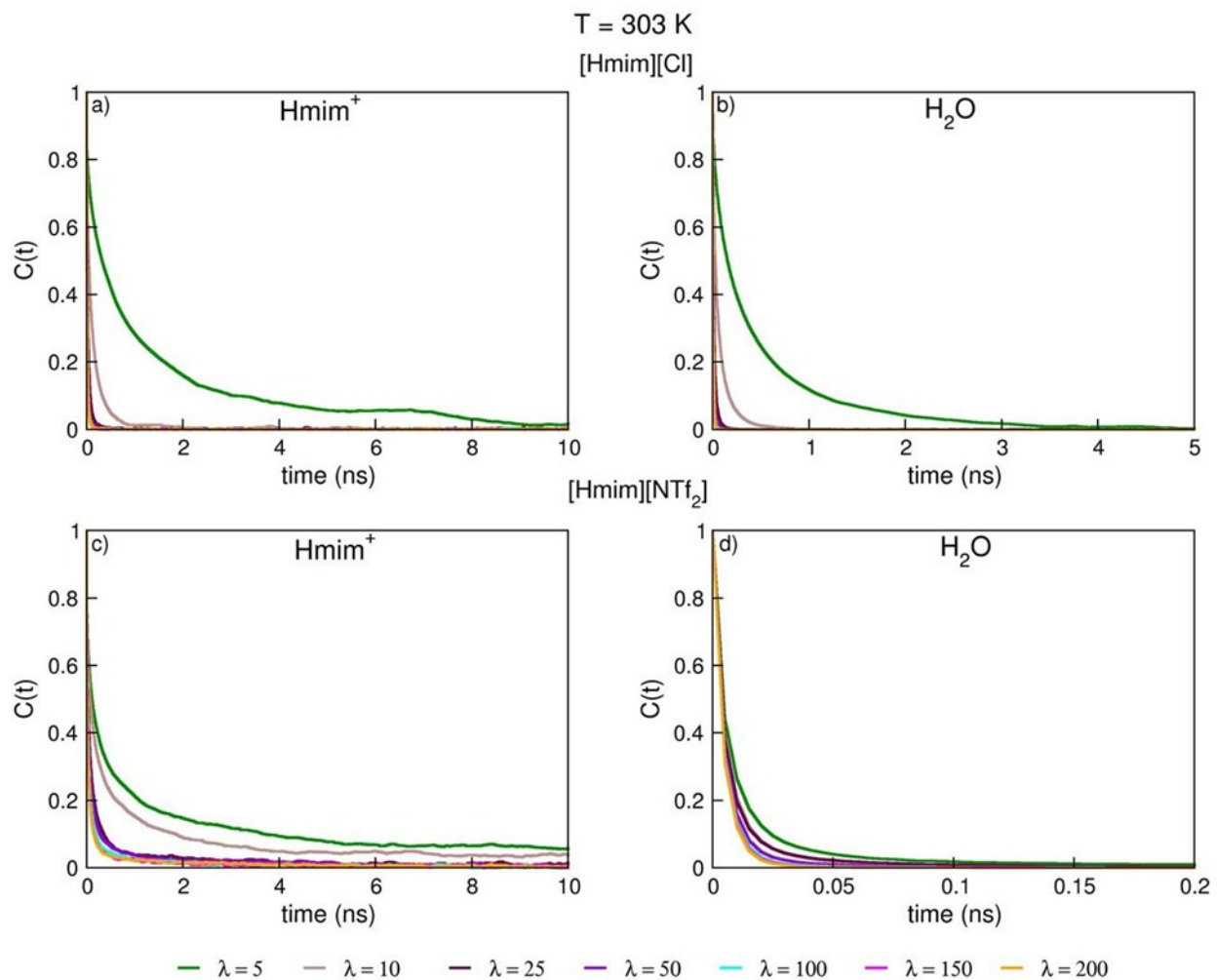


**Figure S5:** RDF (T = 303 K) on site interaction between the hydrogen atoms of Hmim<sup>+</sup> cation and anion (Cl<sup>-</sup> and N of NTf<sub>2</sub><sup>-</sup> anion) in neat IL used for calculation of IP lifetime. Dotted line (Magenta) is the initial distance criterion for calculation of IP lifetime. The final point is chosen as the first minima for the respective interactions.

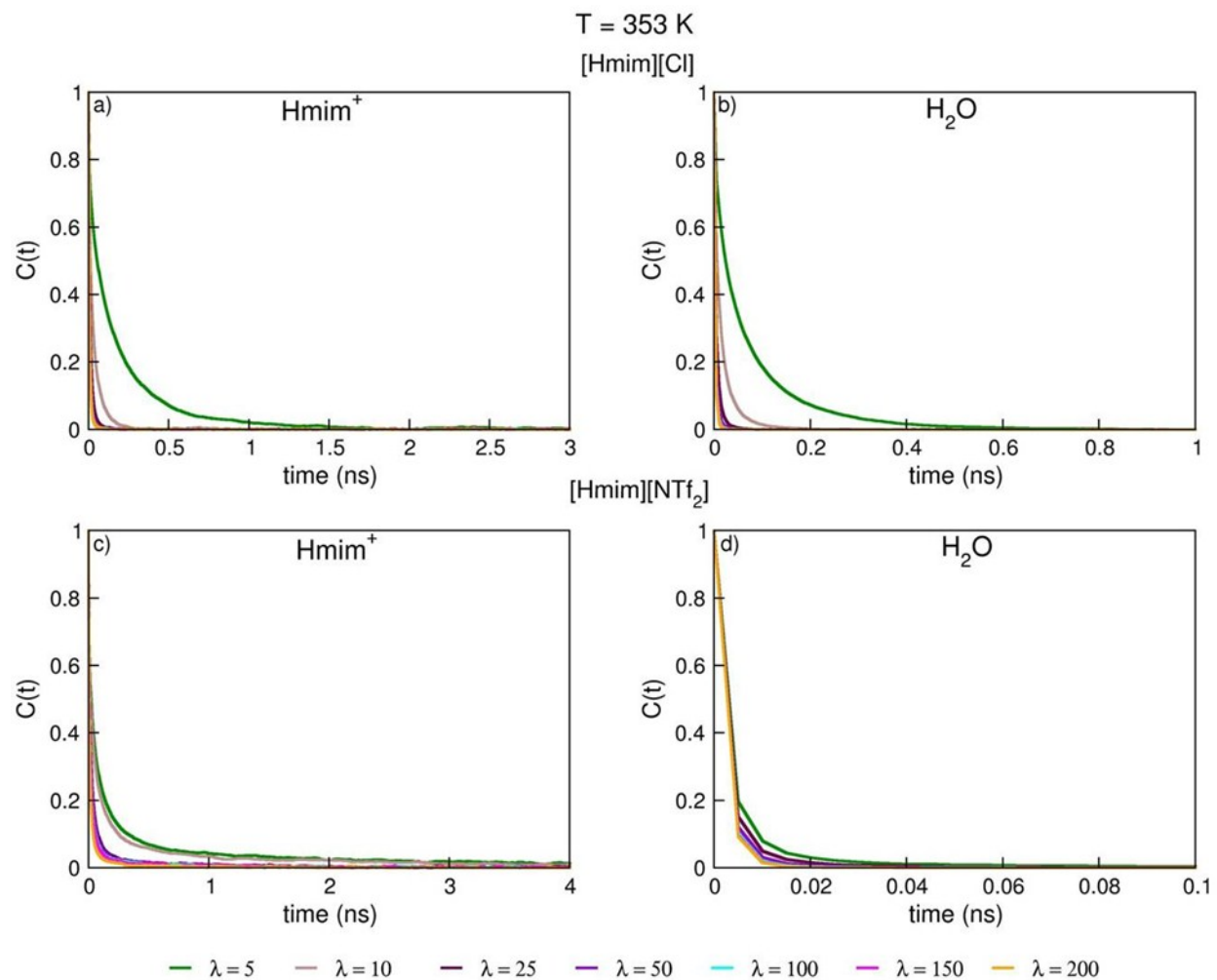
**Table S3:** Ion-Pair Life-time (ps) in hydrated [Hmim][Cl] and [Hmim][NTf<sub>2</sub>] IL**T = 353 K**

$\lambda$		Ion Pair Life-time (ps)					
		[Hmim][Cl]			[Hmim][NTf <sub>2</sub> ]		
		H1..Cl	H2..Cl	H3..Cl	H1..N	H2..N	H3..N
Neat	0	181.1	394.2	639.0	11.6	12.4	10.0
	0.25	171.4	306.5	481.7	11.7	12.5	9.9
	0.5	154.4	254.8	380.7	11.4	12.1	9.5
	1	158.2	206.0	297.5	11.0	11.4	9.1
	2	66.1	55.8	80.5	10.4	10.6	8.5
Low	5	20.1	14.6	19.9	10.1	10.2	9.4
	10	10.4	8.0	9.9	9.8	9.9	9.1
Intermediate	25	7.4	6.3	7.1	8.4	8.4	7.4
	50	6.8	5.9	6.6	8.7	8.2	7.2
	100	6.5	5.8	6.4	8.6	8.1	7.2
	150	6.4	5.7	6.3	8.6	8.2	7.2
	200	6.4	5.8	6.2	8.2	7.6	6.7





**Figure S6:** RACF (simulation) of  $\text{Hmim}^+$  cations and water molecules in low, intermediate and high water concentration of  $[\text{Hmim}][\text{Cl}]$  and  $[\text{Hmim}][\text{NTf}_2]$  IL at  $T = 303 \text{ K}$ .

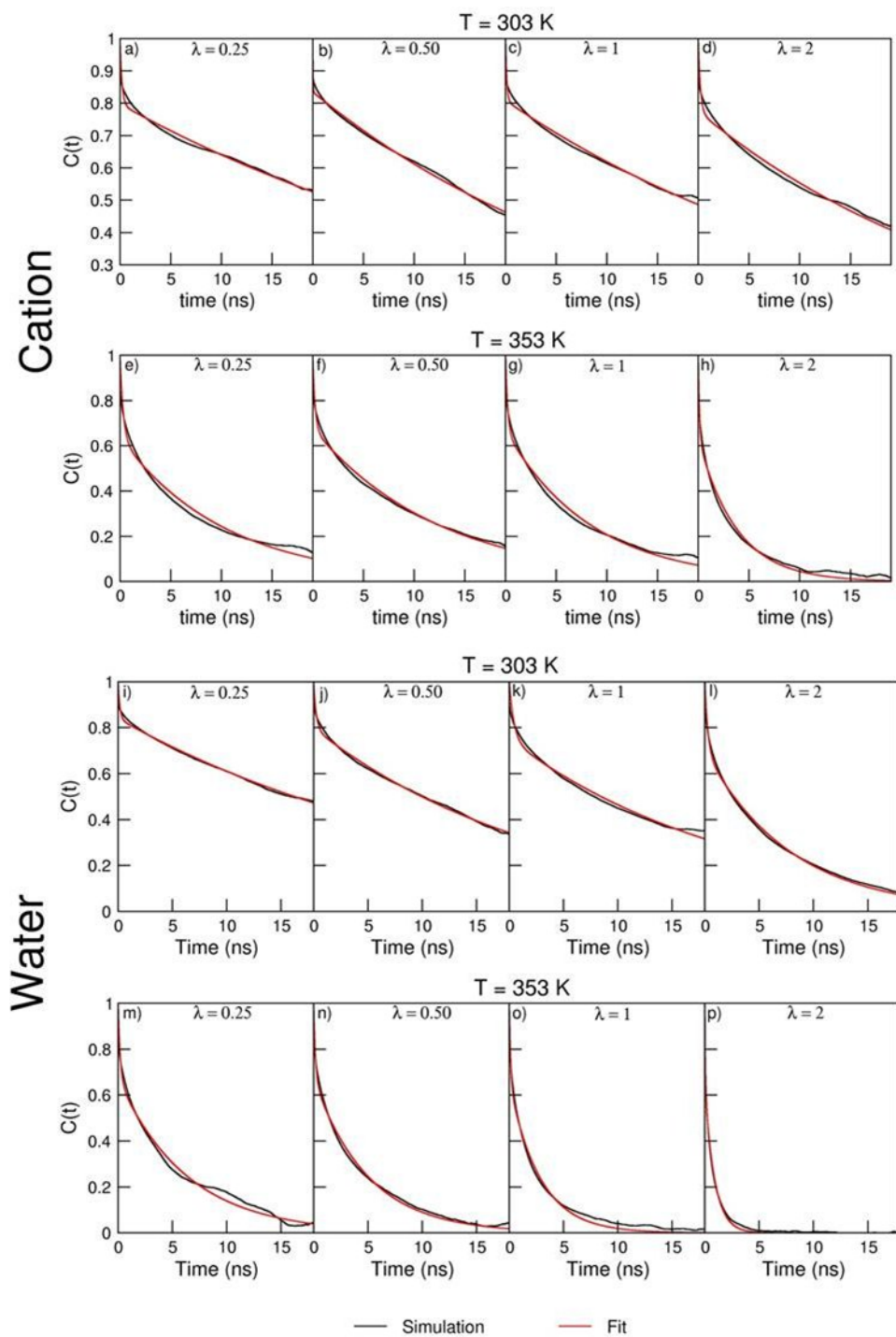


**Figure S7:** RACF (simulation) of Hmim<sup>+</sup> cations and water molecules in low, intermediate and high water concentration of [Hmim][Cl] and [Hmim][NTf<sub>2</sub>] IL at T = 353 K.

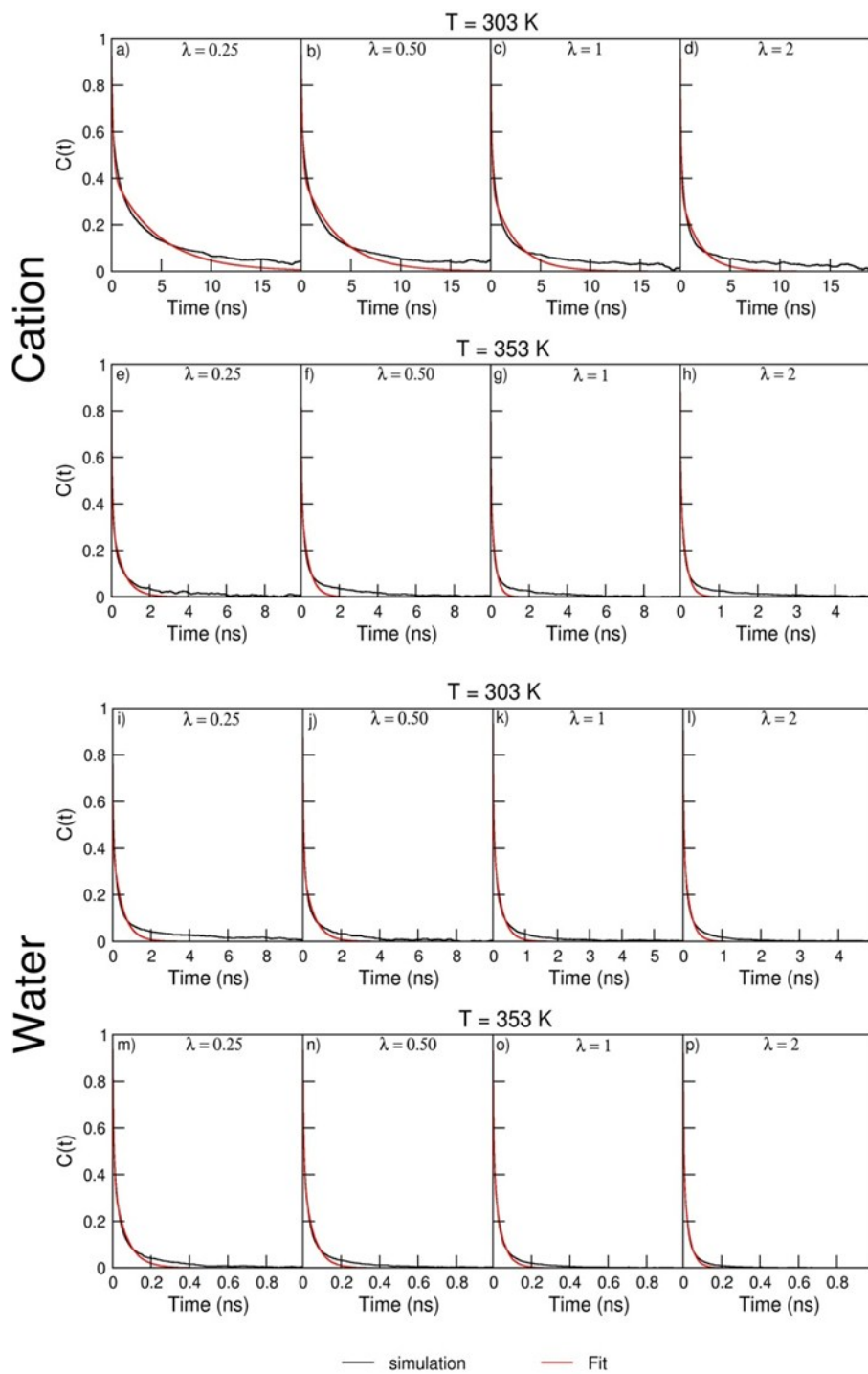
**Table S4:** Rotational Correlation time ( $\tau_{\text{rot}}$ ) in in low, intermediate and high water concentration of [Hmim][Cl] and [Hmim][NTf<sub>2</sub>] IL.

**T = 353 K**

$\lambda$	$\tau_{\text{rot}}$ (ps)			
	[Hmim][Cl]		[Hmim][NTf <sub>2</sub> ]	
	Cation	H <sub>2</sub> O	Cation	H <sub>2</sub> O
5	177.5	67.4	225.8	5.7
10	28.2	14.4	171.3	4.1
25	11.8	5.5	55.9	4.1
50	8.3	4.0	51.5	3.5
100	6.9	3.5	44.7	3.2
150	6.7	3.3	46.6	3.2
200	7.5	3.2	28.3	3.2



**Figure S8:** RACF of Hmim<sup>+</sup> cation and water molecules in ultra-low water concentration of [Hmim][Cl] IL at T = 303 K and T = 353 K.



**Figure S9:** RACF of Hmim<sup>+</sup> cation and water molecules in ultra-low water concentration of [Hmim][NTf<sub>2</sub>] IL at **T = 303 K** and **T = 353 K**.