Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

The Importance of Timescale for Hydrogen Bonding in Imidazolium Chloride Ionic Liquids.

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Additional definitions of time correlation functions (TCFs), used to prepare Figure 8 of the main Paper. Starting from the t=0 state where the HB-criterion has been applied, the individual component x=$R_{H...Cl}$, $R_{C...Cl}$ and ϕH-C-Cl criteria have been applied at t=t to generate *individual* TCFs $C_{HB}^{x}(t)$, which contribute to the (overall) H-bond TCF.

$$C_{HB}^{x}(t) = \frac{\left\langle h_{ij}(0)\cdot h_{ij}^{x}(t)\right\rangle_{t^*}}{\left\langle h_{ij}(0)^2\right\rangle} \qquad C_{HB(n)}^{I}(t) = \frac{\left\langle dh_n(0)\cdot dh_n(t)\right\rangle_{t^*}}{\left\langle dh_n(0)^2\right\rangle} \qquad dh_n(t) = h_n(t) - \left\langle h_n(t)\right\rangle$$

Thus $h_{ij}^{x}(t)=1$ if the distance $R_{H...Cl}$ (or distance $R_{C...Cl}$ or angle ϕH-C-Cl) at time t=0, is less than or equal to the cut-off value employed for the H-bonding criterion (using an angular cut-off of 30º), and the distance or angle has not exceeded the cut-off value for a period longer than t*=0 in which case $h_{ij}^{x}(t)=0$. In addition, the TCFs for the H-bond state dynamics, $C_{HB(n)}(t)$, presented in Figure 10 have been calculated using the definition presented above and in Ref. 68 from the main paper.

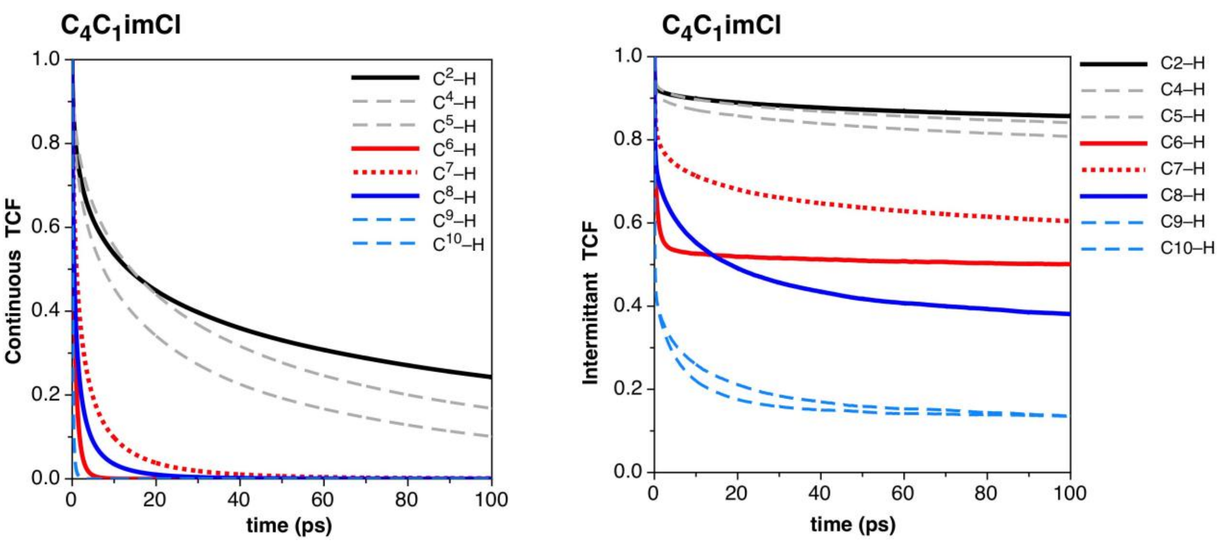

Figure F1 (a) Continuous and (b) intermittent residence TCFs for $[C_4C_1im]Cl$. Black and grey are ring C-H, red are first C-H and blue are alkyl C-H.

H-atom	c1	c2	τ_1	τ_2	τ_3
C^2-H	0.09316	0.04928	0.29326	66.73381	6442.50647
C^4-H	0.11746	0.08034	0.46206	73.05993	4996.36556
C^5-H	0.09593	0.06746	0.65406	80.07079	5378.54283
C^6-H	0.46440	0.03357	0.41237	49.93836	6657.17580
C^7-H	0.25295	0.14094	0.53165	40.87189	3305.20445
C^8-H	0.34507	0.26897	0.35860	24.47911	2636.96111
C^9-H	0.63470	0.22155	0.12099	18.65015	1137.27163
C^{10}-H	0.60798	0.24773	0.11353	9.316560	1399.78351

Table T1 Parameters for the exponential fit ($C(t) = c_1\exp(-t/t_1) + c_2\exp(-t/t_2) + (1 - c_1 - c_2)\exp(-t/t_3)$) to the intermittent residence TCFs for $[C_4C_1im]Cl$.

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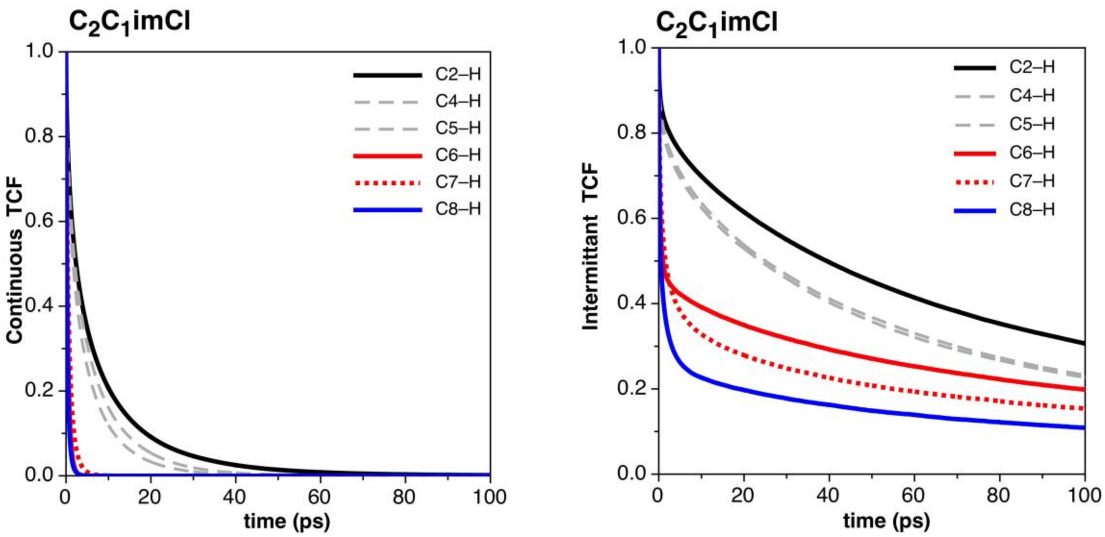

Figure F2 (a) Continuous and (b) intermittent residence TCFs for [C_2C_1im]Cl. Black and grey are ring C-H, red are first C-H and blue are alkyl C-H.

	c_1	c_2	τ_1	τ_2	τ_3
C^2-H	0.21195	0.50136	0.97644	55.11665	383.56014
C^4-H	0.25902	0.48151	0.85079	40.65351	282.71207
C^5-H	0.25211	0.49673	1.06527	42.65733	308.00967
C^6-H	0.55517	0.21305	0.31668	45.26675	340.27127
C^7-H	0.58992	0.21142	0.74235	27.11275	324.3122
C^8-H	0.70591	0.14661	0.45182	25.1938	290.62338

Table T2 Parameters for the exponential fit ($C(t) = c_1 \exp(-t/t_1) + c_2 \exp(-t/t_2) + (1 - c_1 - c_2)\exp(-t/t_3)$) to the intermittent residence TCFs for [C_2C_1im]Cl.

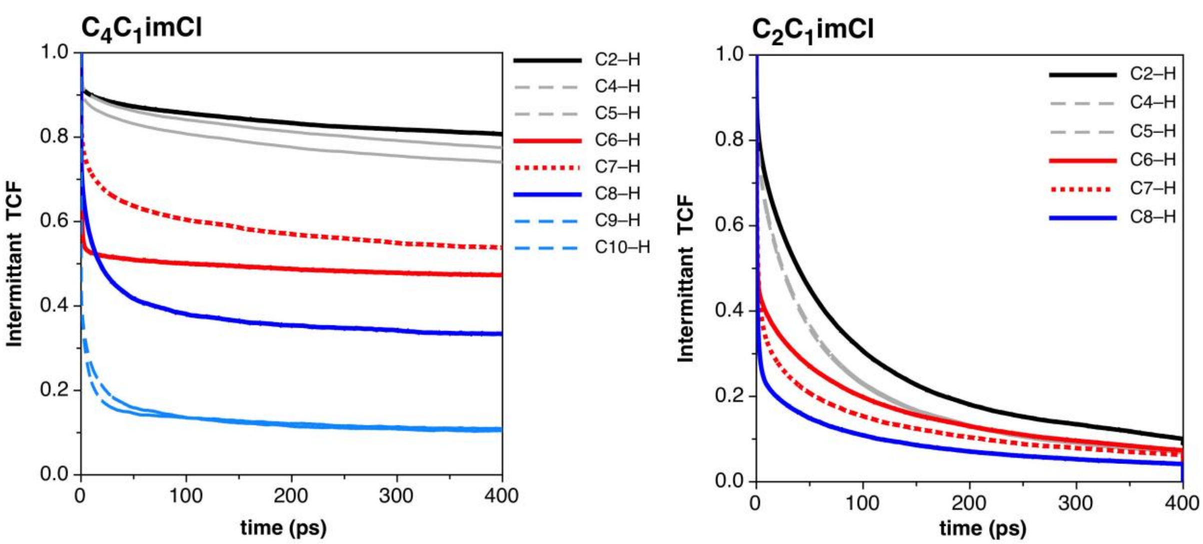

Figure F3 Long time intermittent TCFs for (a) [C_4C_1im]Cl and (b) [C_2C_1im]Cl. Black and grey are ring C-H, red are first C-H and blue are alkyl C-H.

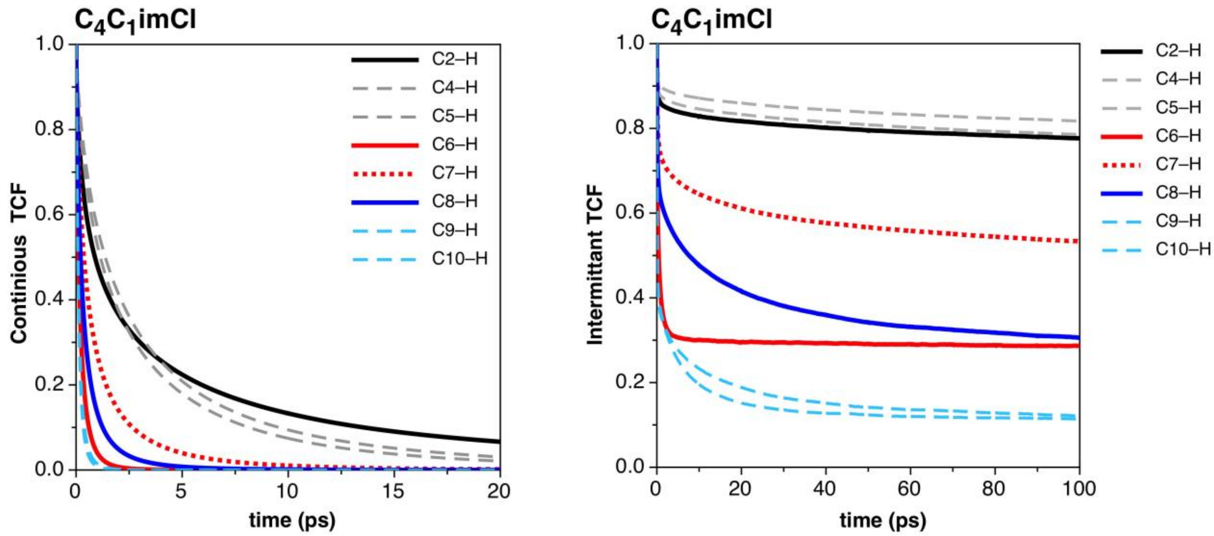

Figure F4 (a) Continuous and (b) intermittent H-bond TCFs for $[C_4C_1im]Cl$. Black and grey are ring C-H, red are first C-H and blue are alkyl C-H.

H-atom	c_1	c_2	τ_1	τ_2	τ_3
C^2-H	0.15883	0.06482	0.20234	58.08314	6027.78672
C^4-H	0.14014	0.07027	0.2418	57.39527	4285.21455
C^5-H	0.11574	0.0567	0.26773	51.09677	4128.78632
C^6-H	0.40824	0.29764	0.08451	1.04379	4458.81171
C^7-H	0.30839	0.14579	0.32754	32.12979	2307.91593
C^8-H	0.40802	0.27149	0.2246	21.5083	1553.47059
C^9-H	0.64496	0.20045	0.09338	12.00476	441.01373
C^{10}-H	0.60791	0.25017	0.09636	6.76139	407.40945

Table T3 Parameters for the exponential fit ($C(t) = c_1 \exp(-t/t_1) + c_2 \exp(-t/t_2) + (1 - c_1 - c_2)\exp(-t/t_3)$) to the intermittent H-bond TCFs for $[C_4C_1im]Cl$, 60º angular cut-off.

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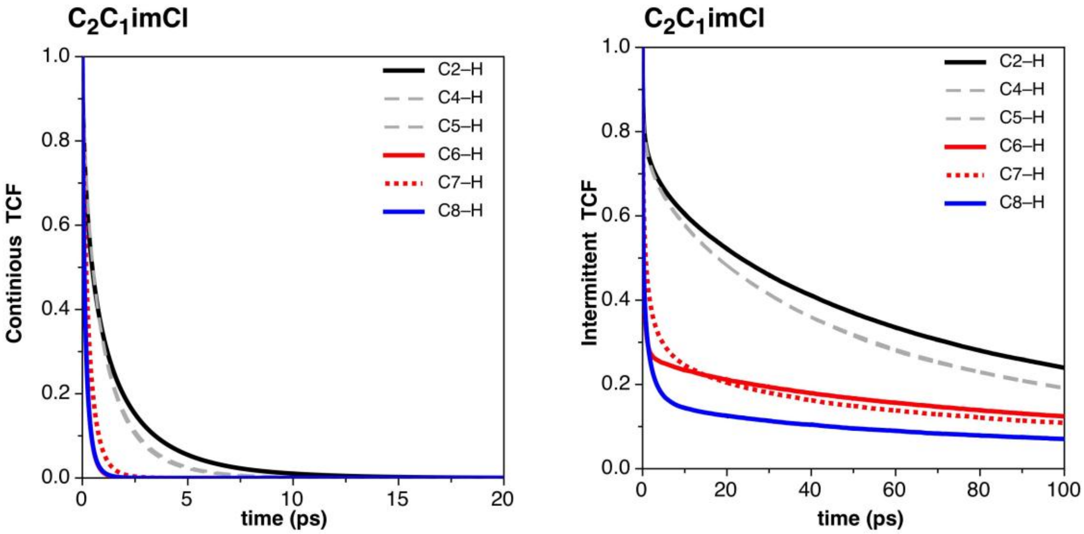

Figure F5 (a) Continuous and (b) intermittent H-bond TCFs for [C_2C_1im]Cl. Black and grey are ring C-H, red are first C-H and blue are alkyl C-H.

	c_1	c_2	τ_1	τ_2	τ_3
C^2-H	0.30078	0.46824	0.59403	49.59836	343.06931
C^4-H	0.3013	0.47434	0.57277	38.56703	254.82172
C^5-H	0.30184	0.48243	0.6381	39.80561	277.06233
C^6-H	0.73358	0.11844	0.22746	44.55992	341.65263
C^7-H	0.6579	0.19201	0.5169	19.85986	296.69665
C^8-H	0.6657	0.21582	0.18041	4.5518	226.95897

Table T4 Parameters for the exponential fit ($C(t) = c_1 \exp(-t/t_1) + c_2 \exp(-t/t_2) + (1 - c_1 - c_2)\exp(-t/t_3)$) to the intermittent H-bond TCFs for [C_2C_1im]Cl, 60º angular cut-off.

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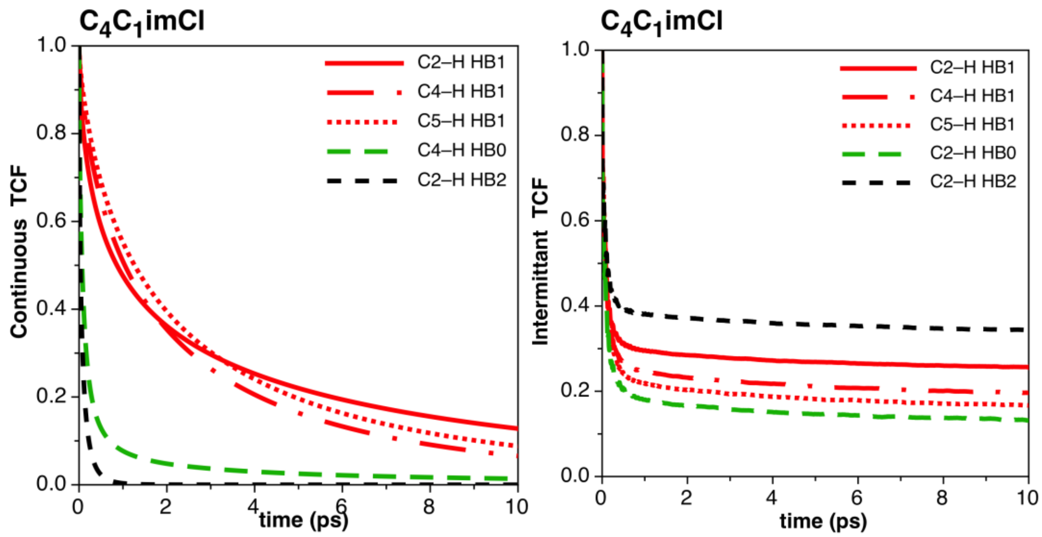

Figure F6 (a) Continuous and (b) intermittent H-bond state TCFs for [C_4C_1im]Cl.

		c_1	c_2	τ_1	τ_2	τ_3
C^2-H	$n_{HB} = 0$	0.80194	0.07362	0.06549	5.17907	212.77892
	$n_{HB} = 1$	0.69191	0.06022	0.05611	5.97582	519.94817
	$n_{HB} = 2$	0.60909	0.05648	0.0553	6.79116	672.94646
C^4-H	$n_{HB} = 0$	0.74887	0.07528	0.09359	7.10524	215.61573
	$n_{HB} = 1$	0.74481	0.06746	0.08043	6.65705	250.89793
	$n_{HB} = 2$	0.69725	0.05945	0.06162	7.57775	375.1323
C^5-H	$n_{HB} = 0$	0.76939	0.07621	0.09855	5.25609	241.34802
	$n_{HB} = 1$	0.774	0.0711	0.08994	6.91465	294.03505
	$n_{HB} = 2$	0.73368	0.07587	0.06583	12.61041	641.65965

Table T5 Parameters for the exponential fit ($C(t) = c_1 \exp(-t/t_1) + c_2 \exp(-t/t_2) + (1 - c_1 - c_2)\exp(-t/t_3)$) to the intermittent H-bond state TCFs for [C_4C_1im]Cl.

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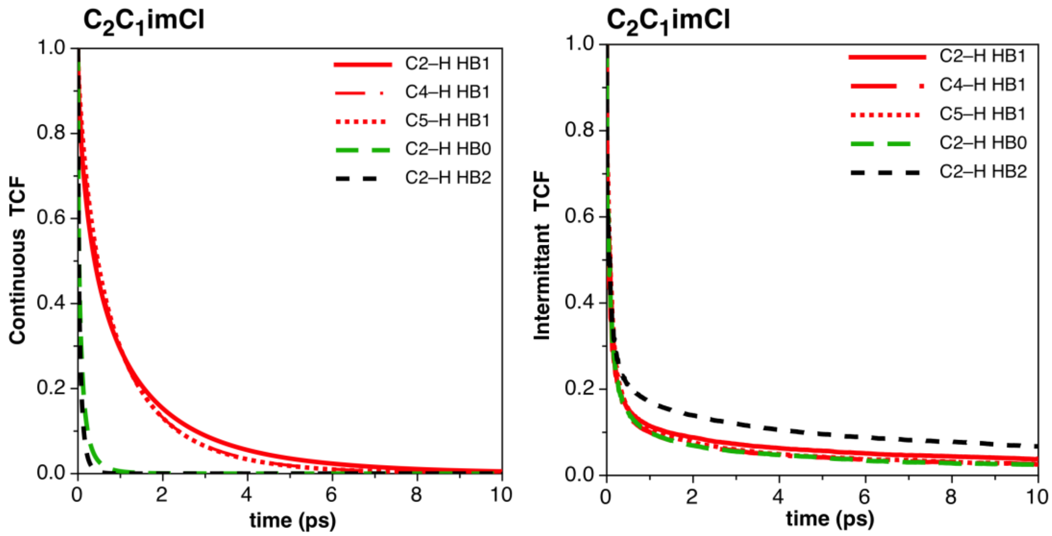

Figure F7 (a) Continuous and (b) intermittent H-bond state TCFs for [C_2C_1im]Cl.

The values presented in below correspond to numerical integrals, however since the TCF have already decayed to zero, the use of these fitting functions was not necessary. However, in order to be complete these are provided.

		c_1	c_2	τ_1	τ_2	τ_3
C^2-H	n_{HB} = 0	0.70974	0.22877	0.0482	0.60832	12.39304
	n_{HB} = 1	0.76407	0.17152	0.04705	1.01871	20.77262
	n_{HB} = 2	0.74661	0.15297	0.05391	1.78484	23.81166
C^4-H	n_{HB} = 0	0.76065	0.17145	0.08504	0.86946	11.40991
	n_{HB} = 1	0.75615	0.18141	0.06754	0.72108	12.27741
	n_{HB} = 2	0.75665	0.16019	0.04555	0.82393	18.52332
C^5-H	n_{HB} = 0	0.76861	0.16641	0.09406	1.10844	12.55995
	n_{HB} = 1	0.77115	0.16707	0.07909	0.94601	12.47833
	n_{HB} = 2	0.76395	0.15766	0.04636	0.86728	16.86652

Table T6 Parameters for the exponential fit ($C(t) = c_1 \exp(-t/t_1) + c_2 \exp(-t/t_2) + (1 - c_1 - c_2)\exp(-t/t_3)$) to the intermittent H-bond state TCFs for [C_4C_1im]Cl.

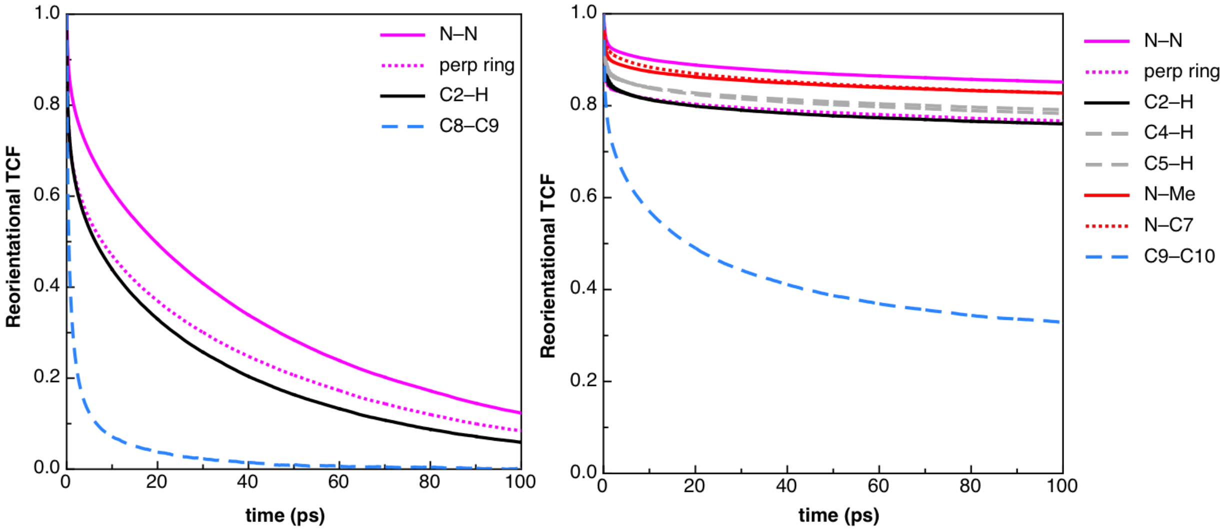

Figure F8 (a) Reorientational dynamics represented by the Legendre polynomial of rank 2 (l=2) for $[C_2C_1im]Cl$ and $[C_4C_1im]Cl$. The specific unit vectors are described in the text below.

Normalised reorientational TCFs for the cationic species have been obtained:

$$C(t) = \frac{\left\langle P_l\left[u_i(t)\cdot u_i(0)\right]\right\rangle}{\left\langle P_l\left[u_i(0)\cdot u_i(0)\right]\right\rangle}$$

where P_l denote the Legendre polynomial of rank l, and u_i are unit vectors, aligned along the C^2-H bond (C^2-H), or aligned along the vector connecting N^1 and N^3 (N-N), or aligned along the cross-product of the N-N and C^2-H vectors, which is a vector perpendicular to the ring (perp ring), or along the terminal bond of the alkyl chain (C^8-C^9) in $C_2C_1im^+$ or C^9-C^{10} in $C_4C_1im^+$, denoted C-C. The exponential fit has been taken to 500ps. Fitting was initiated from c_1=0.33 c_2=0.33, t_1=0.1 t_2=10, t_3=1000 or 10000. Where a poor χ^2 was obtained the fit was restarted using similar values to those obtained for like fits. The "Robust" algorithm from Pro-fit package† was used, integration was undertaken using the "Analyse" feature.

unit vector	c_1	c_2	τ_1	τ_2	τ_3	χ^2
C^2-H	0.33	0.23	0.39	9.43	50.26	0.81
perp ring	0.32	0.20	0.34	9.72	59.60	0.78
N-N	0.23	0.34	1.01	27.77	75.68	0.61
C-C	0.52	0.36	0.29	2.09	19.19	0.08

Table T7 Parameters for the exponential fit ($C(t) = c_1\exp(-t/t_1) + c_2\exp(-t/t_2) + (1-c_1-c_2)\exp(-t/t_3)$) to the reorientational Legendre polynomial of rank 2 (l=2) for $[C_2C_1im]Cl$.

unit vector	c_1	c_2	τ_1	τ_2	τ_3	χ^2
C^2-H	0.17	0.07	0.41	50.77	13761	0.17
perp ring	0.17	0.07	0.32	57.34	15854	0.10
N-N	0.09	0.06	0.81	52.45	13223	0.06
N-C7	0.10	0.07	1.04	50.10	10327	0.10
C-C	0.33	0.35	1.04	31.92	2458	1.37

Table T8 Parameters for the exponential fit ($C(t) = c_1\exp(-t/t_1) + c_2\exp(-t/t_2) + (1-c_1-c_2)\exp(-t/t_3)$) to the reorientational Legendre polynomial of rank 2 (l=2) for $[C_4C_1im]Cl$.

† pro Fit 6.2.11 by QuantumSoft, Bühlstr. 18, CH-8707 Uetikon am See, Switzerland

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To enable a more direct comparison the time correlation functions have been evaluated on an equivalent basis below. The numerical integration time is reduced slightly due to the Legendre polynomial becoming negative before 400ps for the C^2-H reorientation.

unit vector	c_1	c_2	τ_1	τ_2	τ_3	χ^2	numerical to 365ps	τ □□□□
l=1 C^2-H	0.14	0.16	0.65	17.57	74.82	3.72	54.88	56
l=2 C^2-H	0.33	0.23	0.39	9.43	50.26	0.81	24.40	24
$[C_4C_1im]Cl$ *l*=1 C^2-H	0.06	0.03	0.49	58.83	14473	0.03	330	12842
l=1 perp ring	0.12	0.10	0.40	9.90	73.76	0.79	58.16	58
l=2 perp ring	0.32	0.20	0.34	9.72	59.60	0.78	30.54	31
$[C_4C_1im]Cl$ *l*=1 perp ring	0.06	0.03	0.36	57.73	14835	0.002	318	13502
l=1 N^1-N^2	0.08	0.12	1.08	38.97	145.77	0.34	111.95	122
l=2 N^1-N^2	0.23	0.34	1.01	27.77	75.68	0.61	42.42	42
$[C_4C_1im]Cl$ *l*=1 N^1-N^2	0.03	0.03	0.89	56.00	33590	0.001	343	31576
C^2-H Continuous	0.26	0.40	0.38	3.77	15.37	0.05	6.89	7
C^2-H Intermittent	0.21	0.50	0.98	55.12	383.56	0.55	95.29	139
l=1 C-C	0.56	0.18	1.13	17.02	145.25	0.66	39.54	42
l=2 C-C	0.52	0.36	0.29	2.09	19.19	0.08	3.11	3

Table T9 Parameters for the exponential fit ($C(t) = c_1 \exp(-t/t_1) + c_2 \exp(-t/t_2) + (1 - c_1 - c_2)\exp(-t/t_3)$) to the reorientational Legendre polynomial of rank 1 (*l*=1) for $[C_2C_1im]Cl$ (unless otherwise noted) and integration parameters to produce the time constant τ.

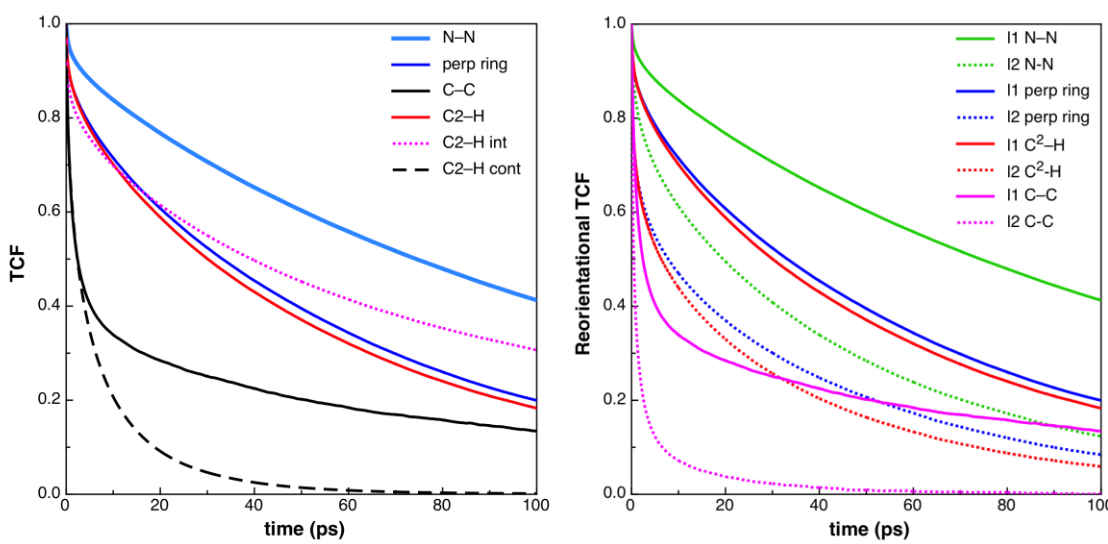

Figure F9 (a) Reorientational dynamics represented by the Legendre polynomial of rank 1 (*l*=1) for $[C_2C_1im]Cl$ compared with the intermittent and continuous residence TCF decay of the C^2-H H-bond, (b) Comparison of the rank 1 (*l*=1) and rank 2 (*l*=2) reorientational Legendre time CFs