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Bond Stretching Potential Parameters

Bond	used for	K_r/ kcal mol^{-1} Å^{-2}	R_{eq}/ Å
CT-CT	*BMI*$^+$,*EMI*$^+$	310.0	1.526
CT-H1	*BMI*$^+$,*EMI*$^+$	340.0	1.090
CT-HC	*BMI*$^+$,*EMI*$^+$	340.0	1.090
CT-NA	*BMI*$^+$,*EMI*$^+$	337.0	1.475
CR-H5	*BMI*$^+$,*EMI*$^+$	367.0	1.080
CR-NA	*BMI*$^+$,*EMI*$^+$	477.0	1.343
CW-H4	*BMI*$^+$,*EMI*$^+$	367.0	1.080
CW-NA	*BMI*$^+$,*EMI*$^+$	427.0	1.381
CW-CW	*BMI*$^+$,*EMI*$^+$	549.0	1.350
AL-Cl	*TCA*$^-$	116.1	2.170
P-F	*PF*$_6^-$	260.3	1.646
NN-ON	*NO*$_3^-$	300.0	1.260

Bond Angle Potential Parameters

Angle	used for	K_θ / kcal mol^{-1} rad^{-2}	θ_{eq} / degree
H1-CT-H1	*BMI*$^+$,*EMI*$^+$	35.0	109.5
H1-CT-NA	*BMI*$^+$,*EMI*$^+$	50.0	109.5
CR-NA-CT	*BMI*$^+$,*EMI*$^+$	70.0	128.2
CW-NA-CT	*BMI*$^+$,*EMI*$^+$	70.0	121.2
CW-CW-H4	*BMI*$^+$,*EMI*$^+$	35.0	119.7
CT-CT-CT	*BMI*$^+$,*EMI*$^+$	40.0	109.5
CT-CT-H1	*BMI*$^+$,*EMI*$^+$	50.0	109.5
CT-CT-HC	*BMI*$^+$,*EMI*$^+$	50.0	109.5
HC-CT-HC	*BMI*$^+$,*EMI*$^+$	35.0	109.5
CT-CT-NA	*BMI*$^+$,*EMI*$^+$	50.0	109.5
NA-CR-NA	*BMI*$^+$,*EMI*$^+$	70.0	120.0
NA-CR-H5	*BMI*$^+$,*EMI*$^+$	35.0	120.0
CR-NA-CW	*BMI*$^+$,*EMI*$^+$	70.0	120.0
NA-CW-H4	*BMI*$^+$,*EMI*$^+$	35.0	120.0
CL-AL-CL	*TCA*$^-$	50.0	109.5
F$^-$P-F	*PF*$_6^-$	194.1	90 / 180
ON-NN-ON	*NO*$_3^-$	150.0	120.0

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Dihedral Torsion Potential Parameters				
Torsion	**Used for**	**V_n / kcal mol^{-1}**	**γ / degree**	**n**
		Proper Torsions		
NA-CR-NA-CT	*BMI*$^+$,*EMI*$^+$	6.80	180.0	2
H5-CR-NA-CT	*BMI*$^+$,*EMI*$^+$	6.80	180.0	2
H5-CR-NA-CW	*BMI*$^+$,*EMI*$^+$	9.30	180.0	2
NA-CR-NA-CW	*BMI*$^+$,*EMI*$^+$	9.30	180.0	2
X-CT-CT-X	*BMI*$^+$,*EMI*$^+$	1.40	0.0	3
X-CT-NA-X	*BMI*$^+$,*EMI*$^+$	0.00	0.0	2
X-CW-CW-X	*BMI*$^+$,*EMI*$^+$	26.60	180.0	2
CW-CW-NA-CR	*BMI*$^+$,*EMI*$^+$	7.40	180.0	2
CW-CW-NA-CT	*BMI*$^+$,*EMI*$^+$	7.40	180.0	2
H4-CW-NA-CR	*BMI*$^+$,*EMI*$^+$	6.00	180.0	2
H4-CW-NA-CT	*BMI*$^+$,*EMI*$^+$	7.40	180.0	2
		Improper Torsions		
X-X-CR-H5	*BMI*$^+$,*EMI*$^+$	1.10	180.0	2
X-X-CW-H4	*BMI*$^+$,*EMI*$^+$	1.10	180.0	2
X-X-CT-NA	*BMI*$^+$,*EMI*$^+$	1.00	180.0	2
ON-NN-ON-ON	*NO3-*	50.0	180.0	2

Nonbonded Van Der Waals Potential Parameters			
Atom type	**used for**	**R_{ij} / Å**	**ε_{ij} / kcal mol^{-1}**
HC	*BMI*$^+$,*EMI*$^+$	1.4870	0.0157
H1	*BMI*$^+$,*EMI*$^+$	1.3870	0.0157
H4	*BMI*$^+$,*EMI*$^+$	1.4090	0.0150
H5	*BMI*$^+$,*EMI*$^+$	1.3590	0.0150
CT	*BMI*$^+$,*EMI*$^+$	1.9080	0.1094
CR	*BMI*$^+$,*EMI*$^+$	1.9080	0.0860
CW	*BMI*$^+$,*EMI*$^+$	1.9080	0.0860
NA	*BMI*$^+$,*EMI*$^+$	1.8240	0.1700
Cl	*TCA*$^-$	1.9430	0.2650
Al	*TCA*$^-$	2.1900	0.3100
F	*PF_6^-*	2.0940	0.2000
P	*PF_6^-*	1.7460	0.0610
NN	*NO_3^-*	1.7680	0.1700
ON	*NO_3^-*	1.6050	0.2100

Table S1: AMBER parameters used to simulate the BMI+, EMI+, PF_6^- , TCA- and NO_3^- species. The corresponding atom types and charges are given in Figure 3.

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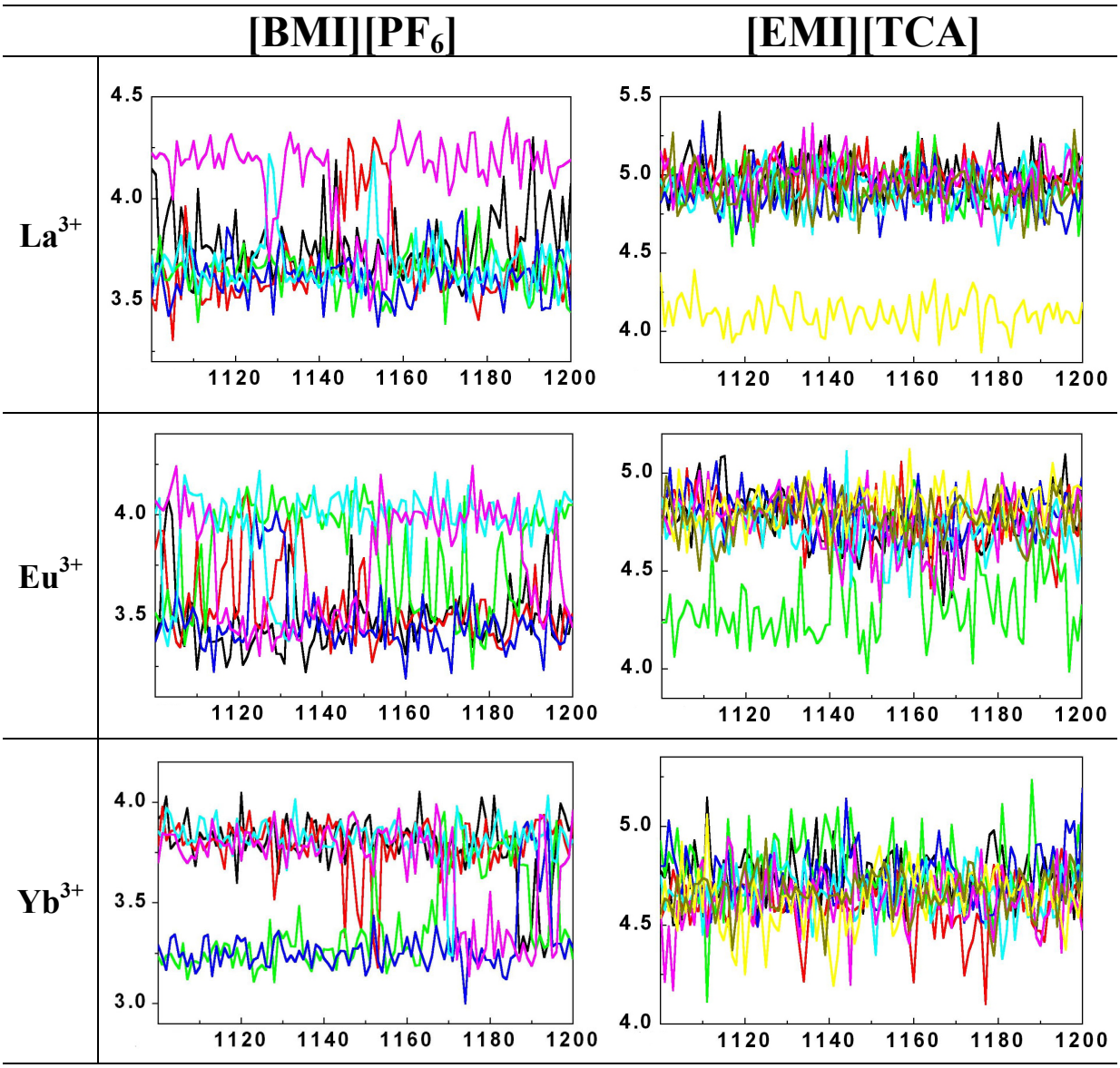

Figure S1: M^{3+} ions in [BMI][PF_6](left) and [EMI][TCA] (right) solutions. Distance between M and first shell P(PF_6) and Al($AlCl_4$) atoms during the last 0.1 ns.

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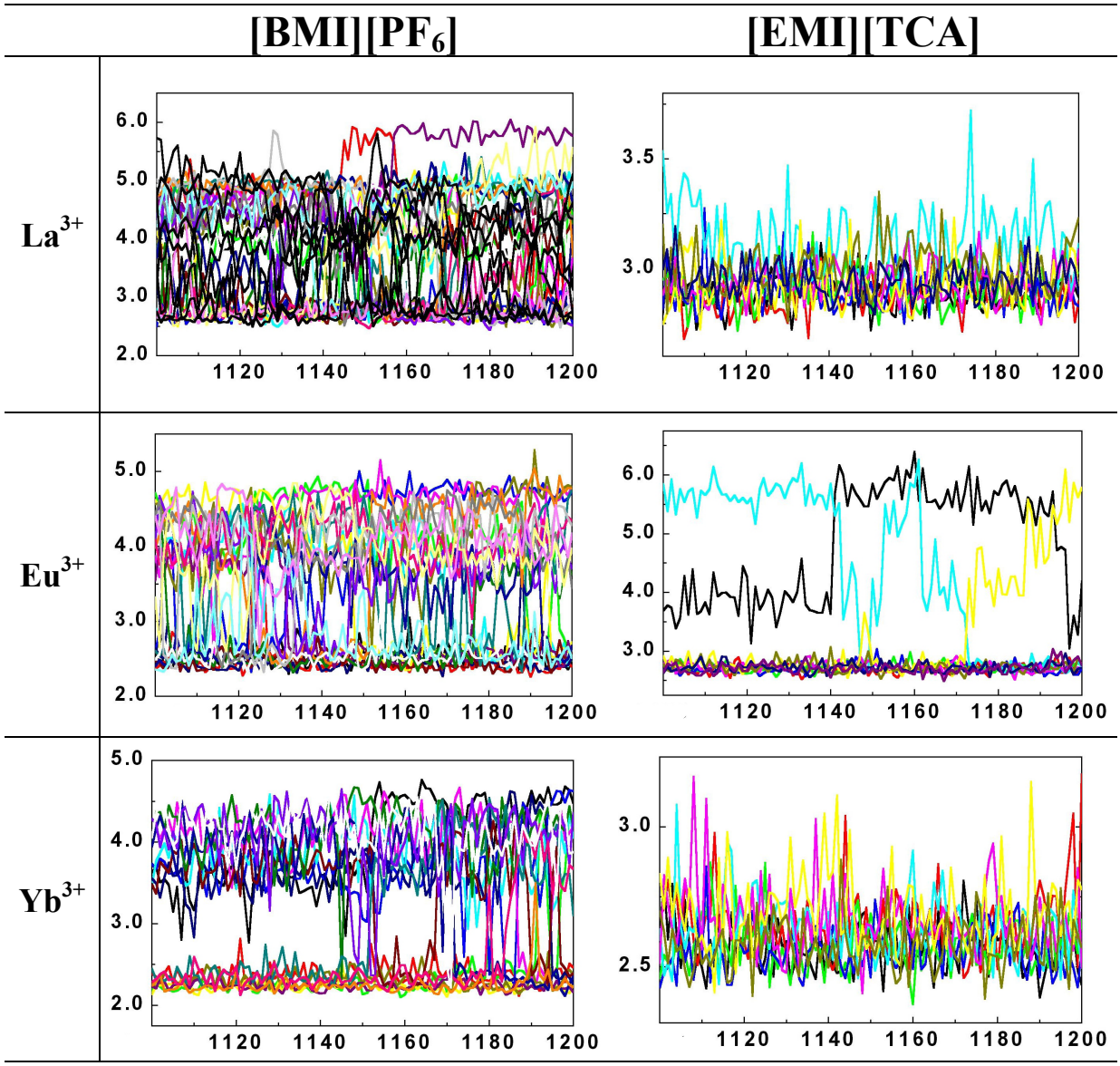

Figure S2: M^{3+} ions in solution: distance between M and first shell $F(PF_6)$ and $Cl(AlCl_4)$ atoms during the last 0.1 ns. The selected F or Cl atoms are those which contribute to the first peak of the RDF (last 0.1 ns).

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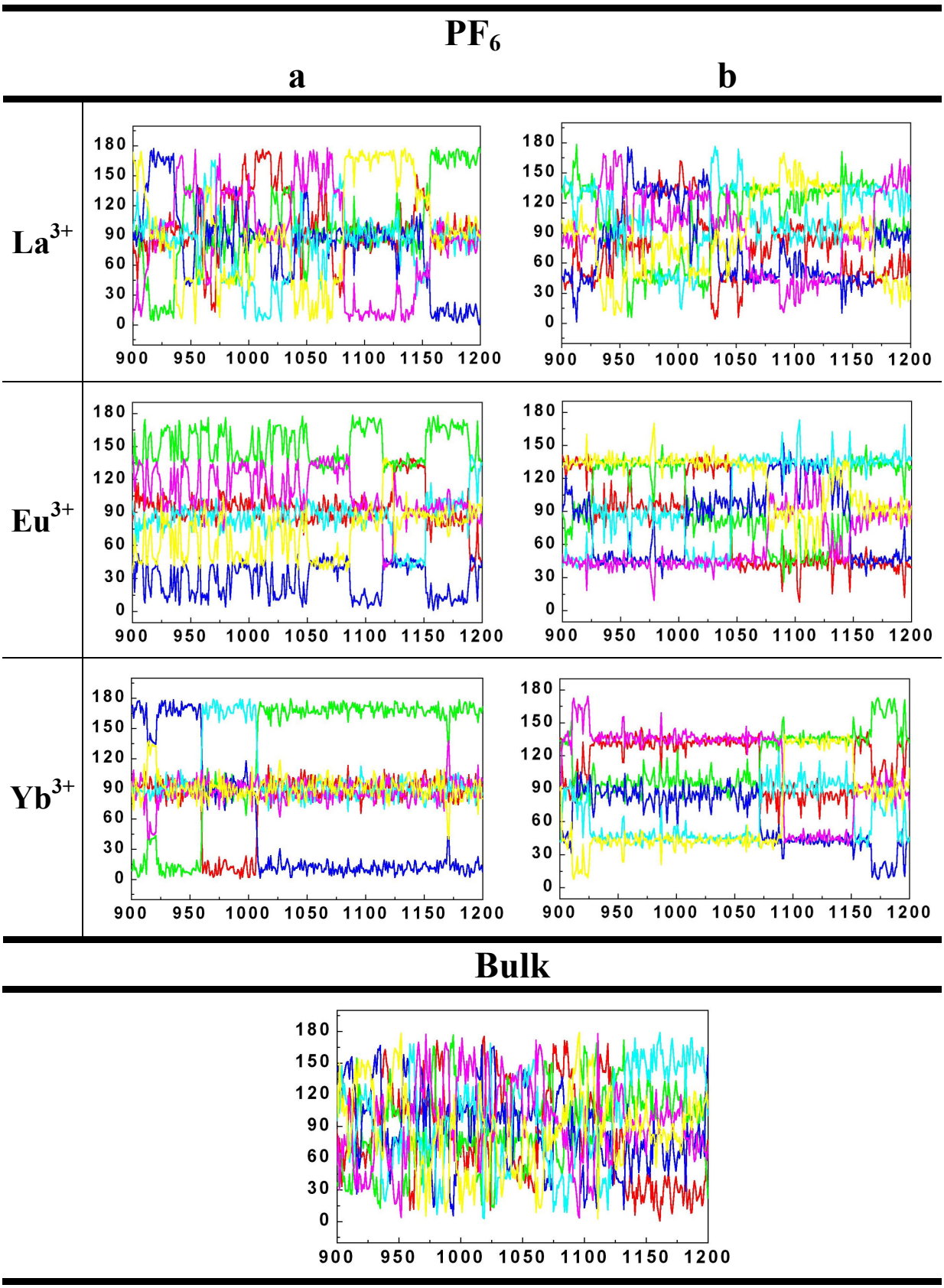

Figure S3: M^{3+} ions in [BMI][PF_6] solution. Angle M-P-F for a "remote" (a) and a "close" anion (b) as a function of time (see definition in Figure 6). "Bulk" corresponds to a PF_6^- anion at 18 Å from M^{3+}.

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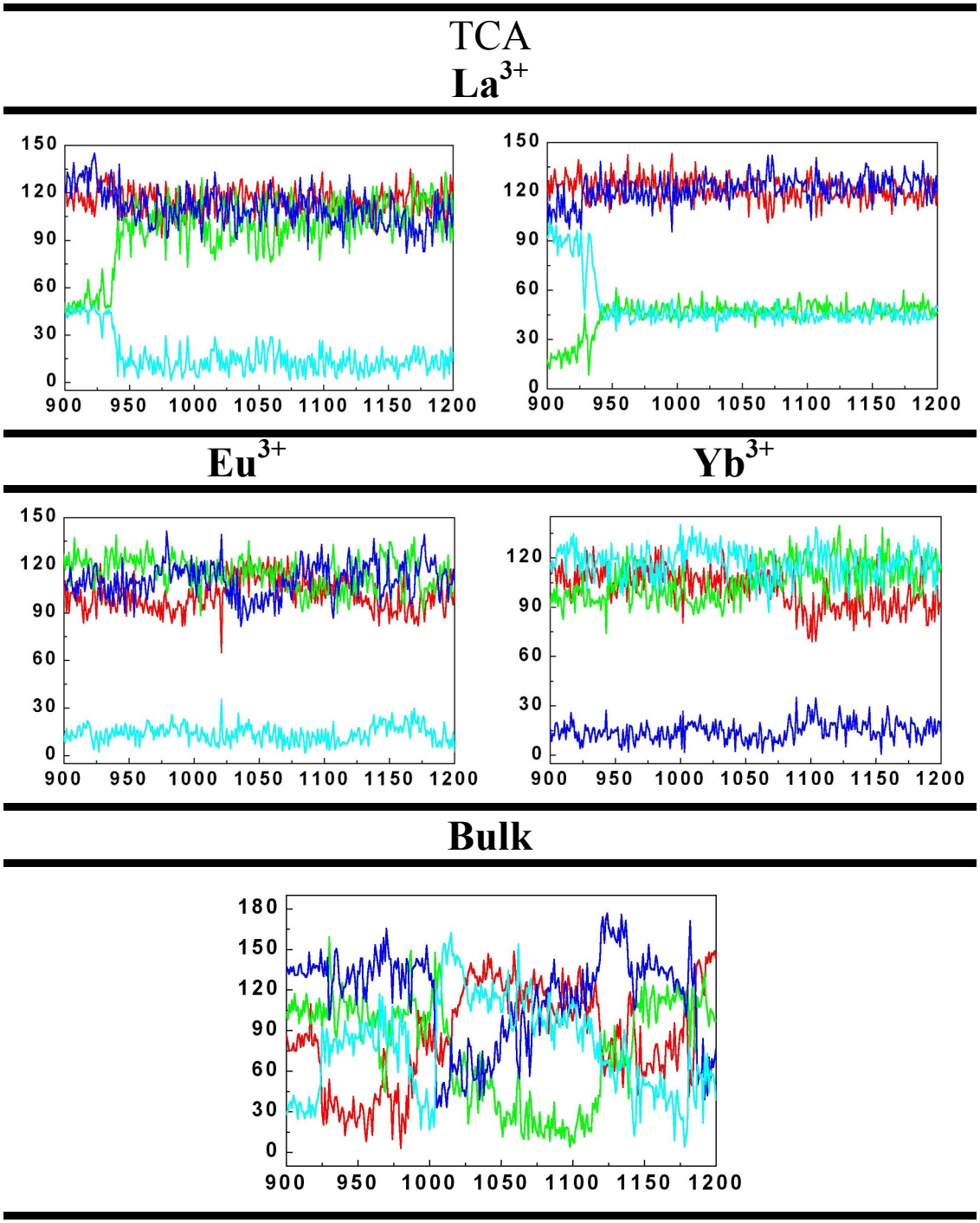

Figure S4: M^{3+} ions in [EMI][TCA] solution. Angle M-Al-Cl of a given anion as a function of time. "Bulk" corresponds to a TCA^- anion at 18 Å from M^{3+}.