Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for

Water modulates the ultraslow dynamics of hydrated ionic liquids near CG rich DNA: consequence to DNA stability

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Cations considered in the study

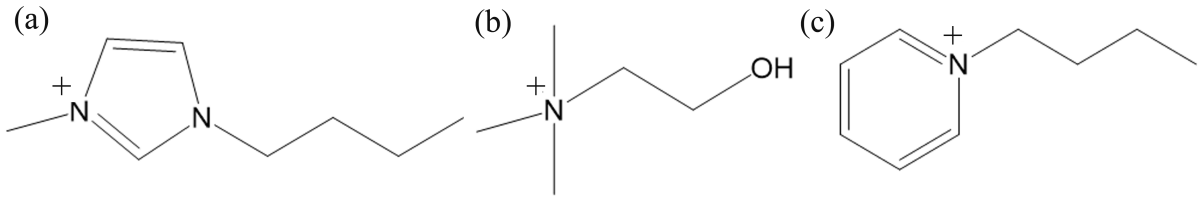

Figure S1. (a) 1-butyl-3-methylimidazolium cation ($[BMIM]^+$), (b) choline cation and (c) 1-butylpyridinum cation ($[BPYR]^+$).

Scheme for stable state picture approach

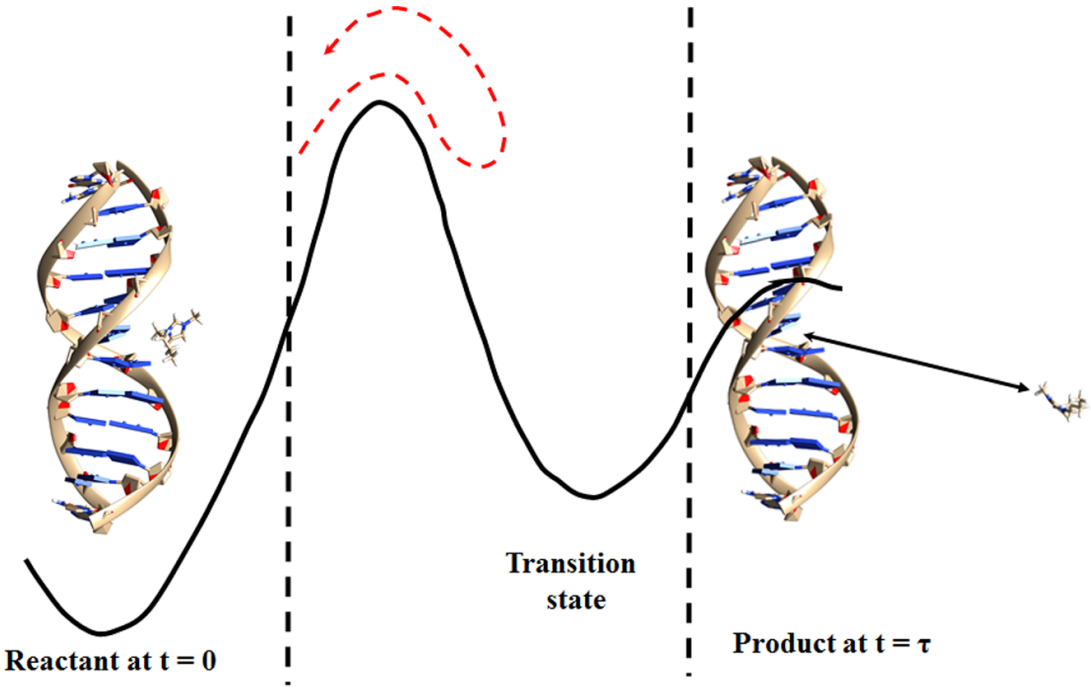

Figure S2. Schematic of the SSP approach involved in the calculation of MRTs. Vertical dashed lines are the stable state boundaries; the left of the left line is considered to be reactant state when a solvent molecule is close to a particular site. The right of the right side line indicates the product state when the solvent is away from the DNA.

RDF and PMF plots for minor groove and phosphate atoms

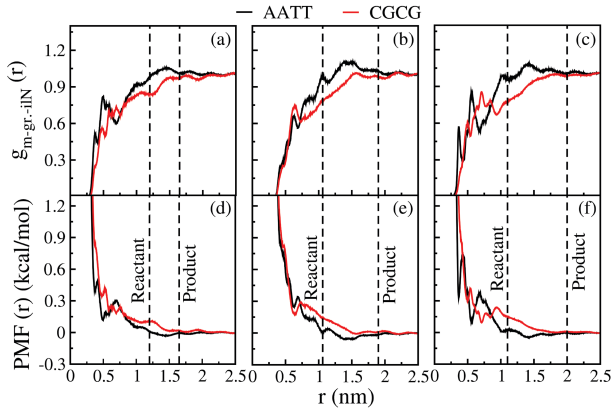

Figure S3. The RDF (top panel) and PMF (bottom panel) plots for minor groove atoms of the DNAs with $[BMIM]^+$ (a and d), $[choline]^+$ (b and e) and $[BPYR]^+$ (c and f) respectively.

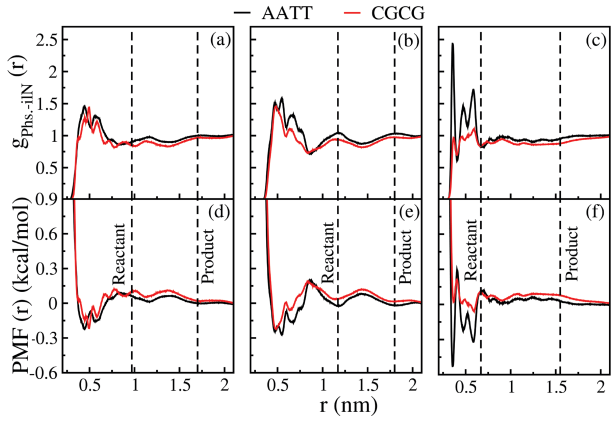

Figure S4. The RDF (top panel) and PMF (bottom panel) plots for phosphate atoms of the DNAs with $[BMIM]^+$ (a and d), $[choline]^+$ (b and e) and $[BPYR]^+$ (c and f) respectively.

Table S1. The distance cut-off taken for calculation of MRTs of IL cations.

IL solution	Reactant state cut-off (nm)			Product state cut-off (nm)		
	Major	Minor	Phosphate	Major	Minor	Phosphate
[BMIM][Cl]	1.32	1.20	0.97	2	1.65	1.7
[Choline][Cl]	1.20	1.06	1.17	2.05	1.9	1.8
[BPYR][Cl]/ [BPYR][PF_6]/[BPYR][BF_4]	1.33	1.10	0.67	2	2	1.55

Comparison between proximal and conventional radial distribution function for water:

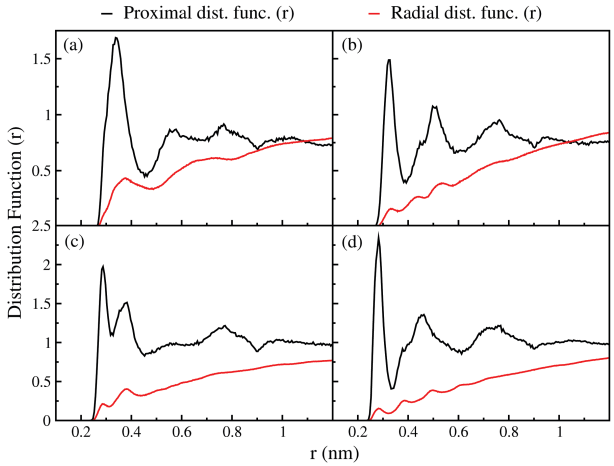

Figure S5. Comparison between proximal radial distribution function (black line) and conventional radial distribution function (red line) between major groove and water oxygen (a and c) and minor groove and water oxygen (b and d) for AT-DNA (a and b) and CG-DNA (c and d). The plots indicate the presence of peaks at similar distances from the site for both proximal and conventional radial distribution function with different peak heights.

Table S2. The coefficients, time scales and the fitting parameters for MRT calculation of IL cations.

IL solution	DNA	Site	C_1 (%)	τ_1 (ns)	C_2 (%)	τ_2 (ns)	Correlation coefficient	χ^2
[BMIM][Cl]	AATT	Maj	91.2	1.79	8.8	59.06	0.99	3.57
		Min	88.3	1.67	11.7	57.5	0.99	5.02
		Phs	90.2	1.37	9.8	60.35	0.99	3.25
	CGCG	Maj	85.2	10.16	14.8	463.23	0.99	7.99
		Min	79.3	9.8	20.7	207.82	0.99	2.24
		Phs	73.8	7.09	26.2	76.69	0.99	1.12
[Choline][Cl]	AATT	Maj	22.6	2.49	77.4	22.34	0.99	0.89
		Min	12.1	2.06	87.9	22.74	0.99	1.97
		Phs	40.9	1.17	59.1	21.92	0.99	0.47
	CGCG	Maj	85.1	15.32	14.9	1.56×10^5	0.99	27.19
		Min	81.8	16.14	18.2	1.1×10^5	0.99	34.52
		Phs	75	7.87	25	59.58	0.99	2.8
[BPYR][Cl]	AATT	Maj	89.9	3.16	10.1	20.22	0.99	1.37
		Min	90.3	3.89	9.7	27.43	0.99	6.84
		Phs	86	2.65	14	24.1	0.99	1.23
	CGCG	Maj	82	7.77	18	407.48	0.99	6.83
		Min	72.3	9.36	27.7	333.46	0.99	11.42
		Phs	79.9	5.76	20.1	282.83	0.99	2.99
[BPYR][PF_6]	AATT	Maj	82.6	2.28	17.4	9.1	0.99	0.97
		Min	83.8	2.83	16.2	10.76	0.99	3.77
		Phs	80.9	1.89	19.1	11.04	0.99	0.9
	CGCG	Maj	86.9	4.04	13.1	35.18	0.99	4.35
		Min	82.3	5.00	17.7	39.29	0.99	5.87
		Phs	76.6	2.58	23.4	26.28	0.99	3.06
	AATT	Maj	88.6	2.21	11.4	15.33	0.99	0.54
		Min	86.6	2.52	13.4	16.77	0.99	4.41
		Phs	82.7	1.91	17.3	16.06	0.99	1.59

[BPYR][BF_4]	CGCG	Maj	83.1	3.58	16.9	24.26	0.99	5.28
		Min	79.1	4.69	20.9	28.73	0.99	7.59
		Phs	77	2.47	23	31.93	0.99	6.78

Error analysis.
To estimate the error in the MRT values, the 100 ns simulation with [BPYR][BF_4] was divided into two 50ns segments and the C(t) was calculated for 25 ns. The [BPYR][BF_4] solution was chosen for this since in this case, the correlation function decays rapidly for the IL cation and hence in 25 ns, the C(t) can be expected to reach close to zero. Fitting the data with a bi-exponential function, the timescales have been calculated from which we have calculated the error as:

S.D.= $\sqrt{((\tau_{100ns} - \tau^1_{50ns})^2 + (\tau_{100ns} - \tau^2_{50ns})^2)/2}$.

Table S3. The timescales with different segment of trajectory and the error associated with the MRT values of $[BPYR]^+$ and water.

Solvent	**Site**	**MRT (ns) from 100ns (τ_{100ns})**	**MRT (ns) from first 50ns (τ^1_{50ns})**	**MRT (ns) from last 50ns (τ^1_{50ns})**	**S. D. (ns)**
$[BPYR]^+$	Maj	3.7	3.77	3.71	0.05
	Min	4.43	4.91	4.69	0.38
	Phs	4.36	4.65	4.49	0.22
Water	Maj	0.27	0.27	0.28	0.003
	Phs	0.18	0.18	0.19	0.008

Table S4. DNA parameters averaged for the middle four base pairs calculated in different IL solutions.

(a) Major Groove Width (Å)

IL solution	**AT-DNA**	**GC-DNA**
[BMIM][Cl]	12.76	11.22
[Choline][Cl]	11.83	11.26
[BPYR][Cl]	13.68	12.13
[BPYR][PF_6]	12.63	12.14
[BPYR][BF_4]	12.43	11.82

(b) Minor Groove Width (Å)

IL solution	**AT-DNA**	**GC-DNA**
[BMIM][Cl]	5.94	6.7
[Choline][Cl]	6.53	7.13
[BPYR][Cl]	5.89	6.65

[BPYR][PF_6]	5.2	6.88
[BPYR][BF_4]	4.99	6.7

(c) Major Groove Depth (Å)

IL solution	**AT-DNA**	**GC-DNA**
[BMIM][Cl]	4.93	3.86
[Choline][Cl]	5.58	4.00
[BPYR][Cl]	5.00	3.46
[BPYR][PF_6]	4.58	4.42
[BPYR][BF_4]	4.81	4.00

(d) Minor Groove Depth (Å)

IL solution	**AT-DNA**	**GC-DNA**
[BMIM][Cl]	4.93	4.96
[Choline][Cl]	4.83	5.07
[BPYR][Cl]	4.92	5.48
[BPYR][PF_6]	5.21	5.05
[BPYR][BF_4]	5.05	5.17

(e) Rise (Å)

IL solution	**AT-DNA**	**GC-DNA**
[BMIM][Cl]	3.43	3.47
[Choline][Cl]	3.45	3.33
[BPYR][Cl]	3.45	3.4
[BPYR][PF_6]	3.54	3.46
[BPYR][BF_4]	3.52	3.41

(f) Roll (°)

IL solution	AT-DNA	GC-DNA
[BMIM][Cl]	1.94	2.45
[Choline][Cl]	2.95	3.4
[BPYR][Cl]	0.1	1.99
[BPYR][PF_6]	-0.06	1.47
[BPYR][BF_4]	0.1	3.3

(g) Tilt (°)

IL solution	AT-DNA	GC-DNA
[BMIM][Cl]	0.92	-0.77
[Choline][Cl]	-0.51	0.51
[BPYR][Cl]	-0.19	1.46
[BPYR][PF_6]	0.22	-1.63
[BPYR][BF_4]	-0.86	0.4

(h) Twist (°)

IL solution	AT-DNA	GC-DNA
[BMIM][Cl]	33.29	36.11
[Choline][Cl]	33.36	32.47
[BPYR][Cl]	33.31	33.87
[BPYR][PF_6]	33.17	33.38
[BPYR][BF_4]	34.57	33.41

(i) Slide (Å)

IL solution	AT-DNA	GC-DNA
[BMIM][Cl]	-0.19	0.34
[Choline][Cl]	-0.34	0.43
[BPYR][Cl]	-0.52	0.32
[BPYR][PF_6]	-0.42	-0.07

[BPYR][BF_4]	-0.29	0.15

(j) Shift (Å)

IL solution	AT-DNA	GC-DNA
[BMIM][Cl]	0.22	-0.11
[Choline][Cl]	-0.14	0.28
[BPYR][Cl]	-0.13	0.26
[BPYR][PF_6]	0.00	-0.24
[BPYR][BF_4]	0.01	0.01

RDF and PMF plot for water near phosphate atoms in different IL solutions.

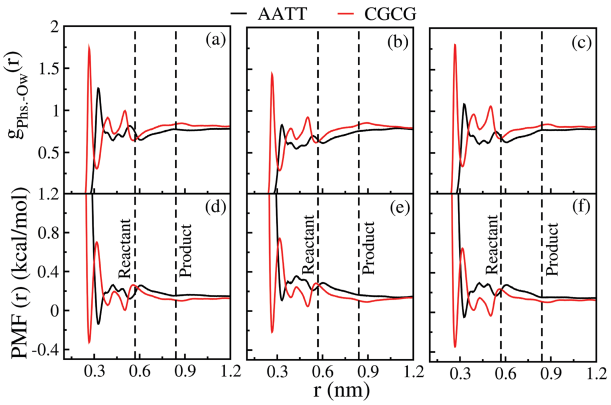

Figure S6. The RDF (top panel) and PMF (bottom panel) plots for the phosphate atoms of the DNAs with water oxygen in [BMIM][Cl] solution (a and d), [Choline][Cl] solution (b and e) and [BPYR][Cl] solution (c and f), respectively.

RDF plots between water and minor groove atom in [BMIM][Cl] and [Choline][Cl] solution.

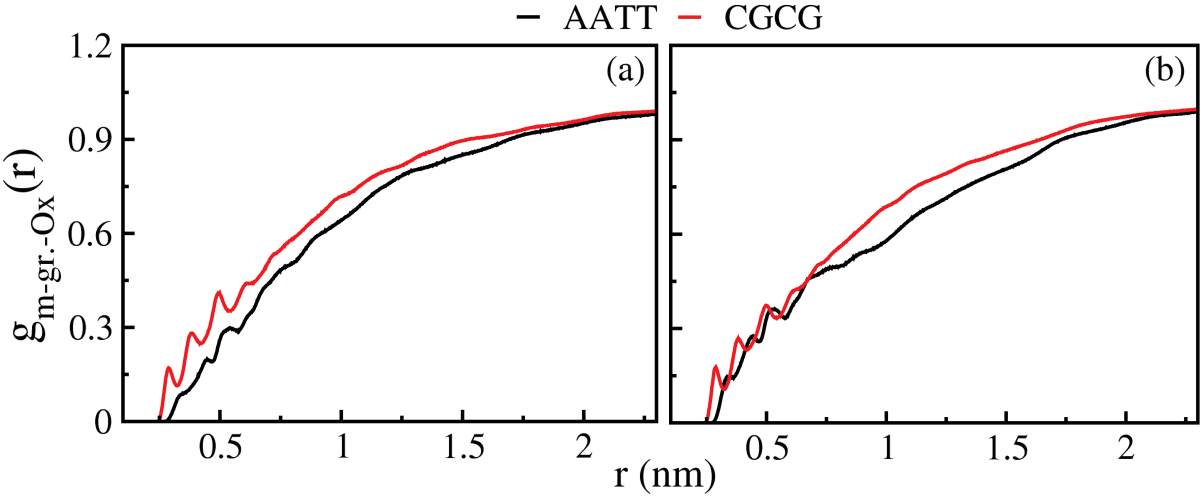

Figure S7. The RDF plot between minor groove atoms of AT and CG-DNA with water oxygen atoms in [BMIM][Cl] solution (a) and [Choline][Cl] solution (b).

Table S5. The MRT calculation results for water in different IL solutions. Sites containing major groove atoms and the phosphate atoms are denoted as Maj, Phs, respectively.

IL solution	DNA	Site	C_1 (%)	τ_1 (ns)	C_2 (%)	τ_2 (ns)	Correlation coefficient	χ^2
[BMIM][Cl]	AATT	Maj	89.3	0.15	10.7	0.84	0.99	0.06
		Phs	91.8	0.08	8.2	0.57	0.99	0.06
	CGCG	Maj	88.4	0.91	11.6	6.55	0.99	0.19
		Phs	23.3	2.15	76.7	0.42	0.99	0.31
[Choline][Cl]	AATT	Maj	82.0	0.21	18	0.83	0.99	0.08
		Phs	21.6	0.54	78.4	0.08	0.99	0.19
	CGCG	Maj	95.1	0.91	4.9	14.74	0.99	0.23
		Phs	75.9	0.42	24.14	1.89	0.99	0.28
[BPYR][Cl]	AATT	Maj	86.8	0.16	13.2	0.71	0.99	0.04
		Phs	84.5	0.08	15.5	0.47	0.99	0.09
	CGCG	Maj	88.5	0.77	11.5	3.96	0.99	0.25
		Phs	80.3	0.36	19.7	1.79	0.99	0.21
[BPYR][PF_6]	AATT	Maj	92.1	0.14	7.9	0.73	0.99	0.05
		Phs	84.1	0.06	15.9	0.35	0.99	0.07
	CGCG	Maj	100	0.46	0	0	0.99	1.84
		Phs	80.1	0.18	19.9	0.73	0.99	0.09
[BPYR][BF_4]	AATT	Maj	93.6	0.15	6.4	2.06	0.99	0.16
		Phs	92.4	0.08	7.6	1.4	0.99	0.37
	CGCG	Maj	92.6	0.42	7.4	2.69	0.99	0.21
		Phs	87.9	0.21	12.1	1.33	0.99	0.21

Table S6. Time scales obtained from calculation at 25 wt% of [BMIM][Cl] for the two DNA systems.

DNA	Solvent	Site	C_1 (%)	τ_1 (ns)	C_2 (%)	τ_2 (ns)	Total time scale (ns)
AT-DNA	BMIM cation	Maj	82.6	0.91	17.4	7.06	1.98
		Min	77.4	0.82	22.6	6.86	2.18
		Phs	79.1	0.63	20.9	6.53	1.87
	Water	Maj	96.4	0.09	3.6	6.28	0.11
		Phs	92.2	0.04	7.8	2.51	0.06
GC-DNA	BMIM cation	Maj	74	2.06	26	10.92	4.37
		Min	66.1	1.73	33.9	10.53	4.71
		Phs	71.8	1.47	28.2	10.39	3.99
	Water	Maj	93.4	2.32	6.6	1.29	0.30
		Phs	86.2	1.13	13.8	0.59	0.18

Table S7. Values obtained from calculation of MRTs for poly-AT DNA system in 50 wt% [BMIM][Cl] solution.

Solvent	Site	C_1 (%)	τ_1 (ns)	C_2 (%)	τ_2 (ns)	Total time scale (ns)
BMIM cation	Maj	88.4	1.47	11.6	33.98	5.23
	Min	84.7	1.31	15.3	33.6	6.25
	Phs	86.8	1.14	13.2	32.99	5.35
Water	Maj	100	0.15	0	0	0.15
	Phs	84	0.07	16	0.22	0.09

Interaction energies between different sites in DNA and water from simulation at 0% IL.

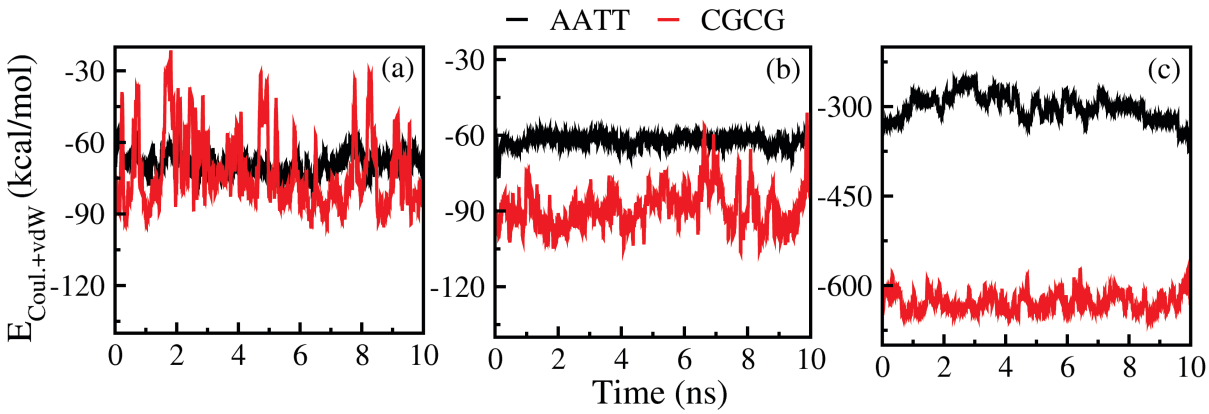

Figure S8. The interaction energies between water and major groove (a), minor groove (b) and phosphate group (c) of the DNAs simulated in pure water.

Table S8. The number of water near different sites and box volume for the two DNA systems in pure water.

Site	Number of water molecules		Box volume (nm^3)	
	AATT	CGCG	AATT	CGCG
Major groove	259	326	398	301
Minor groove	237	314		
Phosphate	537	714		