

## SUPPORTING INFORMATION

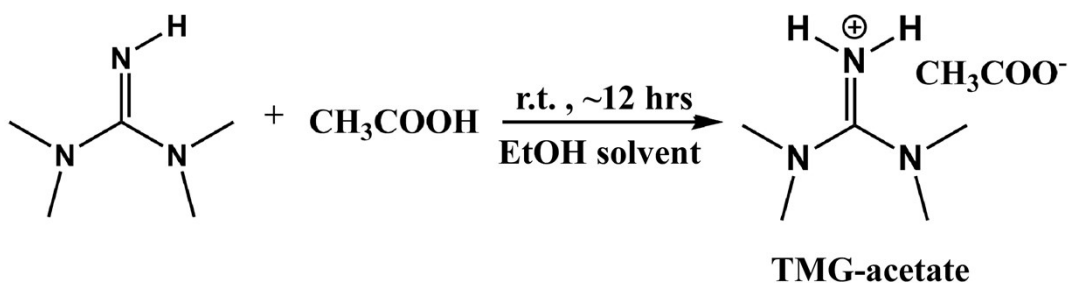
### Hydrogen Bonding of Ionic Liquids in the Groove Region of DNA Controls the Extent of Its Stabilization: Synthesis, Spectroscopic and Simulation Studies

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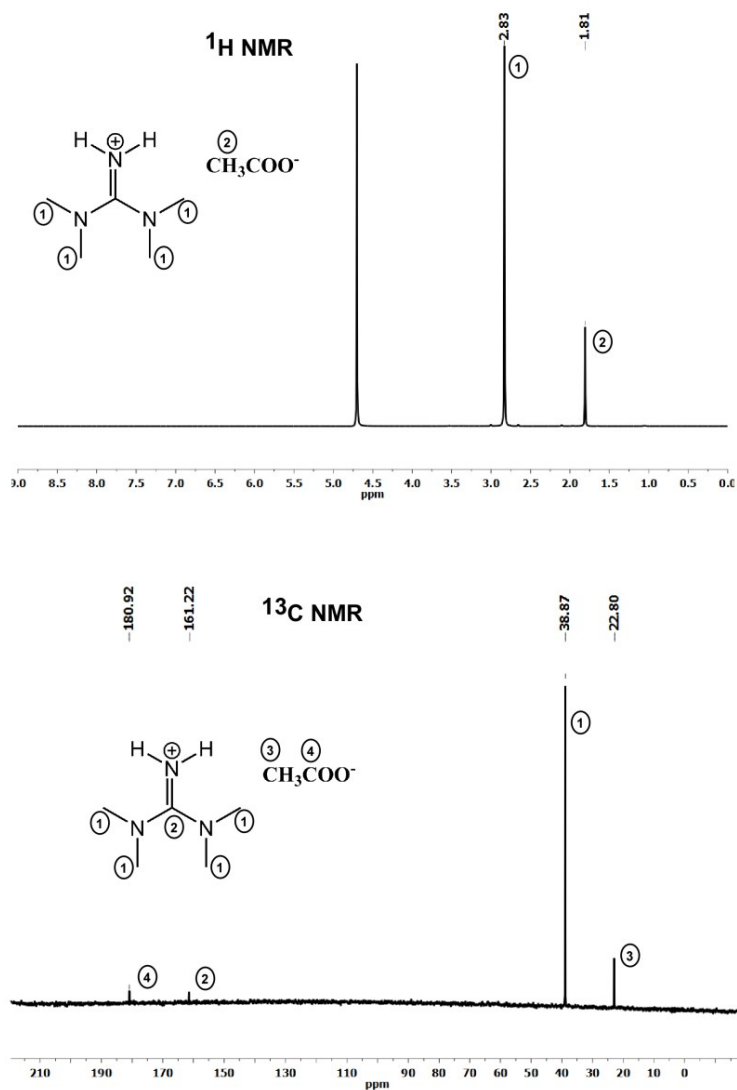
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**Preparation of TMG-acetate:** TMG (25 mmol) in 50 mL of ethanol (EtOH) was taken in a 100 mL round bottom flask. Then acetic acid (25 mmol) was added drop wise keeping the system inside the hood. The reaction was left overnight in a stirring condition. Finally ethanol was dried under vacuum. The mixture was washed with hexane to remove the unreacted compounds (if any). A colourless liquid compound was obtained which was characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectroscopy, data shown in Figure S1 and Table S1.



**Scheme 1:** Preparation scheme of TMG-acetate.



**Figure S1:** <sup>1</sup>H NMR and <sup>13</sup>C NMR of TMG-acetate ionic liquid in D<sub>2</sub>O solvent.

**Preparation of DETMG-acetate:** DETMG-acetate was prepared followed by 2 step reaction. First DETMG-Iodide was prepared then DETMG-acetate was prepared using 5 mmol of DETMG-Iodide and 5 mmol of sodium acetate trihydrate following the previous literature.<sup>1</sup> It was characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and Mass spectroscopy to check the purity; data shown in Figure S2, S3 and Table S1.

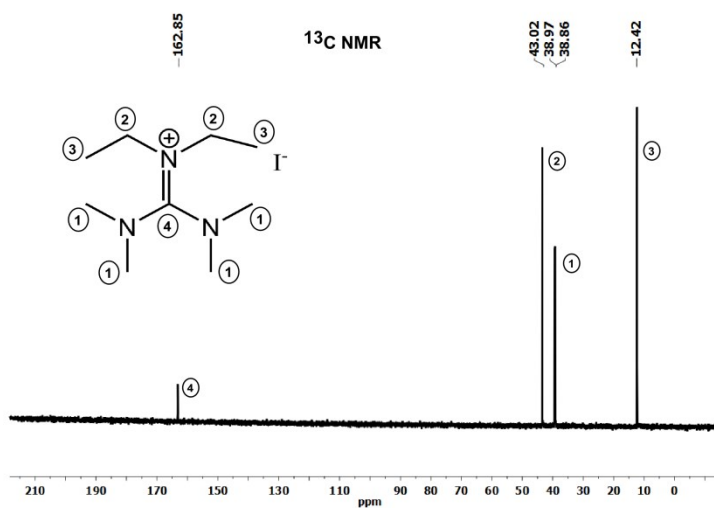
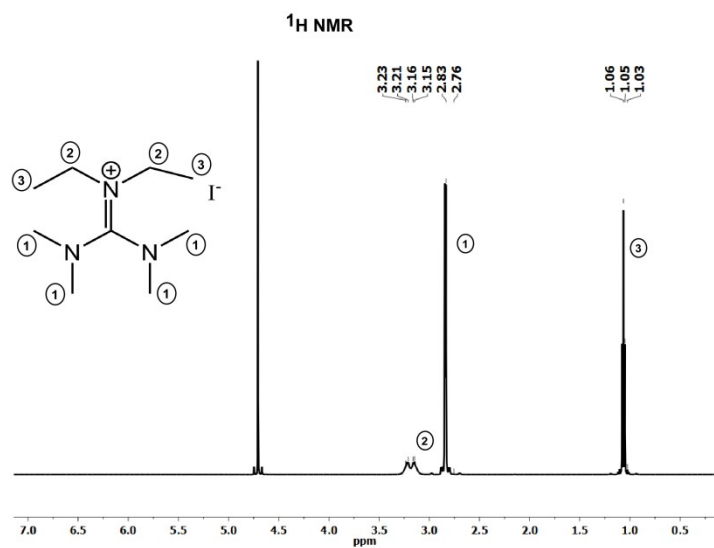
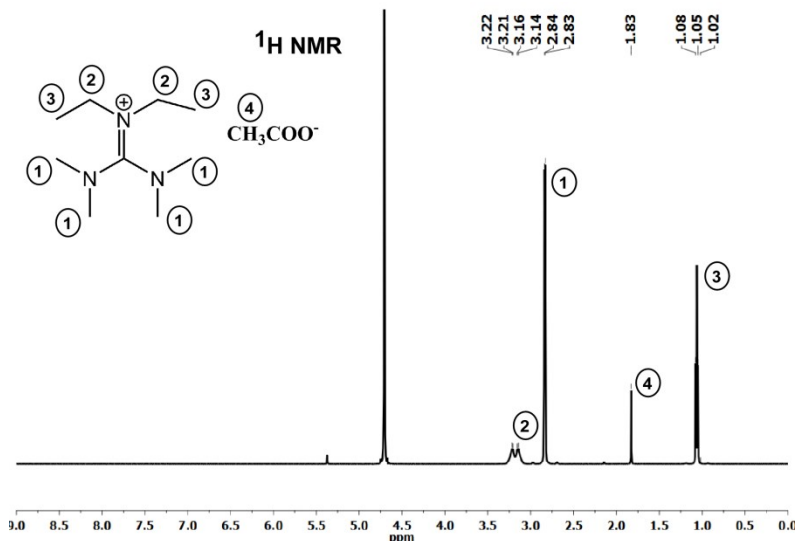


Figure S2: <sup>1</sup>H NMR and <sup>13</sup>C NMR of DETMG-iodide in D<sub>2</sub>O solvent.



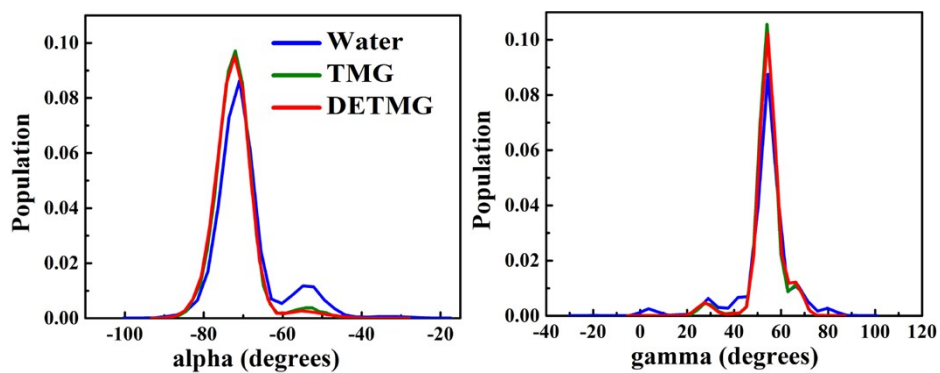
**Figure S3:**  $^1\text{H}$  NMR of DETMG-acetate in  $\text{D}_2\text{O}$  solvent.

**Table S1:** Peak positions (m/z) of the cation and anion fragments in mass spectroscopy.

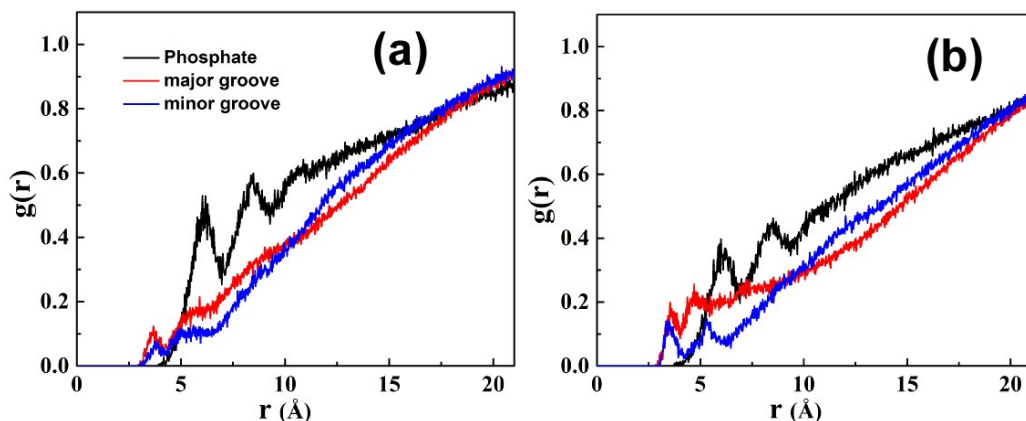
	TMG ( $\text{C}_5\text{N}_3\text{H}_{14}$ )	DETMG ( $\text{C}_9\text{N}_3\text{H}_{22}$ )	Iodide ( $\text{I}^-$ )	acetate ( $\text{C}_2\text{O}_2\text{H}_3$ )
m/z	116	172	127	59

**Table S2:** Disruption free energy ( $\Delta G_{\text{dis}}$ , kJ/mole) along with melting temperature ( $T_m$ ,  $^\circ\text{C}$ ) of DNA estimated using two-state model.  $\Delta G_{\text{dis}}$  has been calculated using Van't Hoff equation,  $\Delta G_{\text{dis}} = -RT_m \ln K_D$ , where,  $K_D$  is the equilibrium constant for the dissociation of duplex DNA =  $[\text{Concentration of DNA}]^2$ .

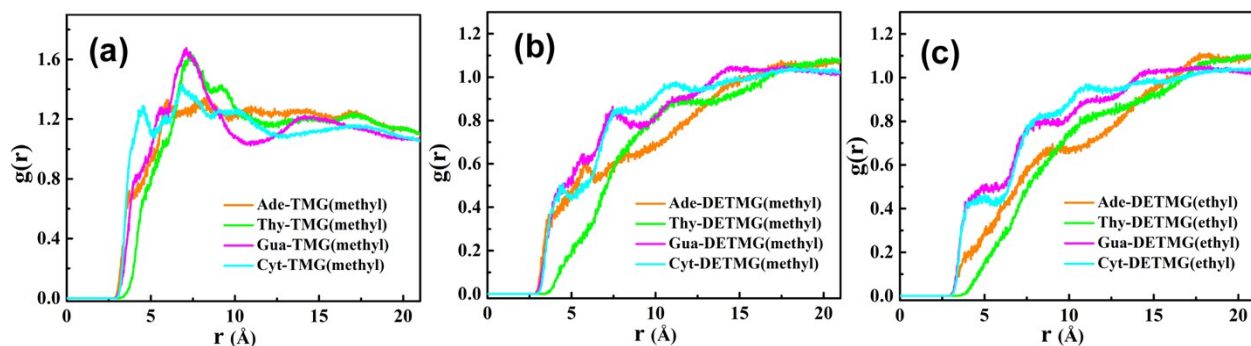
Conc. (mM)	TMG		DETMG	
	$T_m$	$\Delta G_{\text{dis}}$	$T_m$	$\Delta G_{\text{dis}}$
0	64	32.26		
0.7	67	32.54	61	31.92
1	68	32.64	62	32.10
10	68	32.64	55	31.44



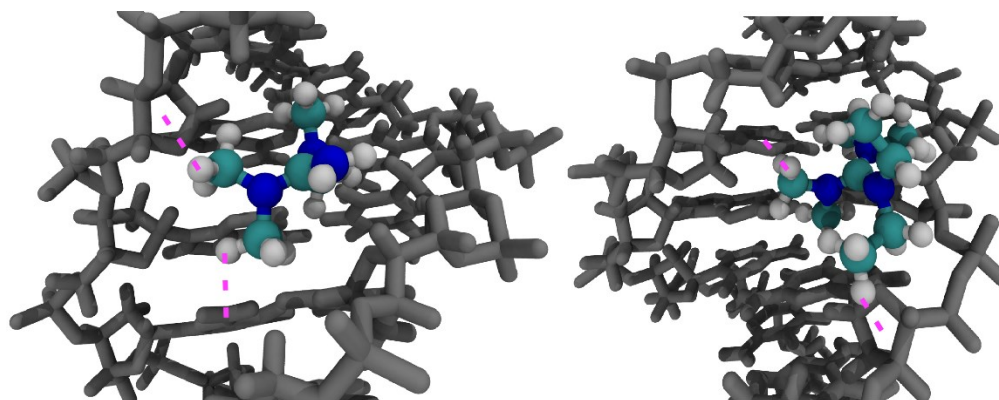
**Figure S4:** Histogram of the dihedral angles of DNA backbone in the presence of water (blue), TMG (green), DETMG (red).



**Figure S5:**  $g(r)$  for the acetate anions with the phosphate, major and minor groove, present as a counter ion of TMG (a) and DETMG (b). Carbon atom of the carboxylate group of acetate ion is considered for  $g(r)$  calculation.



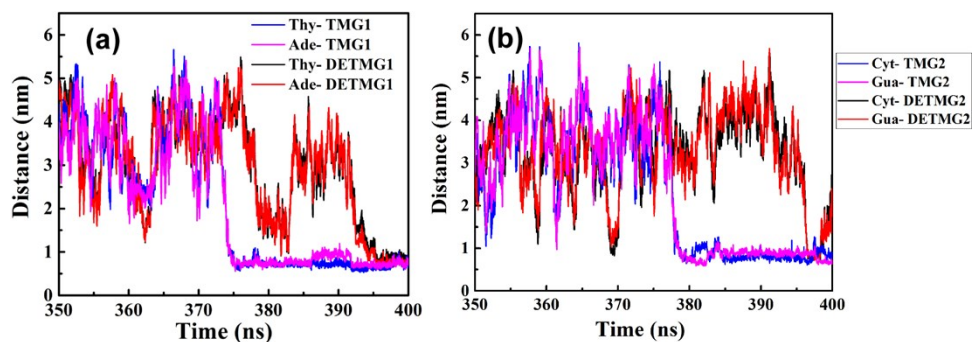
**Figure S6:**  $g(r)$  data for the ring of the nucleobases (heavy atoms only) and the carbon atoms of the methyl groups (TMG and DETMG both) and ethyl groups (only DETMG) are represented in (a), (b), (c) respectively.



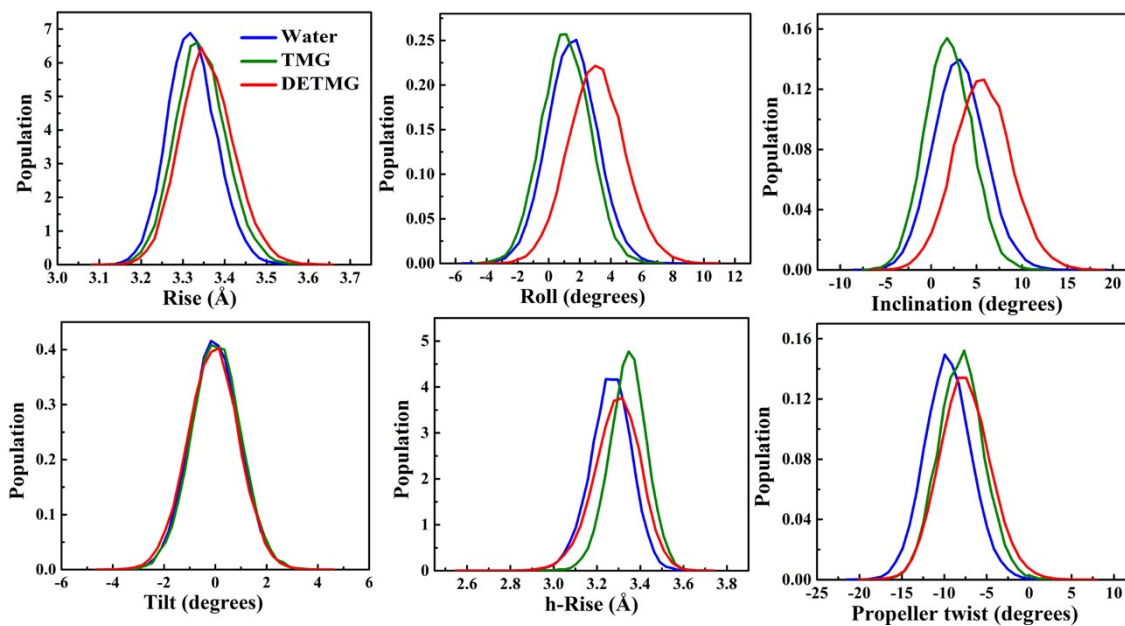
**Figure S7:** Orientation of the C-H group of TMG (left) and DETMG (right) towards the  $\pi$  electron density of nucleobases of DNA. The pink line depict the possibility of the C-H... $\pi$  interaction.

**Table S3:** Total interaction energy (kJ/mole) of methyl groups of ionic liquid cations with the ring of the nucleobases of DNA. The reported energies are the average of last 50 ns simulation time.

	<b>TMG</b>	<b>DETMG</b>
Adenine	$-3.84 \pm 0.4$	$-2.41 \pm 0.1$
Guanine	$-0.32 \pm 0.2$	$-0.08 \pm 0.0$
Thymine	$-0.22 \pm 0.1$	$-0.01 \pm 0.0$
Cytosine	$-1.20 \pm 0.2$	$-0.65 \pm 0.05$



**Figure S8:** Distance between the center of mass of the ring of nucleobases and cations of ILs are plotted with respect to time. Two representative cations for each IL present in the minor groove are shown here.



**Figure S9:** Histogram of the different base pair parameters of DNA in the presence of water (blue), TMG (green), and DETMG (red).

1. X. Lu, J. Yu, J. Wu, Y. Guo, H. Xie and W. Fang, *J. Phys. Chem. B*, 2015, **119**, 8054-8062.