The Effect of a Solvent Modifier in the Cesium Extraction by a Calix[4]arene: A Molecular Dynamics Study of the Oil Phase and the Oil – Water Interface.

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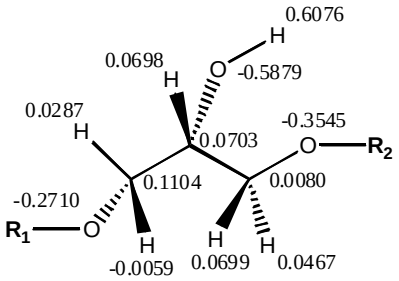
Supplementary Information



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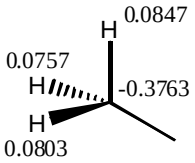

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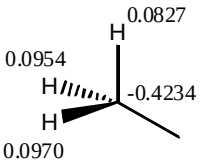

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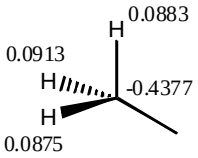

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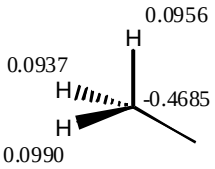
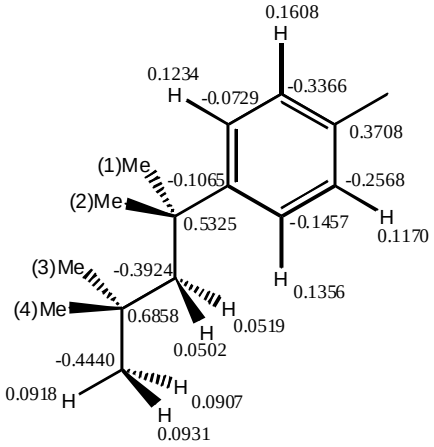
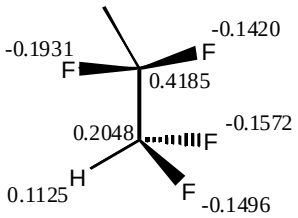




R_1



R_2

Figure S1: Atomic charges on the "cs3" modifier molecule.

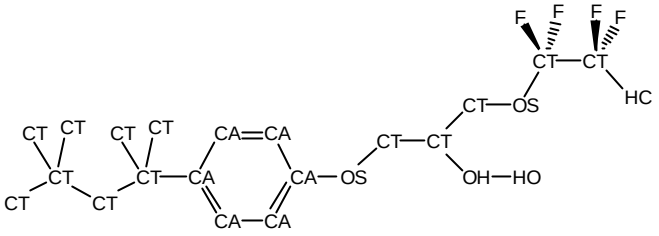


Figure S2: AMBER atom types for the "cs3" modifier molecule. Hidden Hydrogens are of HC type.

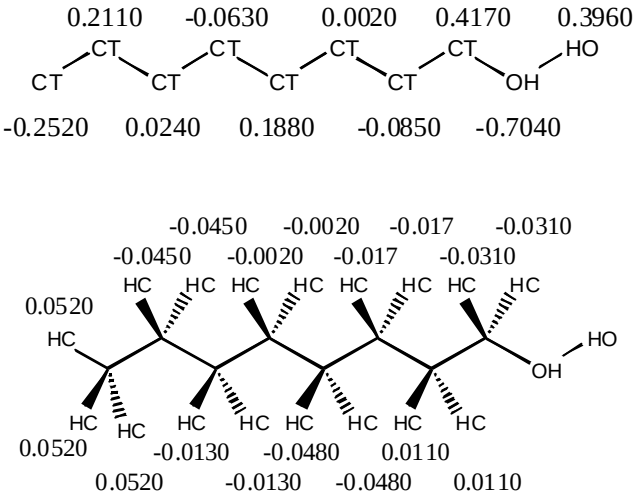


Figure S3: AMBER atom types and atomic charges on the octanol molecule, showing separately the main chain and H-atoms for clarity.

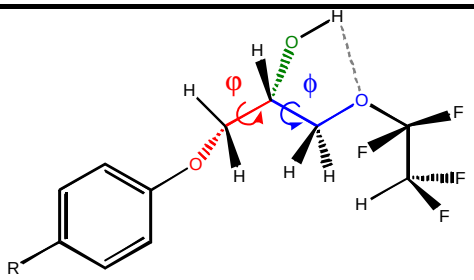
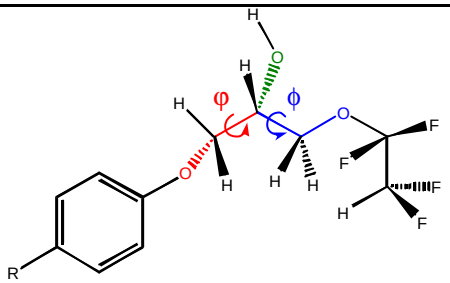
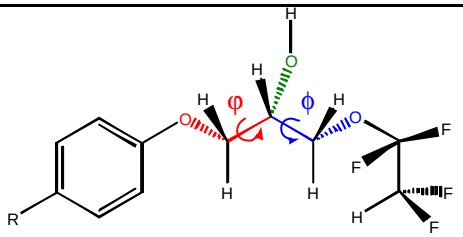
			j	*f*	E_{rel}
Mode 1		**QM**	78.6	59.6	0.0
		AMBER	64.8	51.6	0.0
			j	*f*	E_{rel}
Mode 2		**QM**	67.0	73.9	+3.2
		AMBER	64.2	71.0	+5.3
			j	*f*	E_{rel}
Mode 3		**QM**	55.3	-57.0	+0.4
		AMBER	50.3	-46.7	-0.6

Figure S4 : Selected conformers of the "cs3" modifier. Relative potential energies (E_{rel}, in kcal/mol) obtained by quantum mechanics (QM) and by AMBER, after optimization in the gas phase. *j* = ***O-C-C-O*** *f* = ***O-C-C-O*** ; **R** = H.

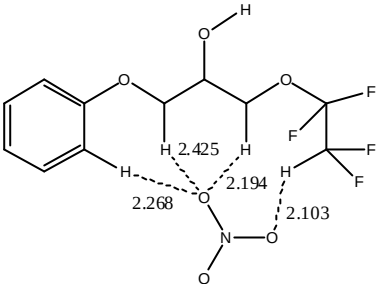
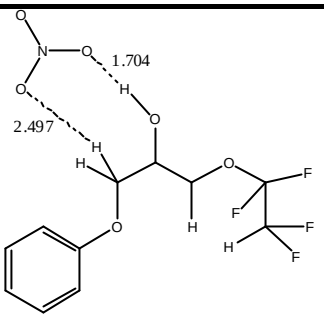
		Dimer 1			Dimer 2		
Nitrate – modifiers pair							
		j	*f*	E_{rel}	*j*	*f*	E_{rel}
	QM	65.9	56.5	0.0	81.1	73.6	-2.6
	AMBER	55.5	39.8	0.0	70.6	68.9	-3.2

Figure S5: Selected cs3 / NO_3^- dimers. Relative potential energies (E_{rel}, in kcal/mol) obtained by quantum mechanics (QM) and by AMBER, after optimization in the gas phase. *j* = ***O-C-C-O*** *f* = ***O-C-C-O*** ; **R** = H.

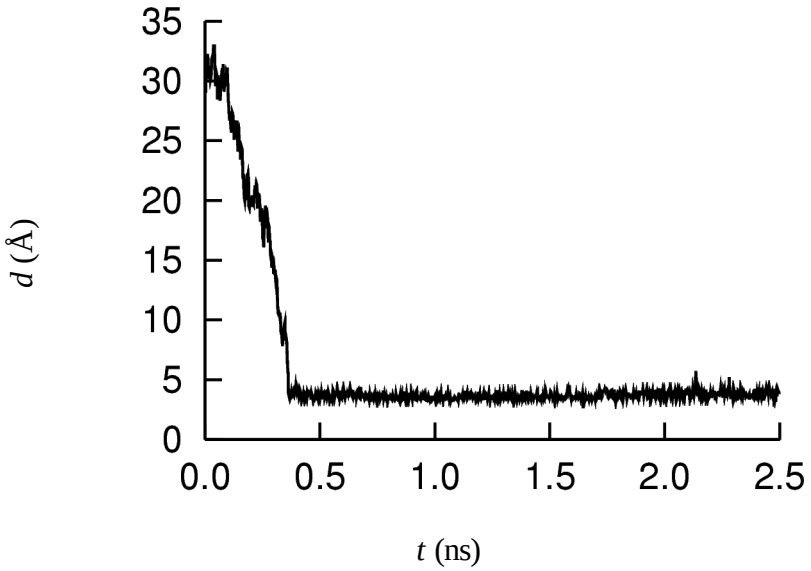


Figure S6 : Spontaneous association of the **L**Cs^+ … NO_3^- pair in the chloroform + cs3 solution (system **B5**). Evolution of the $Cs^+_{complex}$…$N_{nitrate}$ distance ***d*** as a function of time (ns).

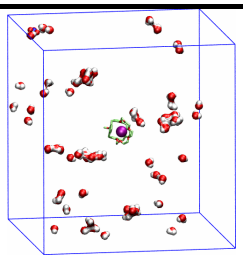
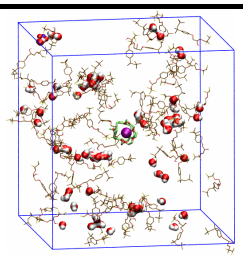
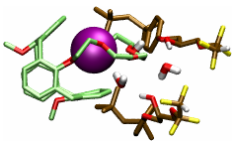
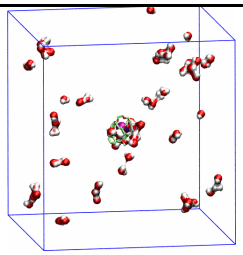
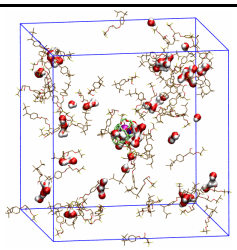
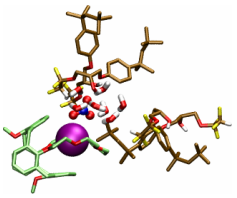
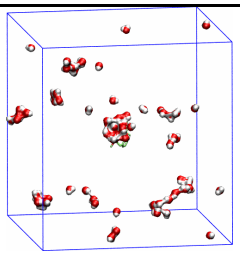
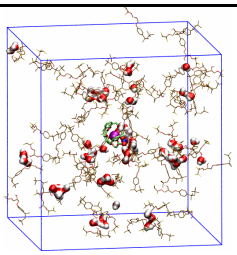
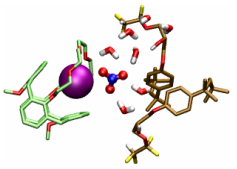
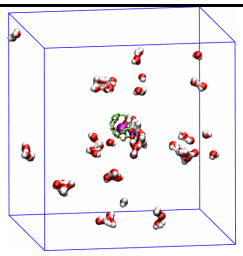
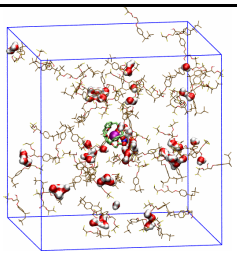
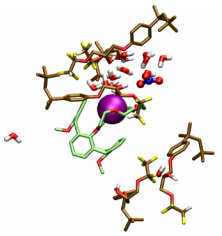
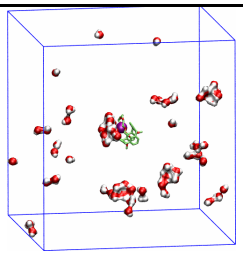
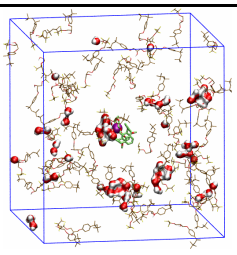
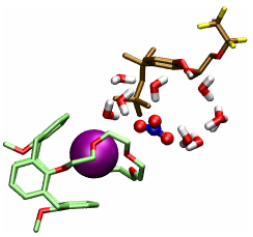
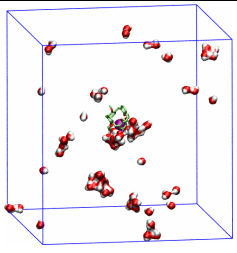
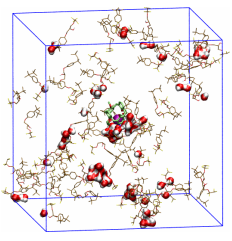
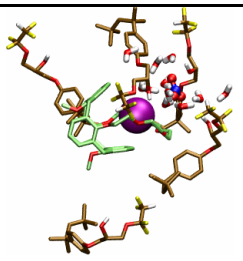
	Water only	Water + modifiers	Zoom
0 ns			
2 ns			
4 ns			
6 ns			
8 ns			
10 ns			

Figure S7 : Selected snapshots of the **C1** solution of **L**Cs^+ NO_3^- (1:1 cs3:water ratio) along the dynamics. Chloroform is hidden for clarity. *Right :* zoomed views on cs3 and water molecules within 14 Å from Cs^+.

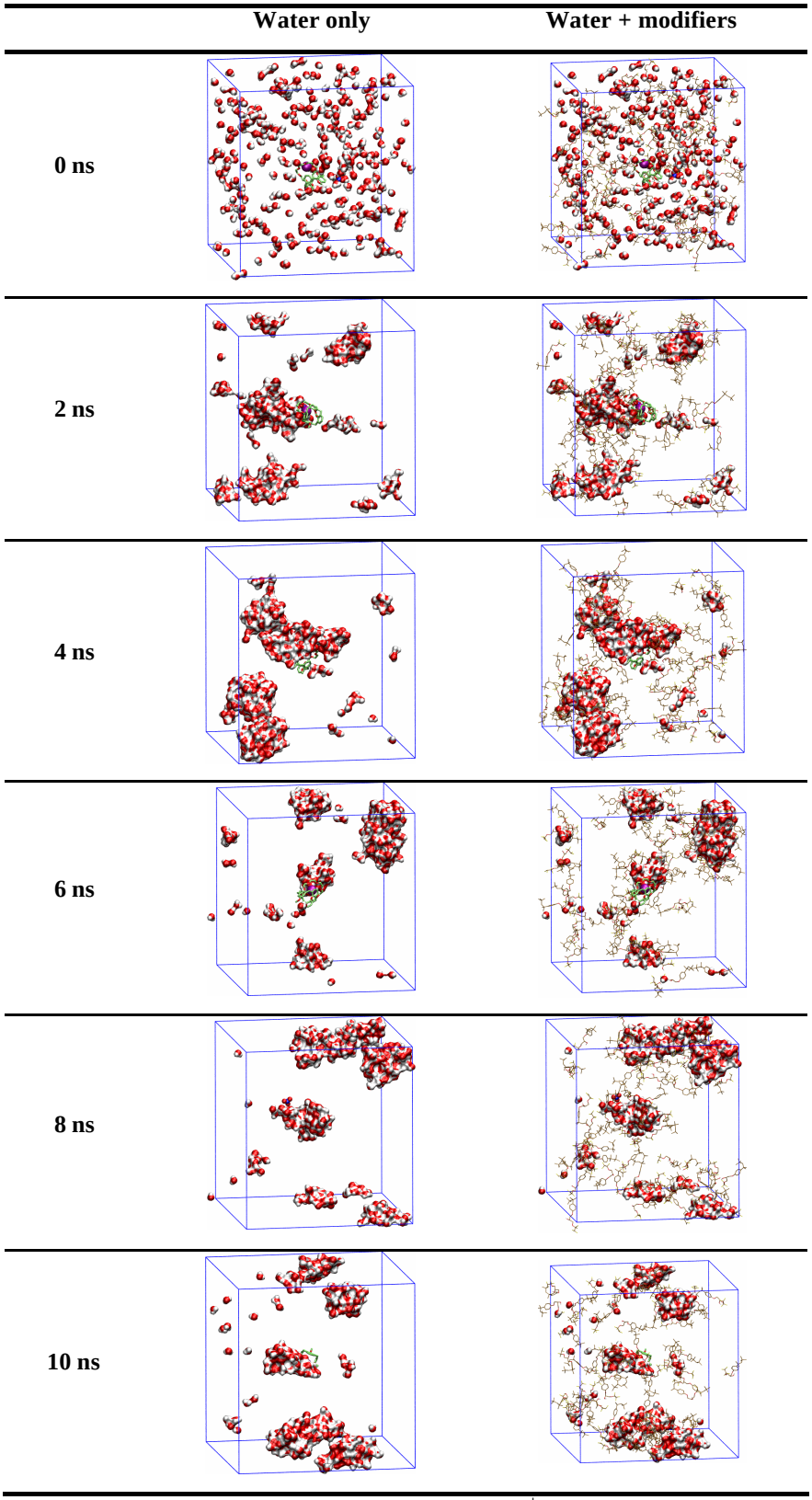


Figure S8 : Selected snapshots of the **C2** solution of **L**Cs^+ NO_3^- (1:5 cs3:water ratio) along the dynamics. Chloroform is hidden for clarity.

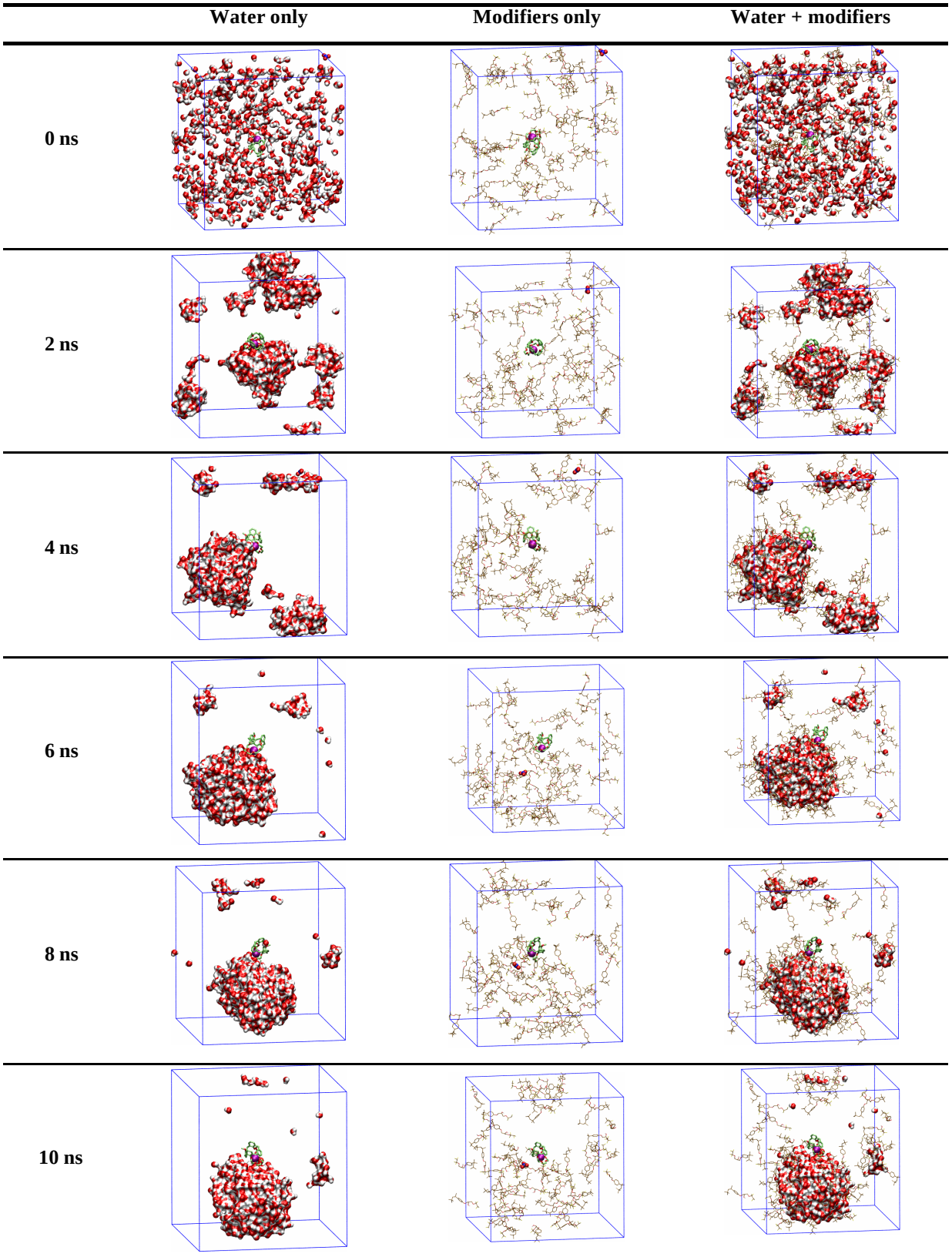


Figure S9 : Selected snapshots of the **C3** solution of **L**Cs^+ NO_3^- (1:10 cs3:water ratio) along the dynamics. Chloroform is hidden for clarity.

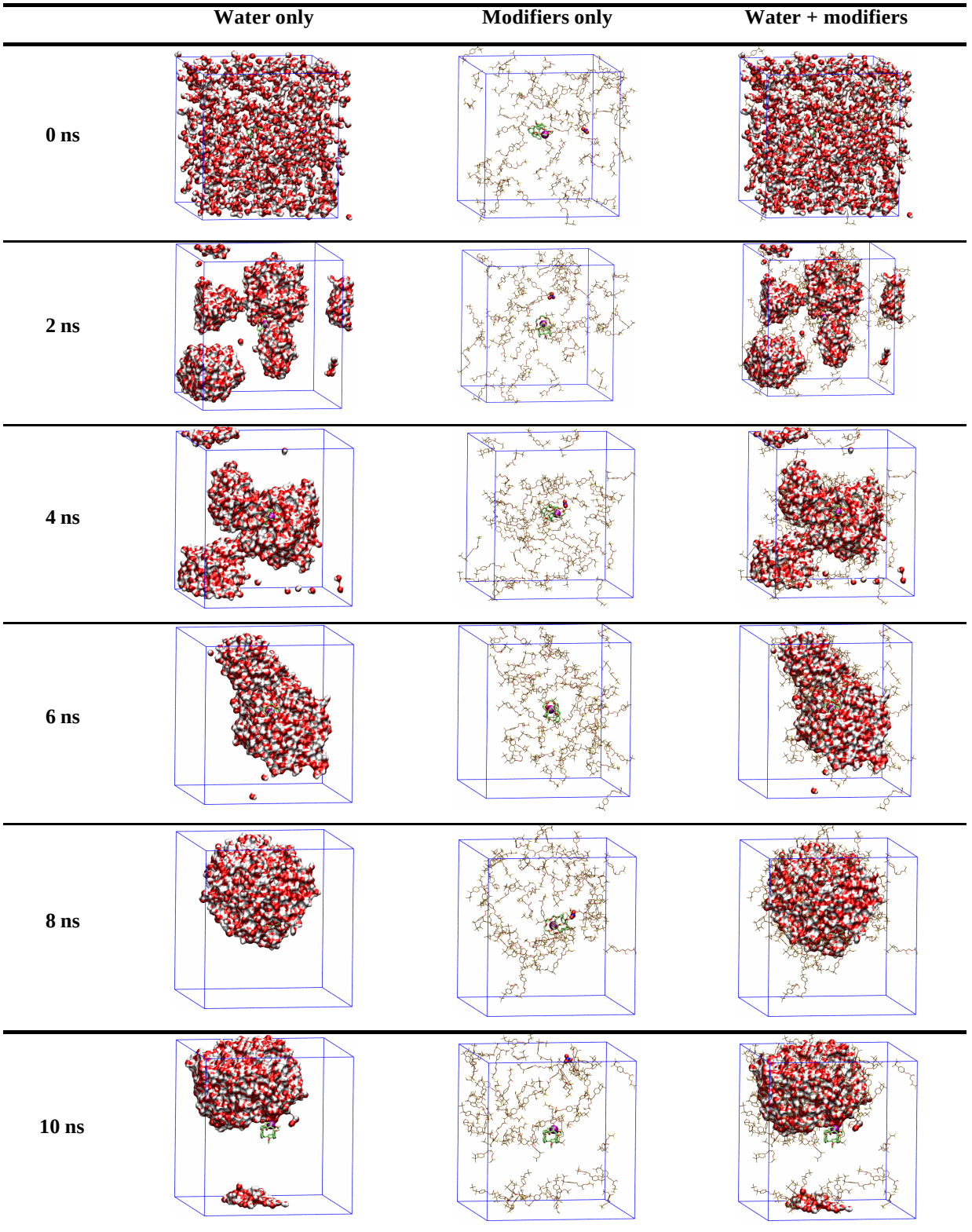


Figure S10 : Selected snapshots of the **C4** solution of **L**Cs^+ NO_3^- (1:20 cs3:water ratio) along the dynamics. Chloroform is hidden for clarity.

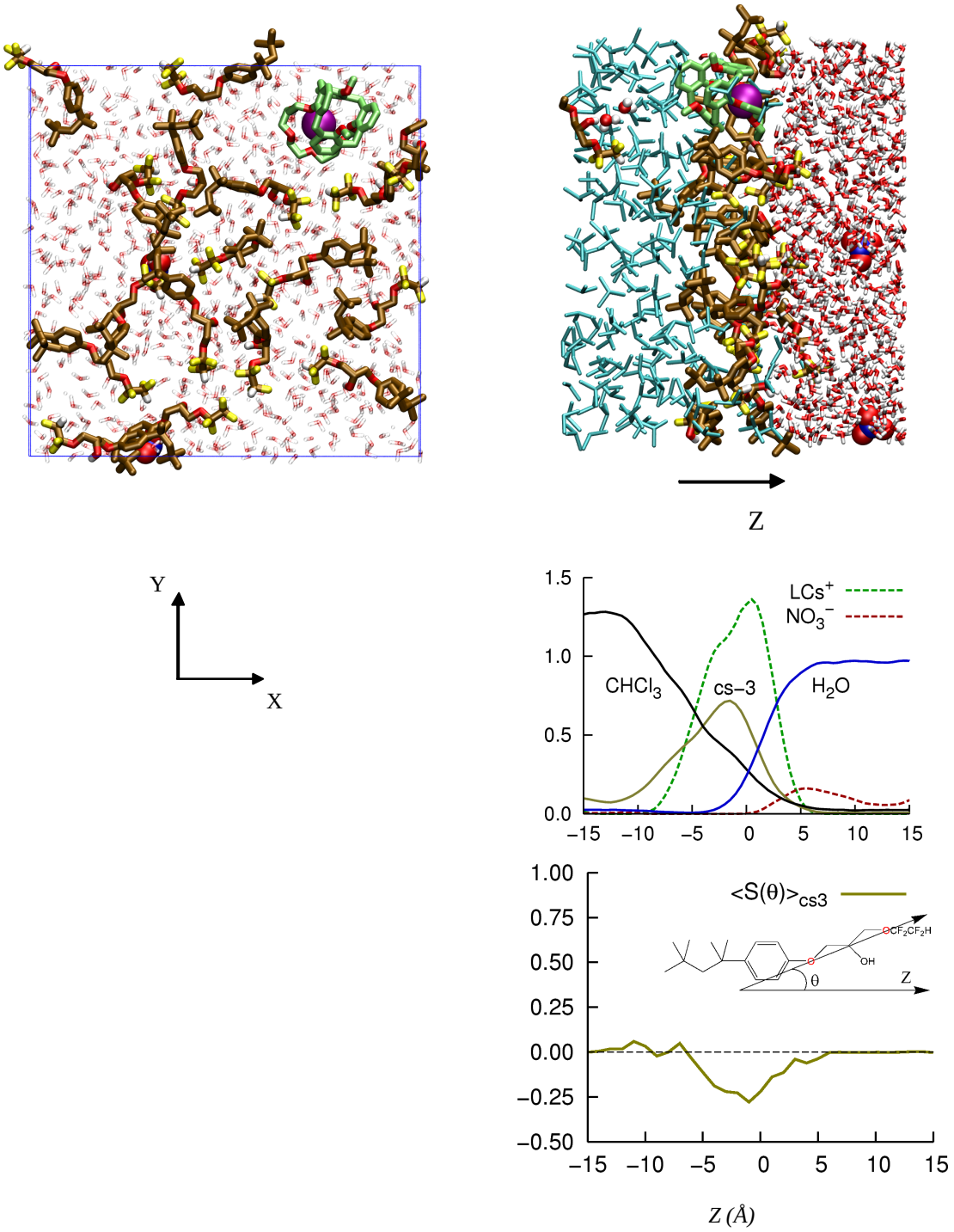


Figure S11 : The "planar" chloroform+cs3 – water interface (extracted from the **D1** system). *First line:* Zoom on the interface seen from the X axis (ΔZ = 30 Å) and from the Z-axis (XY slice). *Second line:* Solvents and solutes densities as a function of Z (Å). The densities of **L**Cs^+ and NO_3^- are scaled up by 12.5 for clarity. *Third line*: Order parameter <*S*(θ)> as a function of the Z-position.