Supplementary Material for PCCP

Molecular dynamics simulations of the aqueous interface with the [BMI][PF_6] ionic liquid: comparison of different solvent models

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Electronic Supplementary Information: Table S1 and Fig. S1–S10.

IL / *Water*	$IL^{\pm1}$ SPC/E PI	$IL^{\pm1}$ TIP5P PI	$IL^{\pm0.9}$ TIP3P PI	$IL^{\pm0.9}$ SPC/E PI	$IL^{\pm0.9}$ TIP5P PI	$IL^{\pm0.9}$ TIP3P DE	$IL^{\pm0.9}$ SPC/E DE	$IL^{\pm0.9}$ TIP5P DE
In water								
H_2O	1356 (70)	2162 (39)	3417 (4)	1671 (37)	2077 (43)	3075 (4)	1744 (57)	2019 (36)
BMI^+	735 (12)	(0)	206 (4)	915 (2)	(0)	2093 (5)	1724 (2)	(0)
PF_6^-	1063 (10)	657 (3)	454 (4)	631 (2)	(0)	1307 (3)	2159 (1)	654 (1)
Interface								
H_2O	859 (48)	1669 (43)	1513 (16)	1211 (65)	(0)	976 (30)	1006 (69)	(0)
BMI^+	420 (12)	206 (15)	165 (9)	270 (12)	337 (13)	411 (7)	288 (12)	491 (8)
PF_6^-	737 (3)	163 (11)	216 (6)	117 (11)	226 (12)	384(12)	354 (11)	436 (11)
In IL								
H_2O	155 (32)	389 (13)	336 (22)	81 (10)	764 (14)	907 (27)	91 (11)	388 (24)
BMI^+	99 (17)	65 (33)	79 (18)	75 (30)	126 (37)	136 (20)	77 (31)	78 (30)
PF_6^-	73 (18)	68 (29)	60 (19)	46 (26)	105 (29)	134 (23)	68 (32)	65 (26)

Table S1: The [BMI][PF_6] / water interface calculated with different models: average diffusion coefficients $\langle D \rangle$ (in 10^{-8} cm^2/s) for H_2O, PF_6^- and BMI^+ species during 0.5 ns for H_2O in water and during 0.1 ns for the others. The averages have been calculated for all molecules that reside during that time within a slice of 10 Å width centered on bulk IL or at the interface, and a slice of 20 Å width centered on the bulk water. Their number is given in parentheses.

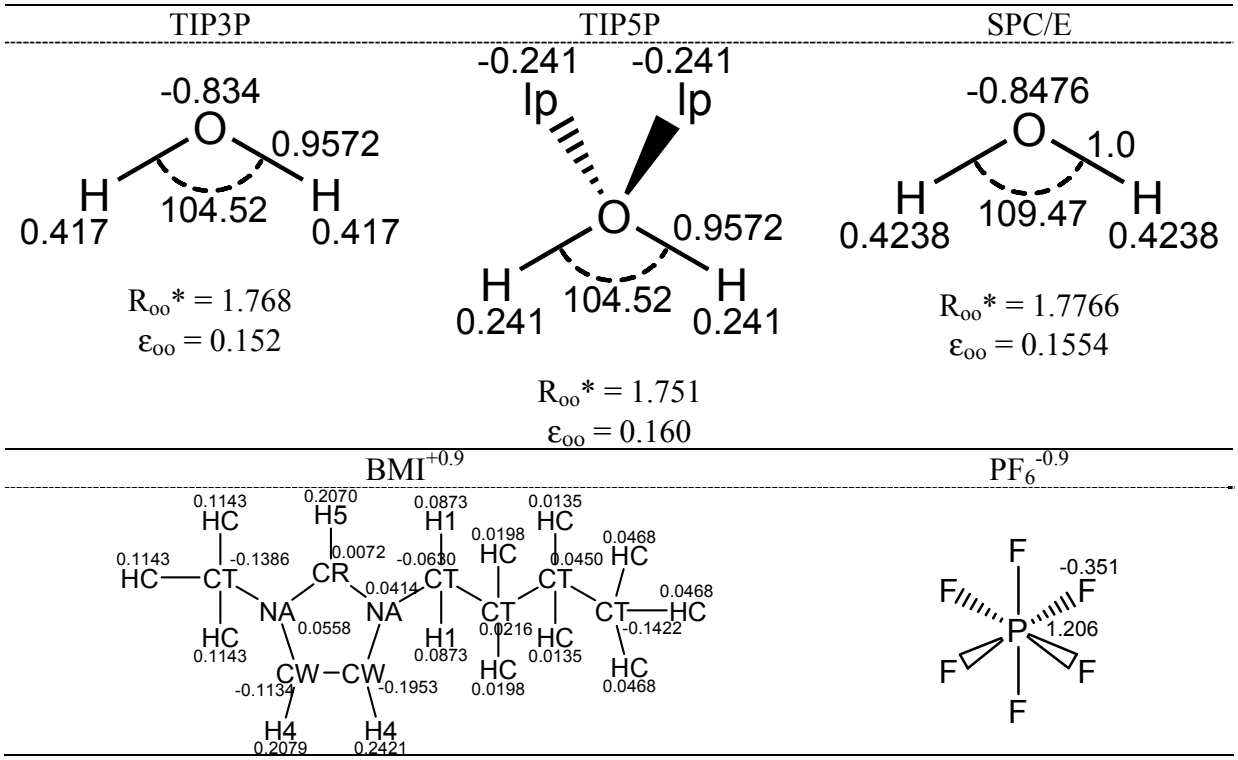


Figure S1 : Water models (distances in Å, angles in degrees, R_{oo}* in Å and ε_{oo} in kcal/mol). $BMI^{+0.9}$ and $PF_6^{-0.9}$ models (atomic charges and atomic atom types).

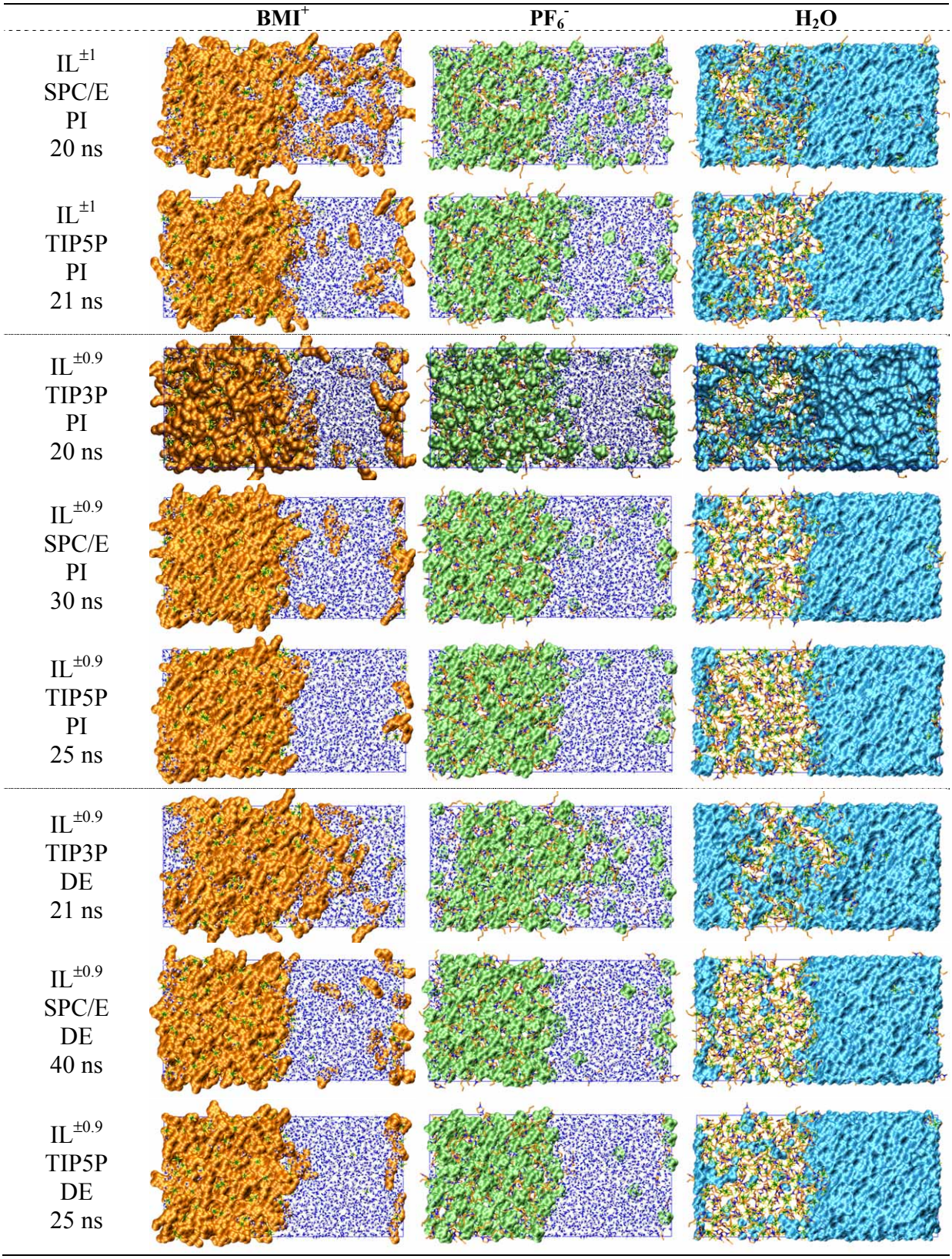


Figure S2: [BMI][PF_6] – water system simulated with different IL and water models. "PI" simulations at the preformed interface and demixing "DE" simulations of randomly mixed liquids: Snapshots at the end of the dynamics, showing separately, from left to right: the BMI^+ cations (orange), the PF_6^- anions (green) and water (blue).

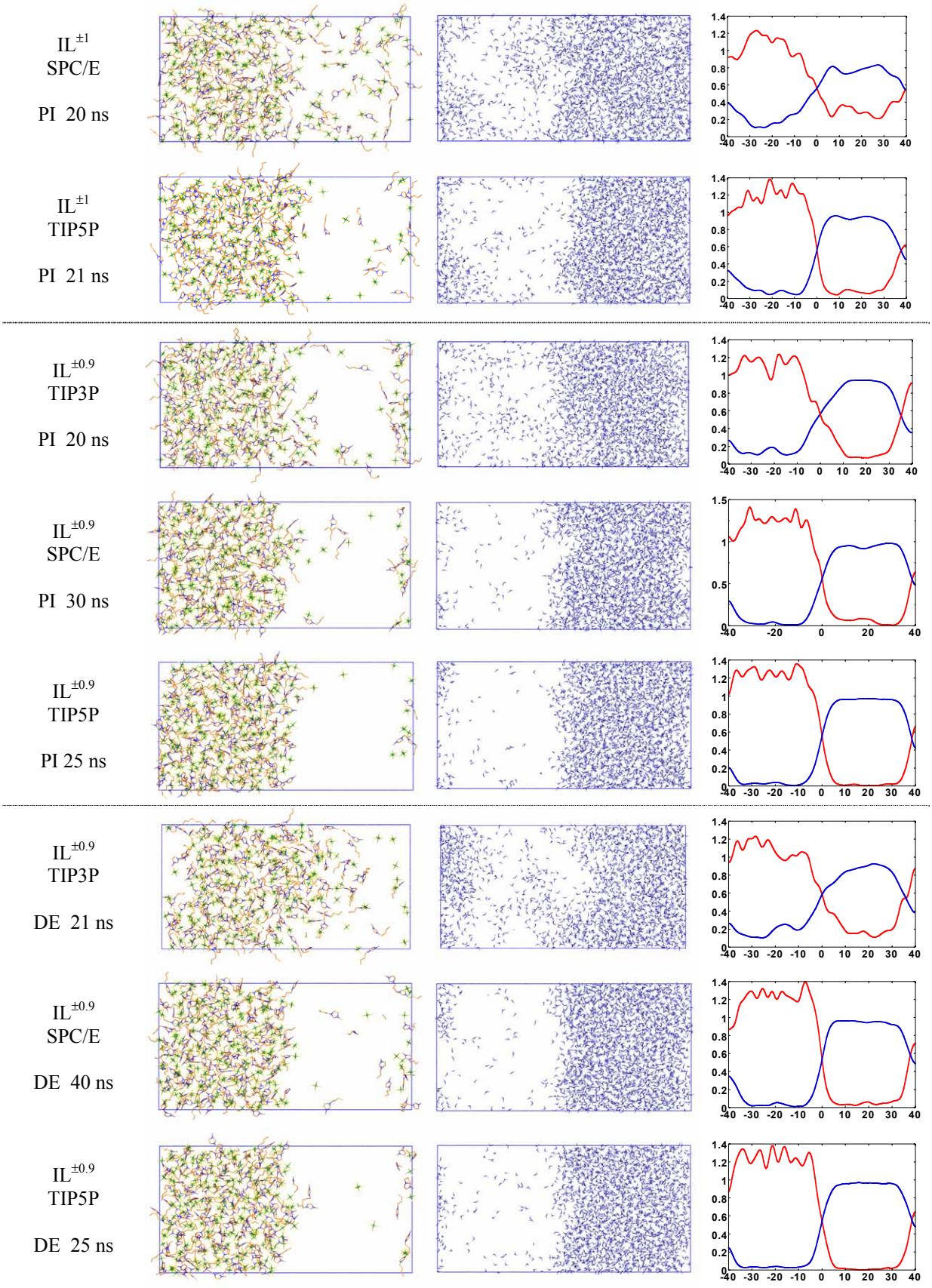


Figure S3: [BMI][PF_6] – water system simulated with different IL and water models. "PI" simulations at the preformed interface and demixing "DE" simulations of randomly mixed liquids: Final snapshots and density curves.

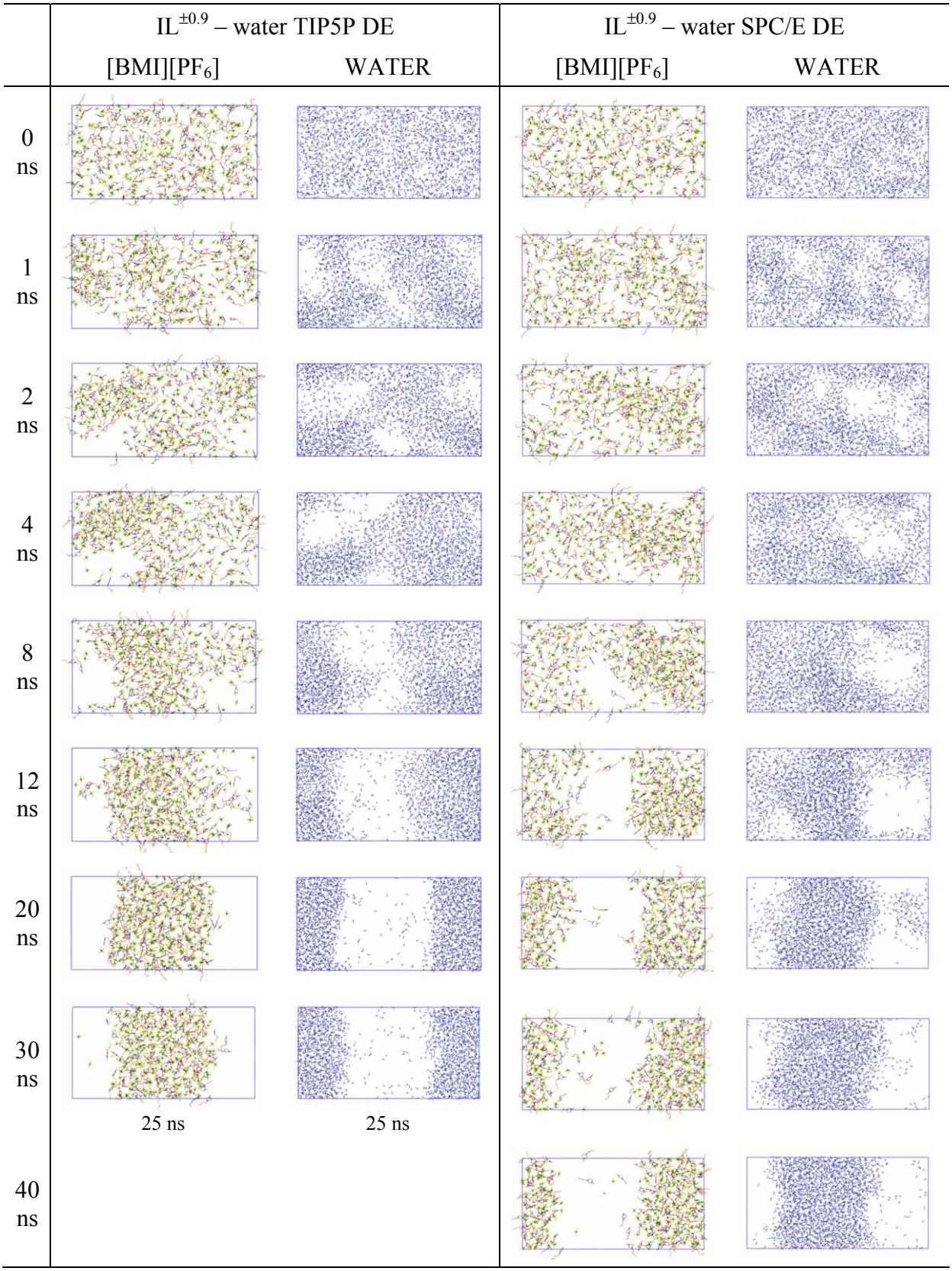


Figure S4: Phase separation of the randomly mixed IL – water liquids: $IL^{\pm 0.9}$ TIP5P and $IL^{\pm 0.9}$ SPC/E models.

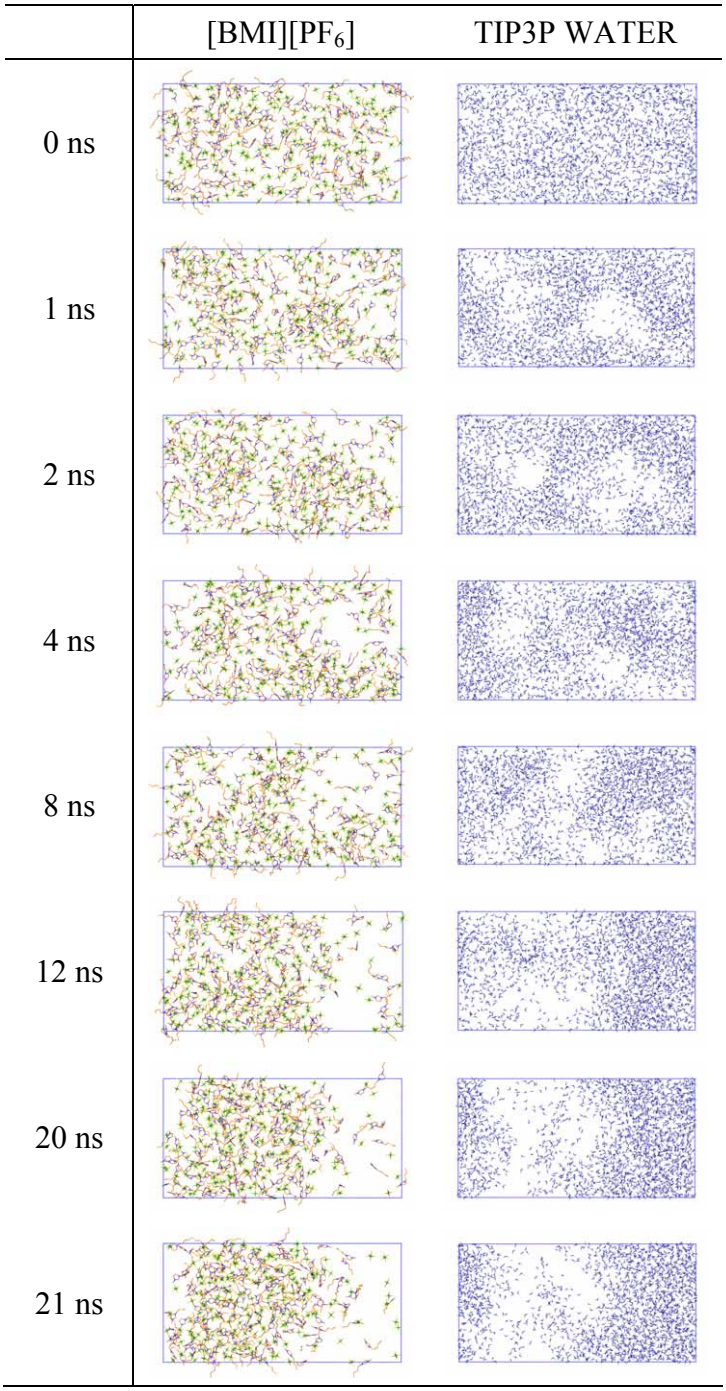


Figure S5: Phase separation of the randomly mixed $IL^{\pm 0.9}$ – water TIP3P liquids.

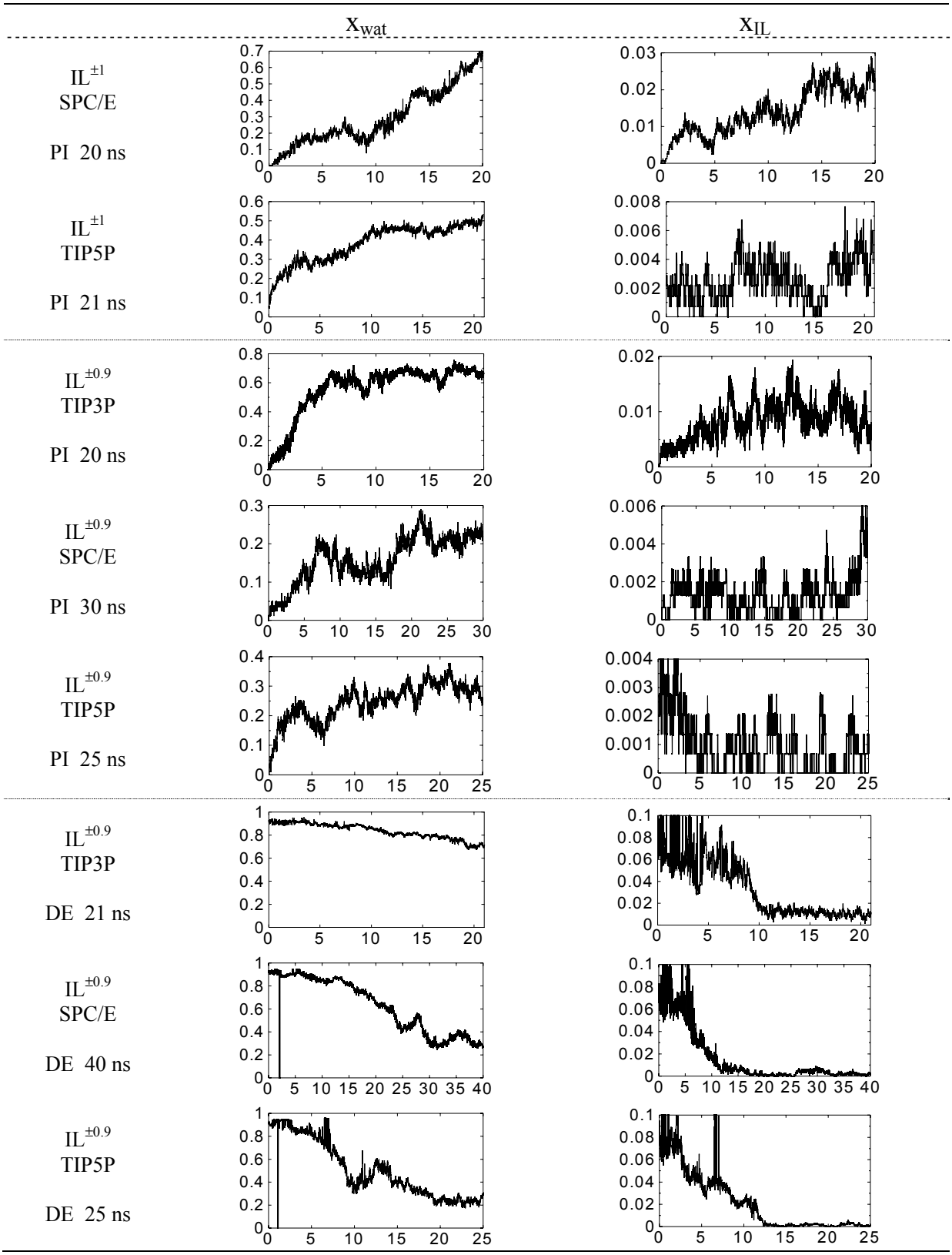


Figure S6: Molar fraction of water in IL (x_{wat}) and molar fraction of IL in water (x_{IL}) as a function of time (ns).

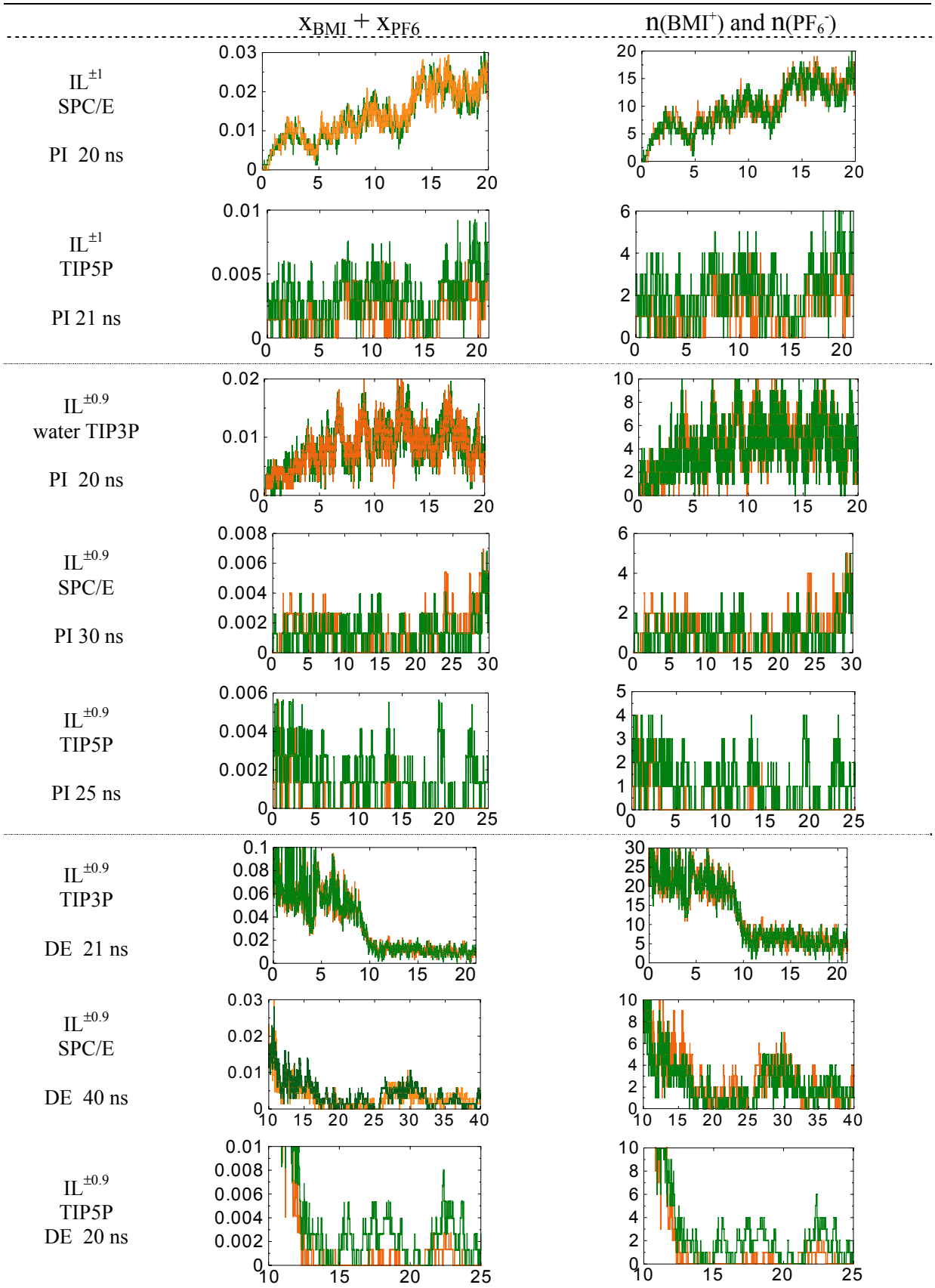


Figure S7: Molar fraction (left) and number of BMI^+ and PF_6^- in water (right) as a function of time (ns) (BMI^+ in orange and PF_6^- in green).

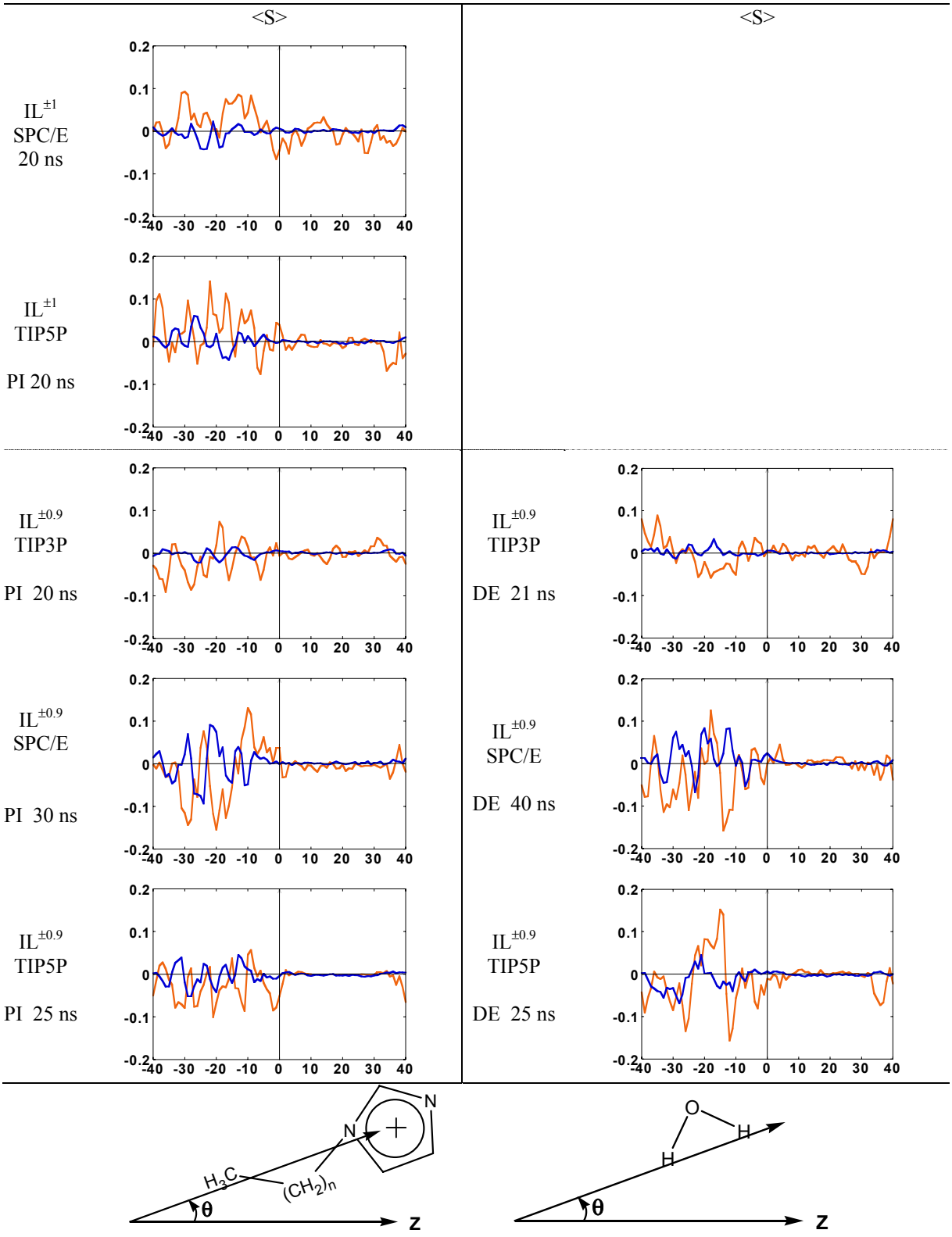


Figure S8: Order parameter *S* of imidazolium cations (orange curves) and water molecules (blue curves), as a function of their z-position (averages over the last 3 ns). Angle θ between the z-axis and the $N_2 - CH_3$ vector of the alkyl chain of BMI^+, or the H – H vector of the H_2O molecules.

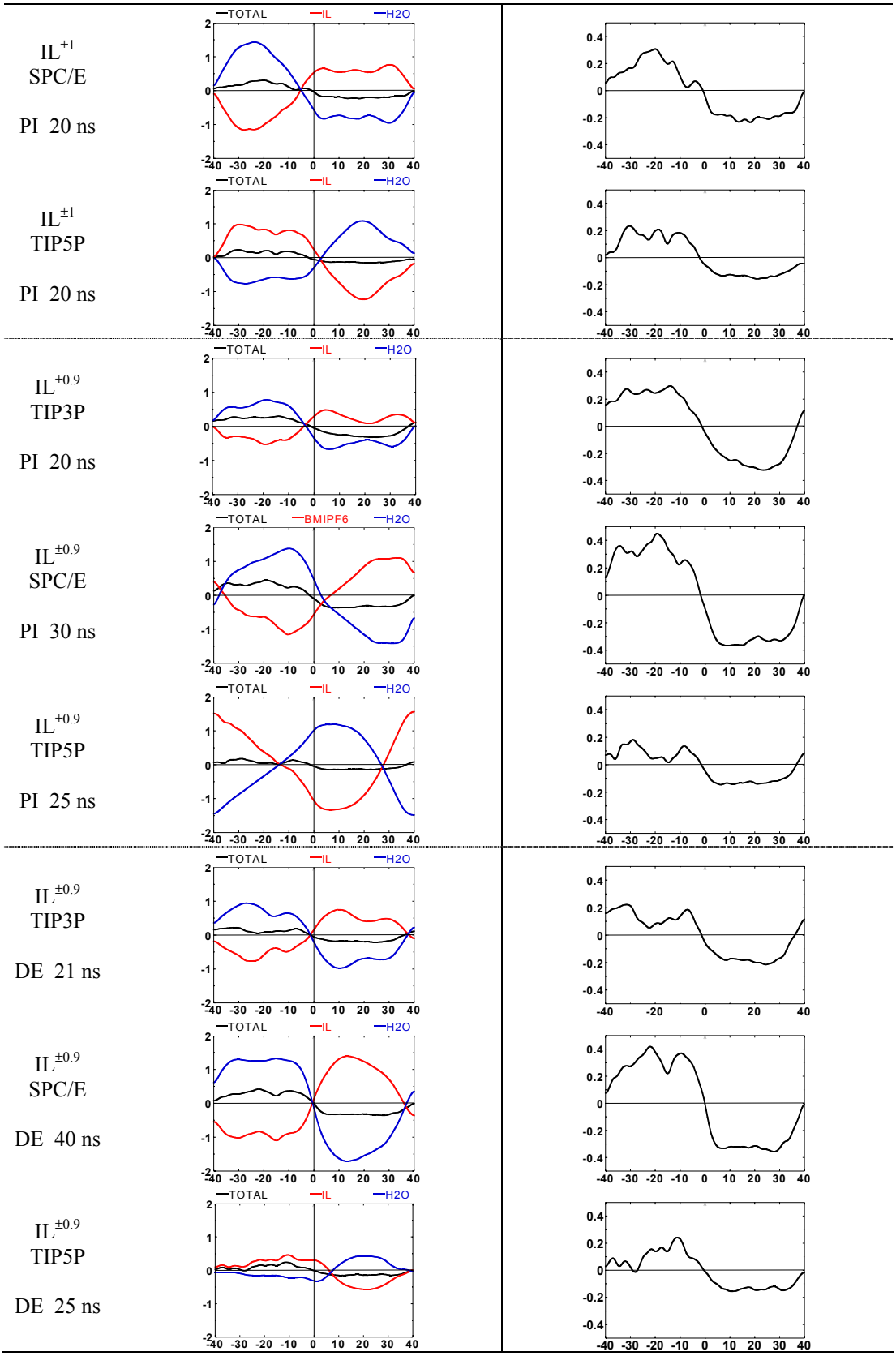


Figure S9: The electrostatic potential ϕ(z) ("TOTAL" in black) and its components $\phi(z)^{IL}$ (in red) + $\phi(z)^{wat}$ (in blue) components (in volts) as a function of the z-distance from the interface. Averages over the last 1 ns of dynamics. The ϕ(z) potential is also displayed separately in the right column.

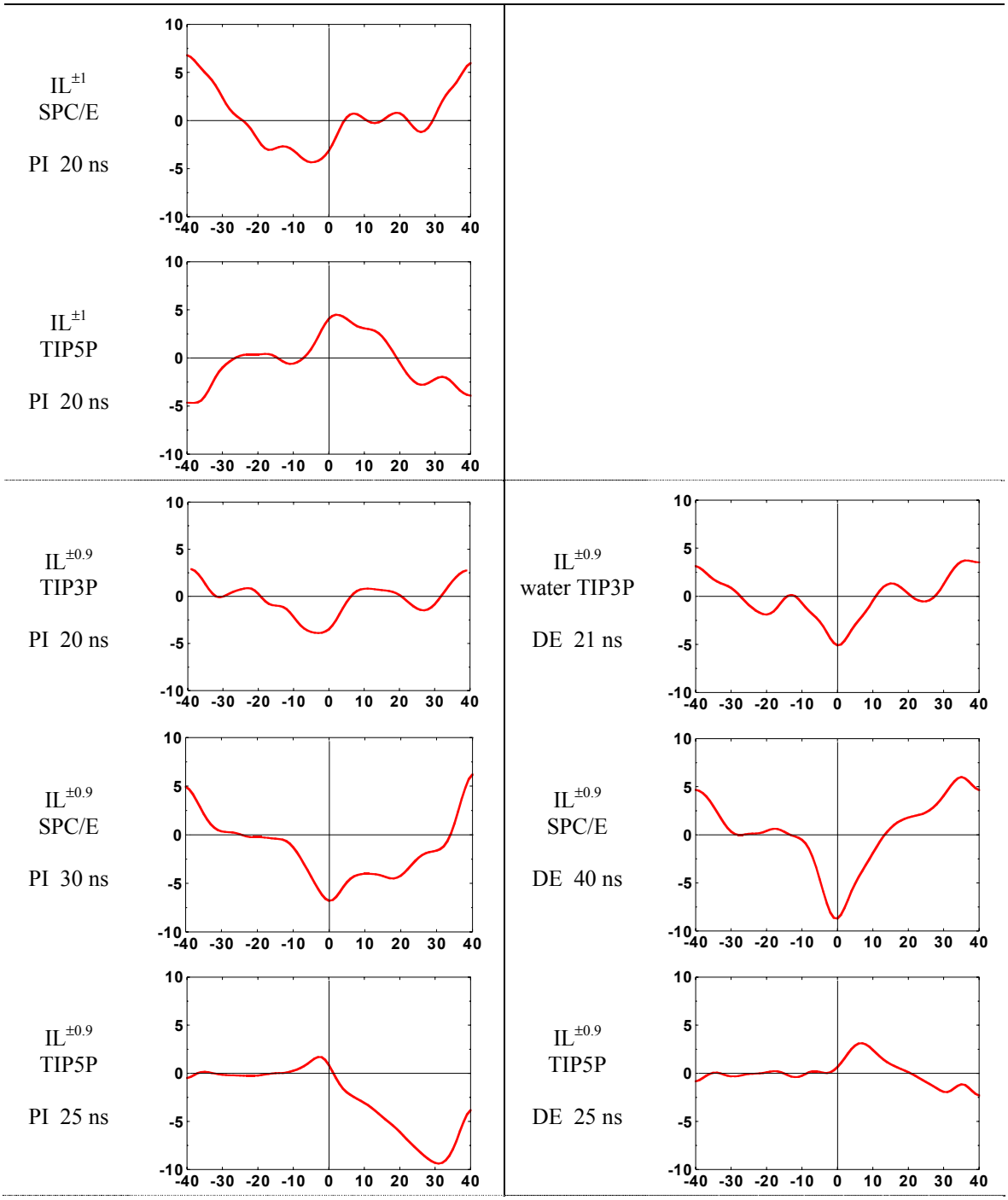
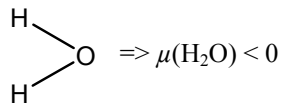
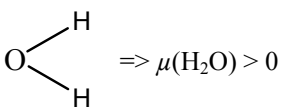


Figure S10: Total z-component of the H_2O dipoles as a function of the distance from the interface. Average over the last ns.



$\Rightarrow \mu(H_2O) < 0$



$\Rightarrow \mu(H_2O) > 0$