

## Supplementary Materials.

Table S1: Average numbers of “extracted” species in the MD simulations "at 400 K" (30 ns at 400 K, followed by 3 ns at 300 K). Species beyond 8 Å from the interface; averages calculated during the last 2 ns of dynamics.

Figure S1: [BMI][Tf<sub>2</sub>N] / "pH neutral" water systems without TBP (left) and with TBP (right). Lines 1 to 4: snapshots highlighting specific solutes. Bottom: density curves of BMI<sup>+</sup> in red, Tf<sub>2</sub>N<sup>-</sup> in green, water in blue, TBP in orange.

Figure S2: [BMI][Tf<sub>2</sub>N] / PTA<sup>mix</sup> systems without TBP (left) and with TBP (right). Lines 1 to 5: snapshots highlighting specific solutes. Bottom: density curves of BMI<sup>+</sup> in red, Tf<sub>2</sub>N<sup>-</sup> in green, water in blue, TBP in orange, HTcO<sub>4</sub> in red, H<sub>3</sub>O<sup>+</sup> in blue and TcO<sub>4</sub><sup>-</sup> in green.

Figure S3: [BMI][Tf<sub>2</sub>N] / PTA<sup>ionic</sup> systems without TBP (left) and with TBP (right). Lines 1 to 5: snapshots highlighting specific solutes. Bottom: density curves of BMI<sup>+</sup> in red, Tf<sub>2</sub>N<sup>-</sup> in green, water in blue, TBP in orange, H<sub>3</sub>O<sup>+</sup> in blue and TcO<sub>4</sub><sup>-</sup> in green.

Figure S4: Number of extracted H<sub>2</sub>O (*in blue*), HA acid (*in red*) and H<sub>3</sub>O<sup>+</sup> (*in black*) molecules during the dynamics (time in ns).

Figure S5: [BMI][Tf<sub>2</sub>N] / H<sub>3</sub>O<sup>+</sup> Tf<sub>2</sub>N<sup>-</sup> system after 100 ns. Snapshots highlighting specific solvents and solutes. Bottom: density curves (BMI<sup>+</sup> in red, Tf<sub>2</sub>N<sup>-</sup> in green, water in blue, H<sub>3</sub>O<sup>+</sup> in black) calculated during the last 1 ns of the dynamics.

"400 K" System			In "bulk" IL				In "bulk" water	
			HA <sub>IL</sub>	A <sup>-</sup> <sub>IL</sub>	H <sub>3</sub> O <sup>+</sup> <sub>IL</sub>	H <sub>2</sub> O <sub>IL</sub>	BMI <sup>+</sup> <sub>aq</sub>	Tf <sub>2</sub> N <sup>-</sup> <sub>aq</sub>
NA	B		-	-	-	206	4	2
	C	TBP	-	-	-	242	4	2
	D <sup>mix</sup>		78	0	0	150	3	3
	D <sup>ionic</sup>		-	0	0	89	1	1
	E <sup>mix</sup>	TBP	50	1	24	90	9	0
	E <sup>ionic</sup>	TBP	-	0	24	50	12	0
PTA	F <sup>mix</sup>		54	1	3	250	9	8
	F <sup>ionic</sup>		-	1	1	114	3	1
	G <sup>mix</sup>	TBP	90	0	6	124	5	2
	G <sup>ionic</sup>	TBP	-	1	19	57	9	0

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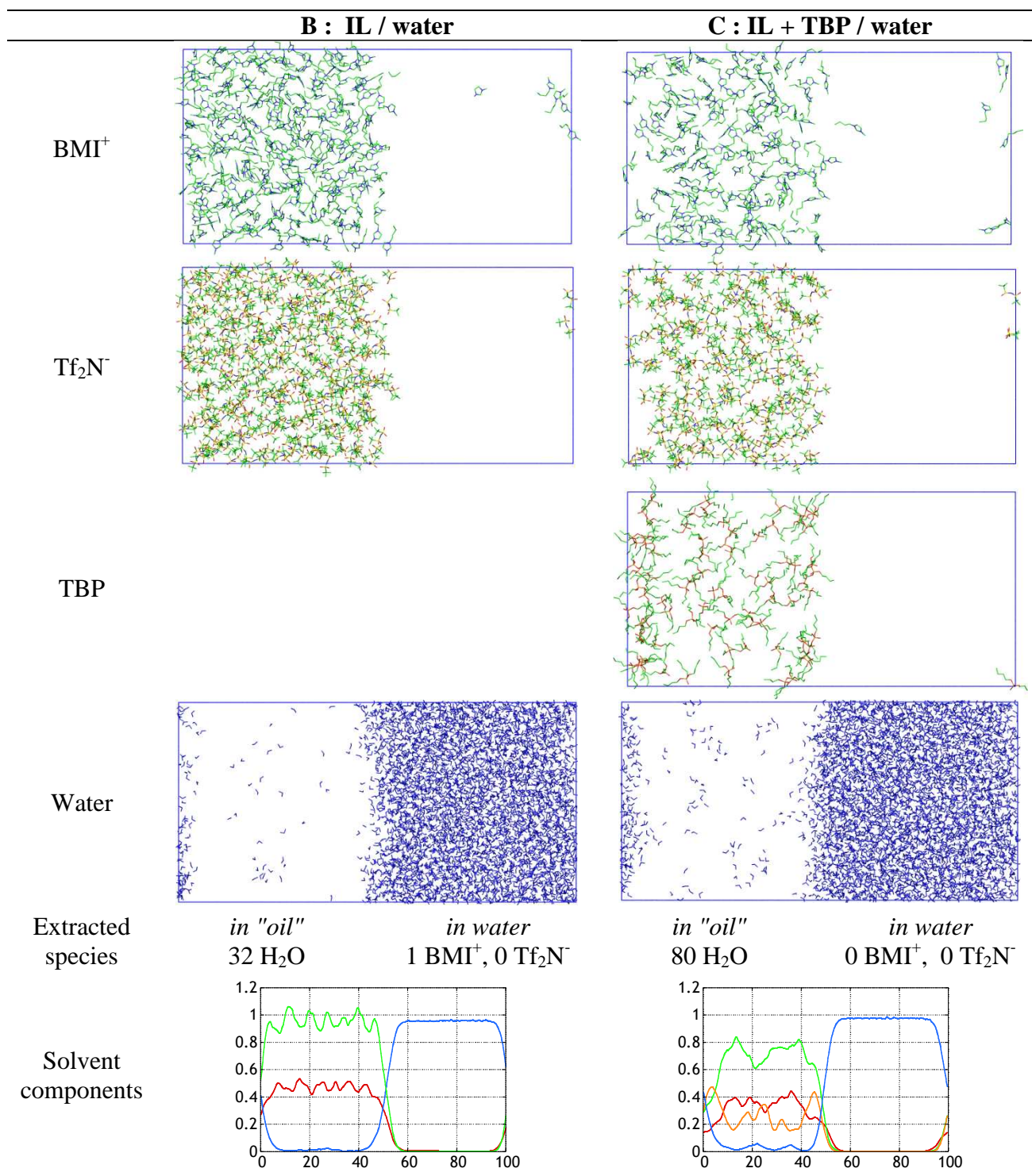


Figure S1: [BMI][Tf<sub>2</sub>N] / "pH neutral" water systems without TBP (left) and with TBP (right). Lines 1 to 4: snapshots highlighting specific solutes. Bottom: density curves of BMI<sup>+</sup> in red, Tf<sub>2</sub>N<sup>-</sup> in green, water in blue, TBP in orange.

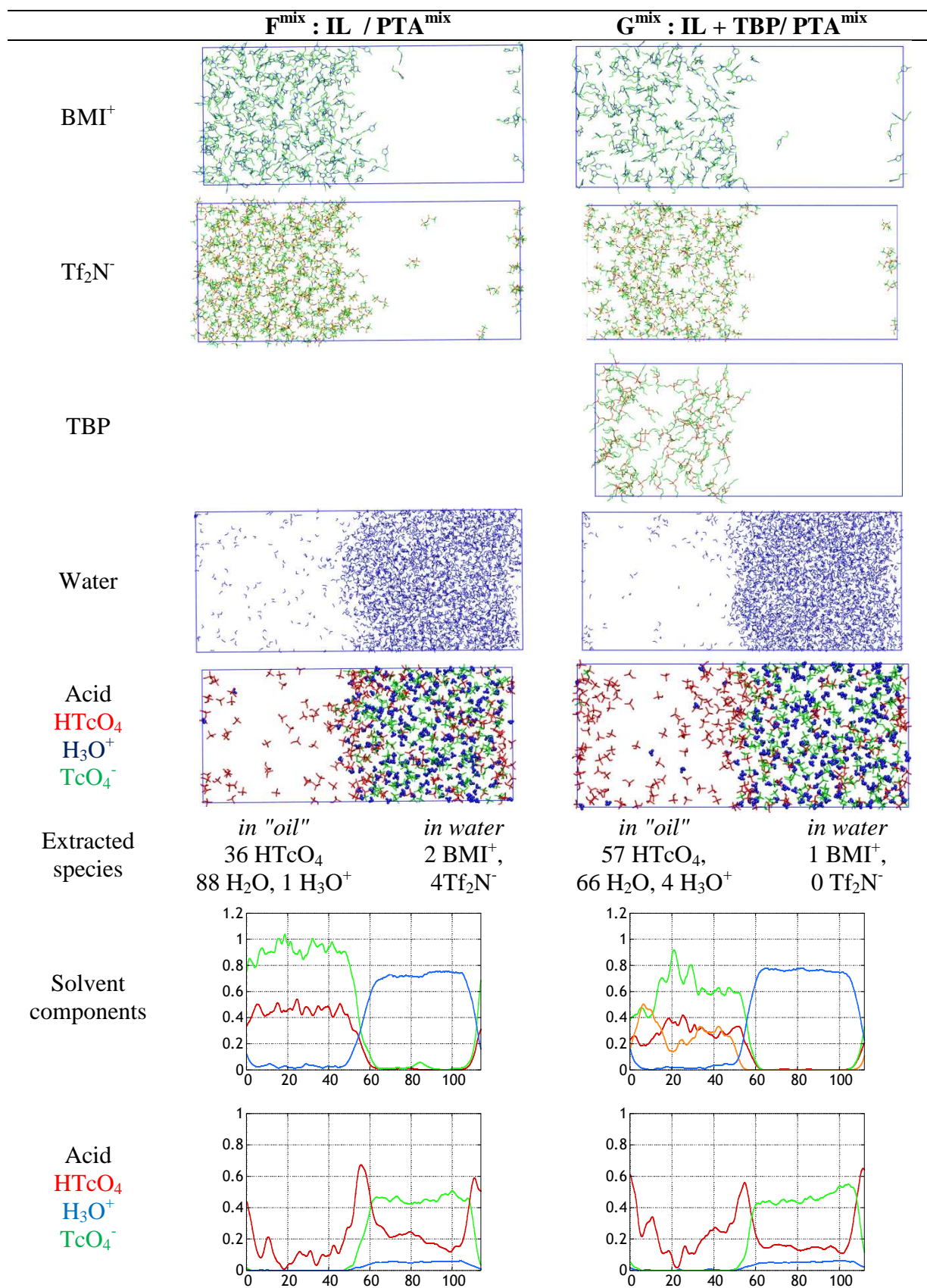


Figure S2: [BMI][Tf<sub>2</sub>N] / PTA<sup>mix</sup> systems without TBP (left) and with TBP (right). Lines 1 to 5: snapshots highlighting specific solutes. Bottom: density curves of BMI<sup>+</sup> in red, Tf<sub>2</sub>N<sup>-</sup> in green, water in blue, TBP in orange, HTcO<sub>4</sub> in red, H<sub>3</sub>O<sup>+</sup> in blue and TcO<sub>4</sub><sup>-</sup> in green.

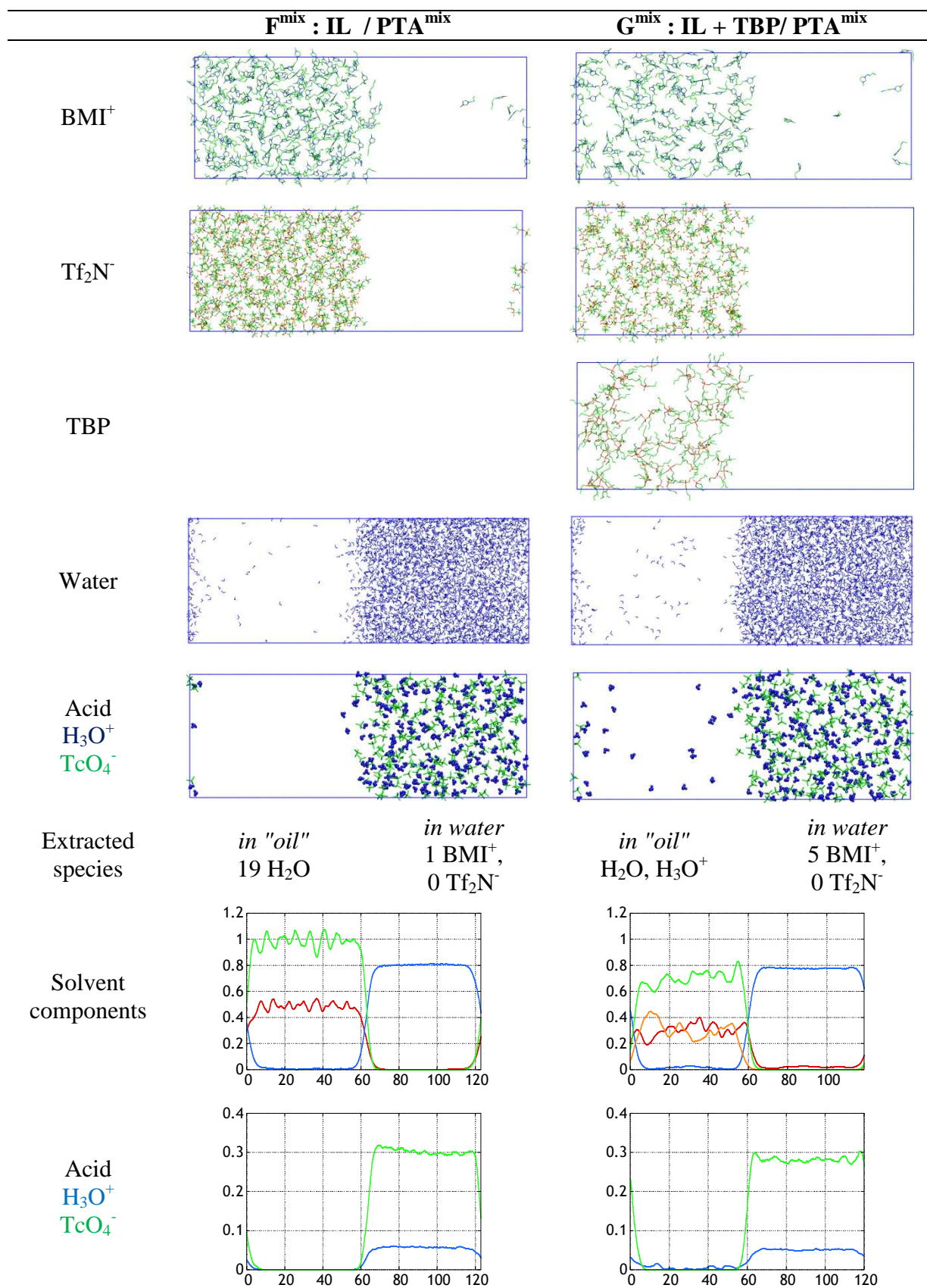


Figure S3: [BMI][Tf<sub>2</sub>N] / PTA<sup>ionic</sup> systems without TBP (left) and with TBP (right). Lines 1 to 5: snapshots highlighting specific solutes. Bottom: density curves of BMI<sup>+</sup> in red, Tf<sub>2</sub>N<sup>-</sup> in green, water in blue, TBP in orange, H<sub>3</sub>O<sup>+</sup> in blue and TcO<sub>4</sub><sup>-</sup> in green.

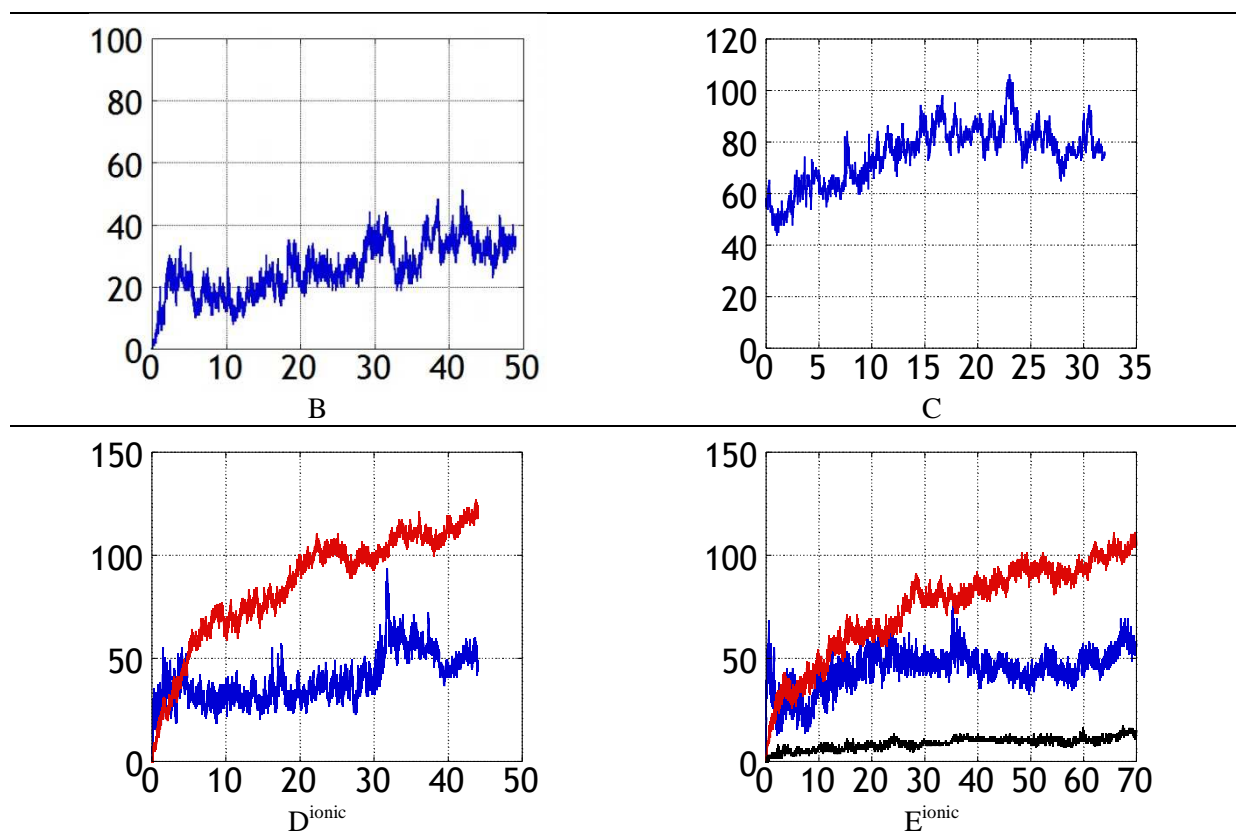
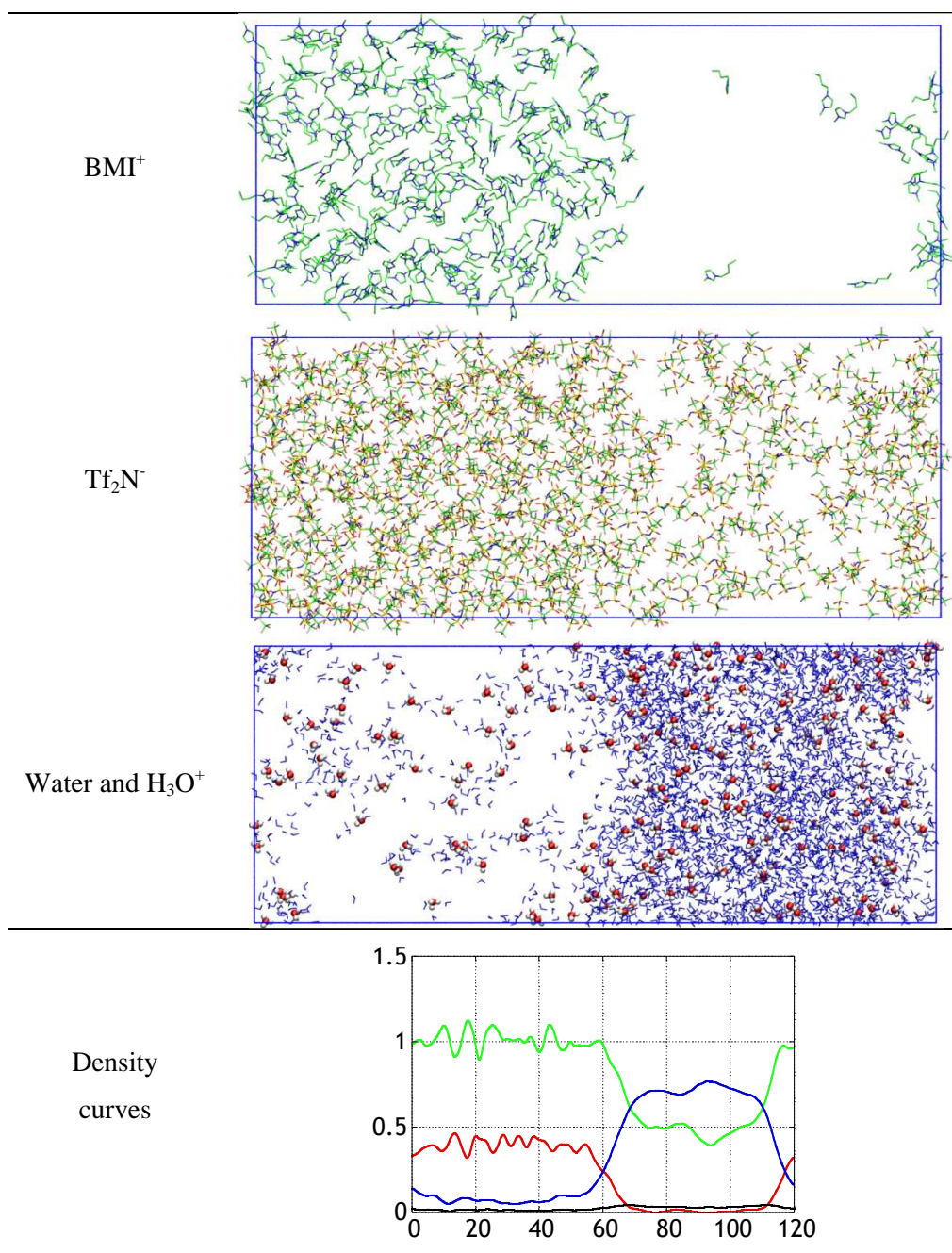


Figure S4: Number of extracted H<sub>2</sub>O (*in blue*), HA acid (*in red*) and H<sub>3</sub>O<sup>+</sup> (*in black*) molecules during the dynamics at 300 K (time in ns).



**Figure S5:** [BMI][Tf<sub>2</sub>N] / H<sub>3</sub>O<sup>+</sup> Tf<sub>2</sub>N<sup>-</sup> system after 100 ns. *Lines 1 to 3:* snapshots highlighting specific solvents or solutes. *Bottom:* density curves of BMI<sup>+</sup> in red, Tf<sub>2</sub>N<sup>-</sup> in green, water in blue, H<sub>3</sub>O<sup>+</sup> in black (calculated during the last 1 ns of the dynamics).

