Ligand	Initial position	Averaging time (ns)	Interaction energy ΔE (kcal/mol)		
			BTP/Oil	BTP/Water	BTP /Oil+Water
$cyMe_4BTP$	Pos 2	0.3	-39 ± 8	-31 ± 8	-70
$^{i}PrBTP$	Pos 1	0.3	-35 ± 12	-36 ± 5	-71
	Pos 2	0.3	-35 ± 8	-37 ± 7	-72
	Pos 3	0.3	-43 ± 8	-25 ± 5	-68
$^{t}But\text{-}^{i}PrBTP$	Pos 1	0.3	-42 ± 11	-32 ± 6	-74
	Pos 2	0.3	-37 ± 9	-38 ± 6	-75
	Pos 3	0.3	-41 ± 7	-34 ± 6	-75
$cyMe_4BTPH^+ NO_3^-$	Pos 2	0.3	-63 ± 12	-67 ± 13	-130
$^{t}But\text{-}cyMe_4BTPH^+ NO_3^-$	Pos 2	1.3	-67 ± 11	-65 ± 14	-132
$^{i}PrBTPH^+ NO_3^-$	Pos 1	1.5	-62 ± 12	-83 ± 13	-145
	Pos 2	1.5	-54 ± 13	-75 ± 28	-129
	Pos 3	1.5	-47 ± 19	-87 ± 16	-134
$^{t}But\text{-}^{i}PrBTPH^+ NO_3^-$	Pos 1	1.5	-63 ± 12	-58 ± 30	-121
	Pos 2	1.5	-48 ± 15	-91 ± 17	-139
	Pos 3	1.5	-53 ± 20	-76 ± 23	-129
$Oct\text{-}^{i}PrBTPH^+ NO_3^-$	Pos 2	0.3	-61 ± 12	-79 ± 11	-140

Table S1. Substituted single BTP and $BTPH^+$ ligands at the OCT-HEX / Water interface. Average interaction energies ΔE (kcal/mol) between BTP(H^+) and the liquids

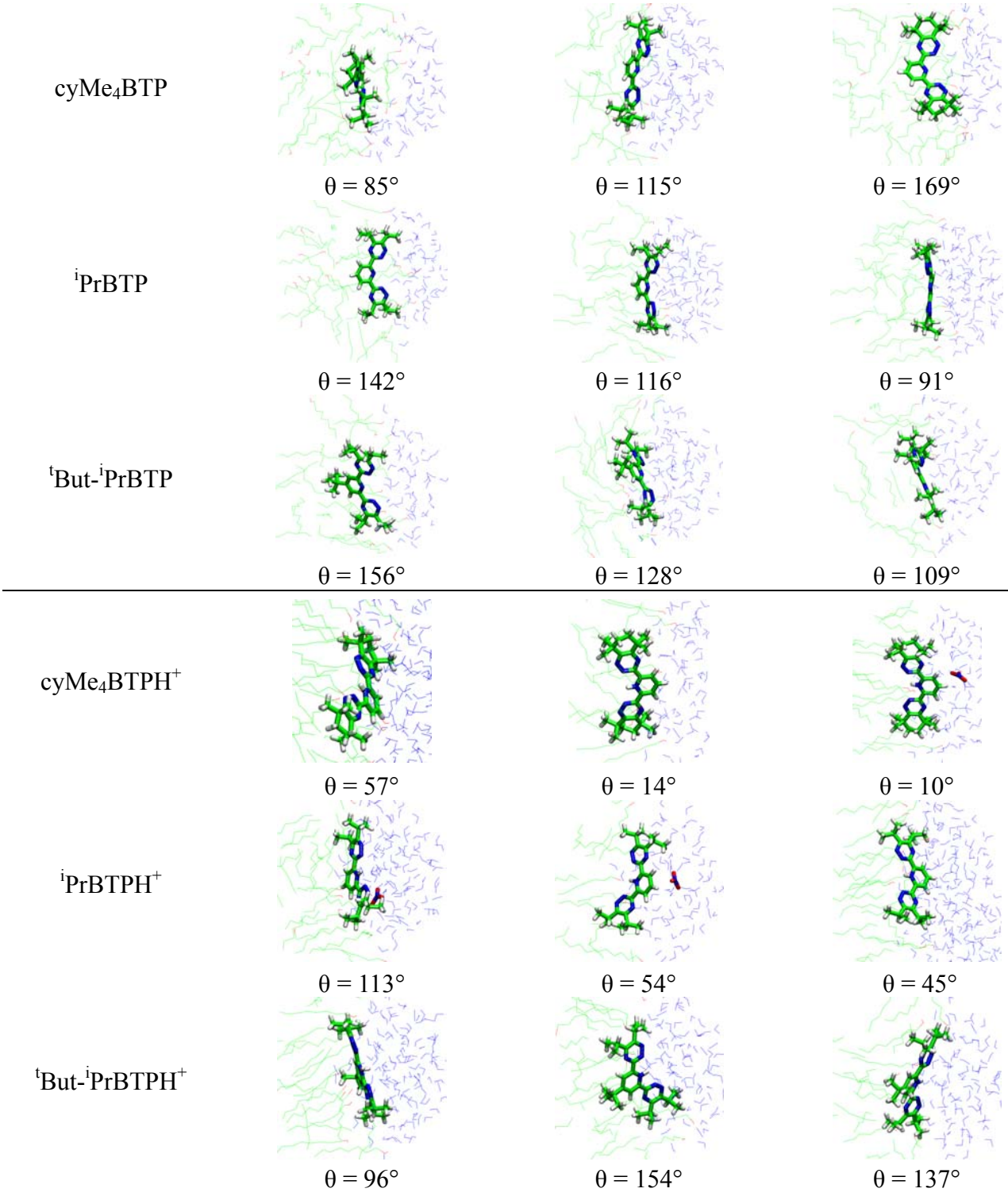


Figure S1 : Snapshots of typical orientations of single R-BTP and R-BTPH$^+$ at the OCT-HEX /water interface along the dynamics starting with Pos 2 ($\theta_0 = 90°$).

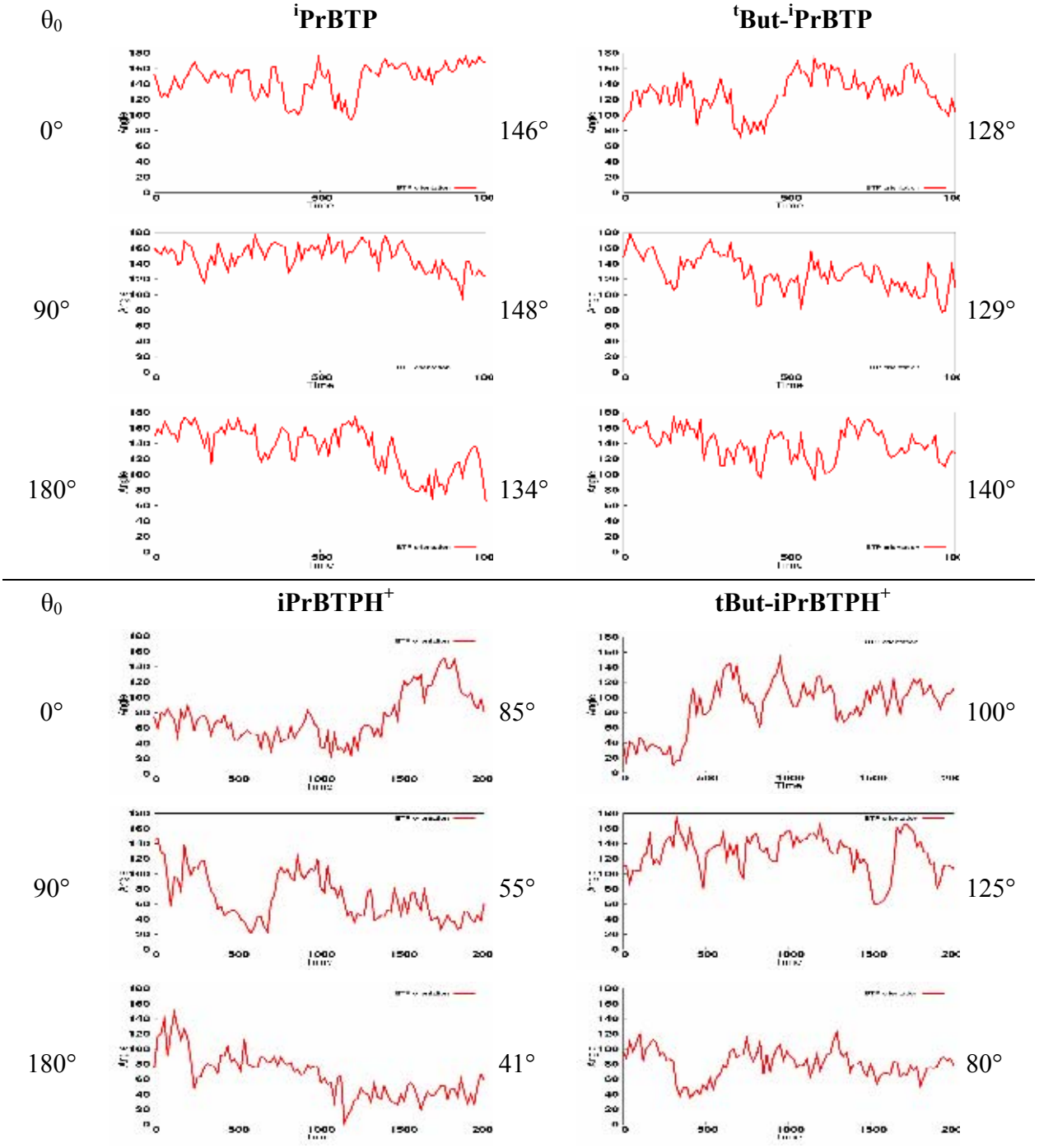


Figure S2 : Orientation of single R-BTPs and $BTPH^+$s at the OCT-HEX / water interface. Time evolution (in ps) of θ for different initial orientations of N_{pyr} (θ_0 = 0, 90 or 180°) and average on the last ns of dynamics.

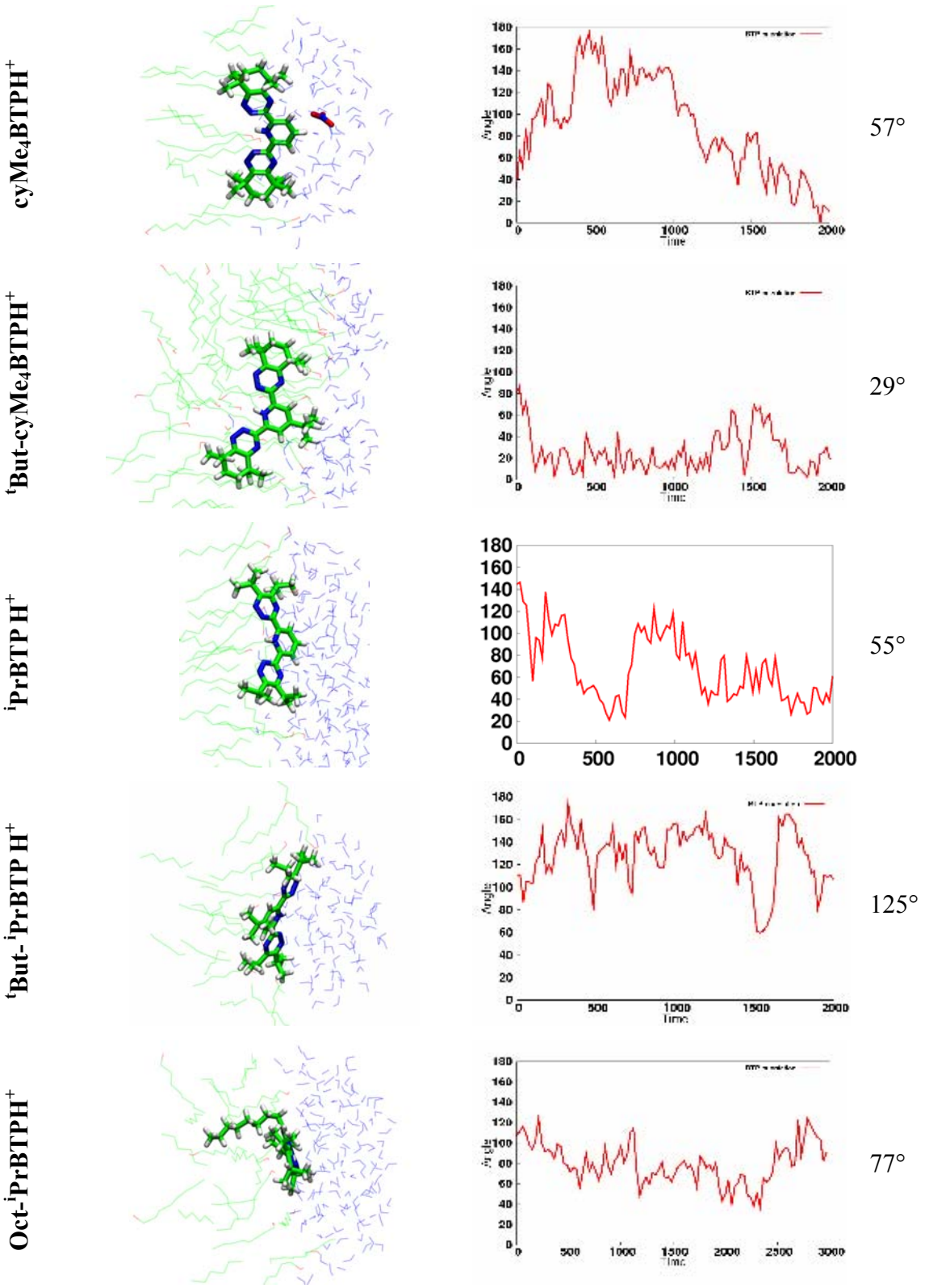


Figure S3 : R-CyMe$_4$BTPH$^+$ and R-^{i}PrBTPH$^+$ single ligands simulated at the OCT-HEX / water interface, starting with $\theta_0 = 90°$ (Pos2 orientation). Snapshots at the end of the dynamics and time evolution (in ps) of θ and average $\langle\theta\rangle$ on the last ns of dynamics.

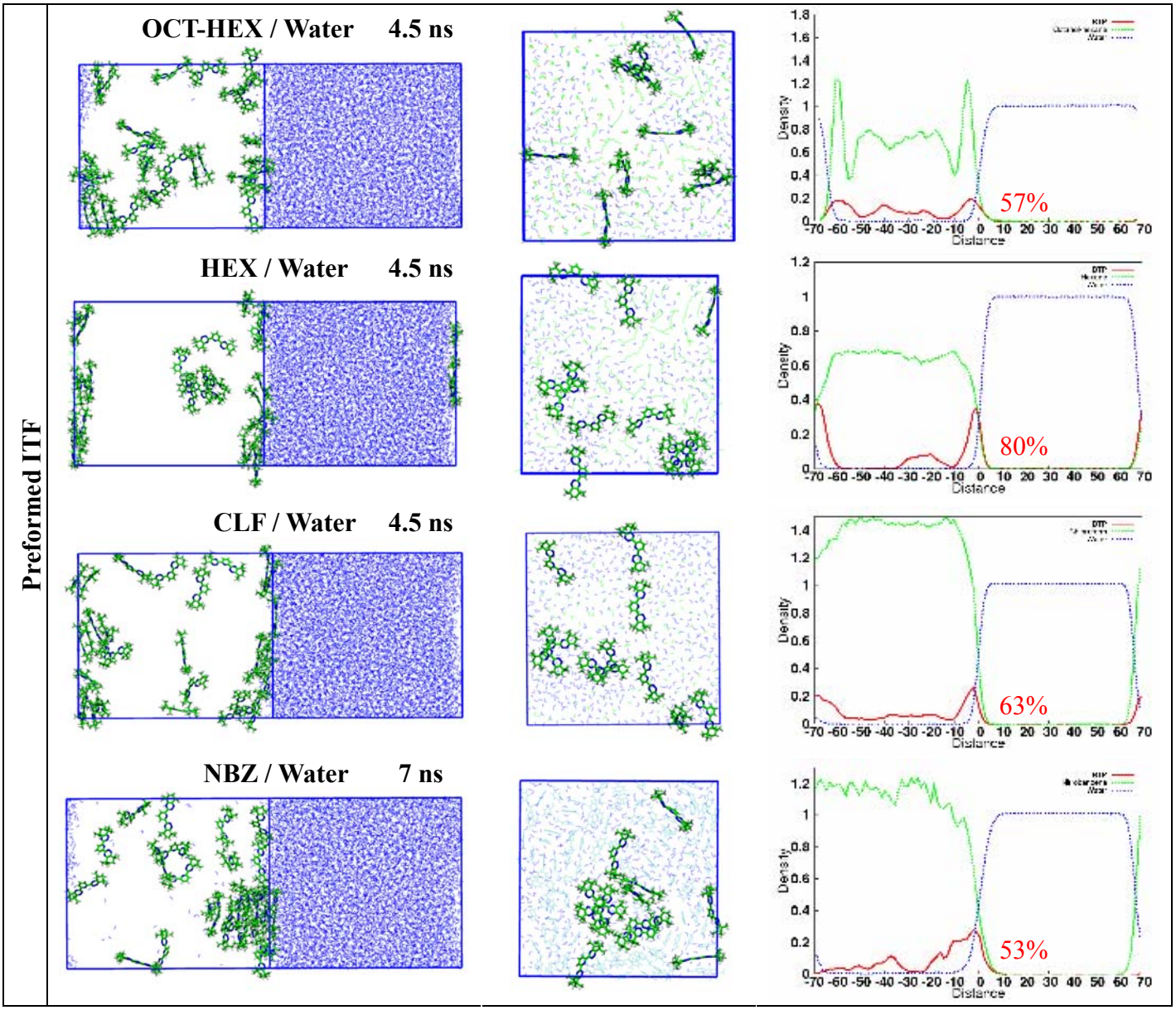


Figure S4 : 30 cyMe$_4$BTP at “oil“ / water preformed interfaces. *Left* : Final snapshots ("oil" hidden for clarity). *Middle*: Cross section of the interface (xy plane, Δz = 10 Å). *Right*: Density curves of BTP (red), “oil” (green) and water (blue) and percentage of cyMe$_4$BTPs within 5Å from the two interfaces.

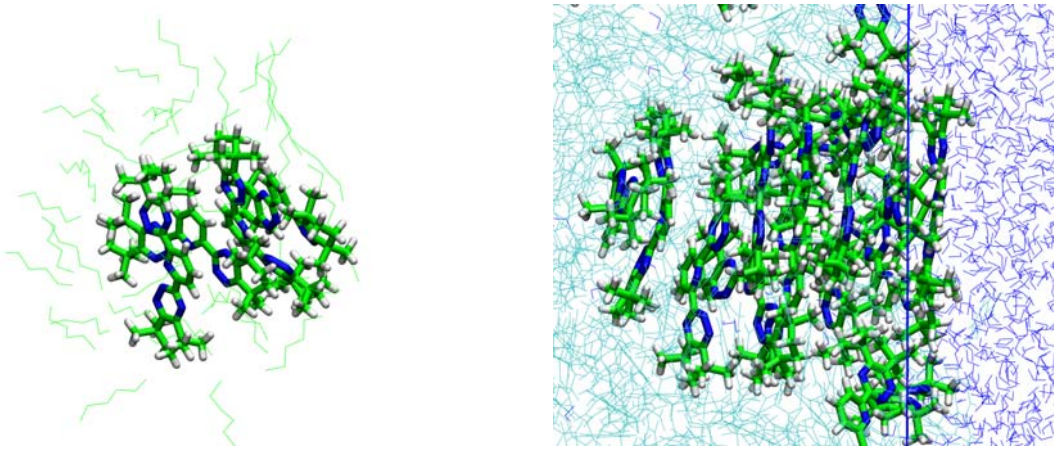


Figure S5 : Zoom on packed neutral $CyMe_4BTPs$ at the end of dynamics (juxtaposed liquids) in the hexane phase (*left*) and in the nitrobenzene phase (*right*).

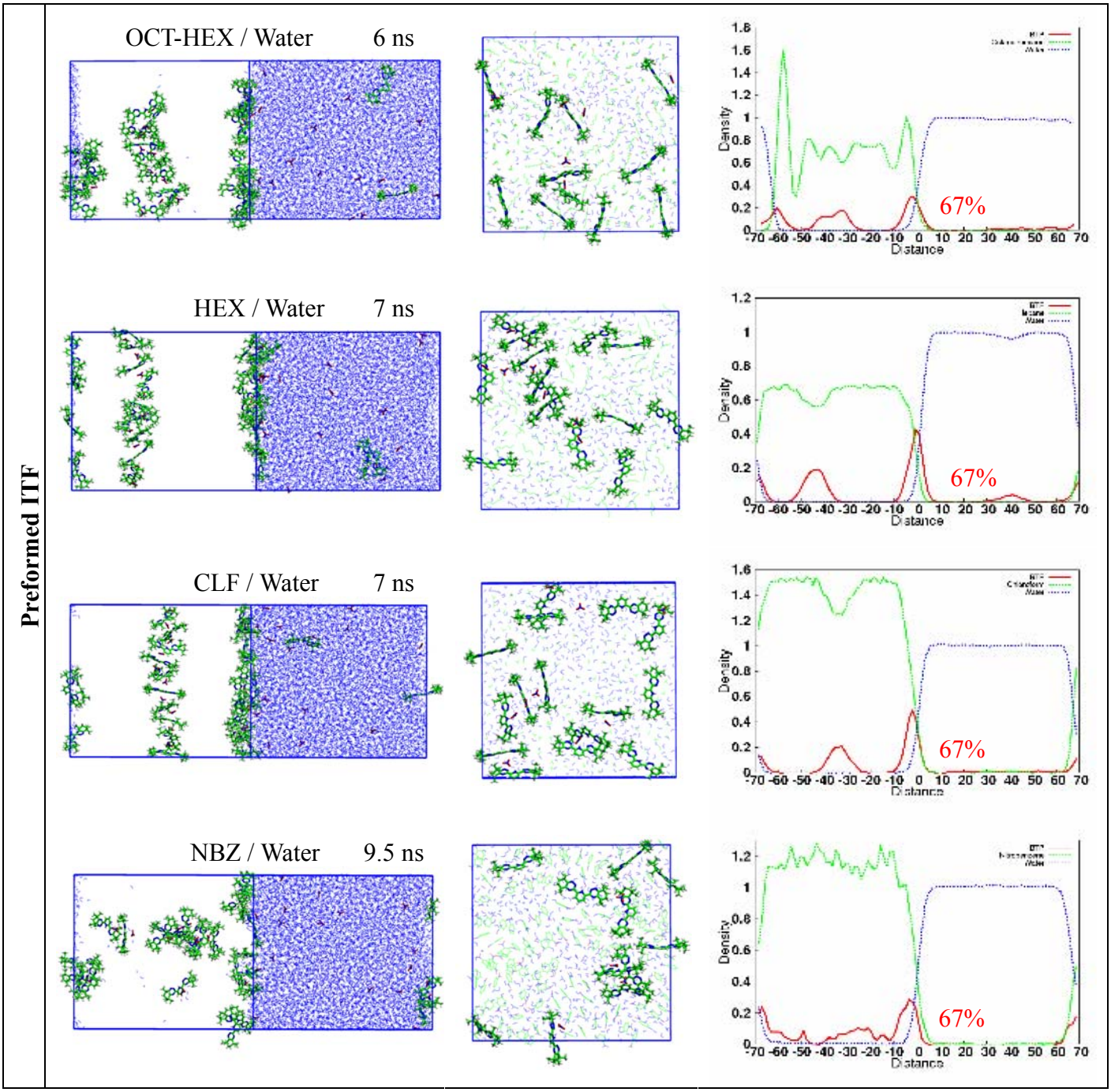
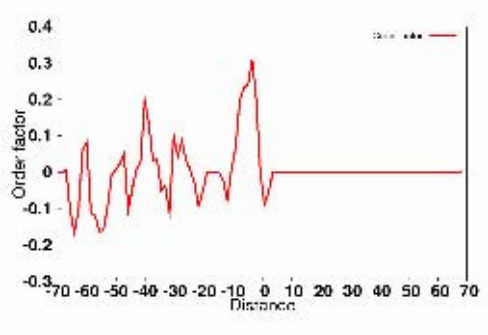
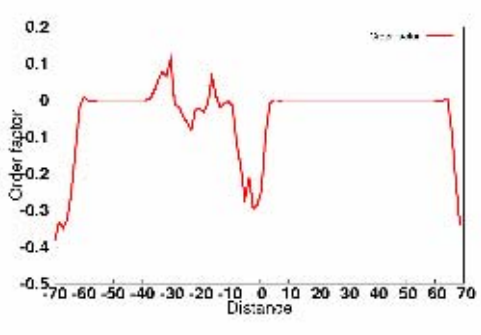


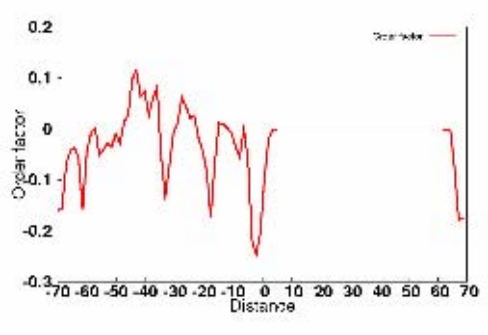
Figure S6 : 30 cyMe$_4$BTPH$^+$ NO_3^- at preformed "oil" / water interfaces. *Left* : Snapshots at the end of the simulations ("oil" phase omitted for clarity). *Middle*: Cross section of the different aqueous interfaces (xy plane, Δz = 10 Å) at the end of the dynamics. *Right*: Density curves of cyMe$_4$BTPH$^+$ (red), "oil" (green) and water (blue) and percentage of cyMe$_4$BTPH$^+$ within 5Å from the two interfaces.



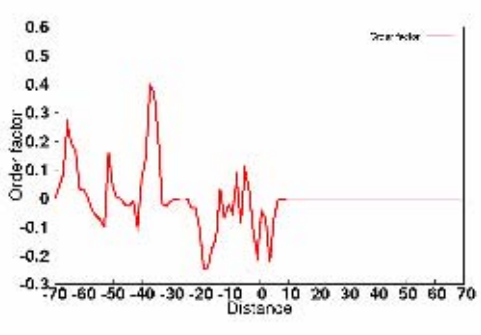
OCT-HEX / Water



HEX / Water

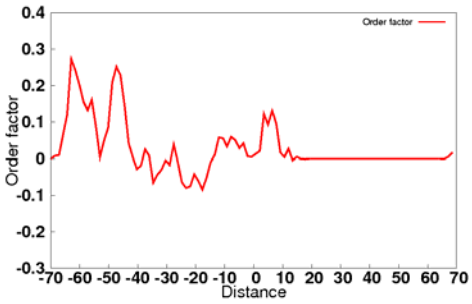


CLF / Water

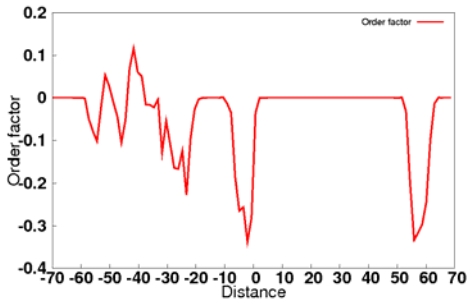


NBZ / Water

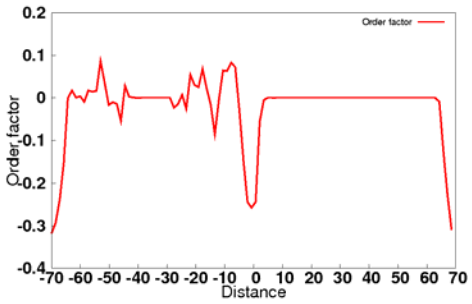
Demix



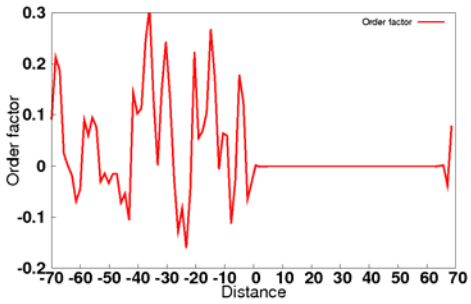
OCT-HEX / Water



HEX / Water



CLF / Water



NBZ / Water

Figure S7 : Order factor S(θ) of $CyMe_4BTP$ as a function of z position. Average over the 30 BTPs for the last 0.5 ns.

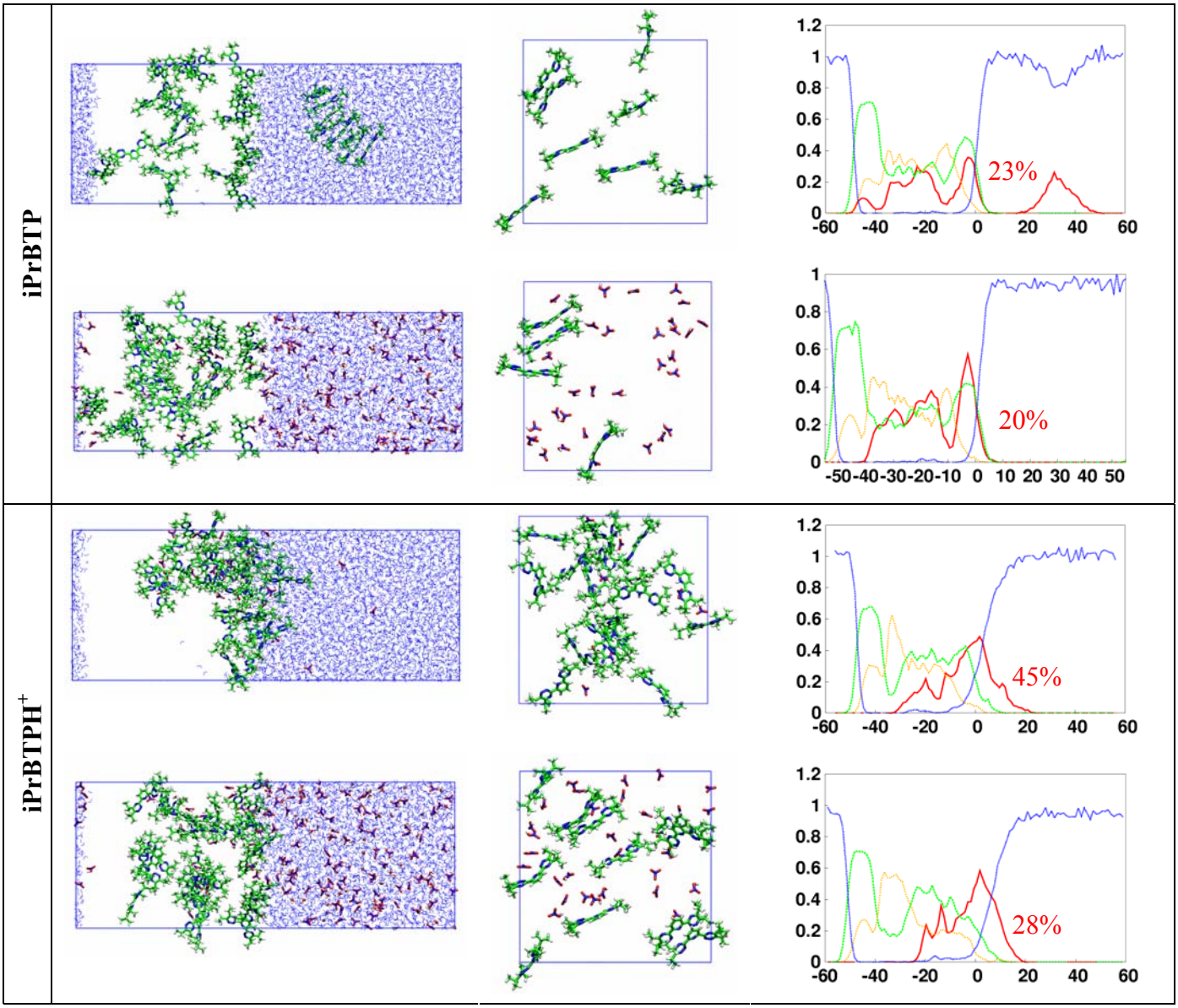


Figure S8 : 30 ^{i}PrBTP and 30 ^{i}PrBTPH^{+} NO_3^{-} at the OCT-HEX / water (*top*) and OCT-HEX / nitric acid (*bottom*) preformed interfaces. *Left* : Final snapshots ("oil" hidden for clarity). *Middle*: Cross section of the interface (xy plane, Δz = 10 Å). *Right*: Density curves of ^{i}PrBTP(H^{+}) (red), octanol (green), hexane (orange) and water (blue), and percentage of ^{i}PrBTP(H^{+}) within 5 Å from the two interfaces.