System	N_{oil} / N_{water}	Time (ns)	Box size ($Å^3$)
NEAT OCTANOL	865 / 0	2	61 x 61 x 61
OCTANOL – WATER INTERFACE			
Juxtaposed 50:50	411 / 3361	16	45 x 45 x 101
Demixing 50:50	411 / 3361	15	45 x 45 x 100
Demixing 50:50 (cubic box)	411 / 3361	15	59 x 59 x 59
Demixing 90:10 (cubic box)	788 / 723	5	60 x 60 x 60
Demixing 10:90 (cubic box)	129 / 5940	5	60 x 60 x 60
30 CCD^- Cs^+ IONS IN OCTANOL	735	5	59 x 59 x 59
30 CCD^- Cs^+ AT THE 50:50 MIXTURE			
Starting at the interface	443 / 3918	5	50 x 50 x 101
Starting in oil	332 / 4102	10	49 x 49 x 98
Starting in water	500 / 3571	14	51 x 51 x 101
30 CCD^- Cs^+ AT THE 90:10 MIXTURE	634 / 742	5	59 x 59 x 59
30 CCD^- 10 Eu^{3+} AT THE 50:50 MIXTURE	507 / 3517	20	50 x 50 x 101
$Eu(BTP)_3^{3+}$ COMPLEX AT THE CHLOROFORM – WATER INTERFACE			
$Eu(BTP)_3(NO_3)_3$ + 3 CMPO + 3 CCD^-, H_3O^+	903 / 4010	2	50 x 50 x 100
$Eu(BTP)_3(NO_3)_3$ + 12 BTP + 12 CMPO + 12 CCD^-, H_3O^+	791 /3697	3.4	50 x 50 x 100
$Eu(BTP)_3^{3+}$ COMPLEX AT THE OCATNOL – WATER INTERFACE			
$Eu(BTP)_3(NO_3)_3$ + 3 CMPO + 3 CCD^-, H_3O^+	464 / 4008	15	50 x 50 x 100
$Eu(BTP)_3(NO_3)_3$ + 12 CCD^-, H_3O^+	445 / 3928	15	50 x 50 x 99
$Eu(BTP)_3(NO_3)_3$ + 12 BTP + 12 CMPO	366 /3712	15	48 x 48 x 97
$Eu(BTP)_3(NO_3)_3$ + 12 BTP + 12 CMPO DEMIX CUBIC	368 / 3742	15	61 x 61 x 61
$Eu(BTP)_3(NO_3)_3$ + 12 BTP + 12 CMPO + 12 CCD^-, H_3O^+	367 / 3706	15	49 x 49 x 98
$Eu(BTP)_3(NO_3)_3$ + 12 BTP + 12 CMPO + 12 CCD^-, H_3O^+ DEMIX	367 / 3706	15	49 x 49 x 98
$Eu(BTP)_3(NO_3)_3$ + 12 BTP + 12 CMPO + 12 CCD^-, H_3O^+ DEMIX CUBIC	336 / 3597	15	61 x 61 x 61

Table S1: Characteristics of the simulated solutions: Number of solvent molecules, simulated time and box size.

	$Cs^+\cdots O_{oct}$	$Cs^+\cdots Cl_{CCD}$	$Cs^+\cdots Co_{CCD}$	$Co\cdots Cs^+$	$Co\cdots H_{oct}$
30 Cs^+, CCD$^-$ in octanol					
	4.0	3.4	1.8	1.8	13.7
	3.1 ; 4.1	*3.7 ; 5.6*	*6.9 ; 10.0*	*6.9 ; 10.0*	*id)*

	$Cs^+\cdots O_{oct}$	$Cs^+\cdots Cl_{CCD}$	$Cs^+\cdots Co_{CCD}$	$Cs^+\cdots O_{H2O}$
30 Cs^+, CCD$^-$ in the 50:50 mixture				
a)	0.8	1.7		5.9
	3.1 ; 4.1	*3.8 ; 5.6*	*id)*	*3.1 ; 4.1*
b)	2.0	2.4	1.5	3.4
	3.1 ; 4.1	*3.8 ; 5.6*	*6.9 ; 9.6*	*3.1 ; 4.1*
a)	1.2	1.3	0.9	5.8
	3.1 ; 4.2	*3.8 ; 5.6*	*6.9 ; 10.0*	*3.1 ; 4.1*
b)	2.7	2.8	1.7	2.3
	3.1 ; 4.2	*3.8 ; 5.6*	*6.9 ; 10.0*	*3.1 ; 4.2*
a)	0.9	0.8	0.8	6.6
	3.1 ; 4.0	*3.8 ; 5.4*	*7.0 ; 9.9*	*3.2 ; 4.1*
b)	3.1	1.1	0.8	3.3
	3.1 ; 4.1	*3.8 ; 5.3*	*7.0 ; 10.3*	*3.1 ; 4.2*
30 Cs^+, CCD$^-$ in the 90:10 mixture				
a)	1.7	1.8	1.2	4.8
	3.1 ; 4.2	*3.8 ; 5.6*	*6.9 ; 9.7*	*3.1 ; 4.1*
10 Eu^{3+}, 30 CCD$^-$ at the octanol – water interface				
a)	1.7			9.0
	4.7 ; 5.5	*id)*	*id)*	*2.5 ; 3.2*
b)	4.4			9.0
	4.7 ; 5.5	*id)*	*id)*	*2.5 ; 3.2*

Table S2: Average coordination numbers of M^{n+} cations and CCD$^-$ anions in neat octanol and in the octanol – water binary mixtures. They are obtained by integration of the first peaks of the RDF's whose maximum and integration distance are given in italics *(second line)*. a) Averages over all Cs^+ or Eu^{3+} ions. b) Averages over Cs^+ or Eu^{3+} ions in the octanol phase. *id)* value not reported because the peak is ill-defined.

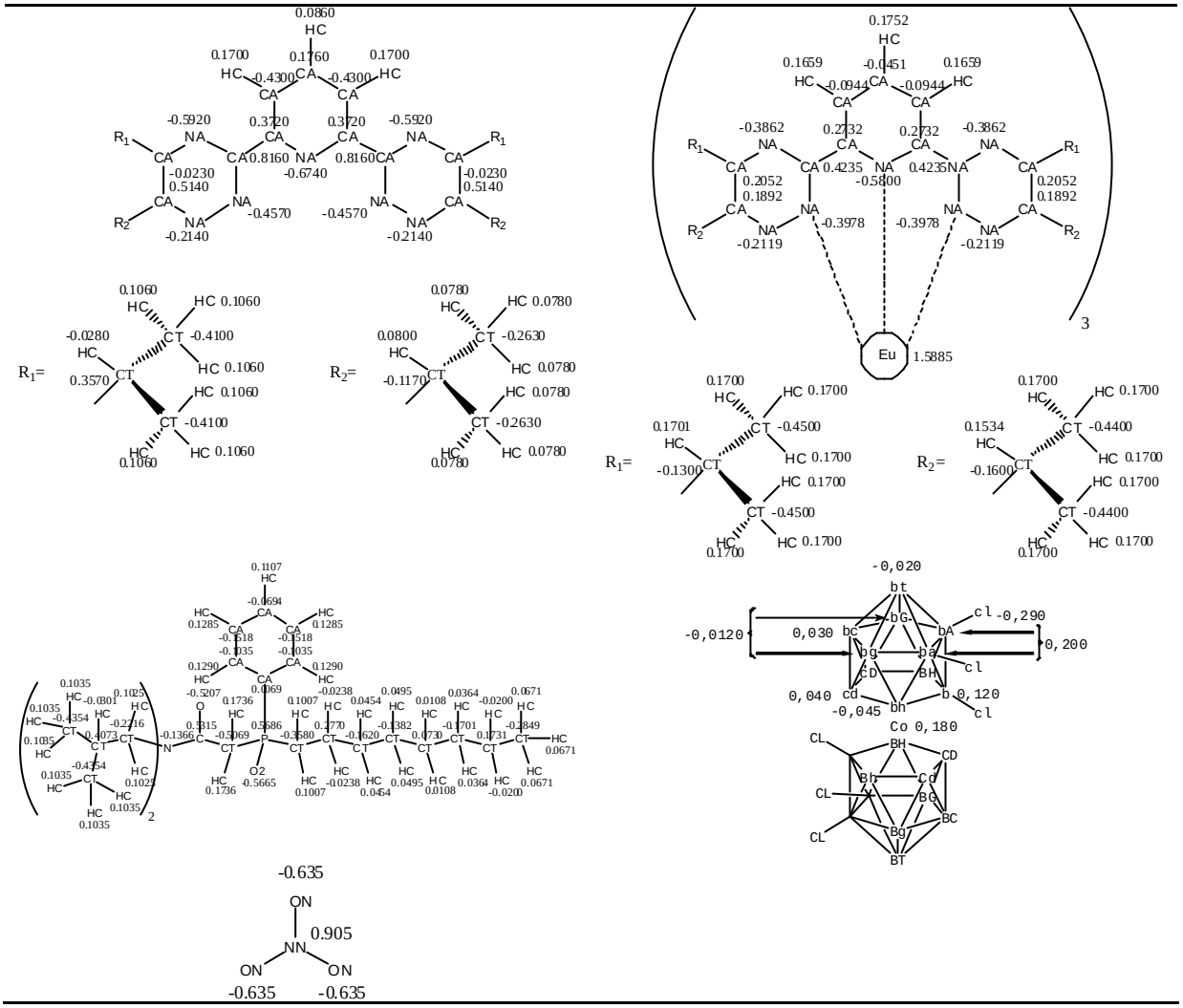


Figure S1: Atomic charges and AMBER atom types used to simulate the free BTP ligand, its $Eu(BTP)_3^{3+}$ complex, the CMPO ligand and the NO_3^- anion.

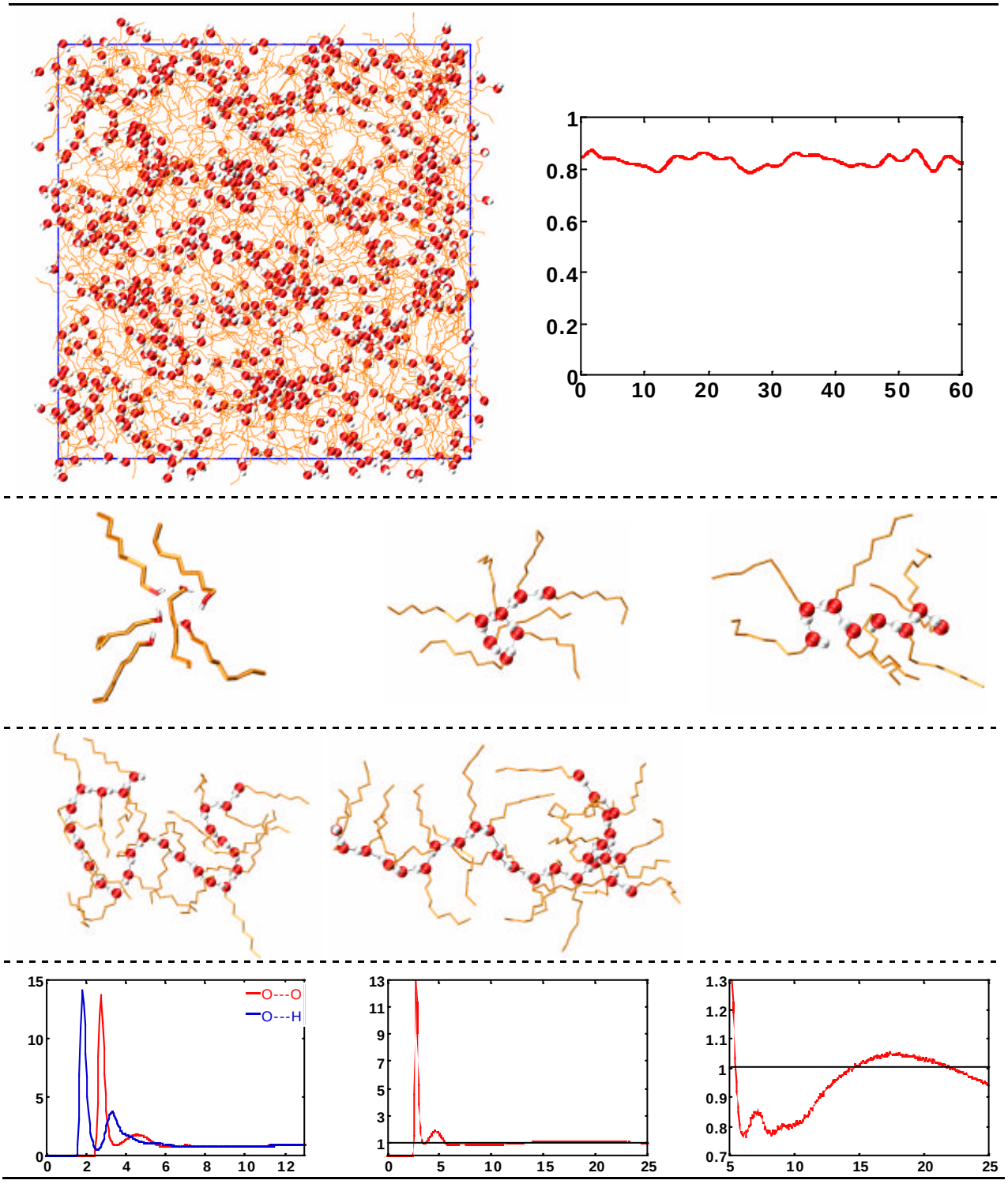


Figure S2: Neat octanol. Snapshot of the simulated box and density curve (*line 1*) and aggregates of 6 7, 8, 25 and 27 molecules (*lines 2 and 3*), and RDF's (*line* 4: O...O in red, and H…O in blue). See also Debolt, S. E. and Kollman, P. A.; *J. Am. Chem. Soc.* **1995**, *117*, 5316; MacCallum, J. L. and Tieleman, D. P. *J. Am. Chem. Soc.* **2002**, *124*, 15093.

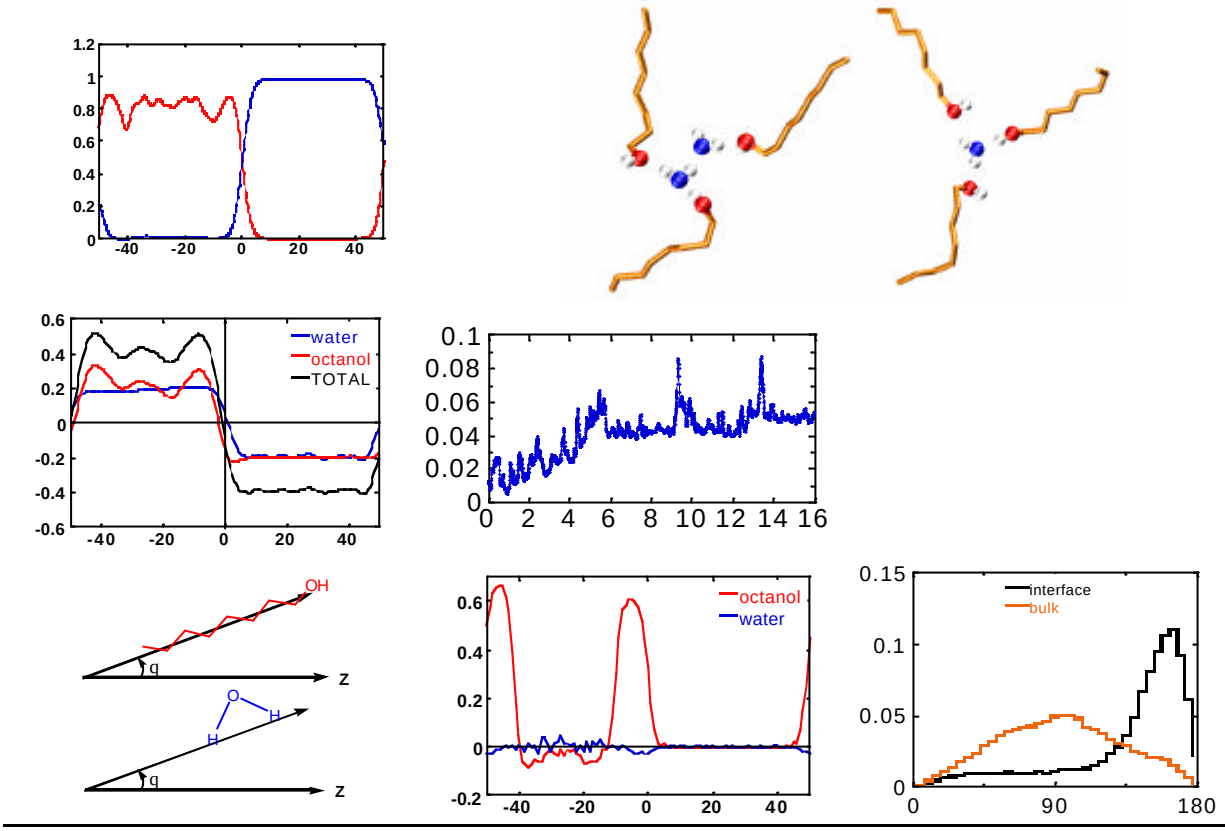


Figure S3: Octanol – water interface simulated from juxtaposed liquids. *First line:* average density curves and snapshots of a water monomer and dimer in the octanol phase. *Second line*: electrostatic potential $\phi(z)$ (volts) and molar fraction of water in octanol as a function of time. *Third line*: order parameter of octanol molecules as a function of their z-position, and $p(\theta)$ populations in bulk octanol and at the interface.

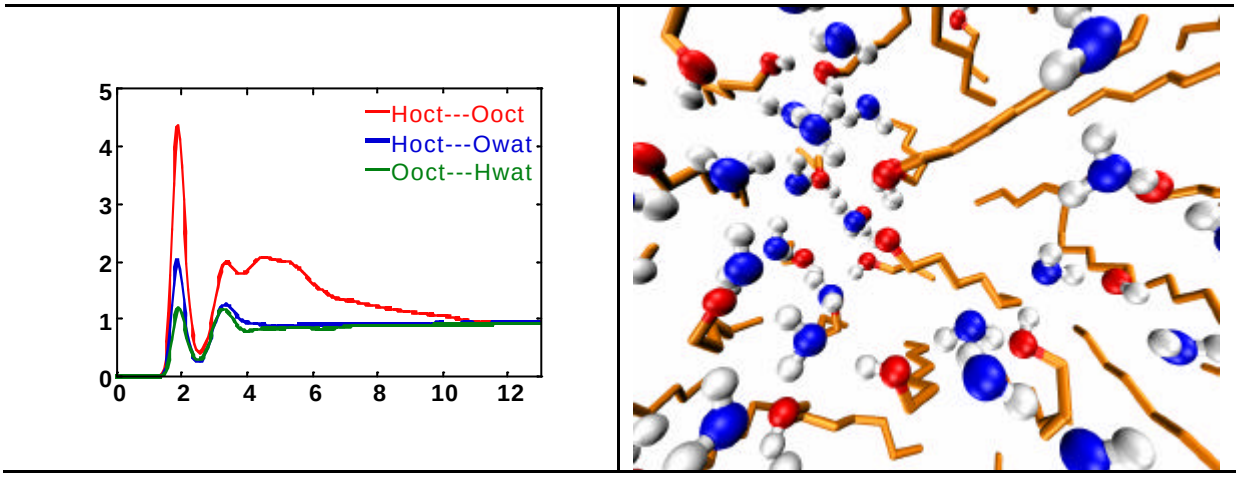
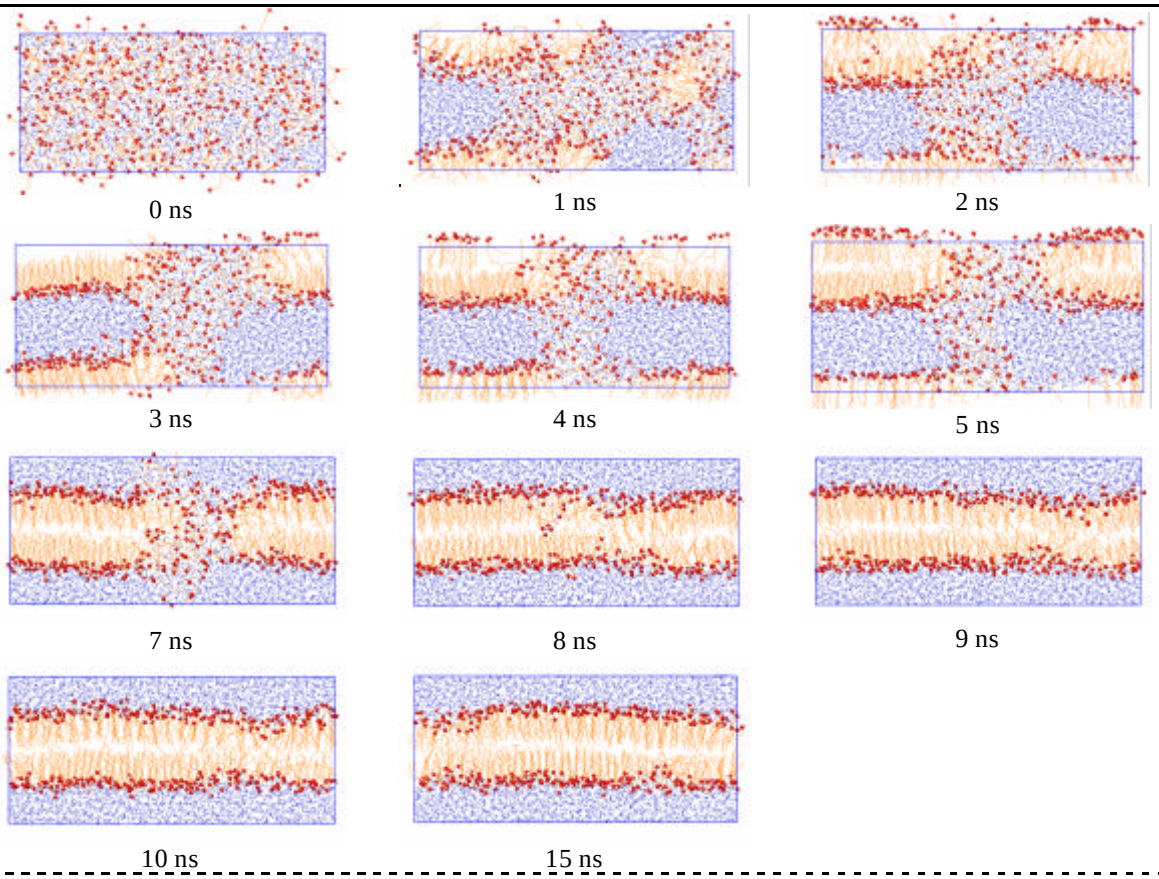
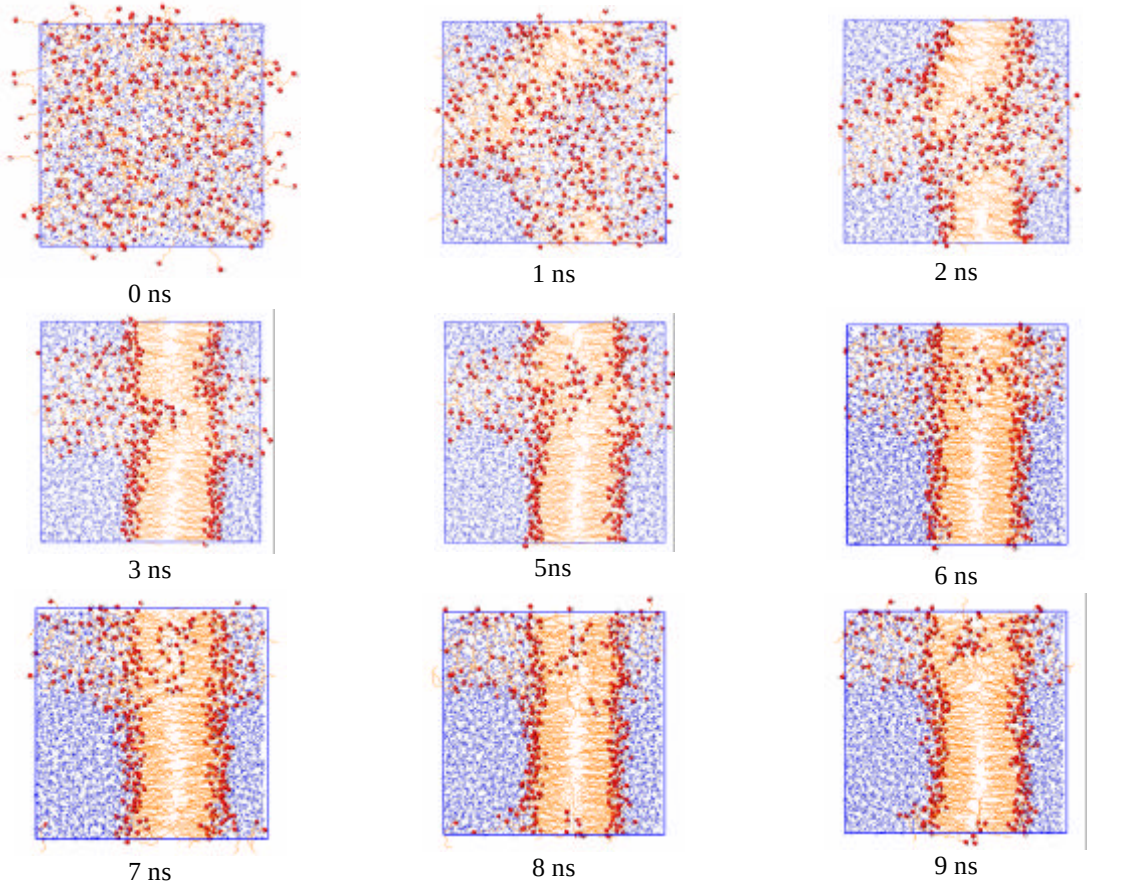


Figure S4: Solvation of octanol at the aqueous interface (z = ± 5Å): RDF's and typical snapshot.


0 ns
1 ns
2 ns
3 ns
4 ns
5 ns
7 ns
8 ns
9 ns
10 ns
15 ns


0 ns
1 ns
2 ns
3 ns
5ns
6 ns
7 ns
8 ns
9 ns

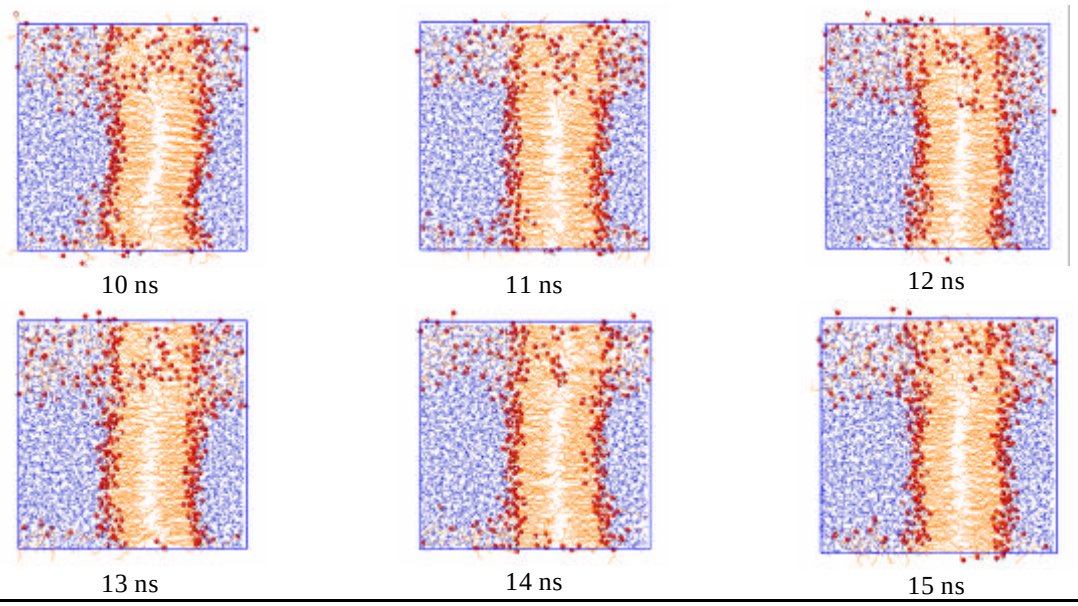


Figure S5: Phase separation of randomly mixed 50:50 octanol – water liquids. Snapshots at selected times in the "rectangular" box and in the cubic box.

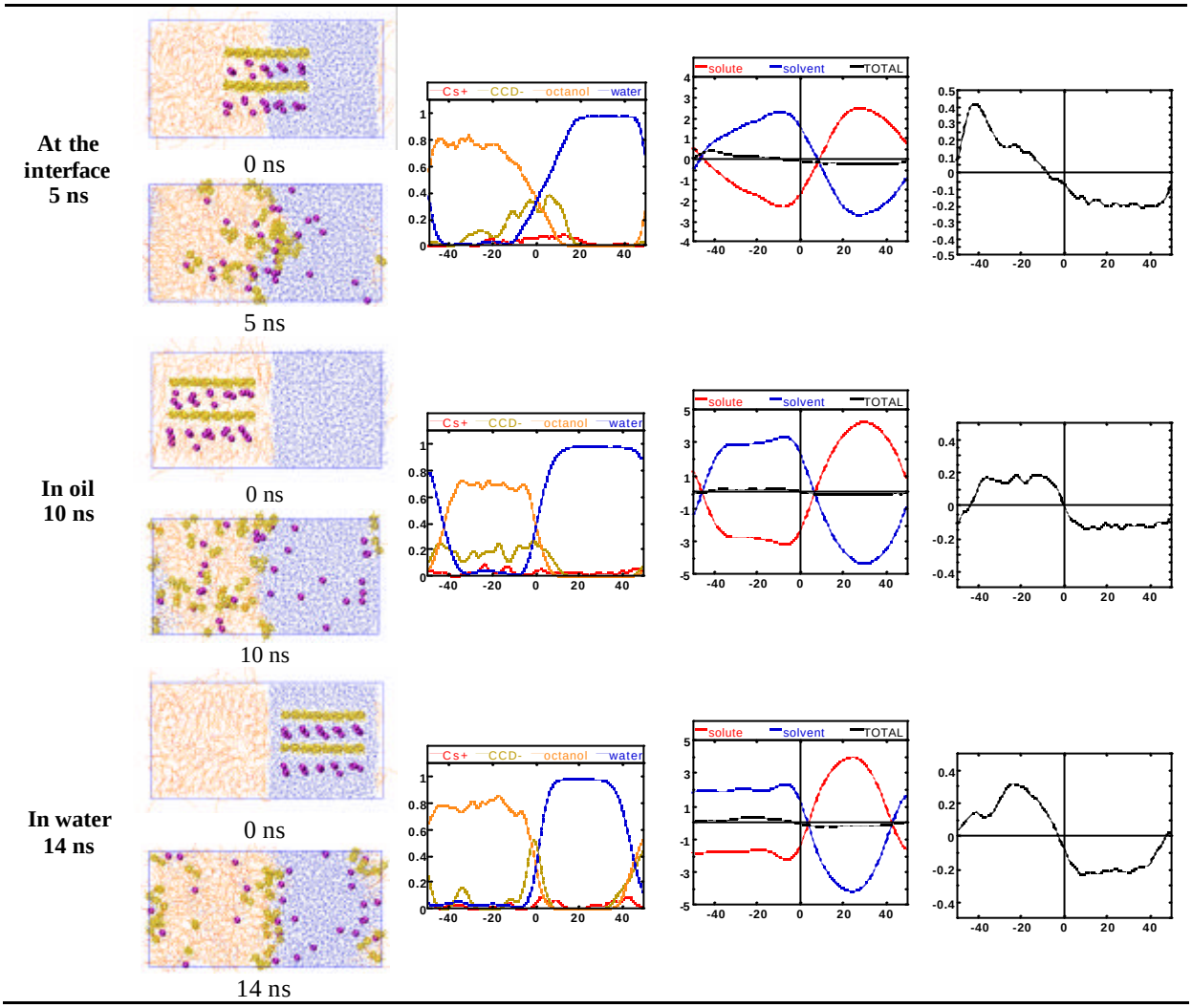


Figure S6: 30 CCD$^-$ Cs$^+$ ions at the octanol – water interface, simulated with the ions initially at the interface, or in octanol, or in water. Initial and final views, average densities as a function of the z-position, electrostatic potentials resulting from the solute (red), the solvents (blue) and their sum (black).

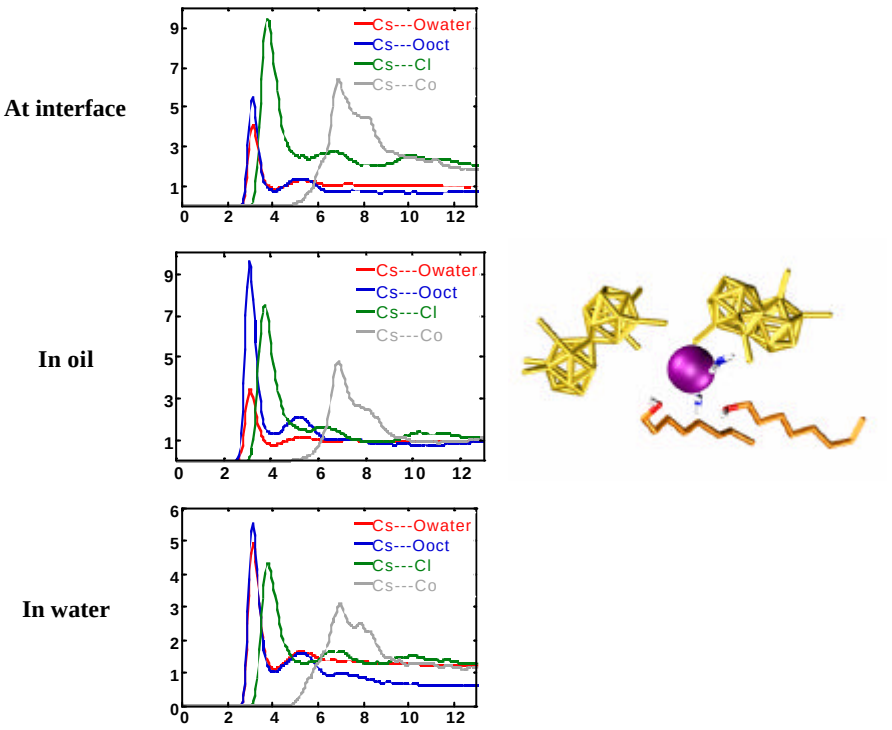


Figure S7: 30 CCD$^-$ Cs$^+$ ions at the octanol – water interface, simulated with the ions initially at the interface, or in octanol, or in water. Average RDF's around all Cs$^+$ atoms and snapshot of Cs$^+$ in octanol.

Starting in water 14 ns

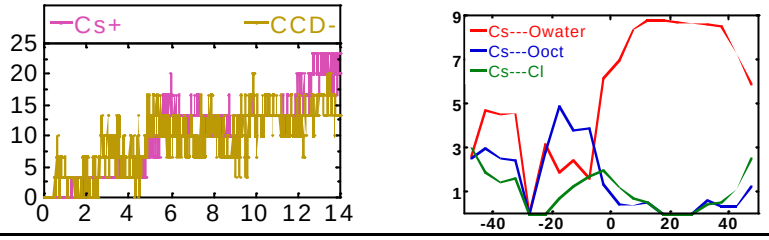


Figure S8: Simulation of 30 CCD^- Cs^+ ions at the octanol – water interface, starting with all ions in water. Percentage of CCD^- and Cs^+ ions found in "bulk octanol" as a function of time. Average number of O(H_2O) (red), O(octanol) (blue) and Cl(CCD) (green) atoms around Cs^+ cations as a function of their z-position.

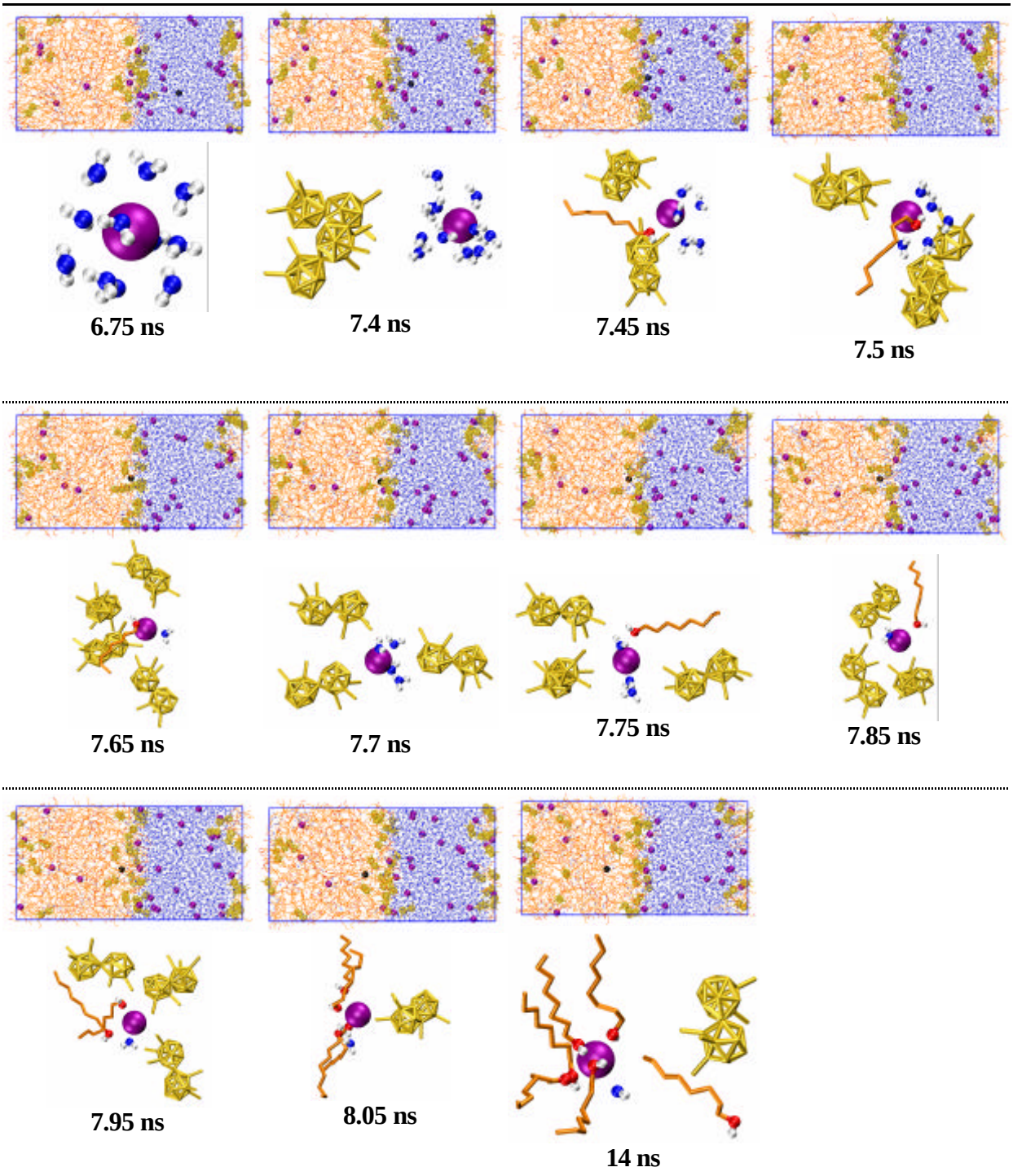


Figure S9: 30 CCD$^-$ Cs^+ ions at the octanol – water interface, simulated with the ions initially in water. Typical snapshots of the solvent box and of a selected Cs^+ ion (colored in black in the solvent box) that migrates from water to octanol.

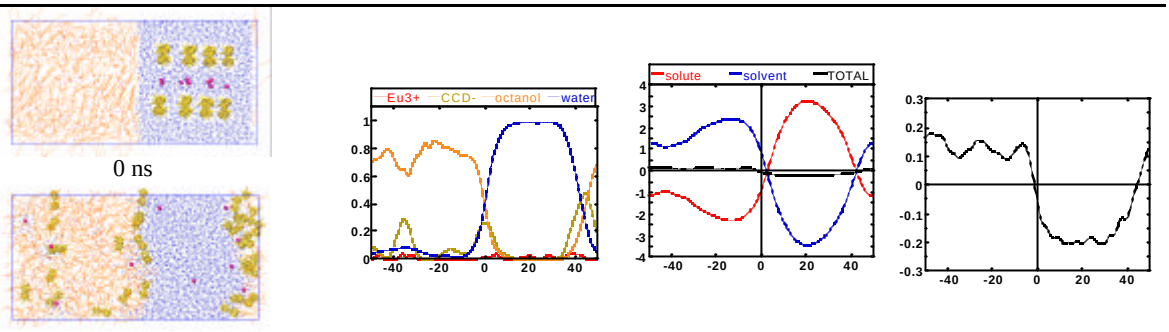


Figure S10: 30 CCD^- and 10 Eu^{3+} ions at the octanol – water interface. Initial and final views, average densities as a function of the z-position, electrostatic potentials resulting from the solute (red), the solvents (blue) and their sum (black).

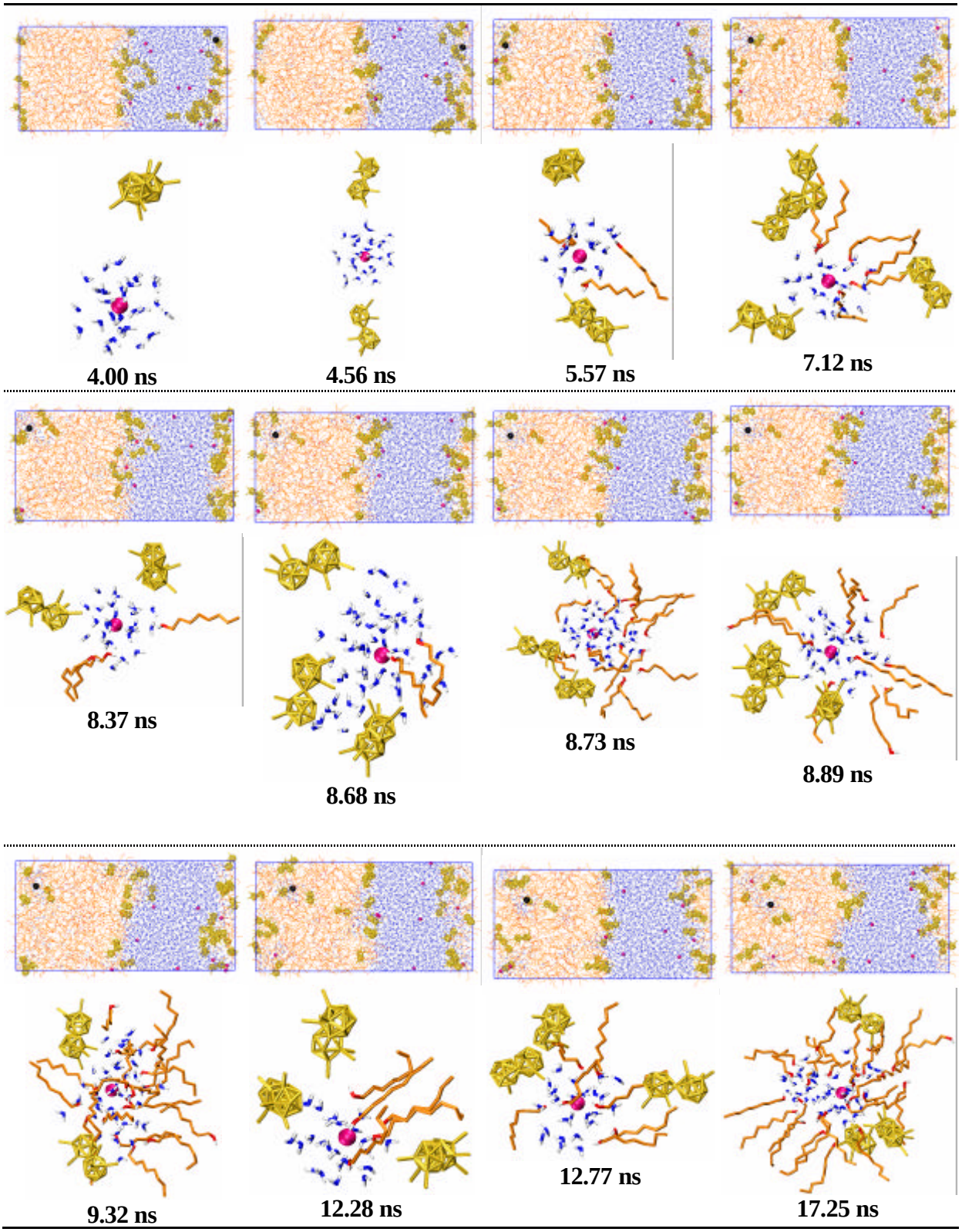
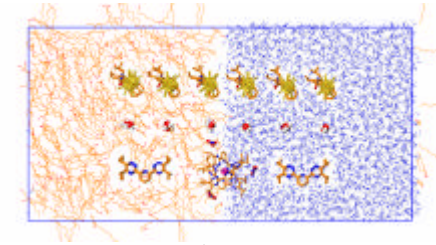
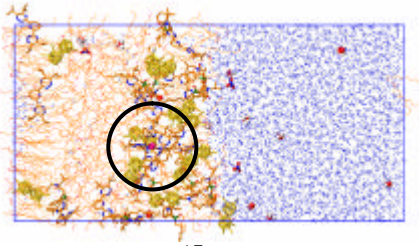


Figure S11: 30 CCD^- and 10 Eu^{3+} ions at octanol – water interface. Typical snapshots of the solvent box and of a selected Eu^{3+} ion (colored in black in the solvent box) that migrates from water to octanol.

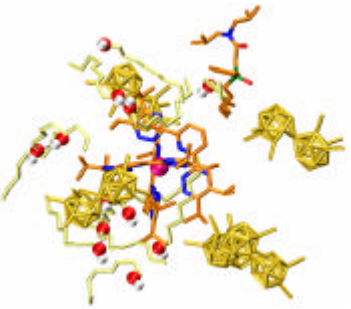
Octanol – water Interface

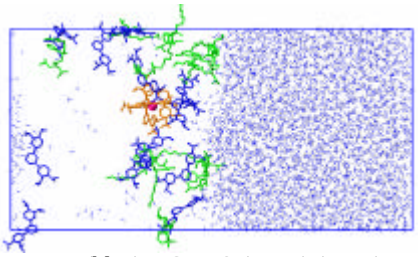


0 ns

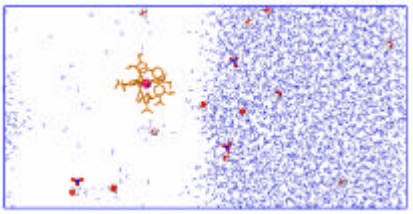


15 ns



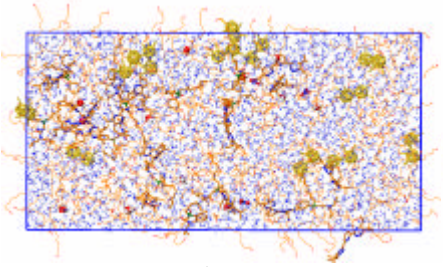


BTP (blue) + CMPO (green) (15 ns)

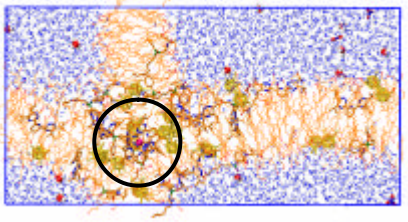


$H_3O^+ + NO_3^-$ (15 ns)

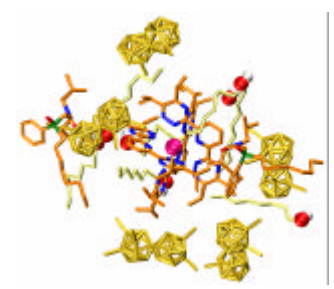
Octanol – water Interface DEMIX

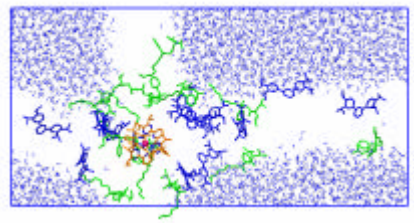


0 ns

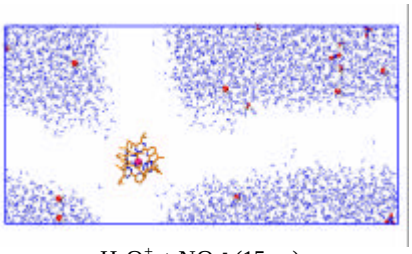


15 ns



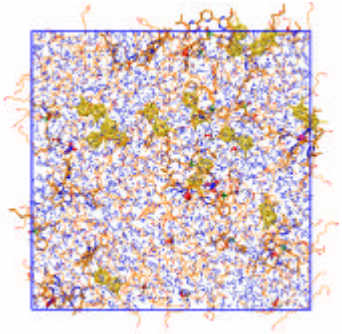


BTP (blue) + CMPO (green) (15 ns)

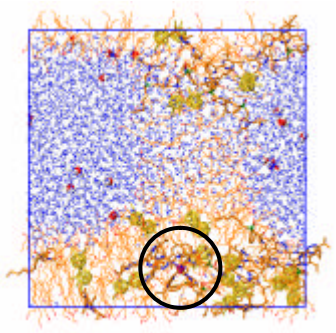


$H_3O^+ + NO_3^-$ (15 ns)

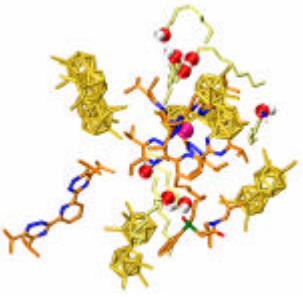
Octanol – water Interface DEMIX CUBIC



0 ns



15 ns



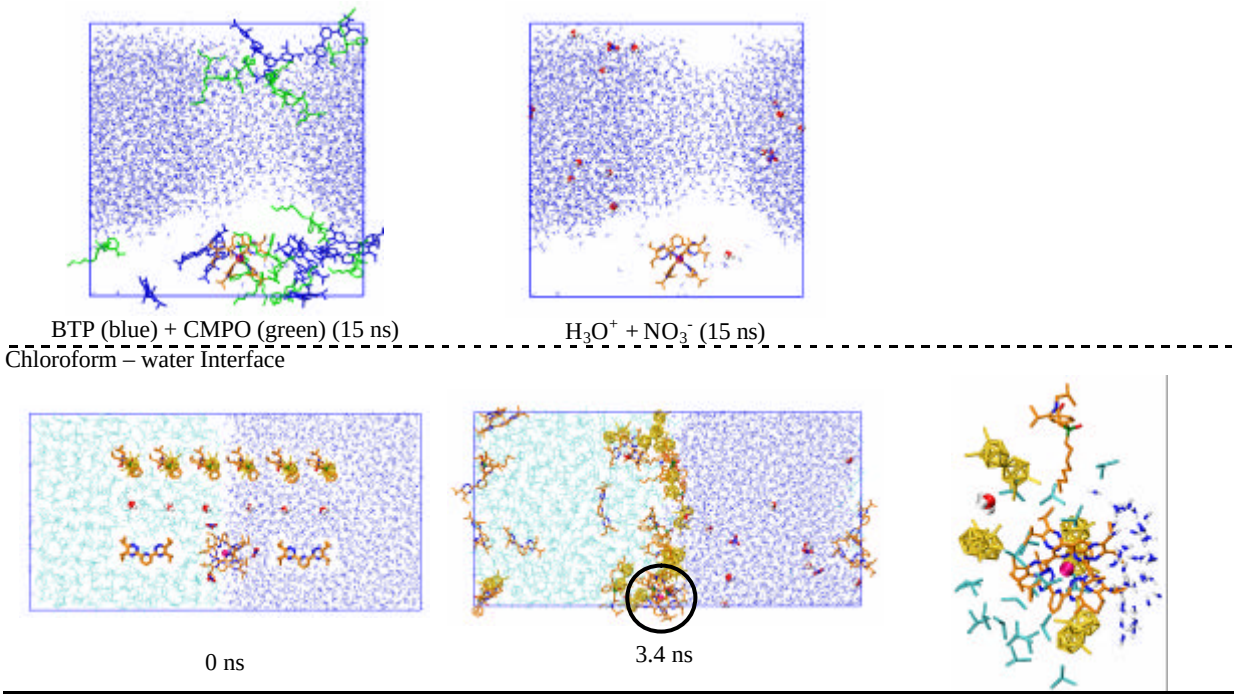


Figure S12: The $Eu(BTP)_3^{3+}$, 3 NO_3^-complex in the presence of 12 CMPO and 12 BTP ligands plus 12 CCD^- H_3O^+ ions. From top to bottom: the octanol – water interface, simulated from juxtaposed liquids (top), from mixed liquids in a rectangular box (middle), or in a cubic box (bottom), and the chloroform – water interface. Initial and final views, with typical snapshots of the $Eu(BTP)_3^{3+}$ complex "extracted" to the octanol phase, or adsorbed at the chloroform interface. At the octanol – water interface, the distribution of CMPO, BTP, H_3O^+ and NO_3^- are also displayed (octanol is not shown for clarity purpose).

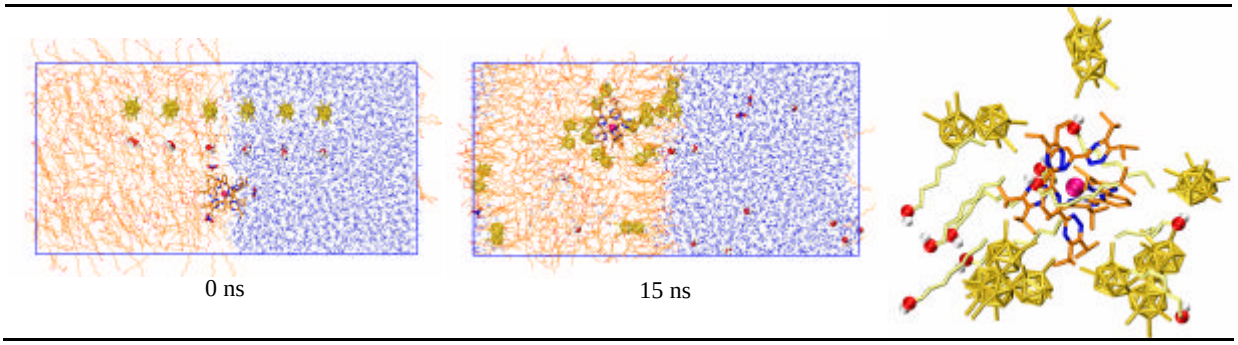


Figure S13: The $Eu(BTP)_3^{3+}$, 3 NO_3^-complex in the presence of 12 CCD^- H_3O^+ ions at the octanol – water interface. Initial and final views of the solvent box and zoom of the $Eu(BTP)_3^{3+}$ complex "extracted" to the octanol phase.

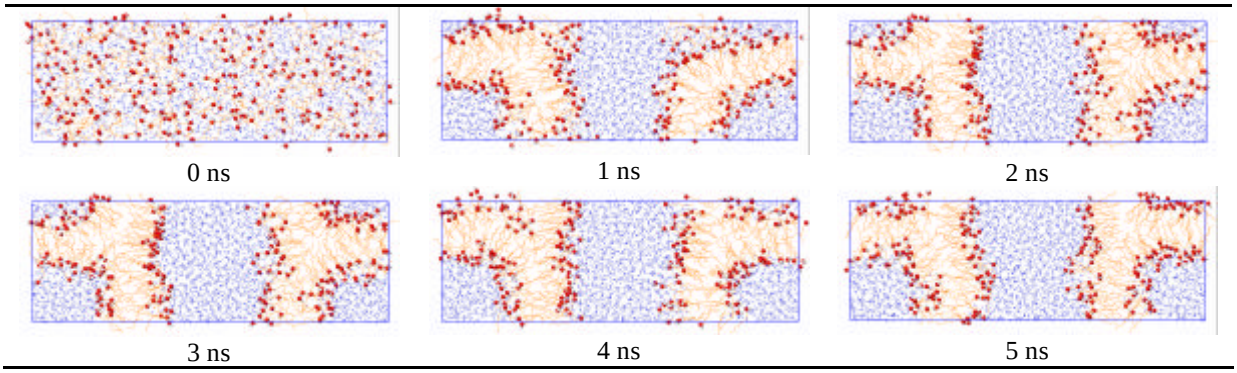


Figure S14: Snapshots of the phase separation of a "random" octanol – water 50:50 mixture (256 H_2O plus 2048 octanol molecules) at 300K, as in the work of R. L. Napoleon and P. B. Moore (*J. Phys. Chem. B*, 2006, **110**, 3666-3673). Our final box size is 35 x 35 x 105 $Å^3$.