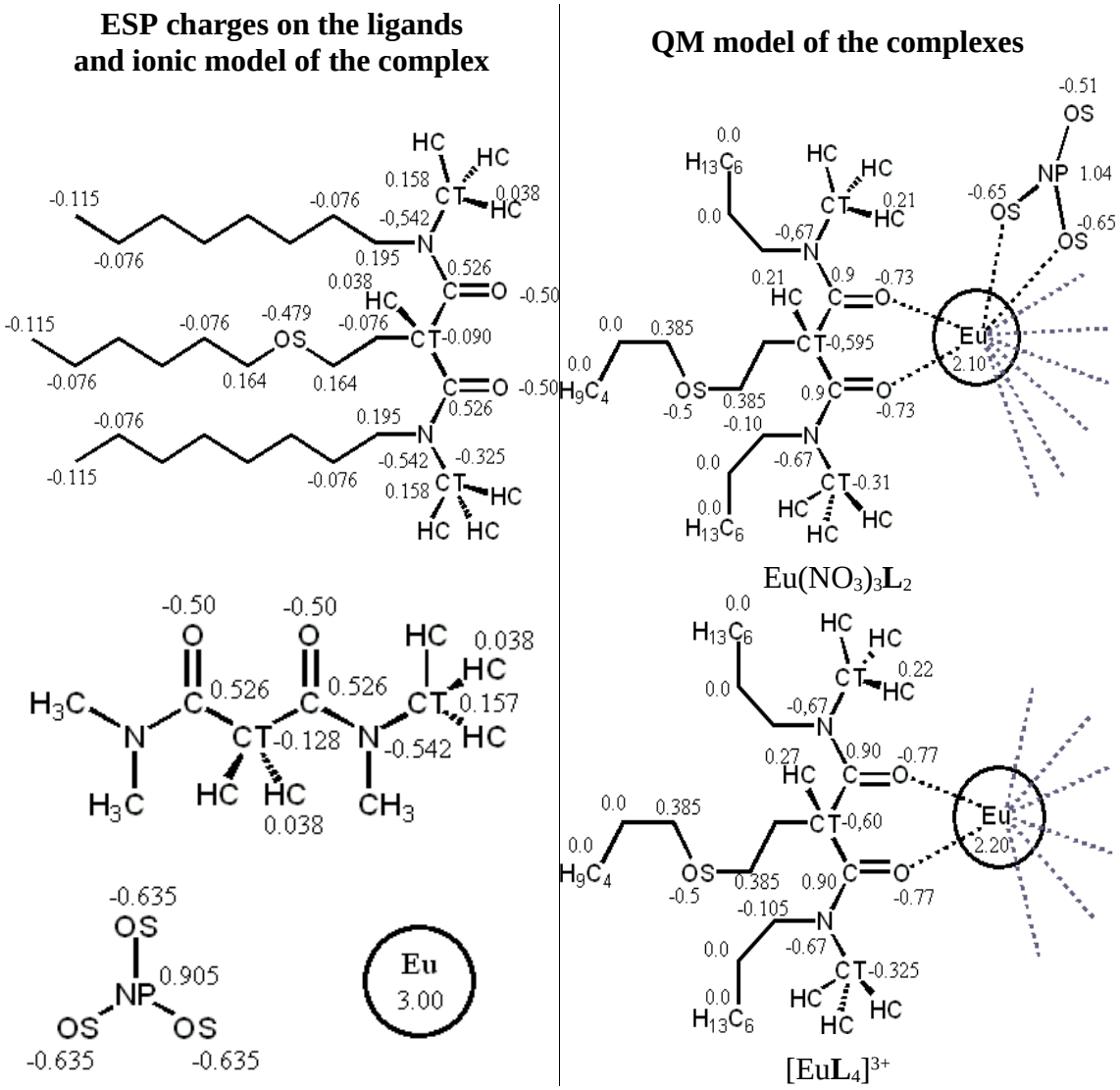

Figure S1. AMBER atom types and atomic charges used to simulate the malonamides and their complexes.

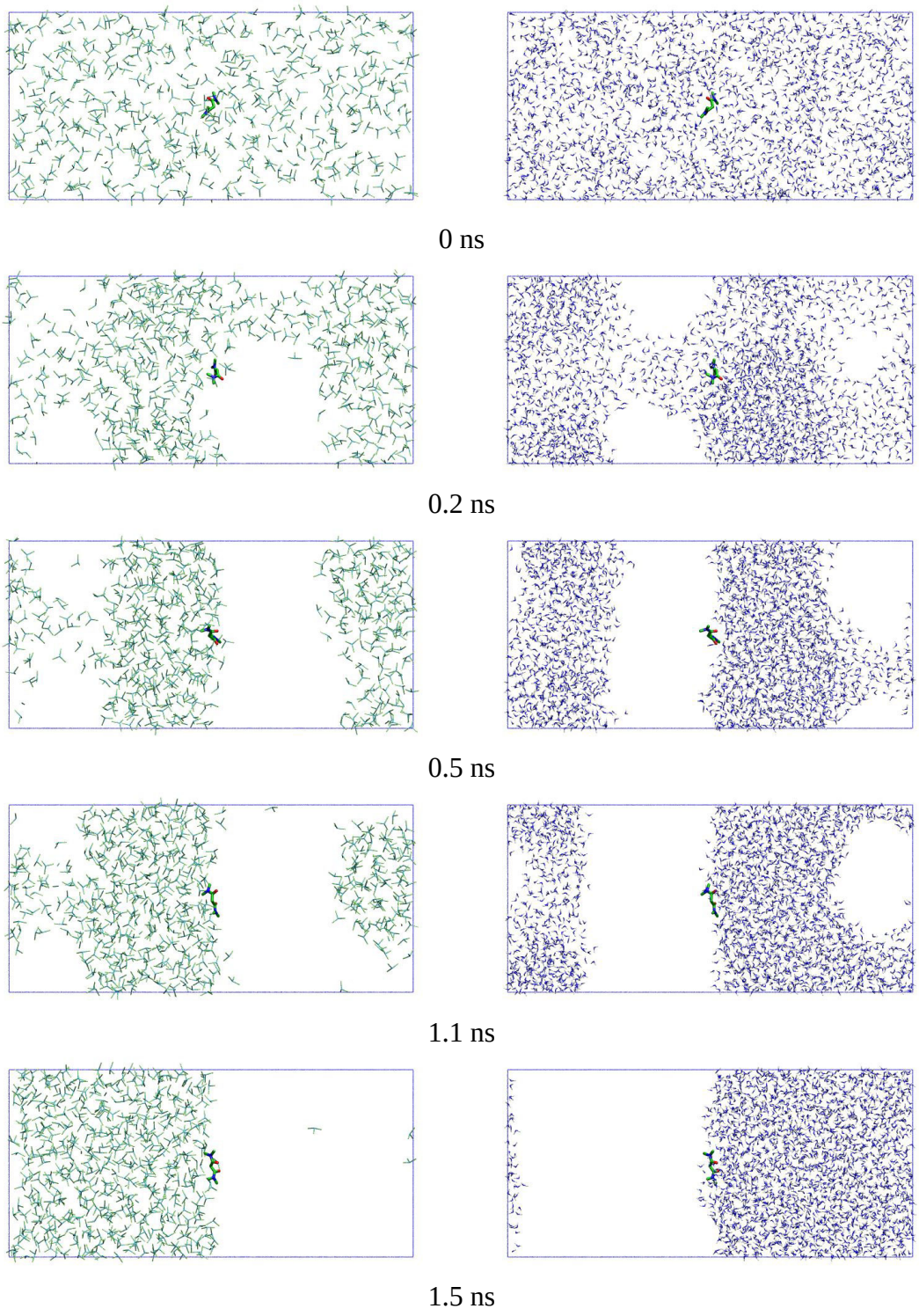

Figure S2. Demixing simulation of a water / chloroform solution with one $\mathbf{L_0}$ malonamide (initially in its *trans* form). Snapshots at different times, showing the chloroform (left) and water (right) solvents separately instead of superimposed, for clarity.

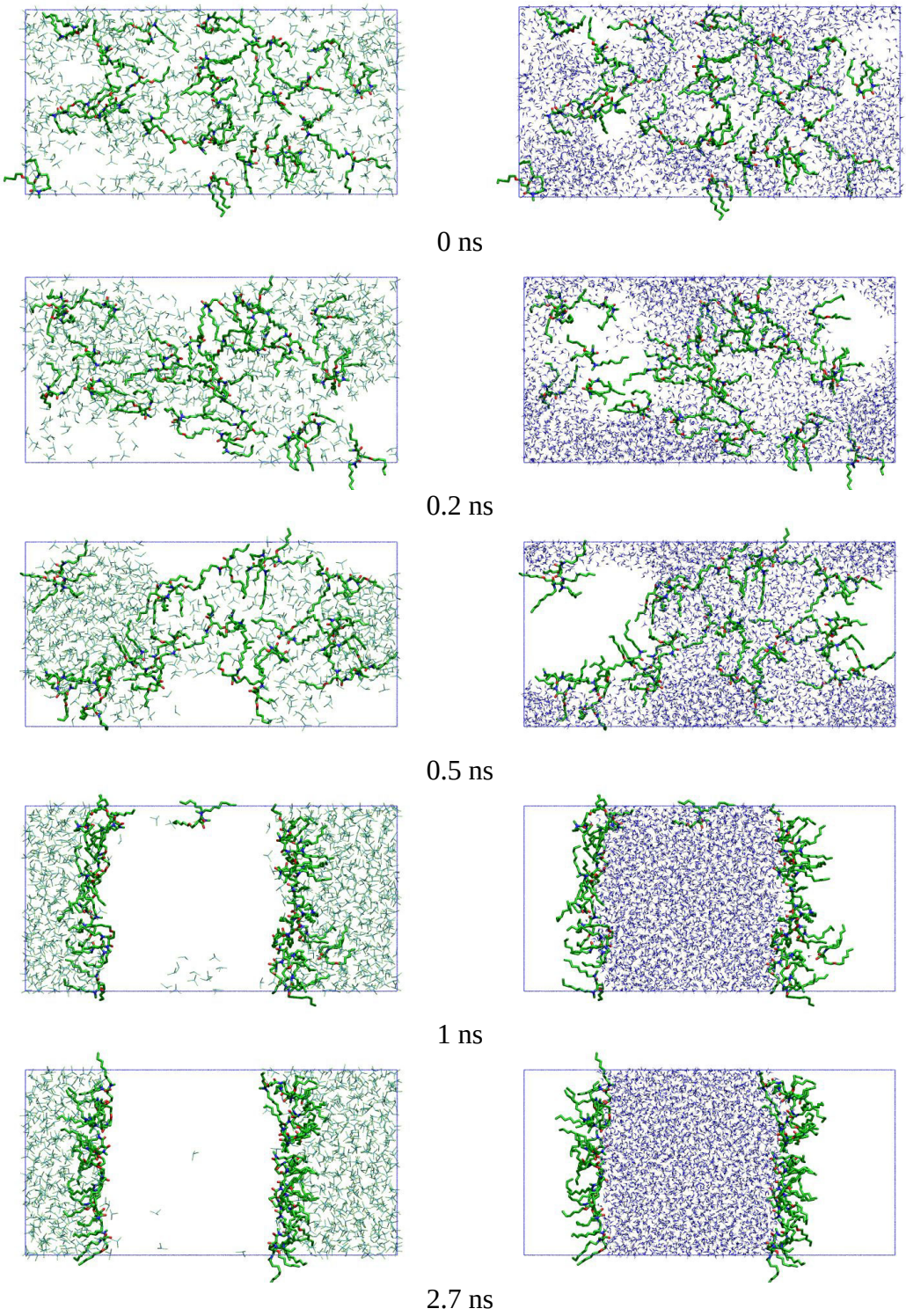

Figure S3. Demixing simulation of a water / chloroform solution with 27 **L** malonamides (initially *EE-gauche*). The amide (O)C-N V_2 torsion parameter was set to 2.5 kcal/mol (from 0 to 2 ns) and to 10.5 kcal/mol after 2 ns. Snapshots at different times, showing the chloroform (left) and water (right) solvents separately instead of superimposed, for clarity.

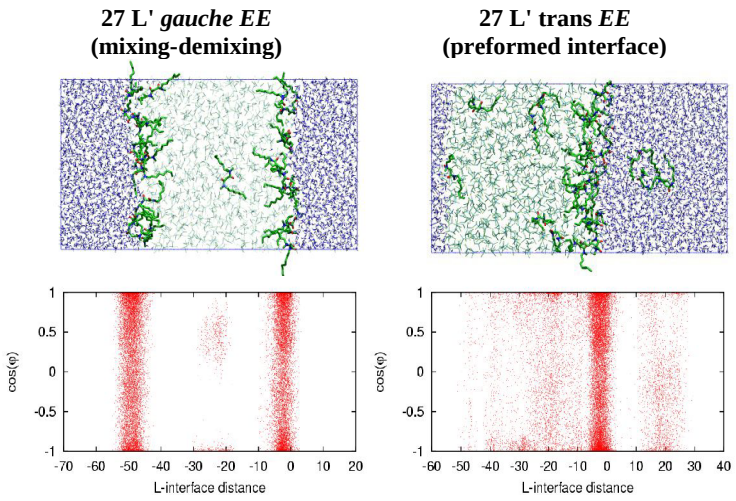

Figure S4: Solutions of 27 **L'** (analogue of **L** with central chain replaced by H) at the interface. Sampling simulations with biased torsional C(O)-N potentials starting with *EE gauche* and *EE trans* forms of **L'**, respectively, in a mixing-demixing simulation and at the preformed interface. *Top*: snapshots after 2 ns; *bottom*: statistical distribution of the O=C--C=O angles (cos(φ)) as a function of z (Å)

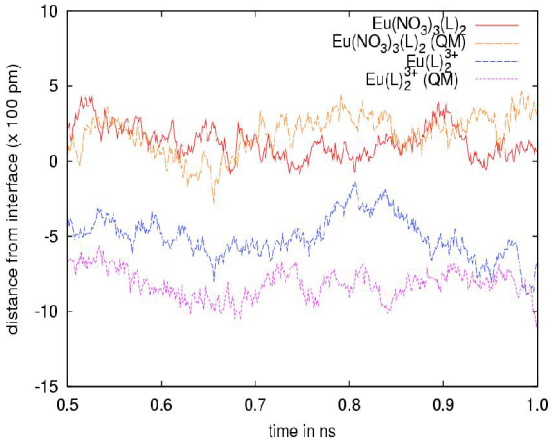

Figure S5. Mixtures of 26 **L** ligands (*EE gauche*) and $Eu(NO_3)_3\mathbf{L}_2$ or $Eu\mathbf{L}_4^{3+}$ complexes at the oil / water interface. Distances between Eu^{3+} and the interface as a function of time (ns).

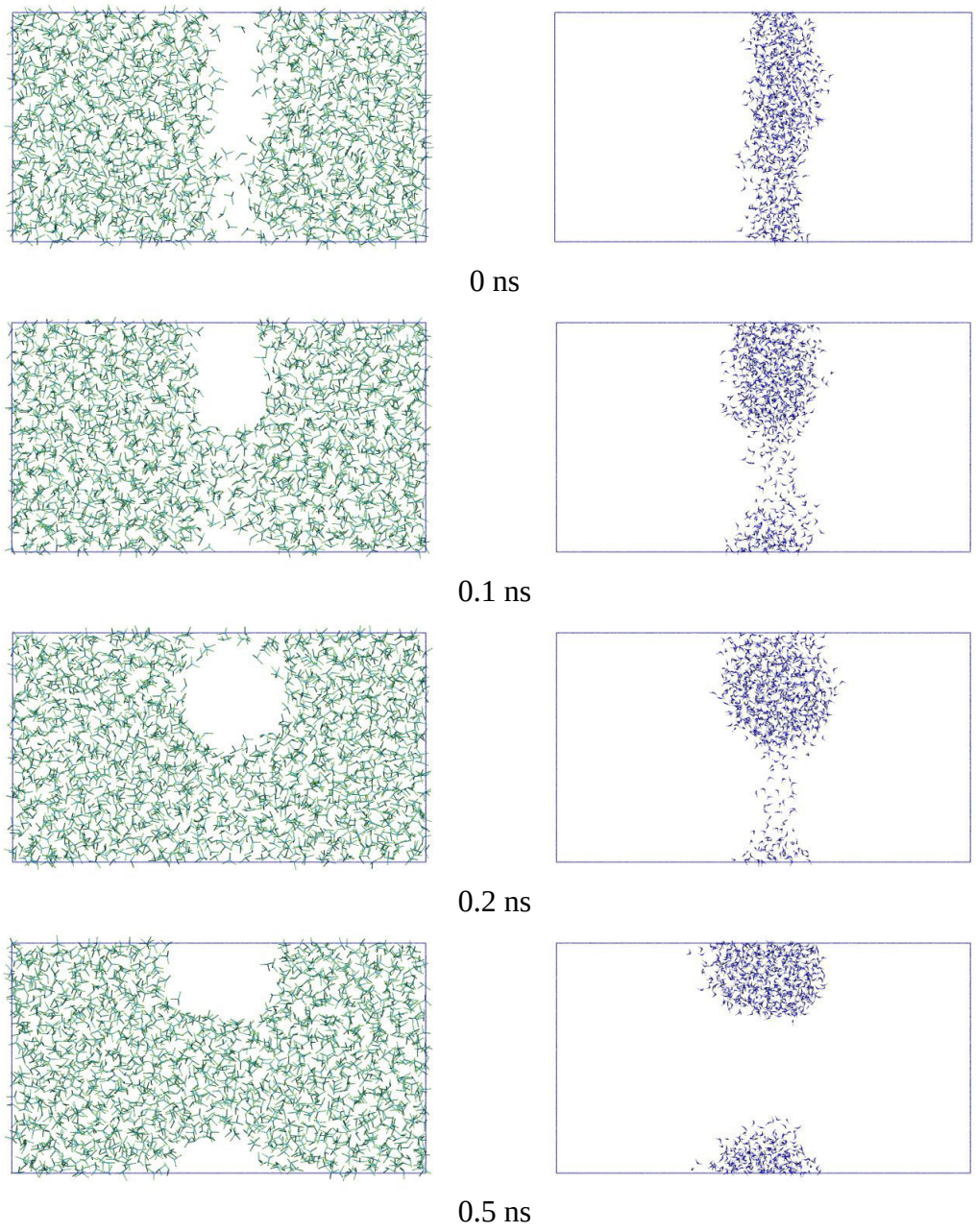

Figure S6. Simulation of a 90:10 chloroform:water "interface" (rectangular box). Snapshots at different times, showing the chloroform (*left*) and water (*right*) solvents separately, instead of superimposed, for clarity.

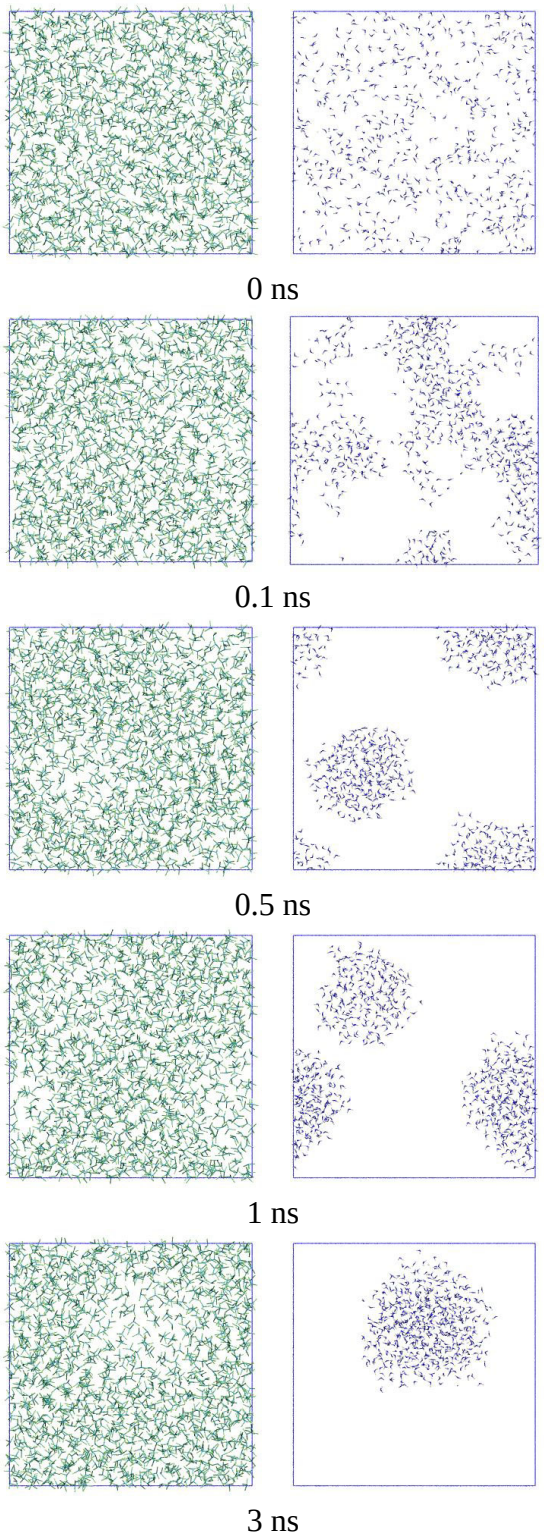

Figure S7. Demixing simulation of a 90:10 chloroform:water mixture ("cubic box"). Snapshots at different times, showing the chloroform (*left*) and water (*right*) solvents separately instead of superimposed, for clarity.

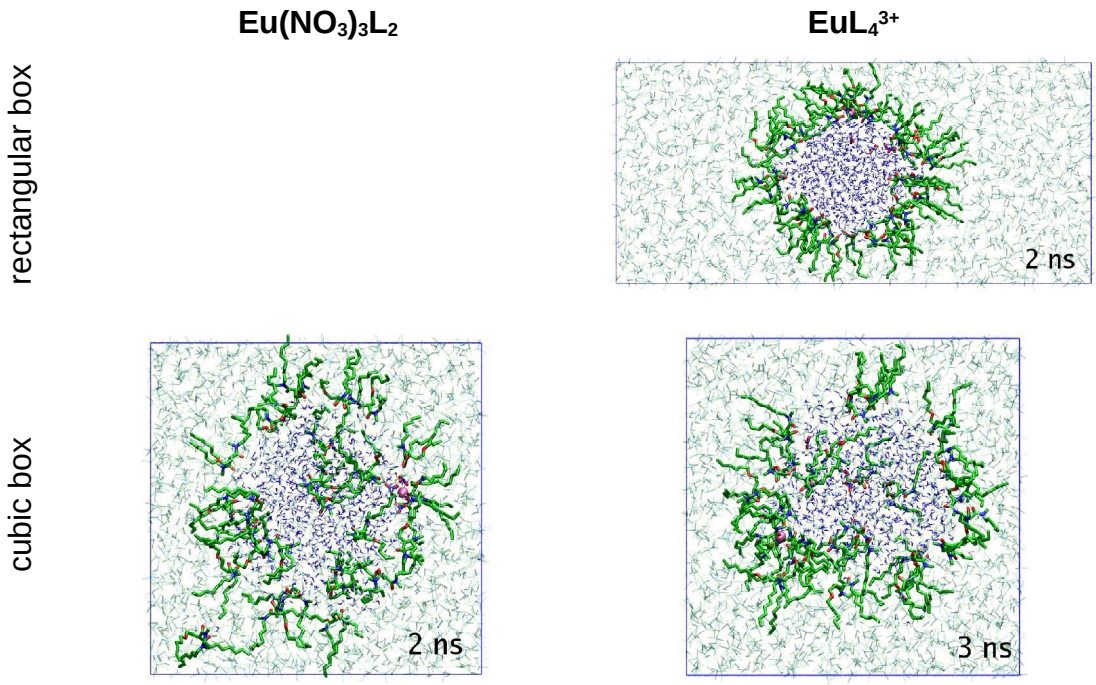

Figure S8. Final snapshots (after 2 ns) of 26 **L** ligands + 1 $Eu(NO_3)_3\mathbf{L}_2$ (*left*) or 1 $Eu\mathbf{L}_4^{3+}$ (*right*) complex (ionic model) in a 95:5 oil:water mixture. *Top*: simulation in a rectangular box starting at a preformed interface. *Bottom*: demixing simulation in a cubic box.

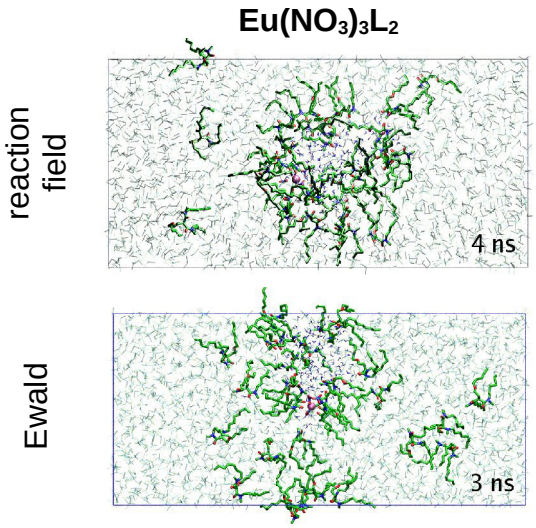

Figure S9. 26 **L** ligands + 1 $Eu(NO_3)_3\mathbf{L}_2$ complex (ionic model) in a 95:5 oil:water mixture. Final snapshots after 1.5 ns of simulations performed with the reaction field (*top*) *versus* Ewald (*bottom*) treatments of electrostatics.

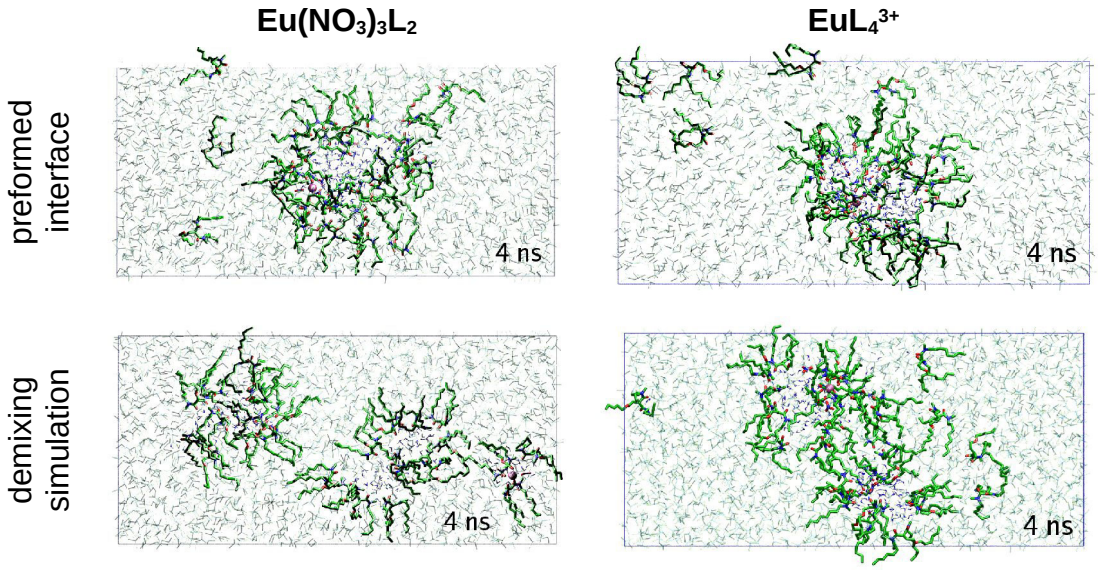

Figure S10. 26 **L** ligands + 1 $Eu(NO_3)_3\mathbf{L}_2$ (*left*) or 1 $Eu\mathbf{L}_4^{3+}$ (*right*) complex (ionic model) in a 95:5 oil:water mixture. Final snapshots from simulations which started at a preformed interface (*top*), and obtained from a mixing-demixing simulation (*bottom*). See also Figure S12 for the demixing results.

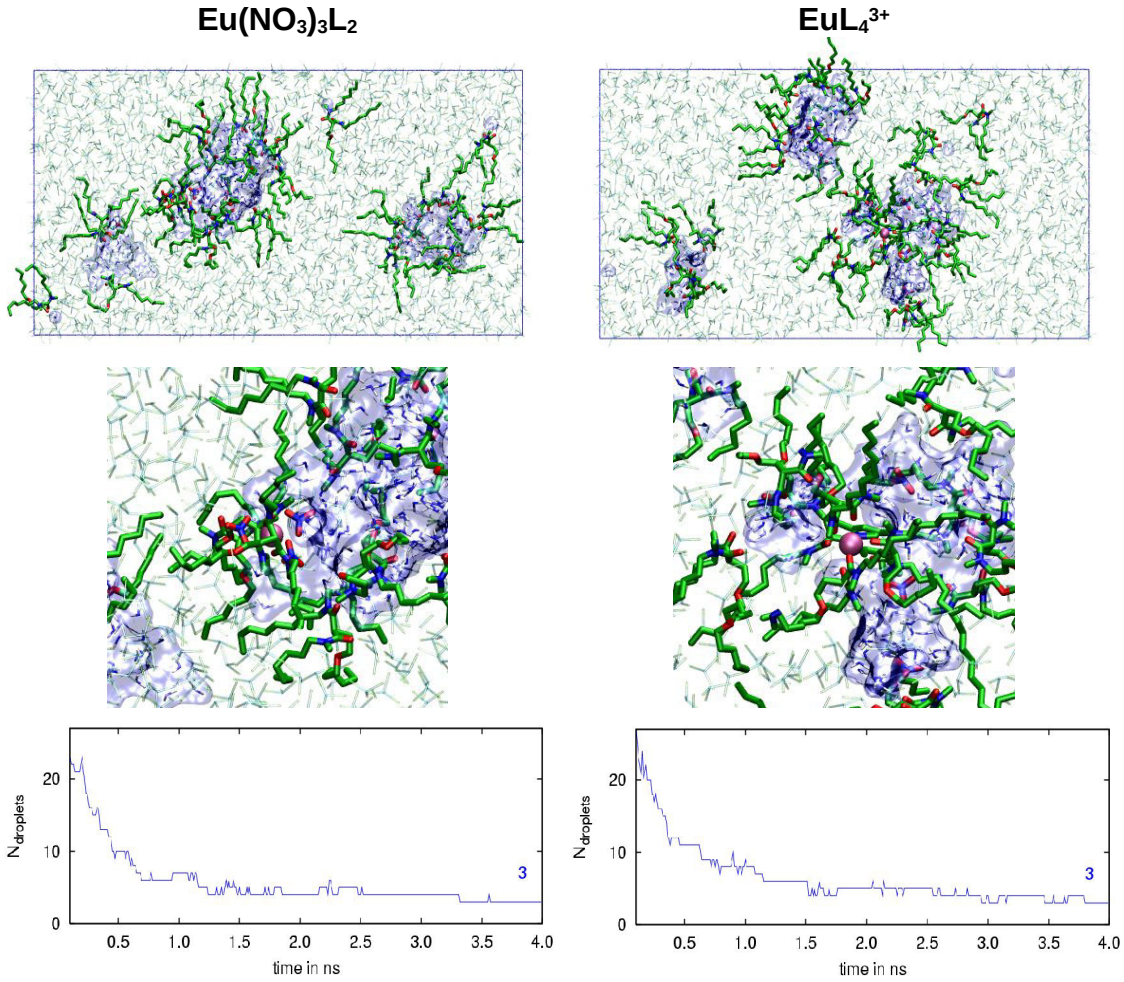

Figure S11. 26 **L** ligands + 1 $Eu(NO_3)_3\mathbf{L}_2$ (*left*) or 1 $Eu\mathbf{L}_4^{3+}$ (*right*) complex (QM model) in a 95:5 oil:water mixture. Final snapshots and zooms after 4 ns of mixing-demixing simulations. *Bottom*: time evolution of the number of water aggregates during the demixing simulation.

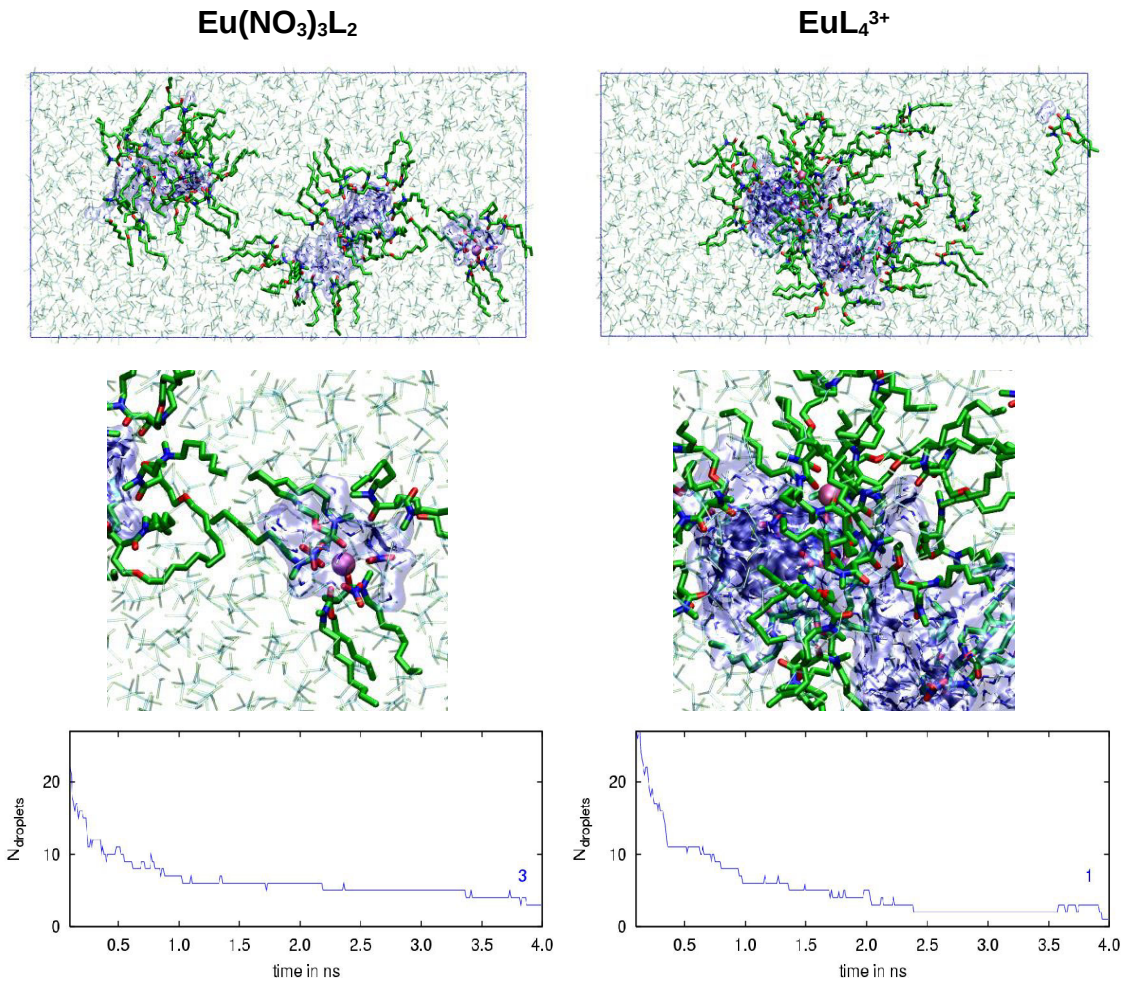

Figure S12. 26 **L** ligands + 1 $Eu(NO_3)_3\mathbf{L}_2$ (*left*) or 1 $Eu\mathbf{L}_4^{3+}$ (*right*) complex (ionic model) in a 95:5 oil:water mixture. Final snapshots and zooms after 4 ns of mixing-demixing simulations. *Bottom*: time evolution of the number of water aggregates during the demixing simulation.