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 $L_0$ 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 V₂ 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$_3$)$_3$L$_2$ or EuL$^{4+}$ 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(NO₃)₃L₂ (left) or 1 EuL₄³⁺ (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$_3$)$_3$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$_3$)$_3$L$_2$ (left) or 1 EuL$_4^{3+}$ (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\textsubscript{3})\textsubscript{3}L\textsubscript{2} (left) or 1 EuL\textsubscript{4}\textsuperscript{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$_3$)$_3$L$_2$ (left) or 1 EuL$_4^{3+}$ (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.