Table S1: Total energies of BTBPs (**L**) neutral, protonated and complexed (in hartrees).

R	**X**	**L** *c-g-c*	**L** *t-t-t* [a)]	**LH**$^+$ *c-c-c*	**LH**$^+$ *t-t-t* [b)]	$Eu(NO_3)_3$ **L**
H	H	-1053.6544	-1053.6718	-1054.0741	-1054.0638	-1930.1810
H	^{t}But	-1210.9223	-1210.9398	-1211.3488	-1211.3394	-2087.4480
Et	H	-1368.2181	-1368.2367	-1368.6488	-1368.6397	-2244.7489
Et	^{t}But	-1525.4857	-1525.5045	-1525.9226	-1525.9139	-2402.0154
$CyMe_4$	H	-1680.3353	-1680.3537	-1680.7668	-1680.7571	-2556.8601
$CyMe_4$	^{t}But	-1837.6030	-1837.6217	-1838.0403	-1838.0313	-2714.1267

a): For **L** *c-t-c* (**R** = $CyMe_4$, **X** = H), E = -1680.3507 hartrees.
b): For **LH**$^+$ *c-t-c* (**R** = $CyMe_4$, **X** = H), E = -1680.7602 hartrees.

Table S2: Total energies of BTPhens (**L**) neutral, protonated and complexed (in hartrees).

R	**X**	**L**	**LH**$^+$	$Eu(NO_3)_3$ **L**
H	H	-1129.8871	-1130.3077	-2006.4153
H	^{t}But	-1287.1382	-1287.5673	-2163.6719
Et	H	-1444.4509	-1444.8826	-2320.9807
Et	^{t}But	-1601.7019	-1602.1411	-2475.2370
$CyMe_4$	H	-1756.5684	-1757.0007	-2633.0943
$CyMe_4$	^{t}But	-1913.8258	-1914.2647	-2790.3508

Table S3: $Eu(NO_3)_3$(**L**) complexes with **L** = BTBP and BTPhen: Optimized distances (in Å) and Mulliken charges of Eu.

R	**X**	**φ (°)**[a)]		**Eu-N and Eu-O Distances (Å)**										**Eu Charge (e)**	
		BTBP	**BTPhen**	**BTBP**					**BTPhen**					**BTBP**	**BTPhen**
				N_1	N_2	$N_{3,4}$	O_{ax}	O_{eq}	N_1	N_2	$N_{3,4}$	O_{ax}	O_{eq}		
H	H	-9.4	0.1	2.68	2.68	2.60	2.53	2.44	2.67	2.67	2.62	2.53	2.44	1.35	1.34
H[b)]	H[b)]	-0.2[b)]	0.2[b)]	2.59[b)]	2.59[b)]	2.59[b)]	2.57[b)]	2.50[b)]	2.60[b)]	2.60[b)]	2.62[b)]	2.57 [b)]	2.51[b)]	1.34[b)]	1.31[b)]
H	^{t}But	-11.2	0.1	2.68	2.66	2.61	2.54	2.45	2.66	2.66	2.60	2.54	2.45	1.34	1.35
Et[c)]	H	-5.7		2.61	2.60	2.60	2.54	2.49							
Et	H	-4.7	0.1	2.66	2.66	2.58	2.54	2.46	2.67	2.67	2.61	2.54	2.45	1.34	1.33
Et	^{t}But	-8.1	0.1	2.67	2.65	2.59	2.54	2.46	2.66	2.66	2.60	2.54	2.46	1.34	1.33
$CyMe_4$	H	1.2	0.1	2.66	2.66	2.58	2.54	2.46	2.66	2.66	2.60	2.54	2.46	1.34	1.34
$CyMe_4$	^{t}But	8.6	0.2	2.65	2.67	2.58	2.54	2.47	2.65	2.65	2.59	2.54	2.47	1.34	1.34

a: Defined in Scheme 2.
b: in PCM -water
c: X-ray structure (ref 19).

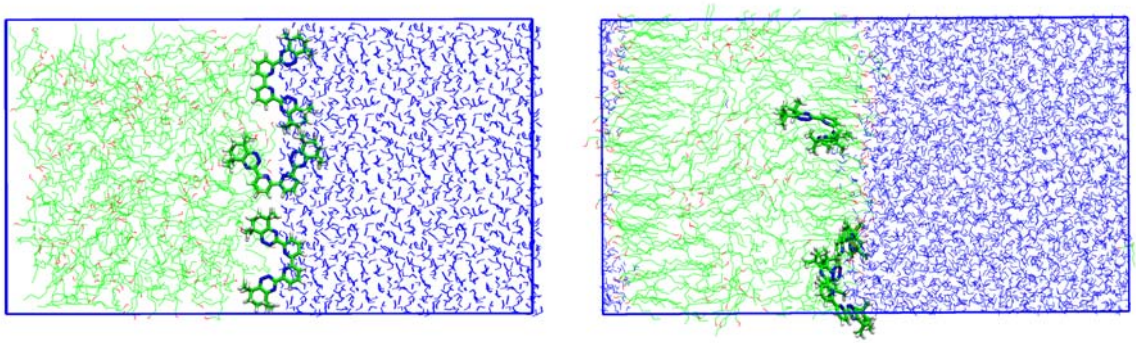


Figure S1: 3 *cis-cis-cis* (*c-c-c*) $CyMe_4BTBP$ (**L**) at the Oct-Hex / water interface. Left: initial position. Right: after 2 ns of dynamics.

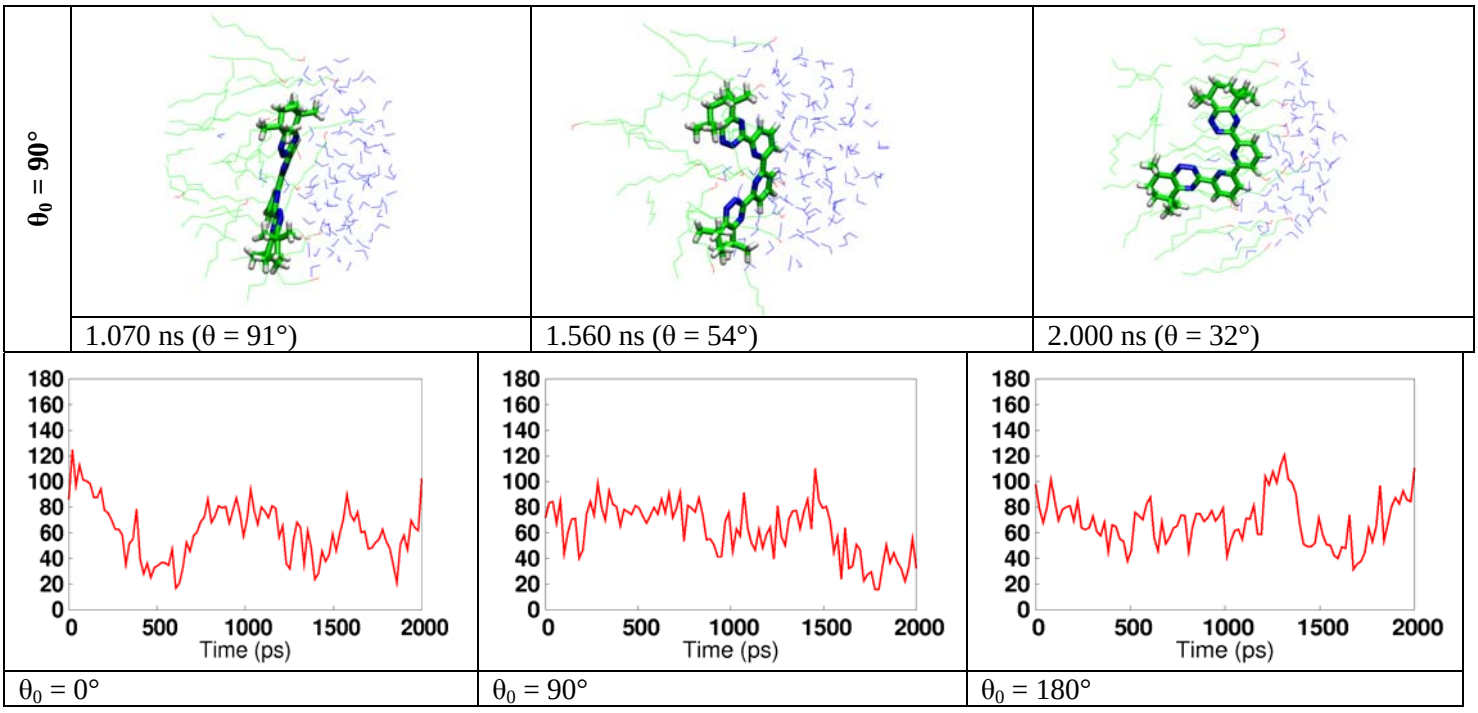


Figure S2: Snapshots of *c-c-c* **L** during the dynamics (top) and evolution of orientation (θ angle, see Scheme 3) with time for different initial positions (bottom).

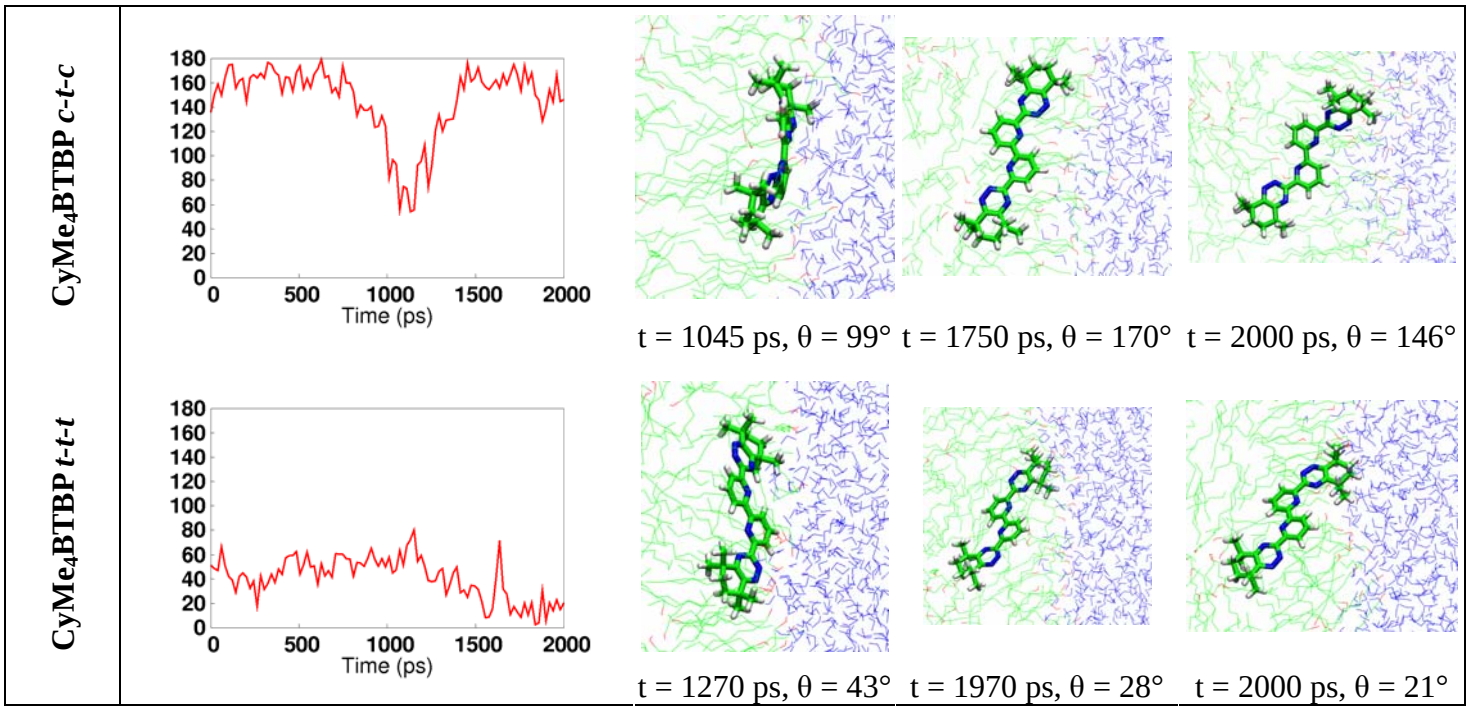


Figure S3: Orientation and snapshots of **L** with *c-t-c* and *t-t-t* conformations with time at the Oct-Hex/water interface.

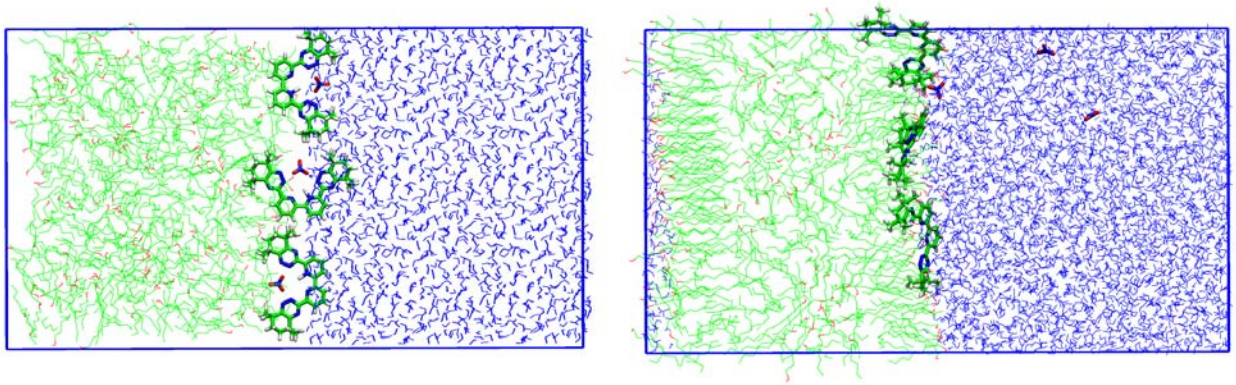


Figure S4: 3 *cis-cis-cis* (*c-c-c*) $CyMe_4BTBPH^+$ ($\mathbf{L}H^+$) at the Oct-Hex / water interface. Left: initial position. Right: after 2 ns of dynamics.

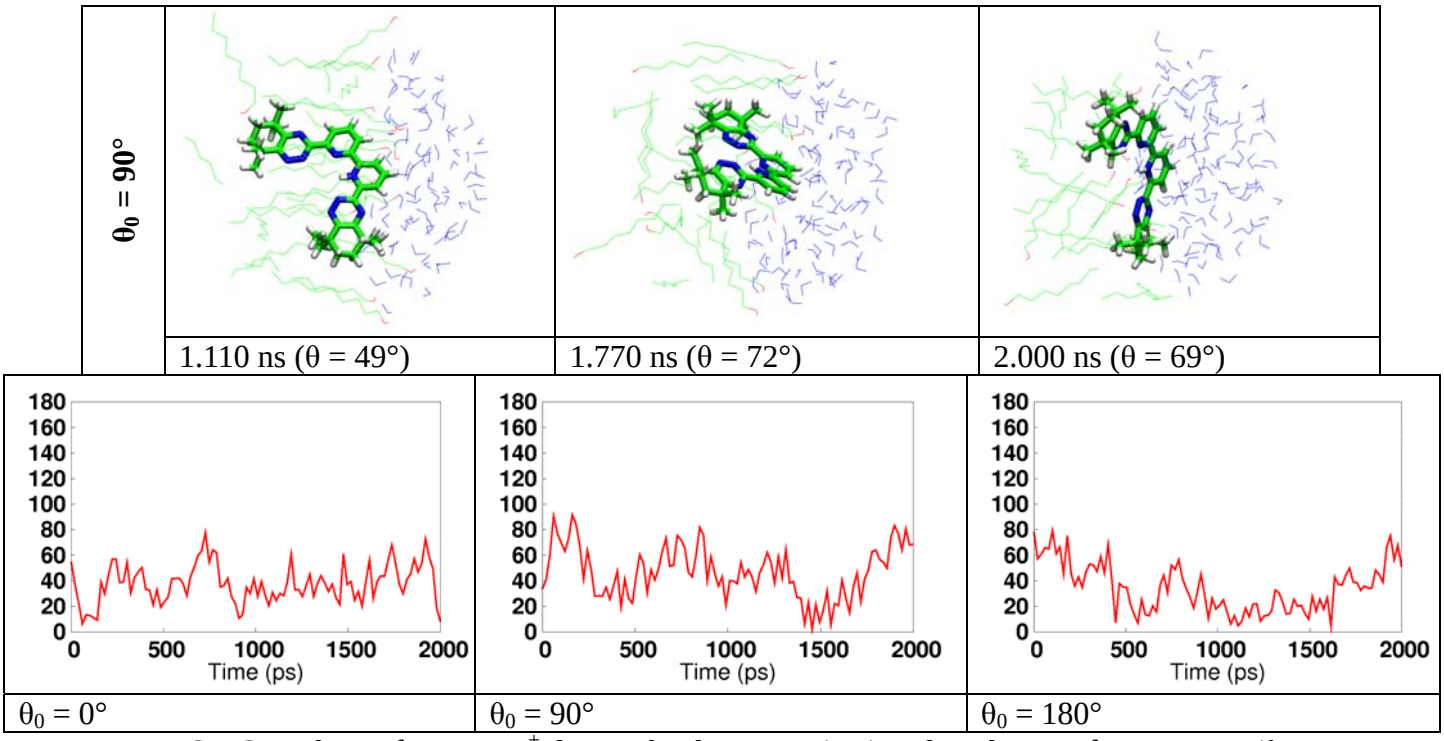


Figure S5: Snapshots of *c-c-c* **L**H^+ during the dynamics (top) and evolution of orientation (θ angle, see Scheme 3) with time for different initial positions (bottom).

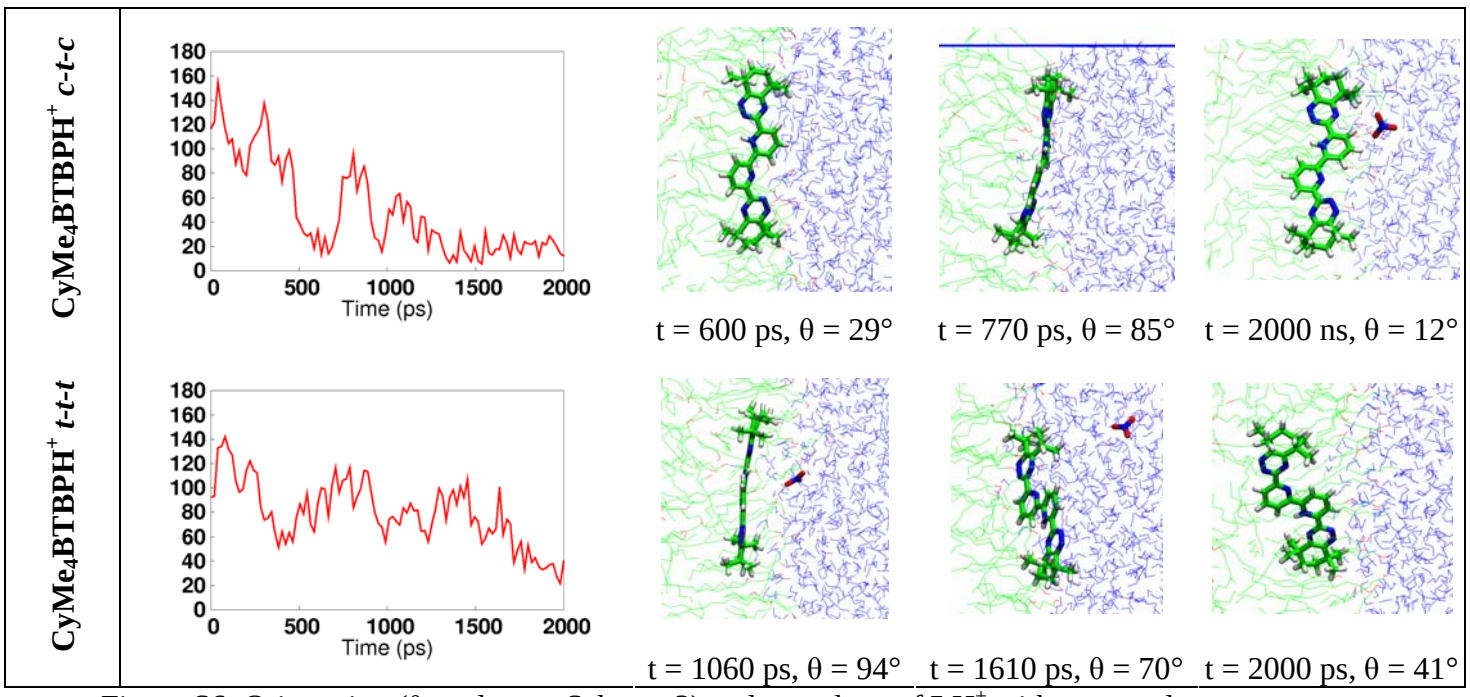
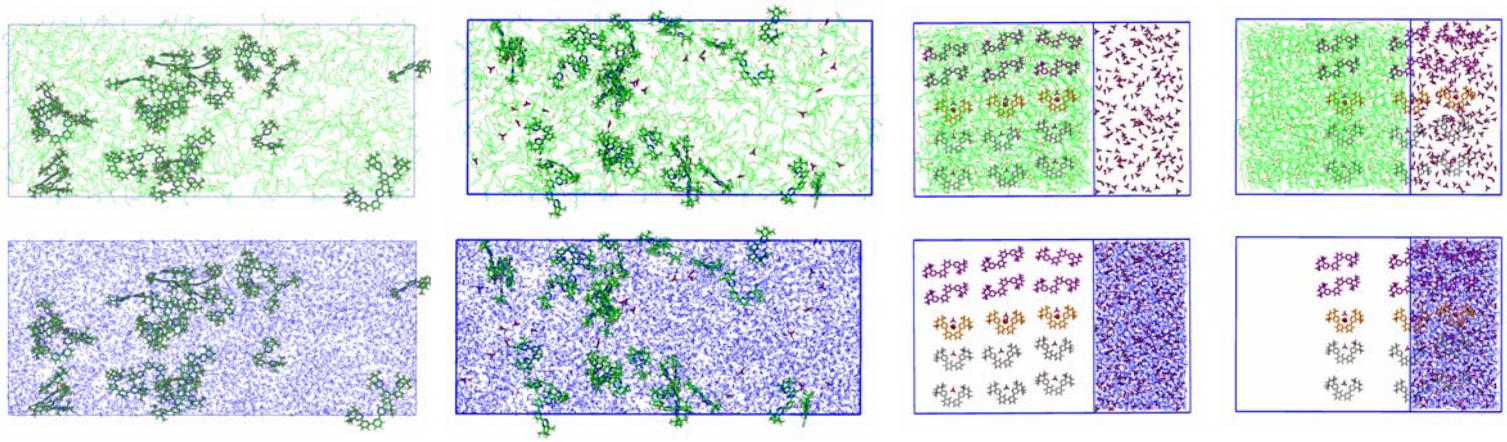


Figure S6: Orientation (θ angle, see Scheme 3) and snapshots of **L**H^+ with *c-t-c* and *t-t-t* conformations with time at Oct-Hex/water interface.



A
30 **L** *cis-cis-cis*

B
30 **L**H^+ *cis-cis-cis*

E
3 [Eu(**L**)$(NO_3)_3$], 6 **L** *t-t-t* and 6 **L**H^+ *c-c-c*

F

Figure S7: Initial positions of concentrated systems with mixed liquids (A and B) and juxtaposed phases (E and F). Solvents shown separately in two lines for clarity: octanol+hexane in green (top) and water in blue (bottom).

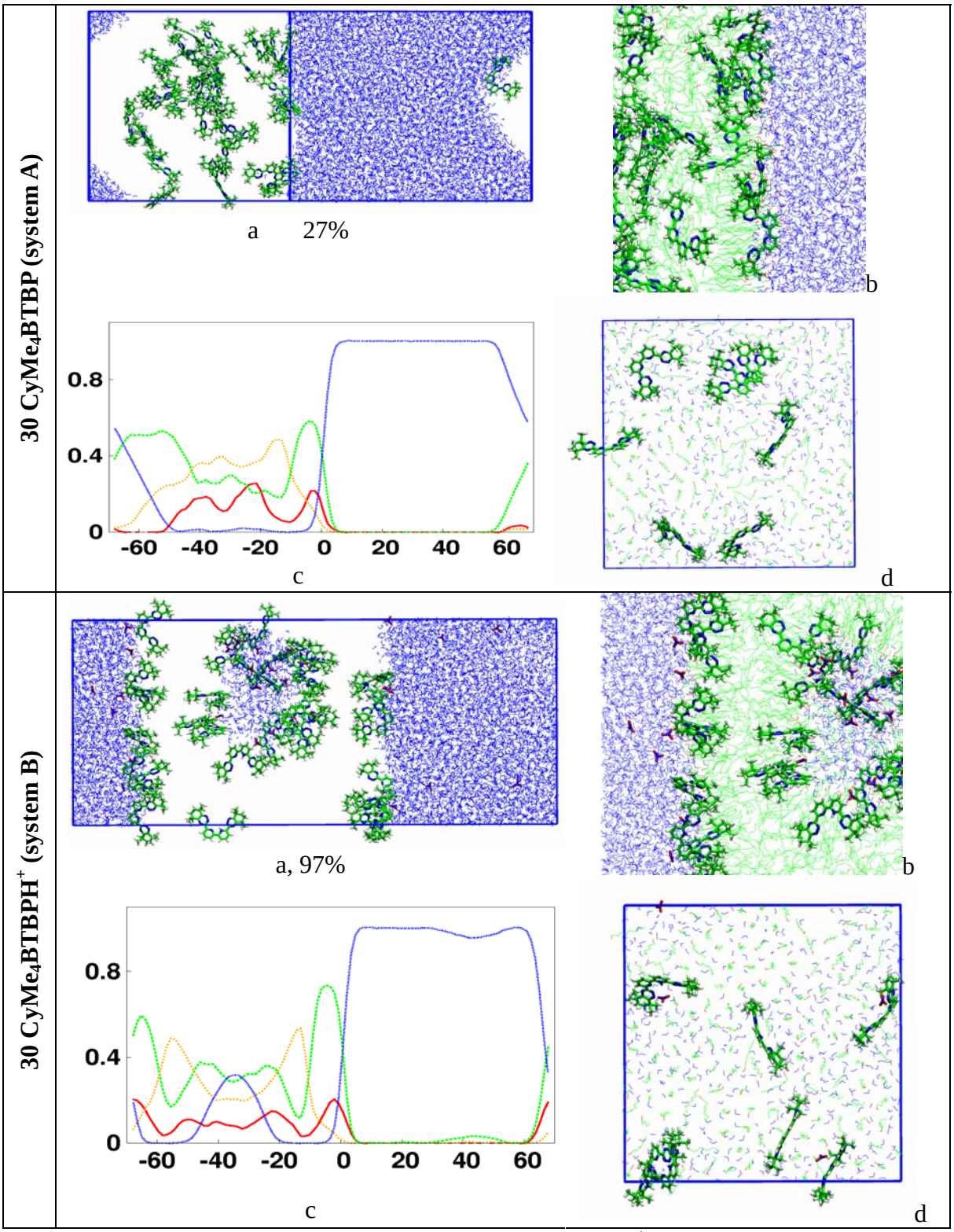


Figure S8: 30 *c-c-c* $CyMe_4BTBP$ and 30 *c-c-c* $CyMe_4BTBPH^+$ in the OCT-HEX/Water mixture. a: Snapshot at the end of the demixing simulations ("oil" phase hidden for clarity). b: Zoom on the interface. c: Density curves of BTBP (red), octanol (green), hexane (orange) and water (blue) and percentage of BTBP within 5Å of the interface (average during the last 0.5 ns of dynamics). d: View of the interface (XY slice with ΔZ = 10 Å).

Supplementary Material (ESI) for Physical Chemistry Chemical Physics

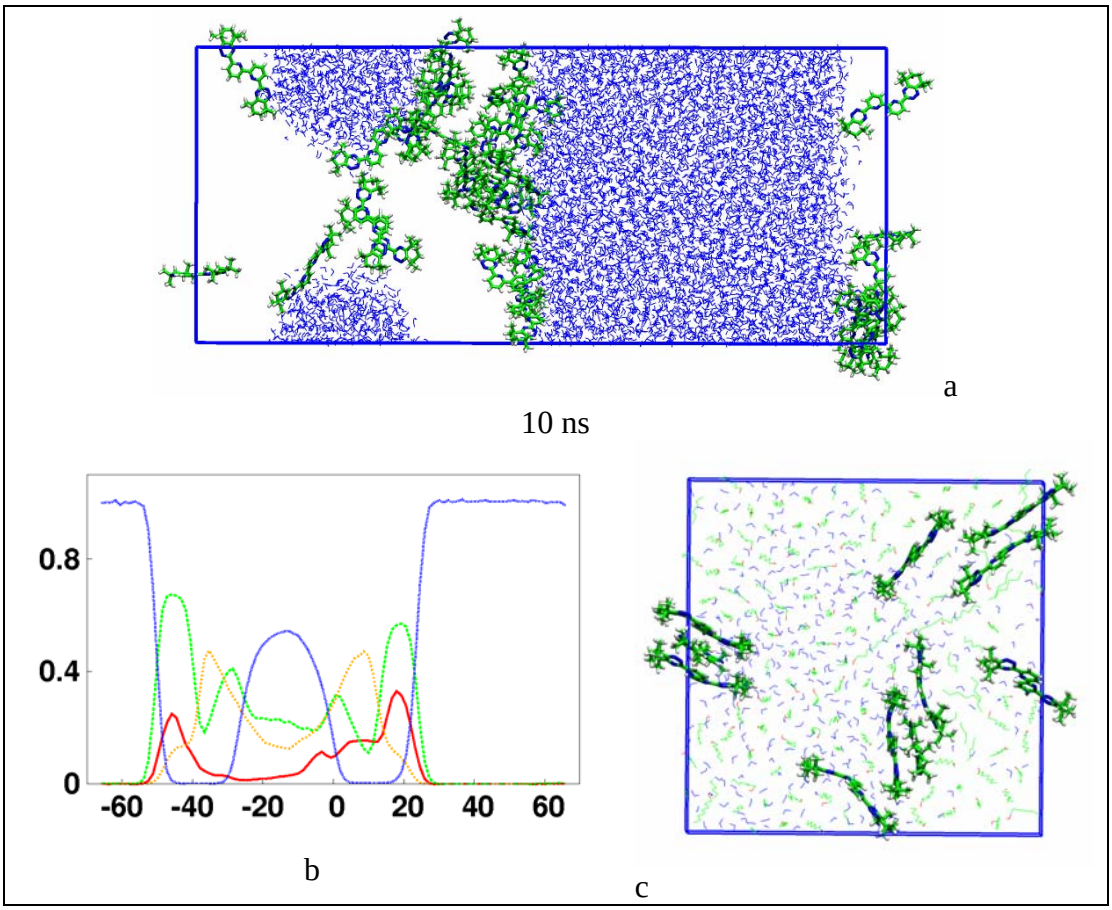


Figure S9: 30 *t-t-t* $CyMe_4BTBP$ in OCT-HEX/Water solution (DEMIX). *a*: Snapshot at the end of the simulations, ("oil" phase is not shown for clarity). *b*: Density curves of BTBP (red), octanol (green), hexane (orange) and water (blue), average during the last 0.5 ns of dynamics. *c*: View of the interface.

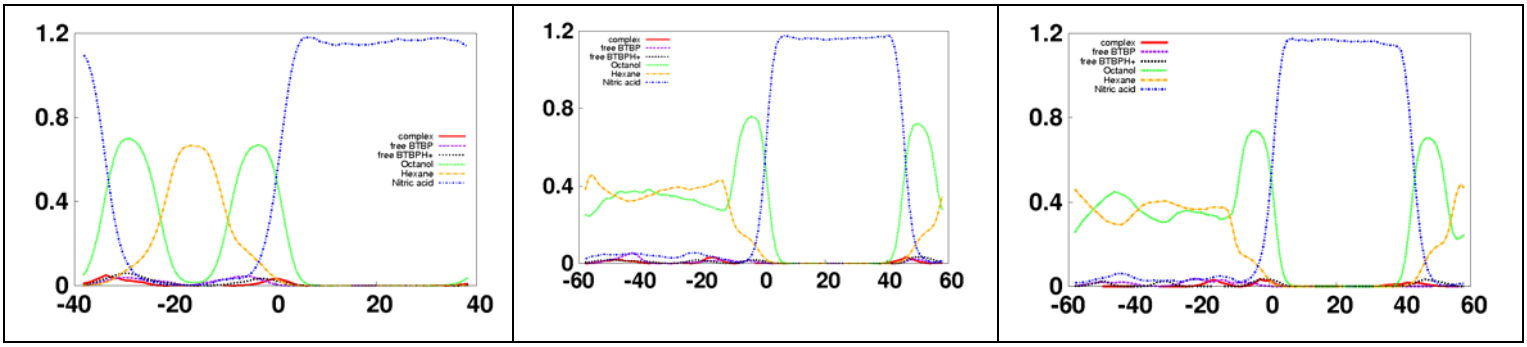


Figure S10: Density curves of systems C (left), E (middle) and F (right), average over the last ns of dynamics (complex in red, neutral BTBP in purple, protonated BTBP in gray, octanol in green, hexane in orange, aqueous phase in blue).

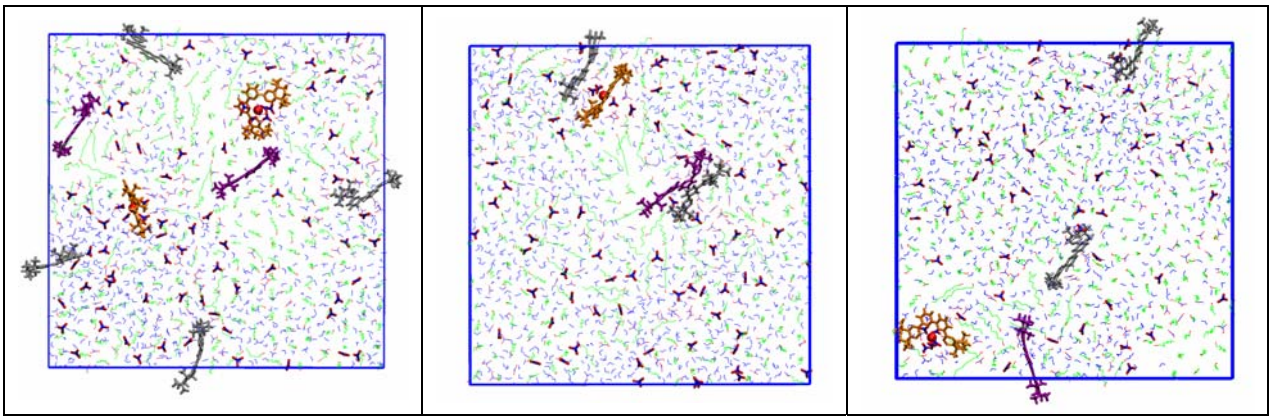


Figure S11: View of the interface (XY slice with ΔZ = 10 Å) of systems C (left), E (middle) and F (right) at the end of the dynamics.

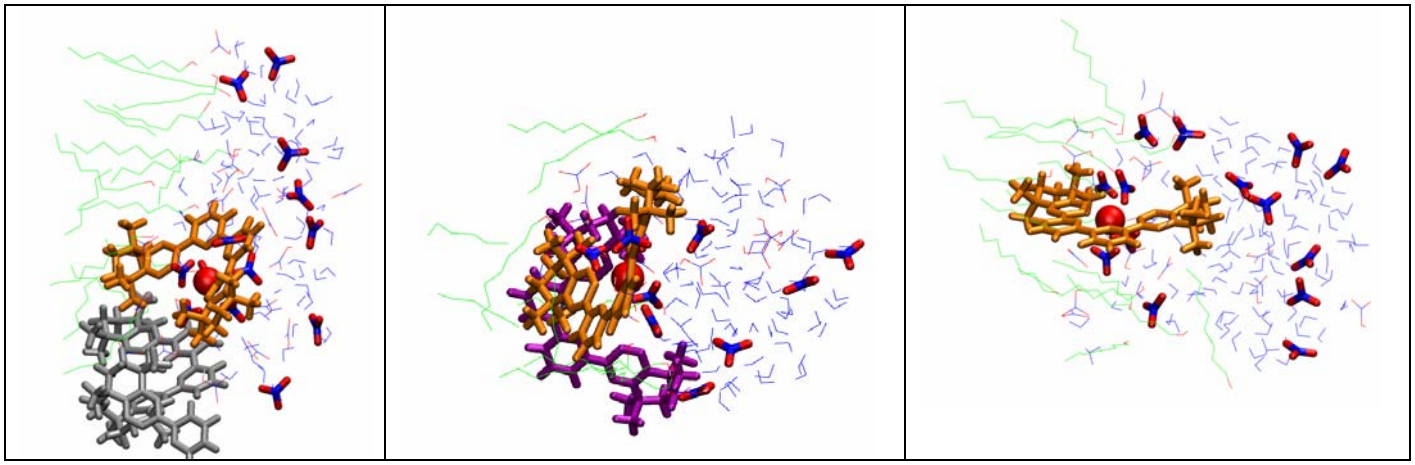


Figure S12: Snapshots of the complexes and their environment in system C.