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Study of the antibacterial activity of *para-tert*-butylcalix[6]arene and its effect on a membrane model: Molecular Dynamics and Langmuir films studies

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Data analysis for Thermodynamic Parameters

The excess area parameter (ΔA^E) values at a given surface pressures were calculated (Eq. (1)) in order to determine the effect of *Calix6* on the lipid monolayer.[1]

$$\Delta A^E = A_{exp} - A_{12} \quad (1)$$

The interactions between the *Calix6* and DPPG molecules in the binary systems were quantitatively analyzed by the excess free energy (ΔG^E)[2] calculated, according to Eq. (2).

$$\Delta G^E = \int_0^{\pi} [A_{exp} - A_{12}] d\pi \quad (2)$$

Ideally mixed or immiscible monolayers exhibit ΔG^E=0. Negative values of ΔG^E are consistent with attractive interactions in the mixed films, i.e., the mixture is thermodynamically more favorable than the separation between respective components and the interactions are energetically more favored than in an ideal mixture. While, positive values of ΔG^E indicate phase separation and/or repulsion in the mixed monolayer, i.e., the interactions between the molecules are weaker than those in the respective pure films.[3,4]

Gibbs energy of mixing (ΔG^M), based on Eq. (3) and (4), was calculated in order to quantitatively analyze the stability of the mixed monolayers.

$$\Delta G^M = \Delta G^E + \Delta G^{ID} \quad (3)$$

$$\Delta G^{ID} = RT (X_1 \ln X_1 + X_2 \ln X_2) \quad (4)$$

where ΔG^{ID} is the Gibbs energy of ideal mixing, which involves entropy terms,[5] X_1 and X_2 denote the mole fraction of the components in mixture, R is the gas constant (8.31451 J K^{-1} mol^{-1}) and T is the temperature in Kelvin.

Thermodynamic parameters reveal the intermolecular interactions and the magnitude of the interaction forces, which can be analyzed in more detail,[2-4] as discussed below. According to the regular solution theory (RST),[2-4] the activity coefficient f_j is given by Eq. (5).[2]

$$\ln f_1 = \frac{\omega (1 - X_1)^2}{RT} \qquad \ln f_2 = \frac{\omega (1 - X_2)^2}{RT} \quad (5)$$

where f_1 and f_2 represent the activity coefficients for the components in mixture (with corresponding mole fractions, X_1 and X_2) and ω is the exchanging energy, which is ascribed to cohesive forces between unlike molecules,[4] calculated from Eq. (6).

$$\omega = \frac{\Delta G^E}{X_1 X_2} \quad (6)$$

The interaction parameter was calculated according to Eq. (7), and the magnitude of the I_p values depended on ΔG^E, where larger negative values of I_p correspond to stronger interactions.[3,4]

$$I_p = \frac{\omega}{RT} \quad (7)$$

Classic Molecular Dynamic (MD)

Water solution was simulated by using the SPCE/FH model,[6] and the force fields between water molecules as well as water-N_2/O_2 (gas) interactions were also

detailed. A pattern of 80290 molecules of water, 176 of N_2 and 56 of O_2 was used for simulating water phase and air phase, respectively. The air phase was defined as two Lennard–Jones sites connected with a rigid bond.[7] *Calix6* molecular geometry was optimized as described in our previous work[8] using CVFF.[9,10] For DPPG molecule the MD calculations were carried out using CHARMM27 (the force field parameters used here are detailed below, in the Table S1, S2 and S3). The convergence criteria for the minimization process was set at 0.001 kcal $Å^{-1}$ mol^{-1}.

Besides the individual components (air, water and monolayers), (1) air/water, (2) water/*Calix6*, (3) *Calix6*/air, (4) water/DPPG, (5) DPPG/air and (6) DPPG:*Calix6* planar interfaces were simulated, which were simulated with a box set to the dimensions $L_x \times L_y \times L_z$, where L_x =12.0 nm, L_y = 24.0 nm and L_z = 8.0 nm (except for the system air/water, where L_z = 10.0 nm). A sequence of NVE (a 1.0 ps run), NVT (a 10.0 ps run) and NPT (a 20.0 ns) calculations were carried out to obtain the thermodynamic properties in equilibrium for each system at 300 K and 1 atm.[8] Periodic boundary conditions have been applied. For long-range electrostatic interactions, the reciprocal PPPM method[8,11-13] was adopted.

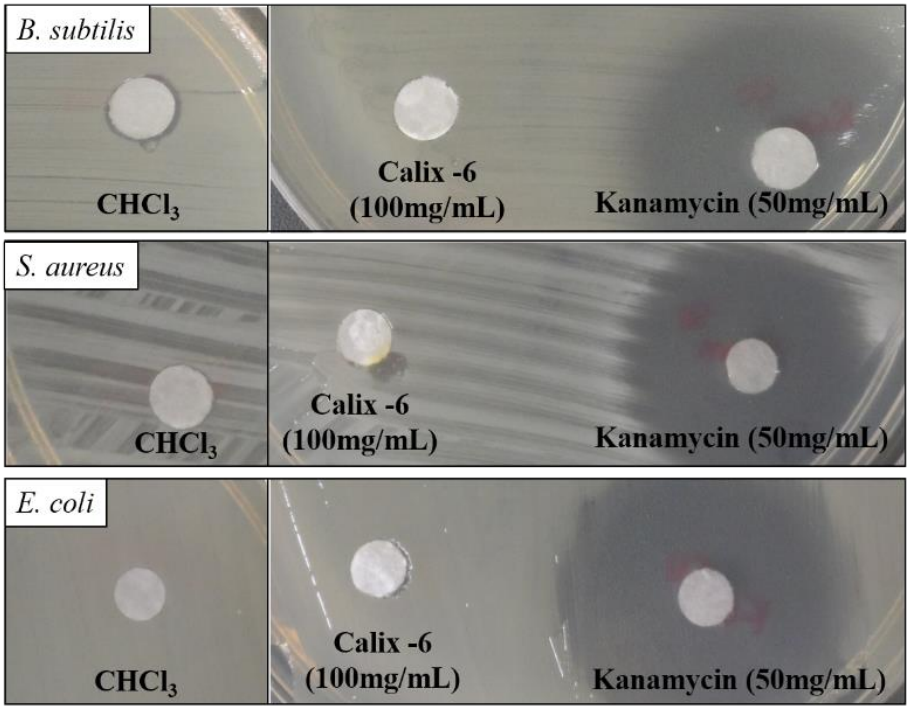

Figure S1. Disc diffusion tests with *Calix6* (100mg mL^{-1}). Gram-negative *E. coli* strain and Gram-positive *S. aureus* and *B. subtilis* strains were incubated in the presence of chloroform, *Calix6* diluted in chloroform and Kanamycin.

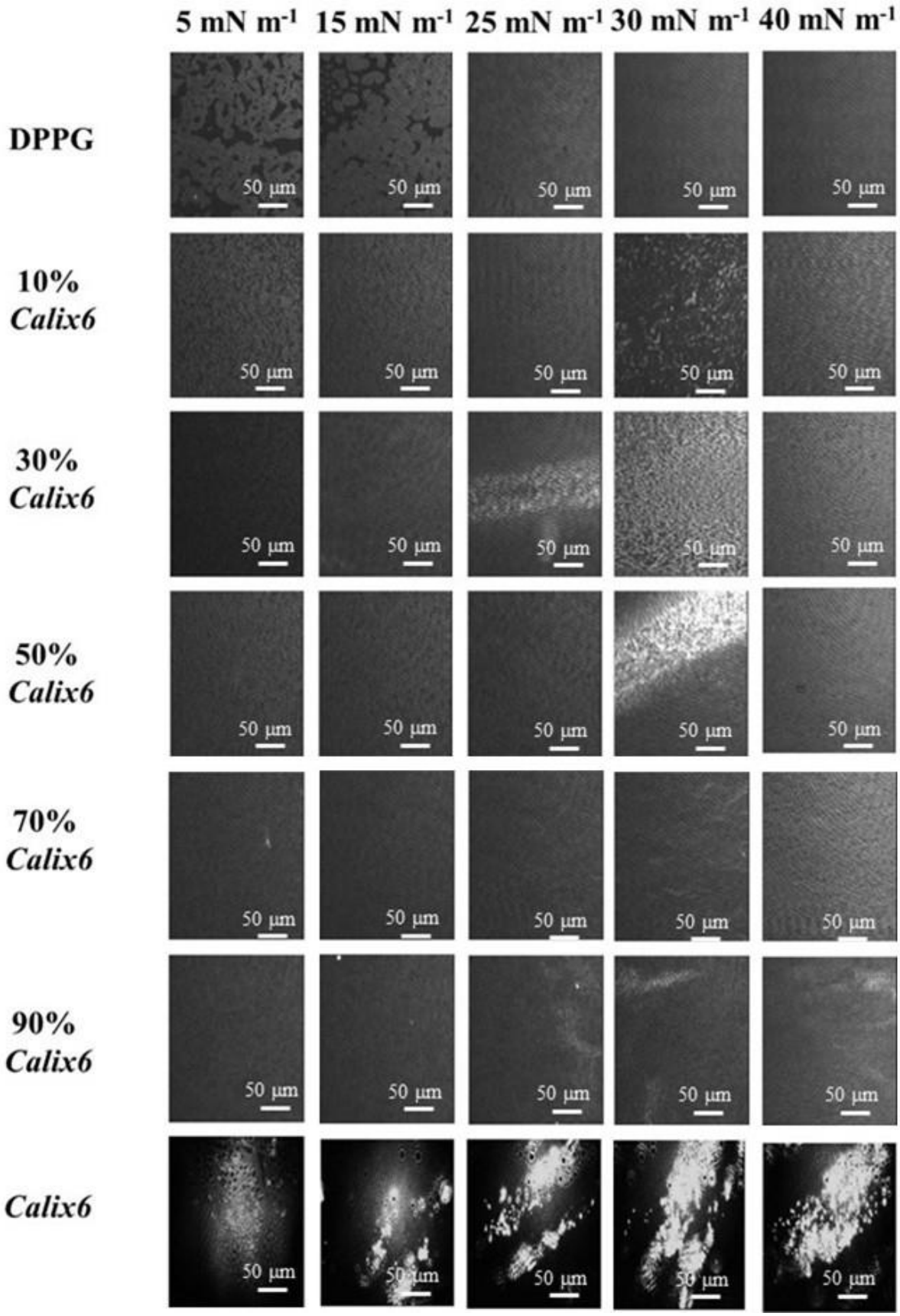

Figure S2. BAM images (width 220 µm) for the DPPG monolayers containing several *Calix6* molar ratios (0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1), at π = 5, 15, 25, 30 and 40 mN m^{-1}.

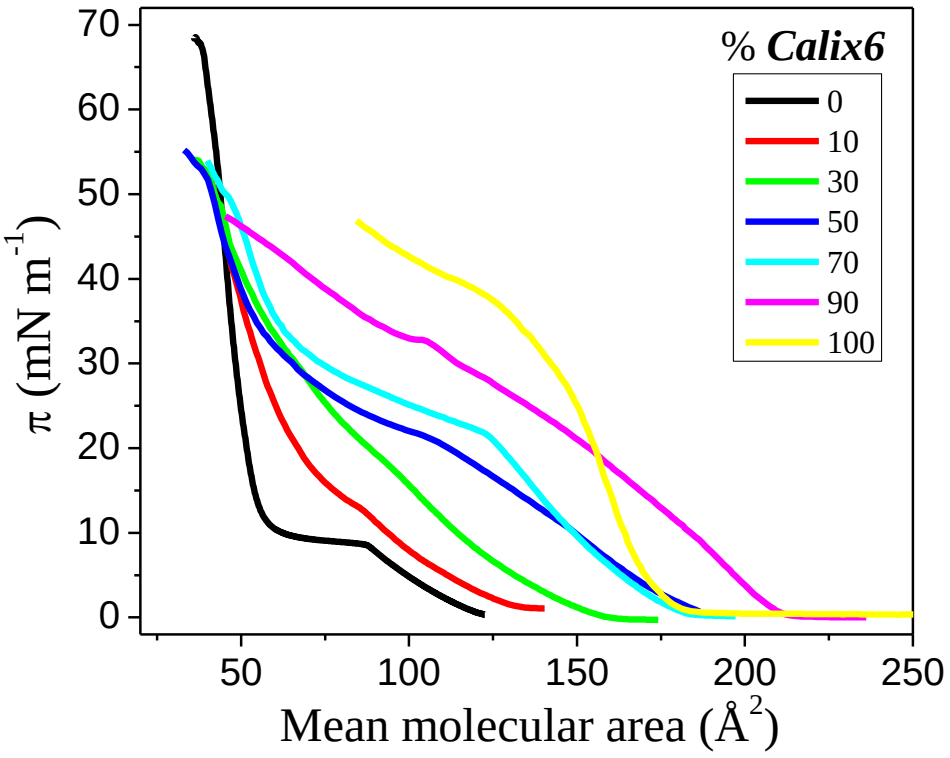

Figure S3. (a) Surface pressure-area isotherms for mixed DPPG:*Calix6* monolayers on PBS buffer, pH = 7.4, for various mole percent of *Calix6*. The area per molecule was calculated assuming that molecules of both DPPG and *Calix6* remain at the interface, and therefore, it is not an area per calixarene molecule.

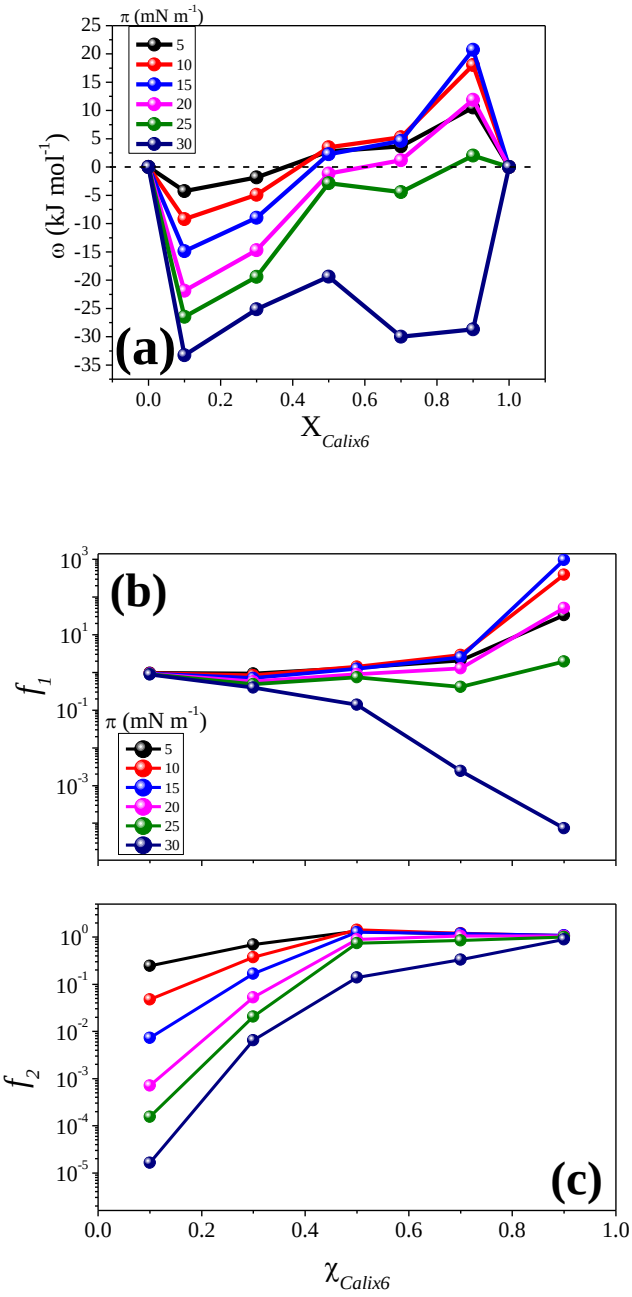

Figure S4. Thermodynamic analysis of **(a)** exchanging energy, and **(b)** f_1 and **(c)** f_2 activity coefficients as a function of molar ratio of *Calix6* for mixed DPPG/*Calix6* monolayers at π =5- 30 mN m^{-1}.

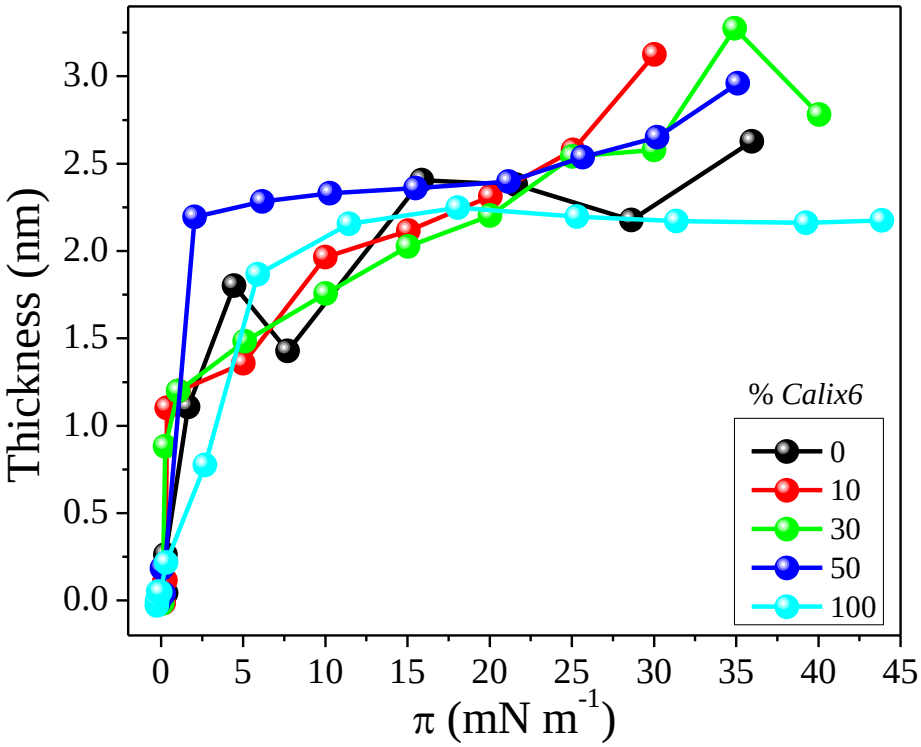

Figure S5. Average thickness for the DPPG/*Calix6* monolayers at the air-water interface, for several *Calix6* molar ratios at different surface pressures, obtained by ellipsometry and fit using a simple box model.

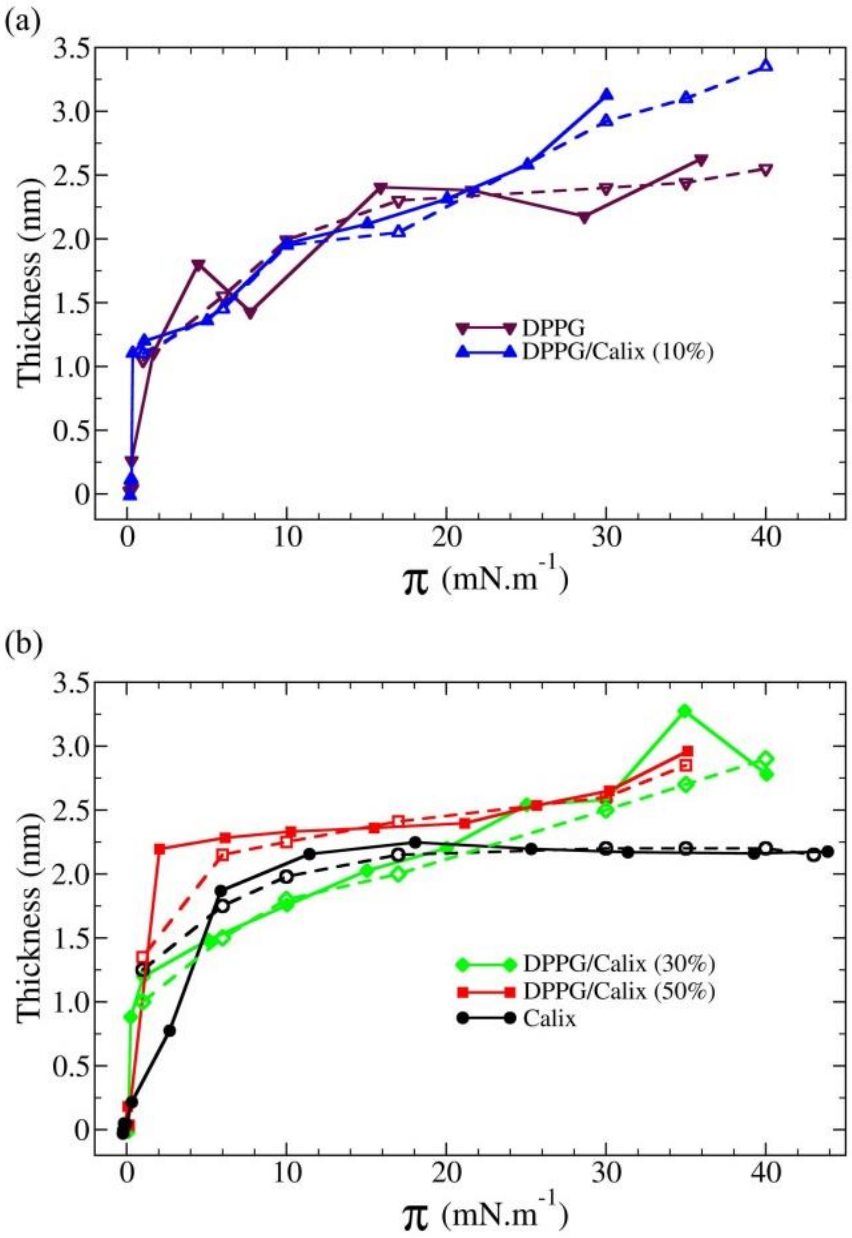

Figure S6. Comparison between the experimental and theoretical thickness values for the DPPG/*Calix6* monolayers on aqueous subphase; full and dotted lines are the experimental and MD results, respectively.

Table S1. Potential parameters for fluids

Parameters of SPC-FH water model			
Site	ε_{ii} *(x10^{-2} kcal/mol)*	σ_{ii} *(Å)*	q_i *(e)*
O	15.525	3.188	-0.8476
H	3.965	0.650	0.4238
	Intramolecular parameters		
	k_b *(kcal/mol/Å^2)*	k_θ *(kcal/mol/rad^2)*	θ-θ_0 *(°)*
O-H	553.92	45.74	109.4
Parameters of N_2 and O_2 gas			
Site	ε_{ii} *(x10^{-2} kcal/mol)*	σ_{ii} *(Å)*	q_i *(e)*
N	16.700	3.320	-
O	22.800	2.990	-

Table S2. Topology and Potential parameters for *Calix6* dimer by LAMMPS style and according to the *Calix6* model.

LAMMPS Calix 6 # units – real

156 atoms
162 bonds
294 angles

7 atom types
9 bond types
13 angle types

0.0000 40.0000 xlo xhi
0.0000 40.0000 ylo yhi
0.0000 40.0000 zlo zhi

Masses

1 12.011150
2 12.011150
3 15.999400
4 12.011150
5 12.011150
6 1.007970
7 1.007970

Pair Coeffs # pair style Lennard-Jones

1 0.14799 3.61704
2 0.03899 3.87540
3 0.22800 2.85978
4 0.15999 3.47450
5 0.03899 3.87540
6 0.03800 2.44997
7 0.03800 2.44997

Bond Coeffs # bond style Harmonic

1 384.0000 1.3700
2 480.0000 1.3400
3 283.0924 1.5100
4 363.4164 1.0800
5 283.0924 1.5100
6 340.6175 1.1050
7 540.6336 0.9600
8 322.7158 1.5260
9 340.6175 1.1050

Angle Coeffs # angle style Harmonic

1 60.0000 120.0000
2 90.0000 120.0000
3 44.2000 120.0000
4 37.0000 120.0000

5	44.2000	120.0000
6	44.4000	110.0000
7	46.6000	110.5000
8	39.5000	106.4000
9	50.0000	109.0000
10	46.6000	110.5000
11	46.6000	110.5000
12	44.4000	110.0000
13	39.5000	106.4000

Atoms # (atom, molecule, type, charge, x, y, z)

1	0	1	0.030000	-15.841334332	21.162318207	-17.359423749
2	0	1	0.000000	-15.841334332	21.162318207	-15.949423783
3	0	1	-0.100000	-14.619334329	21.162318207	-15.282423847
4	0	1	0.000000	-13.407334316	21.154318207	-15.970423691
5	0	1	-0.100000	-13.430334318	21.236318208	-17.359423749
6	0	1	0.000000	-14.628334273	21.224318206	-18.072423749
7	0	2	-0.200000	-17.110334385	21.185318207	-15.147423856
8	0	1	0.000000	-17.412334312	19.887318231	-14.458423726
9	0	1	-0.100000	-16.488334347	19.376318194	-13.549423806
10	0	1	0.000000	-16.723334361	18.200318314	-12.843423955
11	0	1	-0.100000	-17.950334299	17.561318137	-13.005423658
12	0	1	0.000000	-18.898334254	18.020318247	-13.915423744
13	0	1	0.030000	-18.614334334	19.181318261	-14.663423650
14	0	2	-0.200000	-20.186334122	17.262318112	-14.060423724
15	0	1	0.000000	-19.997334469	15.925318219	-14.714423768
16	0	1	-0.100000	-19.242334355	14.960318066	-14.052423827
17	0	1	0.000000	-18.999334324	13.707318284	-14.610423677
18	0	1	-0.100000	-19.611334313	13.385318257	-15.817423694
19	0	1	0.000000	-20.408334244	14.303318001	-16.501423769
20	0	1	0.030000	-20.565334309	15.595318295	-15.961423747
21	0	2	-0.200000	-21.110334385	13.872318245	-17.758423738
22	0	1	0.000000	-20.195334423	13.286318280	-18.789423697
23	0	1	-0.100000	-19.695334423	12.002318360	-18.578423731
24	0	1	0.000000	-18.802334297	11.410318352	-19.465423696
25	0	1	-0.100000	-18.488334406	12.082318284	-20.644423835
26	0	1	0.000000	-18.998334397	13.347318150	-20.921423785
27	0	1	0.030000	-19.828334320	13.969318368	-19.965423696
28	0	2	-0.200000	-18.672334421	13.989318348	-22.237423532
29	0	1	0.000000	-17.244334329	14.432318188	-22.349423520
30	0	1	-0.100000	-16.239334334	13.469318368	-22.352423780
31	0	1	0.000000	-14.894334305	13.809318043	-22.487423532
32	0	1	-0.100000	-14.561334360	15.145318009	-22.692423932
33	0	1	0.000000	-15.534334321	16.143318154	-22.706423871
34	0	1	0.030000	-16.880334366	15.785318352	-22.498423688
35	0	2	-0.200000	-15.120334316	17.557318188	-22.987423532
36	0	1	0.000000	-14.396334279	18.207318284	-21.846423738
37	0	1	0.030000	-14.897334326	19.345318176	-21.185423724
38	0	1	0.000000	-14.128334273	19.998318173	-20.201423757
39	0	1	-0.100000	-12.898334254	19.449318148	-19.846423738
40	0	1	0.000000	-12.417334307	18.282318093	-20.438423745
41	0	1	-0.100000	-13.159334410	17.696318127	-21.459423654
42	0	3	-0.380000	-16.135334332	19.783318259	-21.574423902
43	0	4	0.000000	-11.084334362	17.709318139	-19.997423761

44	0	5	-0.300000	-10.918334473	17.848318316	-18.481423728
45	0	2	-0.200000	-14.566334356	21.287318207	-19.568423860
46	0	4	0.000000	-13.838334311	12.722318627	-22.457423799
47	0	5	-0.300000	-12.458334435	13.290317990	-22.122423761
48	0	3	-0.380000	-17.893334378	16.704318024	-22.451423757
49	0	4	0.000000	-18.178334225	10.060317971	-19.176423781
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51	0	3	-0.380000	-20.329334248	15.231317975	-20.127423637
52	0	4	0.000000	-18.030334223	12.765317894	-13.924423806
53	0	5	-0.300000	-18.178334225	11.327318169	-14.421423785
54	0	3	-0.380000	-21.284334172	16.582318284	-16.581423752
55	0	4	0.000000	-15.649334330	17.568318106	-11.981423967
56	0	5	-0.300000	-14.594334353	18.586318232	-11.546423547
57	0	3	-0.380000	-19.476334322	19.689318158	-15.596423738
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72	0	5	-0.300000	-12.230334271	19.965318181	-14.126423709
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74	0	6	0.100000	-17.926334370	8.679318406	-17.506423749
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131	0	6	0.100000	-10.904334534	22.376318194	-13.944423787
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133	0	6	0.100000	-13.526334275	12.801318146	-24.615423791
134	0	6	0.100000	-12.765334357	16.794318177	-21.968423955
135	0	6	0.100000	-12.474334229	21.278318204	-17.913423769
136	0	6	0.100000	-21.698334206	14.708318211	-18.196423762
137	0	6	0.100000	-12.285334337	19.935318209	-19.062423699
138	0	6	0.100000	-20.937334526	17.874318100	-14.606423728
139	0	6	0.100000	-8.981334198	18.134318091	-20.410423867
140	0	6	0.100000	-17.025334347	21.975318231	-14.372423761
141	0	6	0.100000	-12.646334398	22.686318256	-13.852423780
142	0	6	0.100000	-19.369334448	14.833318211	-22.437423818
143	0	7	0.350000	-21.531334389	16.266318299	-17.447423749
144	0	6	0.100000	-11.730334271	23.201318242	-15.278423660
145	0	7	0.350000	-20.009334553	15.568318345	-20.962423675
146	0	7	0.350000	-20.224334229	19.099318244	-15.656423800
147	0	6	0.100000	-10.030334461	19.561318256	-20.467423789
148	0	6	0.100000	-17.960334290	21.503318198	-15.791423790
149	0	6	0.100000	-10.055334557	18.390318133	-21.796423547
150	0	6	0.100000	-14.450334299	17.561318137	-23.872423761
151	0	7	0.350000	-17.507334340	17.570318200	-22.565423600
152	0	7	0.350000	-17.728334296	21.100318208	-17.496423744
153	0	6	0.100000	-13.841334332	22.076318182	-19.862423770

154	0	6	0.100000	-16.004334334	18.159318186	-23.295423620
155	0	7	0.350000	-16.390334357	20.496318199	-20.994423740
156	0	6	0.100000	-15.541334320	21.628318198	-19.981423728

Bonds # (id, type, atom1, atom2)

1	1	1	60
2	2	1	6
3	2	1	2
4	3	2	7
5	2	2	3
6	4	3	126
7	2	3	4
8	2	4	5
9	5	4	58
10	4	5	135
11	2	5	6
12	3	6	45
13	6	7	140
14	3	8	7
15	6	7	148
16	2	8	13
17	2	8	9
18	2	9	10
19	4	9	121
20	2	10	11
21	5	10	55
22	4	11	105
23	2	11	12
24	2	12	13
25	3	12	14
26	1	13	57
27	3	15	14
28	6	14	138
29	6	14	128
30	2	15	16
31	2	15	20
32	2	16	17
33	4	16	104
34	5	17	52
35	2	17	18
36	4	18	103
37	2	18	19
38	2	19	20
39	3	19	21
40	1	20	54
41	3	22	21
42	6	21	127
43	6	21	136
44	2	22	23
45	2	22	27
46	4	23	102
47	2	23	24
48	2	24	25
82	4	41	134
83	7	42	155
84	8	43	61
85	8	43	62
86	8	43	44
87	9	44	130
88	9	44	118
89	9	44	117
90	6	45	156
91	6	45	153
92	8	46	47
93	8	46	64
94	8	46	63
95	9	47	94
96	9	47	98
97	9	47	113
98	7	48	151
99	8	49	65
100	8	49	66
101	8	49	50
102	9	50	86
103	9	50	74
104	9	50	80
105	7	51	145
106	8	52	68
107	8	52	53
108	8	52	67
109	9	53	79
110	9	53	88
111	9	53	76
112	7	54	143
113	8	55	69
114	8	55	56
115	8	55	70
116	9	56	95
117	9	56	89
118	9	56	82
119	7	57	146
120	8	58	72
121	8	58	71
122	8	58	59
123	9	59	111
124	9	59	125
125	9	59	112
126	7	60	152
127	9	61	139
128	9	61	147
129	9	61	149

49	5	24	49
50	2	25	26
51	4	25	108
52	3	26	28
53	2	26	27
54	1	27	51
55	6	28	142
56	3	29	28
57	6	28	132
58	2	29	34
59	2	29	30
60	4	30	120
61	2	30	31
62	5	31	46
63	2	31	32
64	4	32	129
65	2	32	33
66	3	33	35
67	2	33	34
68	1	34	48
69	6	35	150
70	6	35	154
71	3	36	35
72	2	36	37
73	2	36	41
74	1	37	42
75	2	37	38
76	2	38	39
77	3	38	45
78	2	39	40
79	4	39	137
80	5	40	43
81	2	40	41

130	9	62	109
131	9	62	114
132	9	62	124
133	9	63	123
134	9	63	122
135	9	63	133
136	9	64	100
137	9	64	90
138	9	64	93
139	9	65	101
140	9	65	91
141	9	65	107
142	9	66	81
143	9	66	84
144	9	66	73
145	9	67	99
146	9	67	110
147	9	67	92
148	9	68	75
149	9	68	83
150	9	68	77
151	9	69	116
152	9	69	119
153	9	69	96
154	9	70	78
155	9	70	87
156	9	70	85
157	9	71	131
158	9	71	141
159	9	71	144
160	9	72	97
161	9	72	106
162	9	72	115

Angles # (id, type, atom1, atom2, atom3)

1	1	6	1	60
2	1	2	1	60
3	2	6	1	2
4	3	1	2	7
5	2	1	2	3
6	3	3	2	7
7	4	2	3	126
8	2	2	3	4
9	4	4	3	126
10	2	3	4	5
11	5	3	4	58
12	5	5	4	58
13	4	4	5	135
14	2	4	5	6
15	4	6	5	135
16	2	1	6	5
17	3	1	6	45
18	3	5	6	45
19	6	2	7	140

148	12	43	44	117
149	13	130	44	118
150	13	130	44	117
151	13	118	44	117
152	7	6	45	38
153	6	6	45	156
154	6	6	45	153
155	6	38	45	156
156	6	38	45	153
157	8	156	45	153
158	10	31	46	47
159	10	31	46	64
160	10	31	46	63
161	11	47	46	64
162	11	47	46	63
163	11	64	46	63
164	12	46	47	94
165	12	46	47	98
166	12	46	47	113

20	7	2	7	8
21	6	2	7	148
22	6	8	7	140
23	8	140	7	148
24	6	8	7	148
25	3	13	8	7
26	3	9	8	7
27	2	13	8	9
28	2	8	9	10
29	4	8	9	121
30	4	10	9	121
31	2	9	10	11
32	5	9	10	55
33	5	11	10	55
34	4	10	11	105
35	2	10	11	12
36	4	12	11	105
37	2	11	12	13
38	3	11	12	14
39	3	13	12	14
40	2	8	13	12
41	1	8	13	57
42	1	12	13	57
43	7	12	14	15
44	6	12	14	138
45	6	12	14	128
46	6	15	14	138
47	6	15	14	128
48	8	138	14	128
49	3	16	15	14
50	3	20	15	14
51	2	16	15	20
52	2	15	16	17
53	4	15	16	104
54	4	17	16	104
55	5	16	17	52
56	2	16	17	18
57	5	18	17	52
58	4	17	18	103
59	2	17	18	19
60	4	19	18	103
61	2	18	19	20
62	3	18	19	21
63	3	20	19	21
64	2	15	20	19
65	1	15	20	54
66	1	19	20	54
67	7	19	21	22
68	6	19	21	127
69	6	19	21	136
70	6	22	21	127
71	6	22	21	136
72	8	127	21	136
73	3	23	22	21
74	3	27	22	21
167	13	94	47	98
168	13	94	47	113
169	13	98	47	113
170	9	34	48	151
171	10	24	49	65
172	10	24	49	66
173	10	24	49	50
174	11	65	49	66
175	11	65	49	50
176	11	66	49	50
177	12	49	50	86
178	12	49	50	74
179	12	49	50	80
180	13	86	50	74
181	13	86	50	80
182	13	74	50	80
183	9	27	51	145
184	10	17	52	68
185	10	17	52	53
186	10	17	52	67
187	11	68	52	53
188	11	68	52	67
189	11	53	52	67
190	12	52	53	79
191	12	52	53	88
192	12	52	53	76
193	13	79	53	88
194	13	79	53	76
195	13	88	53	76
196	9	20	54	143
197	10	10	55	69
198	10	10	55	56
199	10	10	55	70
200	11	69	55	56
201	11	69	55	70
202	11	56	55	70
203	12	55	56	95
204	12	55	56	89
205	12	55	56	82
206	13	95	56	89
207	13	95	56	82
208	13	89	56	82
209	9	13	57	146
210	10	4	58	72
211	10	4	58	71
212	10	4	58	59
213	11	72	58	71
214	11	72	58	59
215	11	71	58	59
216	12	58	59	111
217	12	58	59	125
218	12	58	59	112
219	13	111	59	125
220	13	111	59	112
221	13	125	59	112

75	2	23	22	27
76	4	22	23	102
77	2	22	23	24
78	4	24	23	102
79	2	23	24	25
80	5	23	24	49
81	5	25	24	49
82	2	24	25	26
83	4	24	25	108
84	4	26	25	108
85	3	25	26	28
86	2	25	26	27
87	3	27	26	28
88	2	22	27	26
89	1	22	27	51
90	1	26	27	51
91	6	26	28	142
92	7	26	28	29
93	6	26	28	132
94	6	29	28	142
95	8	142	28	132
96	6	29	28	132
97	3	34	29	28
98	3	30	29	28
99	2	34	29	30
100	4	29	30	120
101	2	29	30	31
102	4	31	30	120
103	5	30	31	46
104	2	30	31	32
105	5	32	31	46
106	4	31	32	129
107	2	31	32	33
108	4	33	32	129
109	3	32	33	35
110	2	32	33	34
111	3	34	33	35
112	2	29	34	33
113	1	29	34	48
114	1	33	34	48
115	6	33	35	150
116	6	33	35	154
117	7	33	35	36
118	8	150	35	154
119	6	36	35	150
120	6	36	35	154
121	3	37	36	35
122	3	41	36	35
123	2	37	36	41
124	1	36	37	42
125	2	36	37	38
126	1	38	37	42
127	2	37	38	39
128	3	37	38	45
129	3	39	38	45
222	9	1	60	152
223	12	43	61	139
224	12	43	61	147
225	12	43	61	149
226	13	139	61	147
227	13	139	61	149
228	13	147	61	149
229	12	43	62	109
230	12	43	62	114
231	12	43	62	124
232	13	109	62	114
233	13	109	62	124
234	13	114	62	124
235	12	46	63	123
236	12	46	63	122
237	12	46	63	133
238	13	123	63	122
239	13	123	63	133
240	13	122	63	133
241	12	46	64	100
242	12	46	64	90
243	12	46	64	93
244	13	100	64	90
245	13	100	64	93
246	13	90	64	93
247	12	49	65	101
248	12	49	65	91
249	12	49	65	107
250	13	101	65	91
251	13	101	65	107
252	13	91	65	107
253	12	49	66	81
254	12	49	66	84
255	12	49	66	73
256	13	81	66	84
257	13	81	66	73
258	13	84	66	73
259	12	52	67	99
260	12	52	67	110
261	12	52	67	92
262	13	99	67	110
263	13	99	67	92
264	13	110	67	92
265	12	52	68	75
266	12	52	68	83
267	12	52	68	77
268	13	75	68	83
269	13	75	68	77
270	13	83	68	77
271	12	55	69	116
272	12	55	69	119
273	12	55	69	96
274	13	116	69	119
275	13	116	69	96
276	13	119	69	96

130	2	38	39	40
131	4	38	39	137
132	4	40	39	137
133	5	39	40	43
134	2	39	40	41
135	5	41	40	43
136	2	36	41	40
137	4	36	41	134
138	4	40	41	134
139	9	37	42	155
140	10	40	43	61
141	10	40	43	62
142	10	40	43	44
143	11	61	43	62
144	11	61	43	44
145	11	62	43	44
146	12	43	44	130
147	12	43	44	118

277	12	55	70	78
278	12	55	70	87
279	12	55	70	85
280	13	78	70	87
281	13	78	70	85
282	13	87	70	85
283	12	58	71	131
284	12	58	71	141
285	12	58	71	144
286	13	131	71	141
287	13	131	71	144
288	13	141	71	144
289	12	58	72	97
290	12	58	72	106
291	12	58	72	115
292	13	97	72	106
293	13	97	72	115
294	13	106	72	115

Table S3. Topology and Potential parameters for *DPPG* phospholipid molecule by LAMMPS style and according to the *DPPG* model.

LAMMPS DPPG # units – real

109 atoms
107 bonds
186 angles
246 dihedrals

11 atom types
17 bond types
36 angle types
52 dihedral types

0.000000000 40.000000000 xlo xhi
0.000000000 15.000000000 ylo yhi
0.000000000 15.000000000 zlo zhi

Masses

1	30.973801
2	12.011150
3	15.999400
4	15.999400
5	12.011150
6	12.011150
7	1.007970
8	15.999400
9	1.007970
10	12.011150
11	22.990000

Pair Coeffs

1	0.1999976833	3.7417782334
2	0.0389999952	3.8754094636
3	0.2280000124	2.8597848722
4	0.2280000124	2.8597848722
5	0.0389999952	3.8754094636
6	0.1599999990	3.4745050026
7	0.0380000011	2.4499714540
8	0.2280000124	2.8597848722
9	0.0380000011	2.4499714540
10	0.0389999952	3.8754094636
11	1.6071428571	1.8974388864

Bond Coeffs

1	480.0000	1.5300
2	245.2000	1.6100
3	322.7158	1.5260
4	322.7158	1.5260
5	340.6175	1.1050
6	273.2000	1.4250
7	384.0000	1.4200
8	340.6175	1.1050
9	273.2000	1.4250
10	273.2000	1.4250
11	322.7158	1.5260
12	340.6175	1.1050
13	322.7158	1.5260
14	540.6336	0.9600
15	322.7158	1.5260
16	340.6175	1.1050
17	384.0000	1.4200

Angle Coeffs

1	110.0000	109.5000
2	110.0000	109.5000
3	110.0000	109.5000
4	46.6000	110.5000
5	44.4000	110.0000
6	44.4000	110.0000
7	39.5000	106.4000
8	72.0000	120.0000
9	57.0000	109.5000
10	70.0000	109.5000
11	46.6000	110.5000
12	70.0000	109.5000
13	44.4000	110.0000
14	57.0000	109.5000
15	70.0000	109.5000
16	57.0000	109.5000
17	60.0000	109.5000
18	70.0000	109.5000

19	70.0000	109.5000
20	44.4000	110.0000
21	46.6000	110.5000
22	46.6000	110.5000
23	44.4000	110.0000
24	46.6000	110.5000
25	44.4000	110.0000
26	46.6000	110.5000
27	60.0000	109.5000
28	70.0000	109.5000
29	58.5000	106.0000
30	46.6000	110.5000
31	44.4000	110.0000
32	44.4000	110.0000
33	39.5000	106.4000
34	70.0000	109.5000
35	57.0000	109.5000
36	58.5000	106.0000

Dihedral Coeffs

1	0.2500	1	3
2	0.2500	1	3
3	0.1581	1	3
4	0.1581	1	3
5	0.1581	1	3
6	0.1581	1	3
7	0.1581	1	3
8	0.1581	1	3
9	0.1581	1	3
10	0.1581	1	3
11	0.1581	1	3
12	0.1581	1	3
13	0.1300	1	3
14	0.1300	1	3
15	0.1581	1	3
16	0.1581	1	3
17	0.1581	1	3
18	0.1300	1	3
19	0.1300	1	3
20	0.1581	1	3
21	0.1581	1	3
22	0.1300	1	3
23	0.1300	1	3
24	0.1300	1	3
25	0.1300	1	3
26	0.1950	1	3
27	0.1950	1	3
28	0.2371	1	3
29	0.2371	1	3
30	0.1581	1	3
31	0.1581	1	3
32	0.1581	1	3
33	0.1581	1	3
34	0.2371	1	3
35	0.2371	1	3
36	0.2371	1	3
37	0.2371	1	3
38	0.3556	1	3
39	0.3556	1	3
40	0.3556	1	3
41	0.3556	1	3
42	0.3556	1	3
43	0.1950	1	3
44	0.1950	1	3
45	0.3556	1	3
46	0.3556	1	3
47 to 51	0.1581	1	3

Atoms

1	0	1	1.400000	8.778427525	7.127042974	4.479965264
2	0	2	-0.200000	7.585427685	11.306042875	5.300965244
3	0	3	-0.500000	10.236427231	6.641043032	4.988965208
4	0	3	-0.500000	8.567427082	8.479042972	5.363965208
5	0	4	-0.850000	7.730427189	6.250043000	5.022965247
6	0	4	-0.850000	8.852426930	7.327042962	3.068965251
7	0	2	-0.050000	9.461427136	9.655042971	5.120965177
8	0	5	-0.070000	8.641427441	10.802042927	4.340965325
9	0	2	-0.050000	10.358427448	6.384042944	6.435965220
10	0	5	0.050000	11.892427368	6.610043014	6.708965206
11	0	2	-0.050000	12.782427235	5.823043073	5.787965232
12	0	3	-0.300000	12.203427239	8.071042987	6.454965220
13	0	3	-0.150000	11.910427494	8.418042983	8.696965272
14	0	6	0.300000	12.184427185	8.731043006	7.586965257
15	0	2	-0.200000	12.541427536	10.251043047	7.211965198
16	0	2	-0.200000	13.895427389	10.694042887	7.950965220
17	0	2	-0.200000	15.058427258	9.905042971	7.458965236
18	0	2	-0.200000	16.437427325	10.295042957	8.222965175
19	0	6	-0.100000	17.646427347	9.602042998	7.658965165

20	0	6	-0.100000	18.863427324	10.217042888	8.482965285
21	0	6	-0.100000	20.184427424	9.614042963	7.767965252
22	0	6	-0.100000	21.401427431	10.310043062	8.612965161
23	0	6	-0.100000	22.697427197	9.662042941	7.815965230
24	0	6	-0.100000	23.823427124	10.262042965	8.648965174
25	0	6	-0.100000	25.231427117	9.707043017	7.954965169
26	0	3	-0.300000	14.172427340	6.037042941	6.346965218
27	0	3	-0.150000	14.975427313	4.924042906	4.619965250
28	0	6	0.300000	15.136427326	5.434042896	5.630965227
29	0	6	-0.100000	16.461427374	6.018043007	6.358965220
30	0	6	-0.100000	17.683427347	5.400042976	5.671965236
31	0	6	-0.100000	18.981427355	5.785042967	6.513965221
32	0	6	-0.100000	20.144427462	5.342042888	5.754965240
33	0	6	-0.100000	21.445427342	5.824043001	6.453965220
34	0	6	-0.100000	22.746427460	5.418043102	5.686965221
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36	0	6	-0.100000	25.253427429	5.487042869	5.653965229
37	0	6	-0.100000	26.465427799	5.894042934	6.494965220
38	0	6	-0.100000	27.724427624	5.328042949	5.728965217
39	0	6	-0.100000	28.894427700	6.235043014	6.381965222
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46	0	7	0.100000	12.518427296	4.775042976	5.802965218
47	0	7	0.100000	12.714427395	6.196042980	4.775965268
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229	50	91	90	93	96
230	50	91	90	93	95
231	50	91	90	93	94
232	50	92	90	93	96
233	50	92	90	93	95
234	50	92	90	93	94
235	49	81	97	100	101
236	49	81	97	100	102
237	49	81	97	100	103
238	50	98	97	100	101
239	50	98	97	100	102
240	50	98	97	100	103
241	50	99	97	100	101
242	50	99	97	100	102
243	50	99	97	100	103
244	51	2	104	106	107
245	52	105	104	106	107
246	52	108	104	106	107

Table S4. Summary of thermodynamic parameter changes from Figure S4.

Parameter	10% - 30% *Calix6*	50% - 70% *Calix 6*	-90% *Calix 6*
ω, I_P	At all π values, ω, $I_P < 0$ indicating attractive molecular interactions. Values become more negative with increasing pressure due increasing impact of the intermolecular interactions when the film is more densely packed. For any given pressure, the most negative value is found for 10% *Calix6*, evidence of strong favourable interactions.	At low π, ω, $I_P > 0$ indicating repulsive interactions At high π, $\omega < 0$ attributed to a thermodynamic instability of the monolayer (expulsion of *Calix6*).	Same as 50% *Calix6*, except that as % Calix6 increases, the pressure at which ω, I_P become negative increases.
$f_1 = f_{DPPG}$ (effect of *Calix6* on DPPG)	f_{DPPG} close to 1 but deviate (decrease) slightly as π increases = no impact on DPPG.	f_{DPPG} still relatively close to 1 = little impact on DPPG for π <30 mN m^{-1}; deviation increases at high π attributed to expulsion of *Calix6*	Strong deviations from ideality. For $\pi \leq 25$ mN m^{-1}, $f_{DPPG} > 1$ indicating repulsive interactions, i.e. DPPG:DPPG interactions are favored instead of DPPG:*Calix6,* especially at low π. For $\pi = 30$ mN m^{-1} , f_1 is significantly lower than 1 due to expulsion of *Calix6* from the monolayer inducing a film contraction.
$f_2 = f_{Calix6}$ (effect of DPPG on *Calix6*)	f_2 is less than 1, and decreases significantly with increasing surface pressure. This behavior indicates that the attractive DPPG:*Calix6* interactions are stronger than *Calix6*:*Calix6*.	By increasing the *Calix6* molar ratio in the mixed monolayer, f_2 values are close to 1, indicating that there is no difference between the DPPG:*Calix6*, DPPG:DPPG and *Calix6*:*Calix6* interactions. Only at 30 mN m^{-1} is there significant deviation due to expulsion.	

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