Supporting Information

Distinctive Formation of PEG-Lipid Nanopatches onto Solid Polymer Surfaces Interfacing Solvents from Atomistic Simulation

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S1 The DSPE-PEG Macromolecule

The block copolymer DSPE-PEG(2000), 1, 2-Distearoyl-sn-glycero-3-phosphoethanolamine-poly(ethylene glycol)$_{45}$amine is shown in Fig. S1.

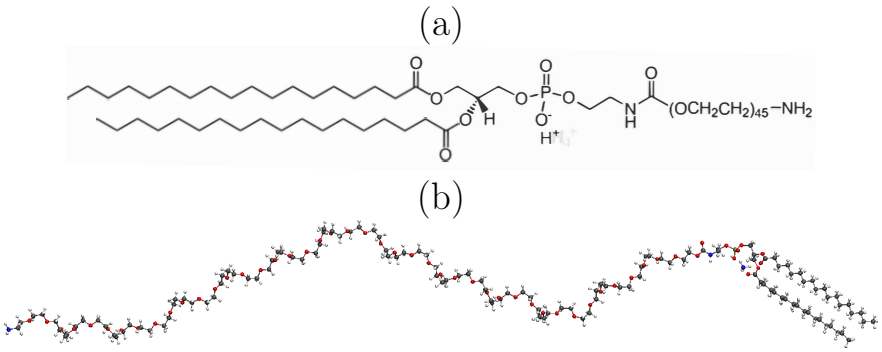

Figure S1: Illustration of the DSPE-PEG macromolecule. (a) Chemical representation, from https://avantilipids.com/product/880128; the PEG component has molecular weight 2000 u. (b) Rendering of the DFT-optimized structure.

This macromolecule was modeled with the GAFF force field for which the RESP atomic charges were calculated and are shown in Table S1. The atomic charges correspond to the DSPE-PEG structure depicted in Fig. S1b. Figure S2 shows the atomic charges values across the length of the macromolecule.

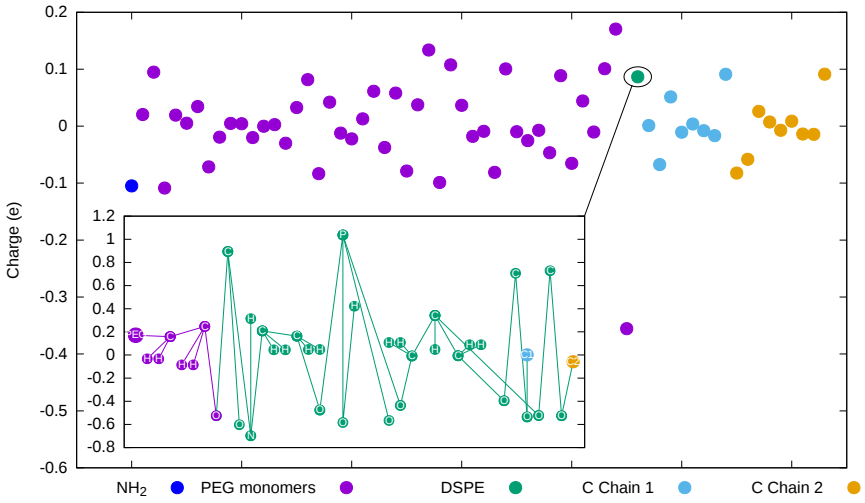

Figure S2: Atomic charges of the DSPE-PEG macromolecule summed over each PEG monomer, in full detail around the phosphorus atom (insert), and every two backbone carbons of each DSPE acyl chain.

S2 Energetics of the PLGA Solid Slab Interfacing Solutions with DSPE-PEG solute

The MD simulations of DSPE-PEG droplet formed on the PLGA surface were 100 ns long and 200 ns long in cases containing EA. These simulations allowed for the collection of significant statistical data showing how the macromolecules composing the droplet accommodate while anchored on the PLGA surface. Figure S3 shows the potential energy of the full PLGA+solvent+DSPE-PEG droplet along the last half of the full NVT trajectory for the three solvents considered in this work. Figure S4(a) shows the interaction energy of the

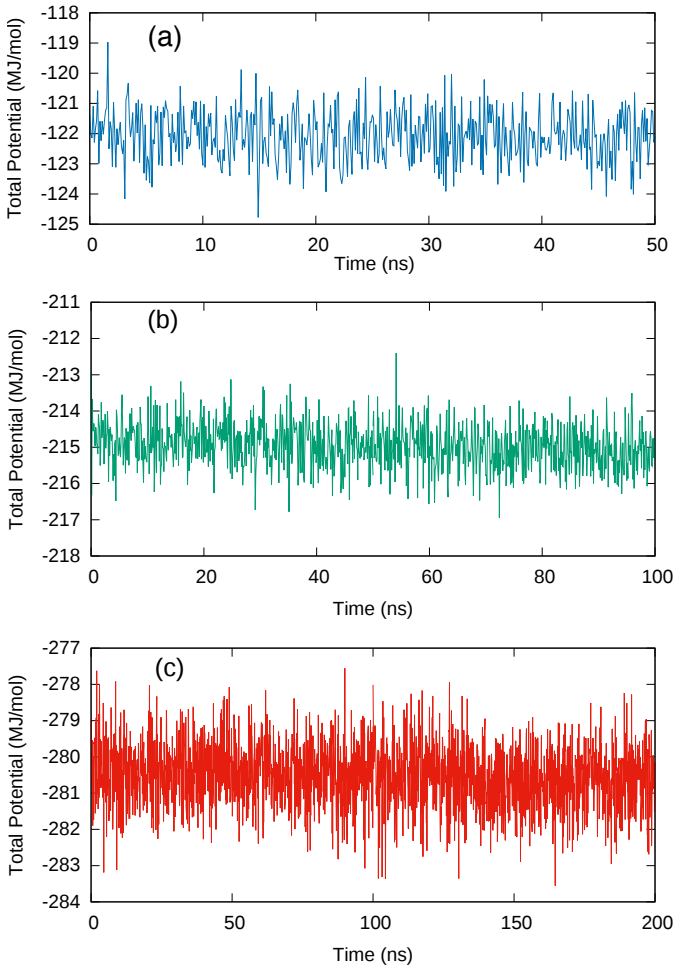

Figure S3: Total potential energy of the ternary systems PLGA+solvent+DSPE-PEG droplet along the NVT simulation at 300 K and at the corresponding equilibrated volume from previous Parrinello-Rahman NPT runs at 300 K and 101.325 kPa. (a) Solvent is water, with depicted last 50 ns of the 100 ns trajectory; (b) solvent is ethyl acetate, with depicted last 100 ns of a 200 ns trajectory; (c) solvent is ethyl acetate:water mixture along the full 200 ns trajectory.

DSPE-PEG droplet with the PLGA solid block split per contribution of the PEG portion

and the DSPE portion of the copolymer. Figure S4(b) shows the interaction energy of the DSPE-PEG droplet with the solvent split per contribution of the PEG portion and the DSPE portion of the lipid copolymer.

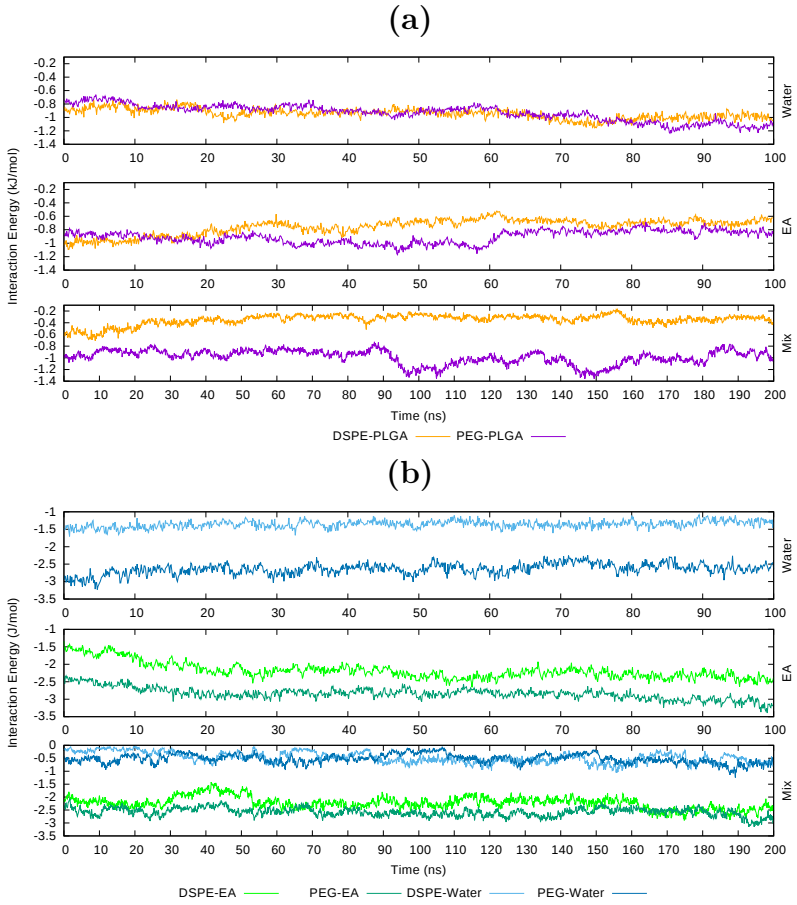

Figure S4: (a) DSPE-PEG droplet interaction energy with the PLGA solid split per contribution of the PEG and DSPE portions of the polymer; (b) DSPE-PEG droplet interaction energy with the solvent split per contribution of the PEG and DSPE portions of the polymer.

When analyzing the characteristics of the DSPE-PEG droplet formation, the hight of each atom within the droplet with respect to the PLGA surface was evaluated. Figure S5 has histograms of the distribution of heights with respect to the surface of all the atoms in either the PEG or DSPE portions of the droplets. For visualization purposes, an idealized enveloping hemispherical cap was proposed to identify the wetting contact angle of the formed DSPE-PEG droplets on the PLGA surface. Figure S6 (left) depicts the idealized enveloping sphere cap. Two possible definitions of the contact angle are either θ_a the angle

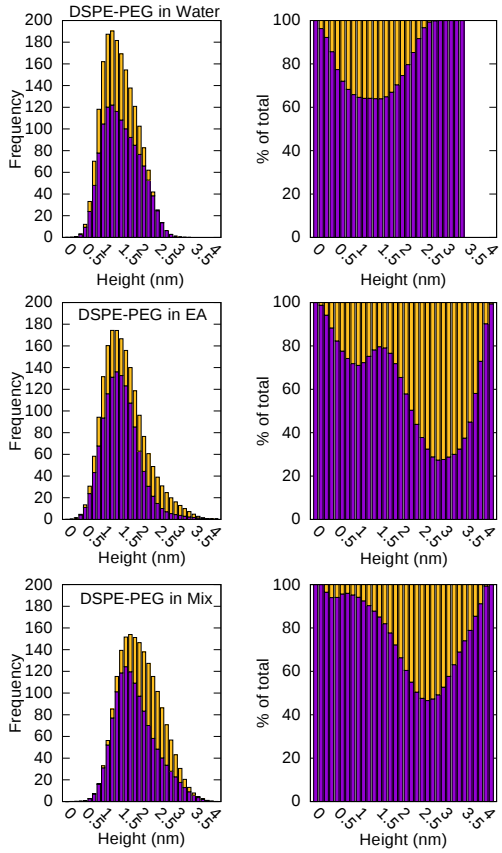

Figure S5: Distribution of DSPE and PEG atom heights with respect to the PLGA surface in the DSPE-PEG droplets formed within water (top), EA (middle), and mixed solvent (bottom). Left panels are stacked histograms where magenta is PEG and gold is DSPE; their sum represents the full droplet. Right panels are the corresponding percent distributions of DSPE and of PEG atomic heights within the droplet.

between the cup radius and the secant reaching the cup apex, or θ_b the angle between the sphere tangent with the horizontal axis along the surface, as illustrated in Fig. S6 (right).

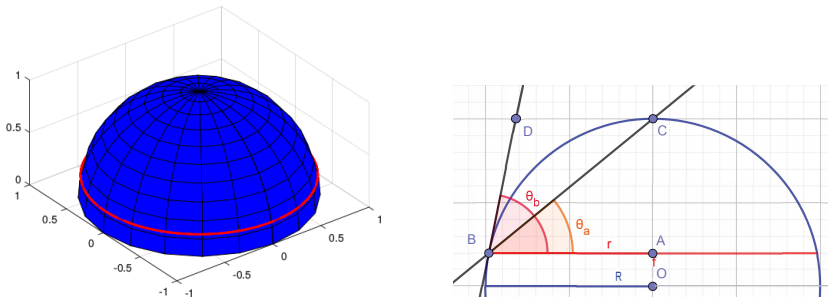

Figure S6: Diagram visualizing the variables leading to the wetting contact angle of an idealized spherical envelope of the DSPE-PEG droplet on the PLGA solid surface. AB is the radius r of the circle fitting the droplet footprint depicted in the main paper Fig. 6. ABC and ABD are two possible definitions of the wetting contact angle termed β_a and β_b, respectively.

S3 Table of the DSPE-PEG Macromolecule Atomic Charges.

Table S1: Atom number, type, name, and charge (e) for atoms belonging to the DSPE-PEG-amine macromolecule.

No.	Type	Name	Charge
1	cA	C1	0.20796600
2	cA	C2	0.16302000
3	oS	O1	-0.47568600
4	pA	P1	1.03785700
5	oH	O2	-0.58357900
6	hO	H5	0.42166800
7	oC	O3	-0.56570700
8	oS	O4	-0.43536100
9	cA	C3	-0.00840100
10	cA	C4	0.34160000
11	cA	C5	-0.00689800
12	oS	O6	-0.39504400
13	cC	C6	0.70645200
14	oC	O7	-0.53564800
15	cD	C8	-0.30087000
16	cD	C9	0.00797900
17	cD	C10	0.04293000
18	cD	C11	-0.01950700
19	cD	C12	-0.00606800
20	cD	C13	0.01107300
21	cD	C14	-0.00401600
22	cD	C15	-0.01097500
23	cD	C16	0.00940700
24	cD	C17	0.00327300
25	cD	C18	-0.01351400
26	cD	C19	0.00145000
27	cD	C20	0.03604600
28	cD	C21	-0.05057500
29	cD	C22	-0.01992800
30	cD	C23	0.12438000
31	cD	C24	-0.23752800
32	hL	H43	0.05122600
33	hL	H44	0.05122600
34	hL	H45	0.05122600
35	hL	H41	-0.01647100
36	hL	H42	-0.01647100
37	hL	H39	0.00988200
38	hL	H40	0.00988200
39	hL	H37	0.00721200
40	hL	H38	0.00721200
41	hL	H35	-0.00709700
42	hL	H36	-0.00709700
43	hL	H33	0.000938
44	hL	H34	0.000938
45	hL	H31	0.002241
46	hL	H32	0.002241
47	hL	H29	-0.000573
48	hL	H30	-0.000573
49	hL	H27	-0.001399
50	hL	H28	-0.001399
51	hL	H25	0.002453
52	hL	H26	0.002453
53	hL	H23	0.001453
54	hL	H24	0.001453
55	hL	H21	-0.000445
56	hL	H22	-0.000445
57	hL	H19	0.001564
58	hL	H20	0.001564
59	hL	H17	0.005030
60	hL	H18	0.005030
61	hL	H15	-0.003753
62	hL	H16	-0.003753
63	hL	H13	0.017335
64	hL	H14	0.017335
65	hL	H11	0.100012
66	hL	H12	0.100012
67	hE	H9	0.088537
68	hE	H10	0.088537
69	oS	O5	-0.522604
70	cC	C7	0.728247
71	oC	O8	-0.524813
72	cD	C25	-0.215636
73	cD	C26	0.172788
74	cD	C27	-0.047623
75	cD	C28	-0.078516
76	cD	C29	0.087991

No.	Type	Name	Charge
77	cD	C30	-0.008889
78	cD	C31	-0.018980
79	cD	C32	0.007940
80	cD	C33	0.013919
81	cD	C34	-0.007079
82	cD	C35	-0.006007
83	cD	C36	0.004834
84	cD	C37	0.034997
85	cD	C38	-0.050163
86	cD	C39	-0.015145
87	cD	C40	0.121912
88	cD	C41	-0.233669
89	hL	H78	0.050410
90	hL	H79	0.050410
91	hL	H80	0.050410
92	hL	H76	-0.016498
93	hL	H77	-0.016498
94	hL	H74	0.008730
95	hL	H75	0.008730
96	hL	H72	0.006671
97	hL	H73	0.006671
98	hL	H70	-0.007408
99	hL	H71	-0.007408
100	hL	H68	-0.000163
101	hL	H69	-0.000163
102	hL	H66	0.000435
103	hL	H67	0.000435
104	hL	H64	0.000249
105	hL	H65	0.000249
106	hL	H62	-0.001802
107	hL	H63	-0.001802
108	hL	H60	-0.001790
109	hL	H61	-0.001790
110	hL	H58	0.001976
111	hL	H59	0.001976
112	hL	H56	0.002634
113	hL	H57	0.002634
114	hL	H54	-0.016503
115	hL	H55	-0.016503
116	hL	H52	0.010216
117	hL	H53	0.010216
118	hL	H50	0.019149
119	hL	H51	0.019149
120	hL	H48	-0.029435
121	hL	H49	-0.029435
122	hL	H46	0.051454
123	hL	H47	0.051454
124	hE	H8	0.047916
125	hE	H6	0.107804
126	hE	H7	0.107804
127	hE	H1	0.047804
128	hE	H2	0.047804
129	hX	H3	0.044779
130	hX	H4	0.044779
131	nA	N1	-0.698150
132	hN	H81	0.314190
133	c	C42	0.894354
134	o	O10	-0.602550
135	os	O9	-0.524511
136	c3	C43	0.246681
137	h1	H82	-0.085219
138	h1	H83	-0.085219
139	c3	C44	0.158824
140	h1	H84	-0.033100
141	h1	H85	-0.033100
142	os	O2	-0.410000
143	c3	C3	0.021600
144	h1	H6	0.096600
145	h1	H7	0.096600
146	c3	C4	0.142660
147	h1	H8	0.111500
148	h1	H9	0.111500
149	os	O3	-0.190512
150	c3	C5	-0.001530
151	h1	H10	0.050150
152	h1	H11	0.050150
153	c3	C6	0.157500
154	h1	H12	0.017600
155	h1	H13	0.017600
156	os	O4	-0.400000
157	c3	C7	0.222579
158	h1	H14	0.003450
159	h1	H15	0.003450
160	c3	C8	0.135370
161	h1	H16	0.012440
162	h1	H17	0.012440
163	os	O5	-0.361000
164	c3	C9	-0.014461
165	h1	H18	0.100600
166	h1	H19	0.100600
167	c3	C10	0.139290
168	h1	H20	0.039650
169	h1	H21	0.039650
170	os	O6	-0.400000
171	c3	C11	0.065690
172	h1	H22	0.058570
173	h1	H23	0.058570
174	c3	C12	0.045980
175	h1	H24	0.052910
176	h1	H25	0.052910
177	os	O7	-0.280000
178	c3	C13	-0.081739
179	h1	H26	0.071700
180	h1	H27	0.071700
181	c3	C14	0.249790
182	h1	H28	0.028560
183	h1	H29	0.028560
184	os	O8	-0.440000
185	c3	C15	0.262235
186	h1	H30	0.000880
187	h1	H31	0.000880
188	c3	C16	0.012200

No.	Type	Name	Charge
189	h1	H32	0.058570
190	h1	H33	0.058570
191	os	O9	-0.412400
192	c3	C17	0.193110
193	h1	H34	0.026370
194	h1	H35	0.026370
195	c3	C18	0.107400
196	h1	H36	0.025970
197	h1	H37	0.025970
198	os	O10	-0.390006
199	c3	C19	0.120190
200	h1	H38	0.042280
201	h1	H39	0.042280
202	c3	C20	0.068800
203	h1	H40	0.045590
204	h1	H41	0.045590
205	os	O11	-0.360000
206	c3	C21	0.053000
207	h1	H42	0.058800
208	h1	H43	0.058800
209	c3	C22	0.011060
210	h1	H44	0.084270
211	h1	H45	0.084270
212	os	O12	-0.370000
213	c3	C23	0.077300
214	h1	H46	0.060800
215	h1	H47	0.060800
216	c3	C24	0.330000
217	h1	H48	-0.029140
218	h1	H49	-0.029140
219	os	O13	-0.466633
220	c3	C25	0.240000
221	h1	H50	-0.011644
222	h1	H51	-0.011644
223	c3	C26	0.085420
224	h1	H52	0.041690
225	h1	H53	0.041690
226	os	O14	-0.380300
227	c3	C27	0.160550
228	h1	H54	0.014000
229	h1	H55	0.014000
230	c3	C28	0.080800
231	h1	H56	0.050950
232	h1	H57	0.050950
233	os	O15	-0.400943
234	c3	C29	0.241400
235	h1	H58	0.004750
236	h1	H59	0.004750
237	c3	C30	0.019870
238	h1	H60	0.056100
239	h1	H61	0.056100
240	os	O16	-0.350000
241	c3	C31	0.161660
242	h1	H62	0.041870
243	h1	H63	0.041870
244	c3	C32	0.032280
245	h1	H64	0.054450
246	h1	H65	0.054450
247	os	O17	-0.240000
248	c3	C33	0.009930
249	h1	H66	0.059870
250	h1	H67	0.059870
251	c3	C34	0.198660
252	h1	H68	0.009670
253	h1	H69	0.009670
254	os	O18	-0.431000
255	c3	C35	0.225570

No.	Type	Name	Charge
256	h1	H70	0.007690
257	h1	H71	0.007690
258	c3	C36	-0.009025
259	h1	H72	0.050100
260	h1	H73	0.050100
261	os	O19	-0.290000
262	c3	C37	0.101100
263	h1	H74	0.047070
264	h1	H75	0.047070
265	c3	C38	0.046490
266	h1	H76	0.091000
267	h1	H77	0.091000
268	os	O20	-0.342100
269	c3	C39	0.117400
270	h1	H78	0.026750
271	h1	H79	0.026750
272	c3	C40	0.208000
273	h1	H80	0.000400
274	h1	H81	0.000400
275	os	O21	-0.402000
276	c3	C41	0.087700
277	h1	H82	0.031700
278	h1	H83	0.031700
279	c3	C42	0.135700
280	h1	H84	0.018190
281	h1	H85	0.018190
282	os	O22	-0.310300
283	c3	C43	-0.011060
284	h1	H86	0.120200
285	h1	H87	0.120200
286	c3	C44	-0.111540
287	h1	H88	0.125300
288	h1	H89	0.125300
289	os	O23	-0.307000
290	c3	C45	-0.128600
291	h1	H90	0.131700
292	h1	H91	0.131700
293	c3	C46	-0.128600
294	h1	H92	0.131700
295	h1	H93	0.131700
296	os	O24	-0.307000
297	c3	C47	-0.111540
298	h1	H94	0.125300
299	h1	H95	0.125300
300	c3	C48	-0.011100
301	h1	H96	0.120200
302	h1	H97	0.120200
303	os	O25	-0.310300
304	c3	C49	0.135700
305	h1	H98	0.018190
306	h1	H99	0.018190
307	c3	C50	0.087700
308	h1	H100	0.031700
309	h1	H101	0.031700
310	os	O26	-0.402000
311	c3	C51	0.208030
312	h1	H102	0.000400
313	h1	H103	0.000400
314	c3	C52	0.117440
315	h1	H104	0.026700
316	h1	H105	0.026700
317	os	O27	-0.343000
318	c3	C53	-0.046499
319	h1	H106	0.091000
320	h1	H107	0.091000
321	c3	C54	0.101100
322	h1	H108	0.047070

No.	Type	Name	Charge
323	h1	H109	0.047070
324	os	O28	-0.290000
325	c3	C55	-0.009025
326	h1	H110	0.050100
327	h1	H111	0.050100
328	c3	C56	0.225570
329	h1	H112	0.007690
330	h1	H113	0.007690
331	os	O29	-0.431000
332	c3	C57	0.198660
333	h1	H114	0.009670
334	h1	H115	0.009670
335	c3	C58	0.009900
336	h1	H116	0.059800
337	h1	H117	0.059800
338	os	O30	-0.240000
339	c3	C59	-0.032300
340	h1	H118	0.054400
341	h1	H119	0.054400
342	c3	C60	0.161600
343	h1	H120	0.041800
344	h1	H121	0.041800
345	os	O31	-0.350000
346	c3	C61	0.019800
347	h1	H122	0.056100
348	h1	H123	0.056100
349	c3	C62	0.241400
350	h1	H124	0.004700
351	h1	H125	0.004700
352	os	O32	-0.401000
353	c3	C63	0.080800
354	h1	H126	0.050900
355	h1	H127	0.050900
356	c3	C64	0.160500
357	h1	H128	0.014000
358	h1	H129	0.014000
359	os	O33	-0.380000
360	c3	C65	0.085400
361	h1	H130	0.041600
362	h1	H131	0.041600
363	c3	C66	0.237300
364	h1	H132	-0.011600
365	h1	H133	-0.011600
366	os	O34	-0.470000
367	c3	C67	0.329150
368	h1	H134	-0.029100
369	h1	H135	-0.029100
370	c3	C68	0.077300
371	h1	H136	0.060800
372	h1	H137	0.060800
373	os	O35	-0.370000
374	c3	C69	0.011060
375	h1	H138	0.084200
376	h1	H139	0.084200
377	c3	C70	0.053000
378	h1	H140	0.058800
379	h1	H141	0.058800
380	os	O36	-0.360000
381	c3	C71	0.068800
382	h1	H142	0.045500
383	h1	H143	0.045500
384	c3	C72	0.120100
385	h1	H144	0.042200
386	h1	H145	0.042200
387	os	O37	-0.400000
388	c3	C73	0.107400
389	h1	H146	0.025900
390	h1	H147	0.025900
391	c3	C74	0.193100
392	h1	H148	0.026300
393	h1	H149	0.026300
394	os	O38	-0.412400
395	c3	C75	0.012200
396	h1	H150	0.058500
397	h1	H151	0.058500
398	c3	C76	0.262200
399	h1	H152	0.000800
400	h1	H153	0.000800
401	os	O39	-0.440000
402	c3	C77	0.249700
403	h1	H154	0.028500
404	h1	H155	0.028500
405	c3	C78	-0.081700
406	h1	H156	0.071700
407	h1	H157	0.071700
408	os	O40	-0.300000
409	c3	C79	0.045980
410	h1	H158	0.052900
411	h1	H159	0.052900
412	c3	C80	0.065700
413	h1	H160	0.058500
414	h1	H161	0.058500
415	os	O41	-0.400000
416	c3	C81	0.139300
417	h1	H162	0.039600
418	h1	H163	0.039600
419	c3	C82	-0.014500
420	h1	H164	0.100600
421	h1	H165	0.100600
422	os	O42	-0.370000
423	c3	C83	0.135300
424	h1	H166	0.012400
425	h1	H167	0.012400
426	c3	C84	0.222500
427	h1	H168	0.003400
428	h1	H169	0.003400
429	os	O43	-0.400000
430	c3	C85	0.157500
431	h1	H170	0.017600
432	h1	H171	0.017600
433	c3	C86	-0.001500
434	h1	H172	0.050100
435	h1	H173	0.050100
436	os	O44	-0.200000
437	c3	C87	-0.142700
438	h1	H174	0.111500
439	h1	H175	0.111500
440	c3	C88	0.021500
441	h1	H176	0.096500
442	h1	H177	0.096500
443	os	O2	-0.531522
444	c3	C3	0.215604
445	h1	H6	-0.033074
446	c3	C4	0.437179
447	h1	H8	-0.017355
448	n3	N1	-0.925440
449	hn	H10	0.410259
450	hn	H11	0.410259
451	h1	H9	-0.017355
452	h1	H7	-0.033074