Supporting Information

Polarization Effect and Electric Potential Changes in the Stimuli-Responsive Molecular Monolayers Under External Electric Field

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- **Table S3.** The values of μ_X, μ_Y, and μ_Z for conformers **a-c** obtained from polarizable force field based on the fragment dipoles (D_{frag}-POL).
- **Table S4.** Relative energies (kcal mol^{-1}) for three conformations **a**–**c** obtained from polarizable force field based on the fragment dipoles (D_{frag}-POL) with mass and geometric centers as fragment center, respectively.
- **Table S5.** The charge parameters for water models.
- **Table S6.** The charge parameters for biotin-4KC chain without (w/o) and with water models.
- **Complete citation for ref. 117.**

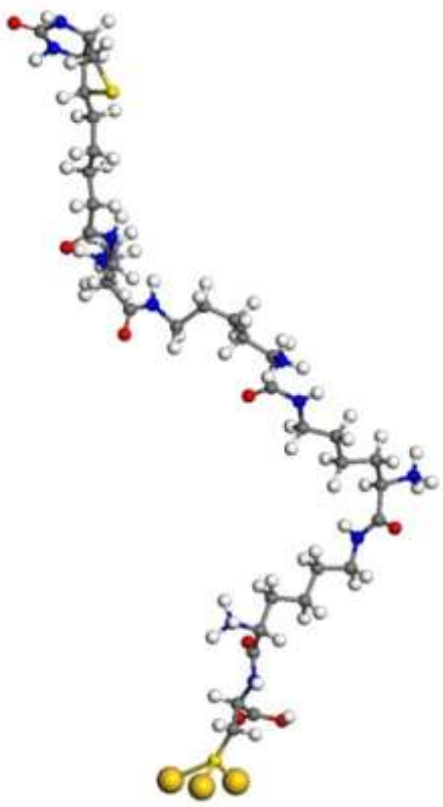


Figure S1. The biotin-4KC/Au_3 cluster model.

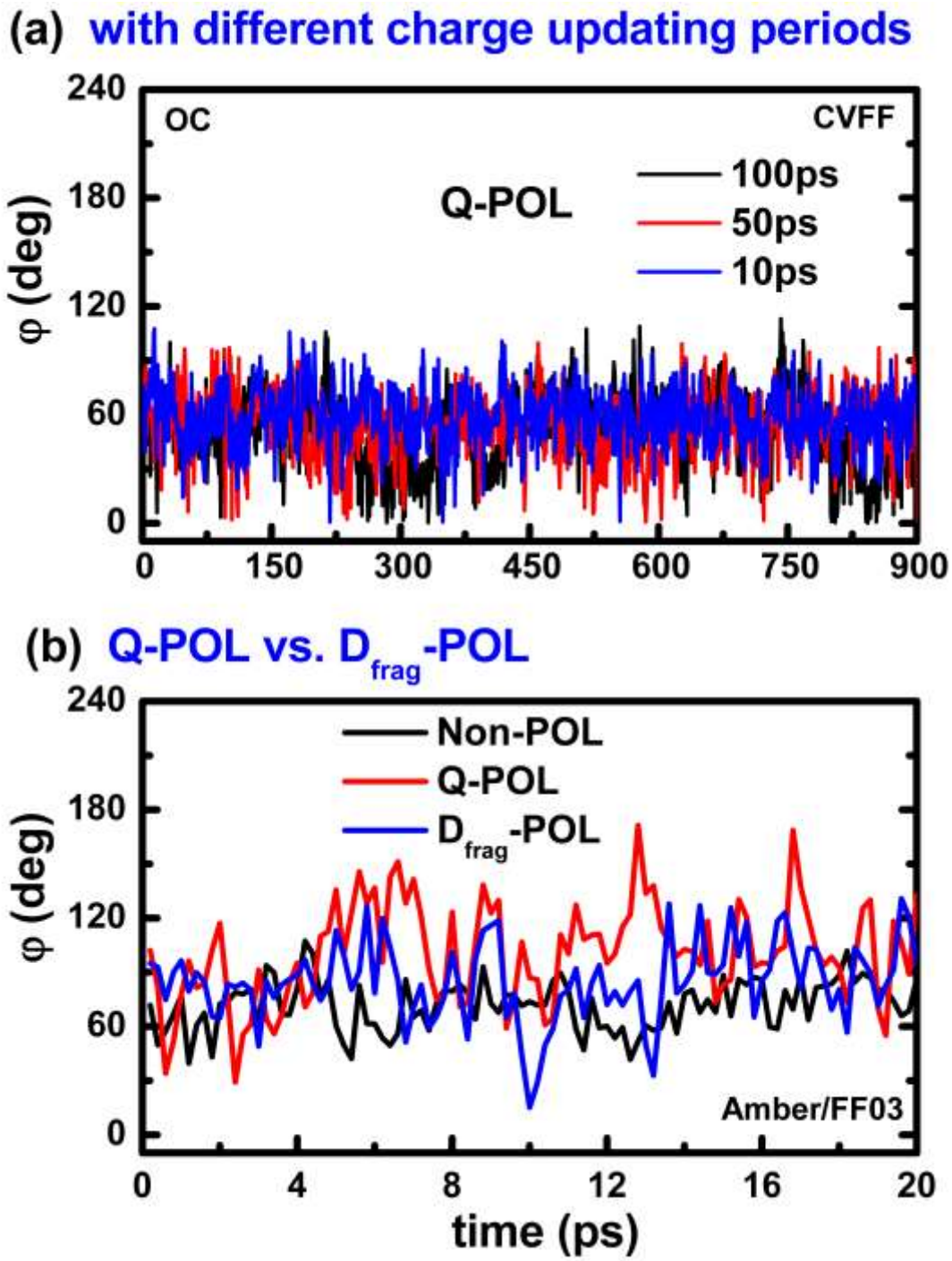


Figure S2. The torsion angle (ϕ, in units of deg) of biotin-4KC/TEGT chain obtained (a) by using charge updating period of 100ps, 50ps and 10ps for Q-POL-OC model within the framework of CVFF; (b) from the Non-POL, Q-POL and D_{frag}-POL models by using charge updating period of 0.2 ps within the framework of Amber/FF03 along the MD simulations. The electrostatic parameters in polarization models are calculated at M06-2X/6-31 level.

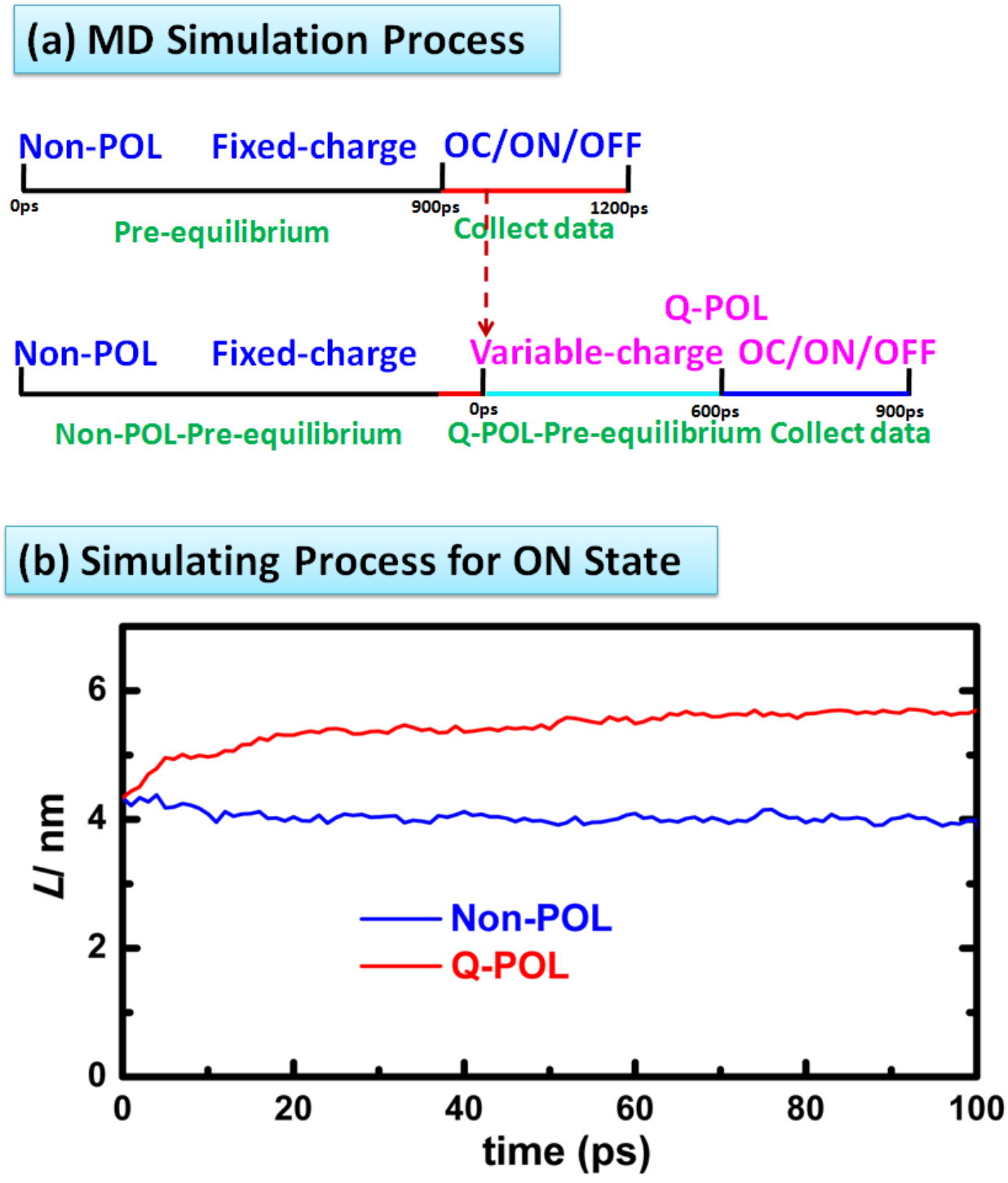


Figure S3. Illustration of (a) MD simulation process and (b) simulating process for ON state.

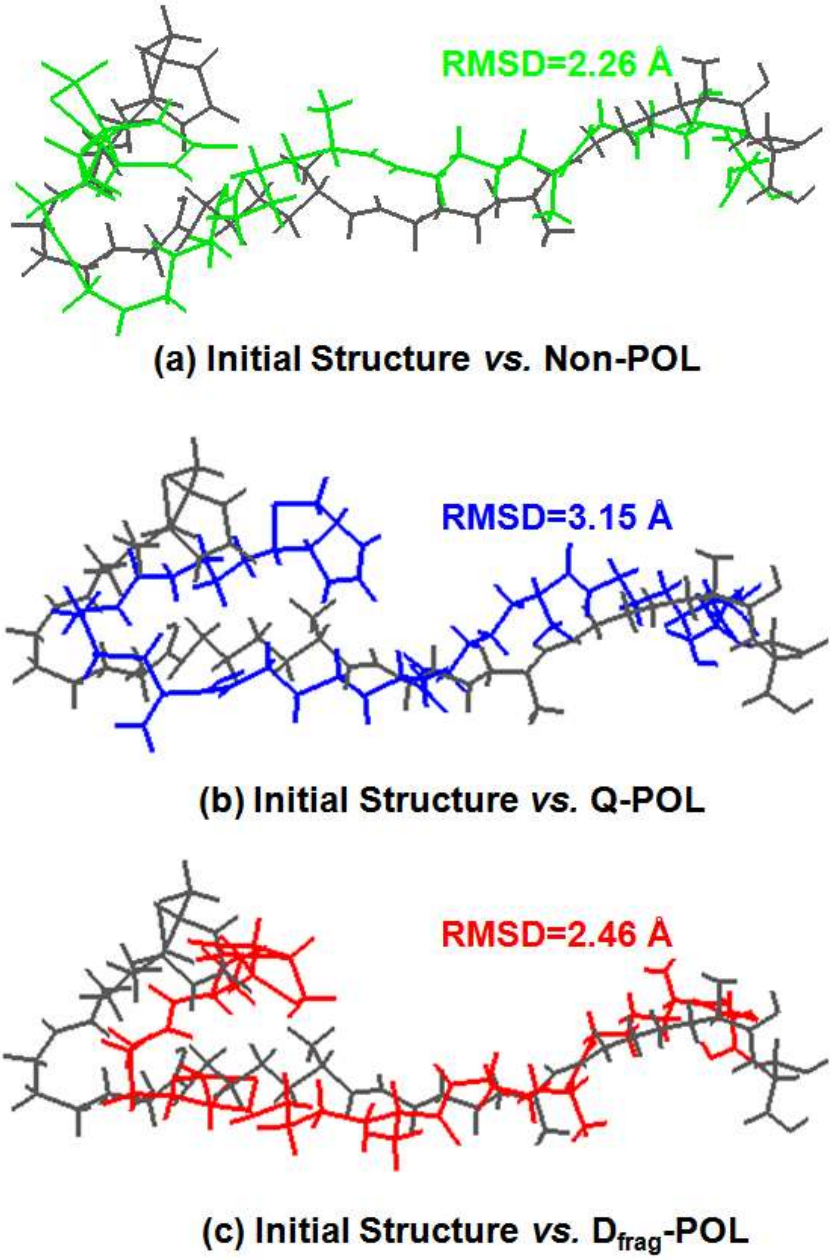


Figure S4. The structure of solvated biotin-4KC/TEGT calculated from (a) the non-polarizable Amber/FF03 force field (in green) and polarization models with DFT-based (b) NBO atomic partial charges (Q-POL-Amber/FF03, in blue) and (c) fragment dipoles (D_{frag}-POL-Amber/FF03, in red), in comparison with the initial structure (in grey). All the electrostatic parameters in polarization models were calculated at M06-2X/6-31 level and scaled by a factor of 0.10. The root-mean-root deviations (RMSD) of calculated structures from the initial one were also shown.

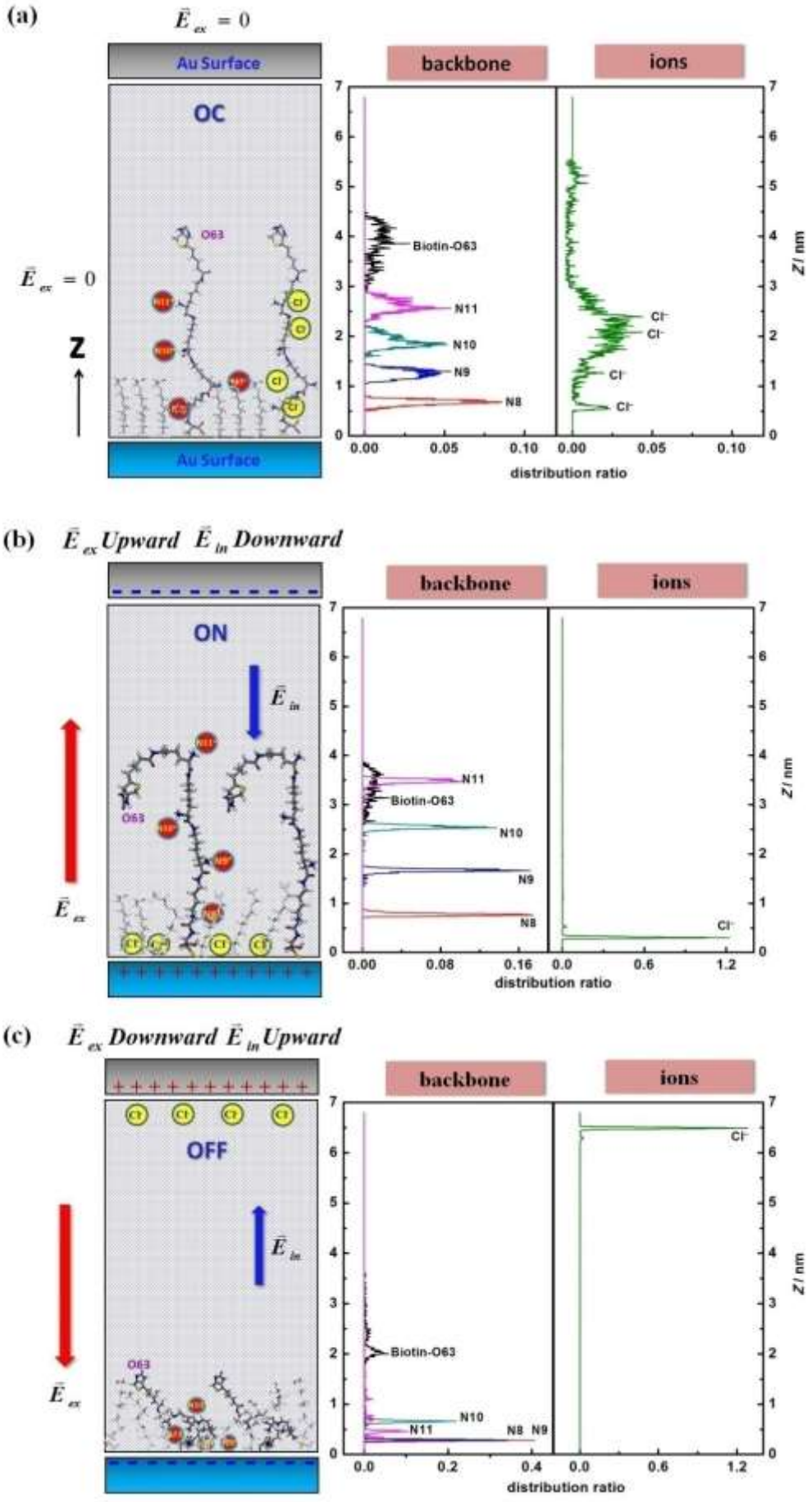

(a)
$\vec{E}_{ex} = 0$
Au Surface
OC
$\vec{E}_{ex} = 0$
Z
Au Surface
backbone
ions
Biotin-O63
N11
N10
N9
N8
Cl⁻
Cl⁻
Cl⁻
Cl⁻
distribution ratio
Z / nm
(b) $\vec{E}_{ex}$ Upward $\vec{E}_{in}$ Downward
ON
$\vec{E}_{in}$
$\vec{E}_{ex}$
backbone
ions
N11
Biotin-O63
N10
N9
N8
Cl⁻
distribution ratio
Z / nm
(c) $\vec{E}_{ex}$ Downward $\vec{E}_{in}$ Upward
OFF
$\vec{E}_{in}$
$\vec{E}_{ex}$
backbone
ions
Cl⁻
Biotin-O63
N10
N11
N8 N9
distribution ratio
Z / nm

Figure S5. The schematic illustrations of the internal E-field induced by the applied external E-field for (a) OC, (b) ON and (c) OFF states by using Non-POL model. $\vec{E}_{ex}$ colored in red refers to the applied external E-field and $\vec{E}_{in}$ colored in blue denotes the internal induced E-field in SAMs. The position distributions of the OC/ON/OFF configurations during 400 ps MD simulations for atoms N8, N9, N10, N11, O63 and four Cl ions are displayed on the right side of each figure.

Table S1. NBO, Mulliken, MK-ESP and CHelpG-ESP charges for biotin-4KC molecular chain.

index	*q*-Mulliken	*q*-NBO	*q*-MK-ESP	*q*-CHelpG-ESP
Conformer a				
N1	-0.414	-0.649	-0.799	-0.749
H2	0.468	0.447	0.337	0.322
C3	-0.452	-0.205	0.656	0.540
H4	0.315	0.311	-0.029	-0.019
C5	-0.495	-0.648	-0.346	-0.238
H6	0.301	0.295	0.136	0.108
H7	0.285	0.283	0.189	0.154
S8	0.076	0.020	-0.133	-0.133
C9	0.677	0.843	0.402	0.515
O10	-0.444	-0.642	-0.481	-0.520
O11	-0.502	-0.705	-0.403	-0.427
H12	0.491	0.527	0.283	0.272
N13	-0.543	-0.649	-0.506	-0.593
C14	0.342	0.742	0.741	0.767
C15	-0.430	-0.552	-0.585	-0.419
C16	-0.187	-0.467	0.222	0.204
C17	-0.889	-0.484	-0.194	-0.191
C18	-0.617	-0.471	0.301	0.336
C19	0.119	-0.428	-0.720	-0.472
C20	-0.764	-0.083	0.555	0.382
N21	-0.479	-0.693	-0.665	-0.632
C22	1.038	0.866	0.670	0.788
O23	-0.732	-0.779	-0.679	-0.692
H24	0.281	0.284	0.027	0.021
C25	0.072	-0.084	-0.203	0.035
N26	-0.657	-0.678	-0.399	-0.539
H27	0.276	0.282	0.158	0.074
C28	-0.793	-0.637	-0.046	0.105

S29	0.408	0.271	-0.112	-0.189
O30	-0.532	-0.750	-0.585	-0.609
H31	0.462	0.455	0.362	0.363
H32	0.249	0.268	0.164	0.117
H33	0.277	0.289	0.186	0.132
H34	0.229	0.228	0.014	-0.006
H35	0.232	0.242	-0.035	-0.048
H36	0.256	0.265	0.131	0.123
H37	0.252	0.258	0.075	0.060
H38	0.188	0.222	-0.065	-0.094
H39	0.260	0.261	0.022	-0.006
H40	0.273	0.263	0.296	0.195
H41	0.423	0.434	0.296	0.289
H42	0.476	0.466	0.358	0.364
H43	0.279	0.273	0.096	0.037
H44	0.288	0.297	0.164	0.102
C45	-0.298	-0.295	-0.010	0.163
C46	-0.519	-0.494	-0.037	0.003
C47	-0.309	-0.492	-0.111	-0.005
C48	-0.530	-0.487	0.113	0.231
H49	0.250	0.277	0.106	0.059
H50	0.265	0.271	0.101	0.047
H51	0.259	0.285	0.068	0.034
H52	0.233	0.251	0.053	0.019
H53	0.233	0.246	0.075	0.020
H54	0.248	0.266	0.063	0.018
H55	0.236	0.263	0.046	-0.014
H56	0.295	0.256	-0.053	-0.107
C57	0.414	-0.157	-0.370	-0.287
H58	0.300	0.291	0.194	0.125
C59	-0.178	0.697	0.804	0.834
O60	-0.394	-0.656	-0.533	-0.552
N61	-0.396	-0.668	-0.919	-0.927
C62	-0.524	-0.281	0.417	0.460
C63	-0.851	-0.492	-0.360	-0.263
C64	0.780	-0.493	0.157	0.163
C65	-1.407	-0.491	-0.344	-0.156
H66	0.247	0.250	-0.007	-0.012
H67	0.245	0.258	0.034	0.010
H68	0.258	0.267	0.132	0.087
H69	0.240	0.255	0.120	0.082
H70	0.210	0.227	-0.007	-0.037
H71	0.280	0.267	0.070	0.029
H72	0.238	0.267	0.104	0.059

H73	0.264	0.266	0.132	0.069
C74	0.476	-0.160	0.113	0.019
H75	0.324	0.305	0.099	0.099
C76	0.100	0.694	0.583	0.676
O77	-0.486	-0.651	-0.492	-0.525
H78	0.459	0.455	0.468	0.459
N79	-0.492	-0.667	-0.733	-0.806
C80	-0.585	-0.285	0.087	0.306
C81	-0.403	-0.495	0.000	-0.057
C82	-0.251	-0.486	-0.137	-0.058
C83	-0.467	-0.501	0.046	0.075
H84	0.271	0.270	0.092	0.028
H85	0.231	0.259	0.092	0.034
H86	0.262	0.271	0.064	0.058
H87	0.238	0.255	0.048	0.041
H88	0.184	0.225	0.013	-0.012
H89	0.249	0.264	0.062	0.038
H90	0.272	0.287	0.043	0.028
H91	0.271	0.274	0.055	0.031
C92	0.144	-0.153	0.008	0.001
H93	0.291	0.288	0.110	0.091
C94	0.178	0.685	0.514	0.602
O95	-0.473	-0.649	-0.459	-0.484
H96	0.445	0.450	0.423	0.419
N97	-0.451	-0.649	-0.584	-0.695
C98	-0.509	-0.286	-0.031	0.217
C99	-0.380	-0.496	-0.022	-0.051
C100	-0.325	-0.484	-0.054	-0.017
C101	-0.507	-0.515	-0.009	0.013
H102	0.276	0.276	0.126	0.057
H103	0.242	0.265	0.120	0.055
H104	0.258	0.269	0.061	0.048
H105	0.239	0.254	0.055	0.039
H106	0.194	0.230	0.011	-0.007
H107	0.247	0.262	0.039	0.017
H108	0.315	0.313	0.085	0.079
H109	0.267	0.274	0.050	0.034
C110	0.145	-0.152	-0.042	-0.004
H111	0.292	0.288	0.145	0.116
C112	0.075	0.701	0.700	0.677
O113	-0.426	-0.631	-0.508	-0.507
H114	0.452	0.454	0.390	0.400
H115	0.533	0.482	0.355	0.313
H116	0.633	0.514	0.276	0.242

H117	0.538	0.499	0.308	0.252
H118	0.545	0.468	0.318	0.290
H119	0.547	0.502	0.301	0.285
H120	0.609	0.517	0.353	0.293
H121	0.510	0.483	0.400	0.377
H122	0.563	0.518	0.358	0.329
H123	0.535	0.496	0.406	0.376
H124	0.561	0.517	0.387	0.349
H125	0.534	0.495	0.421	0.383
H126	0.508	0.482	0.418	0.380
N127	-1.125	-0.838	-0.674	-0.548
N128	-1.131	-0.840	-0.596	-0.511
N129	-1.303	-0.857	-0.415	-0.309
N130	-1.309	-0.865	-0.336	-0.204
H131	0.153	0.171	0.195	0.191
Conformer b				
N1	-0.410	-0.649	-0.813	-0.754
H2	0.468	0.446	0.340	0.325
C3	-0.465	-0.206	0.636	0.525
H4	0.314	0.311	-0.022	-0.015
C5	-0.506	-0.648	-0.336	-0.233
H6	0.301	0.295	0.135	0.109
H7	0.286	0.283	0.183	0.151
S8	0.082	0.020	-0.136	-0.133
C9	0.692	0.843	0.434	0.524
O10	-0.445	-0.642	-0.497	-0.525
O11	-0.500	-0.705	-0.409	-0.425
H12	0.492	0.528	0.284	0.271
N13	-0.564	-0.658	-0.641	-0.693
C14	0.658	0.740	0.680	0.768
C15	-0.903	-0.561	-0.152	-0.183
C16	-0.286	-0.486	-0.107	-0.098
C17	-0.022	-0.462	0.012	0.107
C18	-0.827	-0.487	-0.396	-0.122
C19	-0.454	-0.412	-0.223	-0.076
C20	0.055	-0.072	0.037	0.323
N21	-0.556	-0.705	-0.484	-0.679
C22	0.944	0.856	0.839	0.901
O23	-0.857	-0.789	-0.727	-0.718
H24	0.259	0.261	0.150	0.031
C25	-0.577	-0.091	0.133	0.146
N26	-0.522	-0.696	-0.735	-0.720
H27	0.280	0.289	0.143	0.069
C28	-0.611	-0.645	-0.277	-0.018
S29	0.287	0.268	-0.108	-0.216
O30	-0.616	-0.749	-0.536	-0.581
H31	0.463	0.454	0.372	0.369
H32	0.267	0.266	0.036	0.038

H33	0.268	0.289	0.088	0.089
H34	0.244	0.268	0.099	0.094
H35	0.261	0.268	0.043	0.028
H36	0.195	0.213	0.100	-0.056
H37	0.214	0.228	0.062	0.025
H38	0.265	0.262	0.125	-0.009
H39	0.248	0.270	0.220	0.139
H40	0.261	0.262	0.187	0.096
H41	0.531	0.466	0.344	0.384
H42	0.443	0.445	0.398	0.369
H43	0.262	0.256	0.130	0.028
H44	0.283	0.290	0.211	0.134
C45	-0.271	-0.293	0.163	0.268
C46	-0.620	-0.494	-0.058	-0.086
C47	-0.239	-0.491	-0.117	0.020
C48	-0.617	-0.494	0.117	0.137
H49	0.252	0.279	0.077	0.050
H50	0.262	0.269	0.056	0.018
H51	0.262	0.286	0.062	0.053
H52	0.235	0.253	0.054	0.045
H53	0.226	0.240	0.058	0.008
H54	0.255	0.270	0.074	0.029
H55	0.235	0.265	0.050	0.012
H56	0.288	0.260	-0.045	-0.078
C57	-0.001	-0.154	-0.390	-0.173
H58	0.312	0.297	0.186	0.100
C59	0.330	0.711	0.775	0.790
O60	-0.569	-0.698	-0.573	-0.616
N61	-0.374	-0.652	-0.780	-0.813
C62	-0.402	-0.284	0.299	0.379
C63	-0.526	-0.491	-0.182	-0.127
C64	-0.350	-0.485	-0.135	-0.033
C65	-0.532	-0.496	0.018	0.070
H66	0.271	0.256	-0.019	-0.039
H67	0.248	0.268	0.070	0.040
H68	0.264	0.256	0.079	0.052
H69	0.250	0.261	0.096	0.062
H70	0.207	0.236	0.042	-0.004
H71	0.255	0.256	0.050	0.009
H72	0.306	0.301	0.067	0.034
H73	0.265	0.263	0.056	0.018
C74	0.176	-0.159	0.069	0.120
H75	0.330	0.307	0.107	0.057
C76	0.242	0.692	0.524	0.559
O77	-0.483	-0.672	-0.486	-0.515
H78	0.458	0.457	0.432	0.422
N79	-0.424	-0.670	-0.643	-0.633
C80	-0.526	-0.283	0.145	0.265
C81	-0.392	-0.491	-0.117	-0.103
C82	-0.425	-0.488	-0.071	-0.013
C83	-0.347	-0.500	0.009	0.082

H84	0.262	0.265	0.062	0.021
H85	0.239	0.262	0.086	0.049
H86	0.259	0.268	0.082	0.063
H87	0.237	0.254	0.065	0.042
H88	0.188	0.228	0.008	-0.020
H89	0.250	0.262	0.059	0.035
H90	0.267	0.284	0.043	0.017
H91	0.272	0.275	0.071	0.040
C92	0.006	-0.153	0.007	-0.042
H93	0.294	0.289	0.108	0.102
C94	0.244	0.685	0.565	0.633
O95	-0.473	-0.650	-0.472	-0.491
H96	0.564	0.488	0.419	0.370
N97	-0.452	-0.649	-0.679	-0.719
C98	-0.527	-0.287	0.103	0.204
C99	-0.366	-0.494	-0.053	-0.045
C100	-0.397	-0.485	-0.044	-0.051
C101	-0.386	-0.511	-0.010	0.028
H102	0.276	0.277	0.091	0.061
H103	0.242	0.264	0.092	0.063
H104	0.253	0.267	0.063	0.049
H105	0.240	0.256	0.053	0.043
H106	0.190	0.228	0.001	-0.002
H107	0.248	0.262	0.037	0.029
H108	0.306	0.308	0.082	0.074
H109	0.273	0.279	0.061	0.046
C110	0.070	-0.153	-0.043	-0.030
H111	0.294	0.288	0.141	0.122
C112	0.105	0.703	0.729	0.693
O113	-0.427	-0.631	-0.521	-0.510
H114	0.452	0.453	0.413	0.410
H115	0.544	0.485	0.315	0.300
H116	0.640	0.514	0.178	0.246
H117	0.535	0.496	0.238	0.249
H118	0.521	0.483	0.390	0.374
H119	0.558	0.514	0.342	0.327
H120	0.534	0.488	0.396	0.376
H121	0.508	0.484	0.387	0.369
H122	0.561	0.518	0.356	0.333
H123	0.535	0.496	0.402	0.377
H124	0.561	0.518	0.383	0.346
H125	0.533	0.495	0.415	0.381
H126	0.504	0.481	0.412	0.375
N127	-1.113	-0.839	-0.659	-0.537
N128	-1.103	-0.840	-0.582	-0.505
N129	-1.151	-0.836	-0.595	-0.546
N130	-1.355	-0.858	-0.128	-0.196
H131	0.151	0.170	0.195	0.191

Conformer c

N1	-0.411	-0.650	-0.827	-0.758
H2	0.466	0.446	0.340	0.320
C3	-0.450	-0.205	0.725	0.558
H4	0.315	0.311	-0.041	-0.024
C5	-0.510	-0.648	-0.402	-0.238
H6	0.301	0.295	0.149	0.107
H7	0.284	0.282	0.195	0.151
S8	0.077	0.016	-0.132	-0.140
C9	0.685	0.843	0.400	0.506
O10	-0.440	-0.639	-0.487	-0.520
O11	-0.503	-0.705	-0.396	-0.420
H12	0.492	0.528	0.275	0.271
N13	-0.539	-0.655	-0.591	-0.711
C14	0.864	0.729	0.808	0.850
C15	-1.397	-0.554	-0.778	-0.531
C16	0.540	-0.469	0.388	0.200
C17	-1.448	-0.486	-0.358	-0.152
C18	0.456	-0.470	-0.130	0.078
C19	-0.741	-0.430	-0.456	-0.346
C20	-0.370	-0.080	-0.142	0.072
N21	-0.747	-0.749	-0.032	-0.132
C22	0.807	0.864	0.607	0.613
O23	-0.695	-0.748	-0.689	-0.675
H24	0.250	0.251	0.130	0.043
C25	-0.165	-0.085	-0.006	0.046
N26	-0.579	-0.679	-0.475	-0.484
H27	0.275	0.280	0.122	0.067
C28	-0.763	-0.640	-0.003	0.093
S29	0.437	0.282	-0.085	-0.156
O30	-0.673	-0.742	-0.607	-0.631
H31	0.448	0.451	0.376	0.379
H32	0.282	0.290	0.229	0.150
H33	0.233	0.259	0.189	0.139
H34	0.226	0.238	-0.010	-0.014
H35	0.232	0.241	0.038	0.033
H36	0.247	0.263	0.166	0.118
H37	0.239	0.256	0.140	0.060
H38	0.218	0.235	0.134	0.043
H39	0.250	0.243	0.133	0.031
H40	0.283	0.269	0.261	0.167
H41	0.490	0.449	0.226	0.228
H42	0.477	0.466	0.364	0.350
H43	0.283	0.272	0.080	0.034
H44	0.295	0.301	0.145	0.113
C45	-0.246	-0.298	0.065	0.302
C46	-0.562	-0.493	-0.084	-0.099
C47	-0.607	-0.499	-0.037	0.005
C48	-0.133	-0.501	0.043	0.150

H49	0.253	0.261	0.073	-0.003
H50	0.258	0.279	0.096	0.039
H51	0.244	0.259	0.061	0.047
H52	0.260	0.282	0.074	0.058
H53	0.259	0.275	0.054	0.038
H54	0.216	0.233	0.020	-0.004
H55	0.291	0.280	-0.016	-0.052
H56	0.264	0.268	0.052	0.008
C57	-0.386	-0.152	-0.050	-0.099
H58	0.339	0.308	0.149	0.153
C59	0.445	0.690	0.545	0.633
O60	-0.489	-0.674	-0.528	-0.547
N61	-0.457	-0.676	-0.426	-0.583
C62	-0.380	-0.282	-0.125	0.145
C63	-0.593	-0.489	0.064	0.031
C64	-0.077	-0.486	-0.224	-0.155
C65	-0.991	-0.495	0.112	0.172
H66	0.254	0.258	0.122	0.055
H67	0.269	0.271	0.137	0.065
H68	0.231	0.240	-0.063	-0.045
H69	0.258	0.267	0.073	0.053
H70	0.210	0.240	0.068	0.035
H71	0.254	0.254	0.063	0.030
H72	0.257	0.267	-0.029	-0.042
H73	0.280	0.275	0.053	0.015
C74	0.725	-0.155	0.032	0.053
H75	0.298	0.286	0.116	0.101
C76	0.127	0.691	0.571	0.591
O77	-0.449	-0.643	-0.496	-0.506
H78	0.539	0.485	0.271	0.311
N79	-0.361	-0.659	-0.506	-0.568
C80	-0.675	-0.284	-0.041	0.221
C81	-0.368	-0.482	-0.005	-0.025
C82	-0.352	-0.491	-0.146	-0.083
C83	-0.573	-0.490	-0.067	0.085
H84	0.291	0.288	0.142	0.072
H85	0.240	0.248	0.077	-0.001
H86	0.256	0.266	0.088	0.055
H87	0.235	0.238	-0.008	-0.012
H88	0.230	0.244	0.055	0.030
H89	0.260	0.268	0.086	0.045
H90	0.274	0.282	0.076	0.022
H91	0.272	0.261	0.078	0.020
C92	0.036	-0.154	0.018	0.014
H93	0.294	0.287	0.092	0.064
C94	0.255	0.691	0.521	0.579
O95	-0.473	-0.652	-0.457	-0.481
H96	0.500	0.449	0.207	0.187
N97	-0.474	-0.654	-0.653	-0.698
C98	-0.545	-0.286	0.120	0.237

C99	-0.318	-0.494	-0.029	-0.012
C100	-0.358	-0.484	-0.087	-0.077
C101	-0.450	-0.511	-0.051	0.043
H102	0.273	0.275	0.086	0.046
H103	0.239	0.263	0.077	0.046
H104	0.256	0.268	0.057	0.039
H105	0.239	0.255	0.048	0.030
H106	0.190	0.228	0.017	0.004
H107	0.245	0.261	0.044	0.030
H108	0.308	0.308	0.097	0.076
H109	0.271	0.277	0.075	0.043
C110	0.102	-0.153	-0.014	-0.055
H111	0.292	0.288	0.144	0.130
C112	0.080	0.703	0.703	0.700
O113	-0.427	-0.630	-0.513	-0.511
H114	0.450	0.452	0.404	0.400
H115	0.557	0.513	0.332	0.313
H116	0.535	0.493	0.368	0.347
H117	0.524	0.487	0.329	0.311
H118	0.517	0.486	0.405	0.395
H119	0.563	0.520	0.378	0.366
H120	0.532	0.495	0.417	0.399
H121	0.626	0.508	0.360	0.333
H122	0.554	0.506	0.274	0.257
H123	0.524	0.484	0.355	0.333
H124	0.561	0.518	0.393	0.346
H125	0.533	0.495	0.424	0.381
H126	0.506	0.481	0.426	0.378
N127	-1.121	-0.838	-0.699	-0.533
N128	-1.199	-0.862	-0.403	-0.347
N129	-1.148	-0.842	-0.654	-0.617
N130	-1.114	-0.838	-0.450	-0.387
H131	0.152	0.172	0.199	0.193

Table S2. Comparison of the atomic partial charges obtained by our proposed strategy and the cluster model.

atom index	*q*(our strategy)	*q*(cluster model)	*Δq*
Au_a	-0.278		
Au_b	0.307		
Au_c	0.300		
N1	-0.674	-0.676	-0.002
H2	0.425	0.423	-0.002
C3	-0.202	-0.202	0.000
H4	0.315	0.317	0.002
C5	-0.724	-0.648	0.076
H6	0.271	0.299	0.027
H7	0.235	0.250	0.015
S8	-0.051	-0.049	0.002
C9	0.835	0.828	-0.007
O10	-0.544	-0.534	0.010
O11	-0.676	-0.671	0.005
H12	0.509	0.505	-0.004
N13	-0.708	-0.705	0.003
C14	0.721	0.713	-0.009
C15	-0.577	-0.575	0.002
C16	-0.478	-0.477	0.001
C17	-0.480	-0.481	0.000
C18	-0.471	-0.471	0.000
C19	-0.407	-0.405	0.003
C20	-0.088	-0.087	0.001
N21	-0.693	-0.686	0.007
C22	0.821	0.803	-0.018
O23	-0.711	-0.700	0.011
H24	0.265	0.267	0.002
C25	-0.090	-0.090	0.000
N26	-0.669	-0.662	0.007
H27	0.280	0.283	0.002
C28	-0.661	-0.659	0.002
S29	0.226	0.227	0.001
O30	-0.637	-0.630	0.007
H31	0.431	0.433	0.002
H32	0.251	0.254	0.003
H33	0.287	0.290	0.003
H34	0.259	0.262	0.002
H35	0.219	0.221	0.002
H36	0.252	0.254	0.002
H37	0.255	0.258	0.003
H38	0.241	0.243	0.002
H39	0.246	0.248	0.002
H40	0.265	0.267	0.002
H41	0.447	0.449	0.002

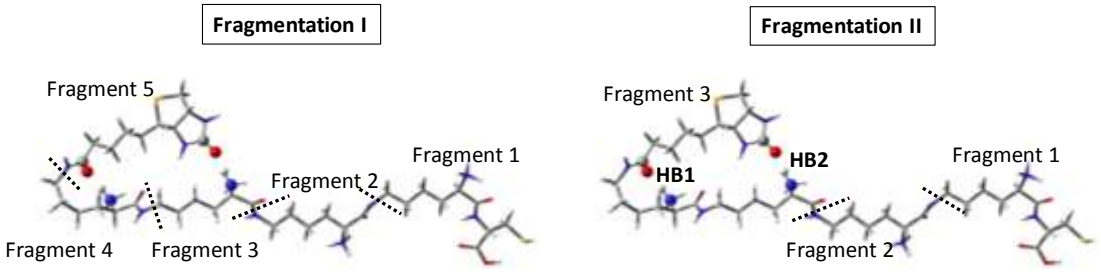
H42	0.441	0.443	0.002
H43	0.266	0.268	0.002
H44	0.290	0.292	0.002
C45	-0.281	-0.281	0.001
C46	-0.500	-0.498	0.001
C47	-0.499	-0.499	0.000
C48	-0.495	-0.494	0.001
H49	0.242	0.244	0.003
H50	0.285	0.287	0.002
H51	0.235	0.237	0.002
H52	0.267	0.270	0.003
H53	0.273	0.275	0.002
H54	0.259	0.262	0.002
H55	0.237	0.240	0.002
H56	0.274	0.276	0.002
C57	-0.173	-0.171	0.002
H58	0.330	0.333	0.002
C59	0.706	0.700	-0.007
O60	-0.597	-0.590	0.007
N61	-0.676	-0.673	0.004
C62	-0.283	-0.282	0.000
C63	-0.513	-0.513	0.001
C64	-0.491	-0.490	0.001
C65	-0.491	-0.491	0.000
H66	0.289	0.291	0.002
H67	0.274	0.277	0.003
H68	0.251	0.254	0.002
H69	0.267	0.269	0.002
H70	0.267	0.270	0.002
H71	0.269	0.271	0.002
H72	0.270	0.273	0.002
H73	0.251	0.253	0.003
C74	-0.130	-0.129	0.001
H75	0.286	0.288	0.003
C76	0.705	0.700	-0.005
O77	-0.572	-0.566	0.006
H78	0.417	0.419	0.002
N79	-0.691	-0.689	0.002
C80	-0.291	-0.290	0.001
C81	-0.504	-0.503	0.001
C82	-0.495	-0.495	0.001
C83	-0.518	-0.517	0.001
H84	0.253	0.255	0.002
H85	0.278	0.280	0.002
H86	0.266	0.268	0.002
H87	0.244	0.246	0.002
H88	0.253	0.256	0.002
H89	0.267	0.269	0.002
H90	0.298	0.300	0.002
H91	0.259	0.262	0.002

C92	-0.134	-0.134	0.001
H93	0.276	0.278	0.002
C94	0.690	0.685	-0.005
O95	-0.618	-0.612	0.006
H96	0.426	0.429	0.003
N97	-0.663	-0.660	0.003
C98	-0.288	-0.288	0.000
C99	-0.484	-0.483	0.001
C100	-0.492	-0.491	0.001
C101	-0.513	-0.513	0.000
H102	0.267	0.270	0.003
H103	0.304	0.307	0.003
H104	0.249	0.252	0.003
H105	0.236	0.238	0.003
H106	0.256	0.259	0.003
H107	0.274	0.276	0.002
H108	0.289	0.291	0.003
H109	0.252	0.255	0.003
C110	-0.159	-0.157	0.002
H111	0.300	0.303	0.003
C112	0.677	0.671	-0.007
O113	-0.576	-0.565	0.011
H114	0.436	0.439	0.003
H115	0.502	0.504	0.002
H116	0.520	0.522	0.002
H117	0.493	0.496	0.002
H118	0.517	0.519	0.002
H119	0.487	0.490	0.002
H120	0.501	0.503	0.002
H121	0.499	0.501	0.002
H122	0.498	0.501	0.003
H123	0.487	0.490	0.003
H124	0.508	0.510	0.002
H125	0.505	0.508	0.003
H126	0.492	0.495	0.003
N127	-0.861	-0.861	0.000
N128	-0.817	-0.819	-0.001
N129	-0.868	-0.869	0.000
N130	-0.880	-0.880	0.000

Table S3. The values of μ_X, μ_Y, and μ_Z for conformers **a-c** obtained from polarizable force field based on the fragment dipoles (D_{frag}-POL)

Fragmentation I	$\|\mu_x\|$	$\|\mu_y\|$	$\|\mu_z\|$	**Fragmentation II**	$\|\mu_x\|$	$\|\mu_y\|$	$\|\mu_z\|$
			Conformer a				
Fragment 1	17.109	3.103	-0.523	Fragment 1	17.109	3.103	-0.523
Fragment 2	3.889	-2.725	1.672	Fragment 2	3.889	-2.725	1.672
Fragment 3	-4.843	0.108	1.291	Fragment 3	7.089	7.267	0.716
Fragment4	12.096	4.158	-1.091				
Fragment 5	-0.164	3.001	0.516				
			Conformer b				
Fragment 1	16.842	-1.916	-1.990	Fragment 1	16.842	-1.916	-1.990
Fragment 2	2.805	-0.235	1.959	Fragment 2	2.805	-0.235	1.959
Fragment 3	-4.941	-3.644	-1.537	Fragment 3	6.711	-2.448	-0.795
Fragment4	12.266	-0.218	2.682				
Fragment 5	-0.614	1.414	-1.940				
			Conformer c				
Fragment 1	15.129	-3.037	-1.608	Fragment 1	15.129	-3.037	-1.608
Fragment 2	-1.245	-0.557	1.882	Fragment 2	-1.245	-0.557	1.882
Fragment 3	-6.371	-4.846	0.315	Fragment 3	5.100	-1.148	-1.054
Fragment4	12.860	1.240	-1.933				
Fragment 5	-1.389	2.458	0.564				

Table S4. Relative energies (kcal mol^{-1}) for three conformations **a–c** obtained from polarizable force field based on the fragment dipoles (D_{frag}-POL) with mass and geometric centers as fragment center, respectively.



	D_{frag}-POL (mass center)			D_{frag}-POL (geometric center)		
	a	**b**	**c**	**a**	**b**	**c**
Fragmentation I[a]						
SF=1.00	0.00	44.75	108.59	0.00	20.00	118.83
SF=0.75	0.00	22.67	60.24	0.00	8.75	66.00
SF=0.50	0.00	6.88	25.68	0.00	0.70	28.25
Fragmentation II[a]						
SF=1.00	0.00	65.36	101.55	0.00	59.74	93.43
SF=0.75	0.00	34.26	56.27	0.00	31.09	51.70
SF=0.50	0.00	12.04	23.93	0.00	10.64	22.06

[a] The scale factors (SF) of the electrostatic parameters (obtained at M06-2X/6-31G(d) level) were set to 1.00, 0.75, and 0.50.

Table S5. The charge parameters for water models

atom index	*q*	*q*	Δ*q*
	NBO	**SPC**	
2W			
O131	-0.979	-0.820	-0.159
H132	0.498	0.410	0.088
H133	0.481	0.410	0.071
O134	-1.032	-0.820	-0.212
H135	0.510	0.410	0.100
H136	0.526	0.410	0.116
14W			
O131	-1.030	-0.820	-0.210
H132	0.517	0.410	0.107
H133	0.522	0.410	0.112
O134	-0.984	-0.820	-0.164
H135	0.497	0.410	0.087
H136	0.488	0.410	0.078
O137	-0.991	-0.820	-0.171
H138	0.500	0.410	0.090
H139	0.490	0.410	0.080
O140	-1.031	-0.820	-0.211
H141	0.511	0.410	0.101
H142	0.523	0.410	0.113
O143	-0.964	-0.820	-0.144
H144	0.492	0.410	0.082
H145	0.472	0.410	0.062
O146	-0.970	-0.820	-0.150
H147	0.497	0.410	0.087
H148	0.476	0.410	0.066
O149	-0.990	-0.820	-0.170
H150	0.494	0.410	0.084
H151	0.496	0.410	0.086
O152	-0.985	-0.820	-0.165
H153	0.489	0.410	0.079
H154	0.490	0.410	0.080
O155	-1.004	-0.820	-0.184
H156	0.498	0.410	0.088
H157	0.506	0.410	0.096
O158	-0.986	-0.820	-0.166
H159	0.488	0.410	0.078
H160	0.498	0.410	0.088
O161	-0.992	-0.820	-0.172
H162	0.477	0.410	0.067
H163	0.491	0.410	0.081
O164	-0.943	-0.820	-0.123
H165	0.466	0.410	0.056

H166	0.502	0.410	0.092
O167	-1.023	-0.820	-0.203
H168	0.512	0.410	0.102
H169	0.511	0.410	0.101
O170	-0.968	-0.820	-0.148
H171	0.496	0.410	0.086
H172	0.472	0.410	0.062
H171	0.496	0.410	0.086
H172	0.472	0.410	0.062

Table S6. The charge parameters of biotin-4KC chain without (w/o) and with water models

atom	**W/O H_2O**	**with 2W**		**with 14W**	
index	***q***	***q***	**Δ*q***	***q***	**Δ*q***
N1	-0.649	-0.663	-0.014	-0.663	-0.013
H2	0.447	0.417	-0.030	0.418	-0.029
C3	-0.205	-0.205	0.000	-0.217	-0.011
H4	0.311	0.316	0.004	0.323	0.012
C5	-0.648	-0.691	-0.043	-0.643	0.005
H6	0.295	0.306	0.010	0.309	0.014
H7	0.283	0.280	-0.003	0.278	-0.005
S8	0.020	-0.047	-0.067	-0.074	-0.094
C9	0.843	0.815	-0.028	0.823	-0.020
O10	-0.642	-0.519	0.123	-0.525	0.117
O11	-0.705	-0.687	0.019	-0.685	0.020
H12	0.527	0.484	-0.043	0.483	-0.044
N13	-0.649	-0.708	-0.059	-0.708	-0.059
C14	0.742	0.695	-0.047	0.694	-0.048
C15	-0.552	-0.564	-0.012	-0.563	-0.011
C16	-0.467	-0.470	-0.003	-0.470	-0.003
C17	-0.484	-0.492	-0.007	-0.491	-0.007
C18	-0.471	-0.474	-0.004	-0.471	-0.001
C19	-0.428	-0.403	0.025	-0.401	0.027
C20	-0.083	-0.097	-0.014	-0.098	-0.014
N21	-0.693	-0.692	0.001	-0.684	0.009
C22	0.866	0.801	-0.066	0.803	-0.063
O23	-0.779	-0.705	0.075	-0.703	0.076
H24	0.284	0.268	-0.017	0.261	-0.023
C25	-0.084	-0.108	-0.024	-0.076	0.007
N26	-0.678	-0.694	-0.016	-0.705	-0.027
H27	0.282	0.285	0.003	0.212	-0.070
C28	-0.637	-0.624	0.013	-0.620	0.017
S29	0.271	0.195	-0.077	0.159	-0.113
O30	-0.750	-0.636	0.114	-0.632	0.118

H31	0.455	0.439	-0.016	0.438	-0.017
H32	0.268	0.238	-0.031	0.236	-0.032
H33	0.289	0.284	-0.004	0.283	-0.006
H34	0.228	0.240	0.013	0.241	0.014
H35	0.242	0.254	0.012	0.253	0.011
H36	0.265	0.262	-0.003	0.260	-0.006
H37	0.258	0.257	-0.001	0.260	0.002
H38	0.222	0.243	0.021	0.244	0.021
H39	0.261	0.264	0.003	0.257	-0.004
H40	0.263	0.257	-0.006	0.260	-0.003
H41	0.434	0.450	0.016	0.452	0.018
H42	0.466	0.462	-0.004	0.467	0.001
H43	0.273	0.264	-0.009	0.261	-0.012
H44	0.297	0.300	0.003	0.368	0.070
C45	-0.295	-0.275	0.020	-0.275	0.020
C46	-0.494	-0.478	0.015	-0.478	0.016
C47	-0.492	-0.499	-0.007	-0.499	-0.007
C48	-0.487	-0.515	-0.027	-0.515	-0.027
H49	0.277	0.292	0.015	0.294	0.016
H50	0.271	0.204	-0.067	0.204	-0.067
H51	0.285	0.290	0.005	0.290	0.005
H52	0.251	0.189	-0.062	0.188	-0.063
H53	0.246	0.294	0.049	0.294	0.049
H54	0.266	0.241	-0.025	0.240	-0.026
H55	0.263	0.294	0.031	0.295	0.032
H56	0.256	0.284	0.028	0.283	0.027
C57	-0.157	-0.178	-0.021	-0.179	-0.022
H58	0.291	0.263	-0.028	0.263	-0.028
C59	0.697	0.691	-0.006	0.692	-0.005
O60	-0.656	-0.611	0.045	-0.612	0.044
N61	-0.668	-0.683	-0.015	-0.683	-0.015
C62	-0.281	-0.275	0.006	-0.275	0.006
C63	-0.492	-0.508	-0.017	-0.509	-0.017
C64	-0.493	-0.489	0.003	-0.489	0.003
C65	-0.491	-0.500	-0.009	-0.500	-0.009
H66	0.250	0.273	0.023	0.273	0.023
H67	0.258	0.272	0.014	0.272	0.014
H68	0.267	0.261	-0.006	0.261	-0.006
H69	0.255	0.255	0.000	0.256	0.001
H70	0.227	0.255	0.028	0.255	0.028
H71	0.267	0.265	-0.002	0.265	-0.003
H72	0.267	0.279	0.012	0.279	0.011
H73	0.266	0.265	0.000	0.266	0.000
C74	-0.160	-0.160	0.000	-0.160	0.000

H75	0.305	0.272	-0.033	0.272	-0.033
C76	0.694	0.676	-0.018	0.676	-0.017
O77	-0.651	-0.643	0.008	-0.643	0.008
H78	0.455	0.451	-0.004	0.451	-0.004
N79	-0.667	-0.654	0.014	-0.654	0.013
C80	-0.285	-0.290	-0.005	-0.290	-0.005
C81	-0.495	-0.482	0.013	-0.482	0.013
C82	-0.486	-0.496	-0.010	-0.496	-0.010
C83	-0.501	-0.495	0.006	-0.495	0.006
H84	0.270	0.278	0.008	0.278	0.008
H85	0.259	0.283	0.023	0.283	0.023
H86	0.271	0.219	-0.052	0.219	-0.052
H87	0.255	0.251	-0.004	0.251	-0.004
H88	0.225	0.287	0.062	0.287	0.062
H89	0.264	0.244	-0.019	0.244	-0.020
H90	0.287	0.287	0.000	0.287	0.000
H91	0.274	0.293	0.018	0.292	0.018
C92	-0.153	-0.174	-0.021	-0.174	-0.021
H93	0.288	0.274	-0.015	0.274	-0.015
C94	0.685	0.663	-0.022	0.663	-0.022
O95	-0.649	-0.619	0.030	-0.619	0.030
H96	0.450	0.453	0.003	0.454	0.003
N97	-0.649	-0.636	0.013	-0.636	0.013
C98	-0.286	-0.280	0.006	-0.280	0.006
C99	-0.496	-0.490	0.005	-0.490	0.005
C100	-0.484	-0.487	-0.003	-0.487	-0.003
C101	-0.515	-0.490	0.025	-0.490	0.025
H102	0.276	0.252	-0.023	0.253	-0.023
H103	0.265	0.282	0.017	0.282	0.017
H104	0.269	0.241	-0.028	0.241	-0.028
H105	0.254	0.266	0.011	0.266	0.011
H106	0.230	0.271	0.041	0.271	0.041
H107	0.262	0.256	-0.005	0.256	-0.005
H108	0.313	0.275	-0.037	0.276	-0.037
H109	0.274	0.233	-0.041	0.233	-0.041
C110	-0.152	-0.163	-0.010	-0.163	-0.010
H111	0.288	0.285	-0.003	0.285	-0.003
C112	0.701	0.690	-0.011	0.690	-0.011
O113	-0.631	-0.604	0.027	-0.602	0.029
H114	0.454	0.428	-0.026	0.428	-0.026
H115	0.482	0.508	0.026	0.508	0.026
H116	0.514	0.512	-0.002	0.512	-0.002
H117	0.499	0.500	0.001	0.500	0.001
H118	0.468	0.507	0.039	0.507	0.039

H119	0.502	0.510	0.007	0.510	0.007
H120	0.517	0.498	-0.019	0.498	-0.019
H121	0.483	0.497	0.014	0.497	0.014
H122	0.518	0.502	-0.017	0.501	-0.017
H123	0.496	0.511	0.016	0.511	0.016
H124	0.517	0.506	-0.011	0.506	-0.011
H125	0.495	0.520	0.025	0.520	0.025
H126	0.482	0.502	0.020	0.502	0.020
N127	-0.838	-0.837	0.001	-0.837	0.001
N128	-0.840	-0.823	0.017	-0.823	0.017
N129	-0.857	-0.822	0.035	-0.822	0.035
N130	-0.865	-0.825	0.040	-0.825	0.040
H131	0.171	0.230	0.059	0.205	0.034
$\Delta\lvert\bar{q}\rvert$			0.026		0.027

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