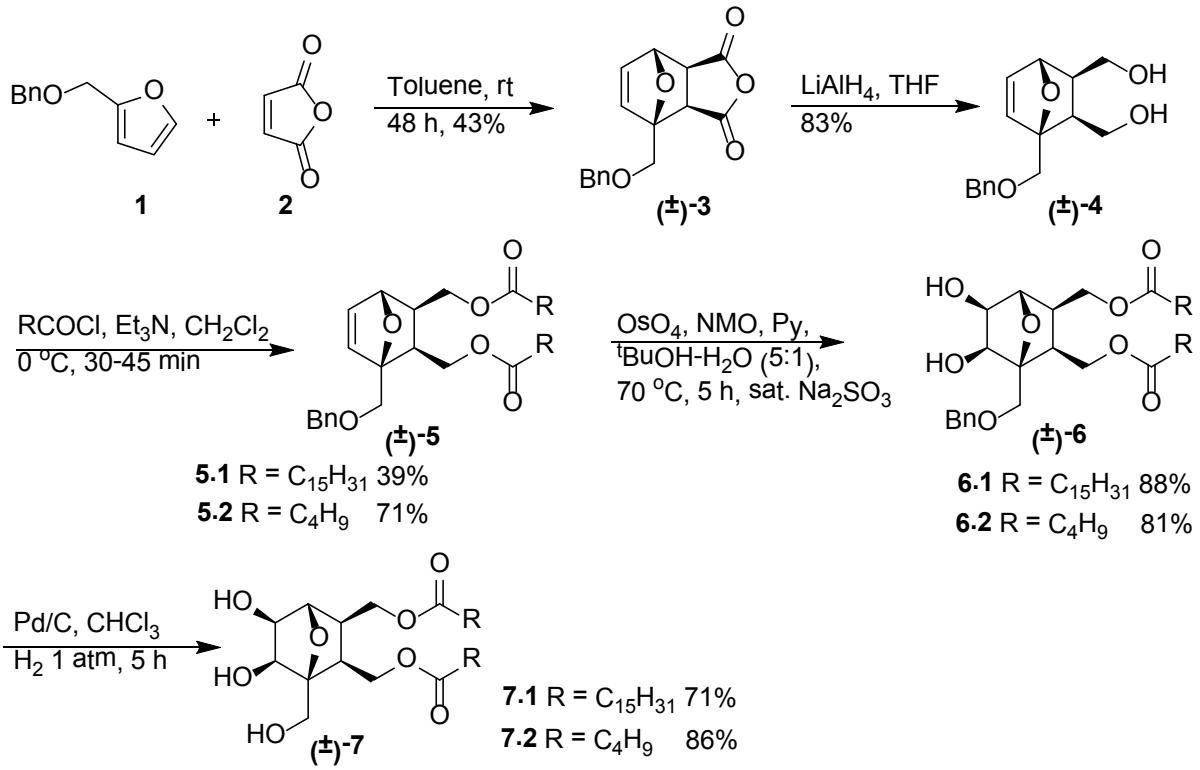
Synthesis of Oxanorbornane based Amphiphilic Systems

(Ref. RSC Advances, 2012, 2, 4048-4051)

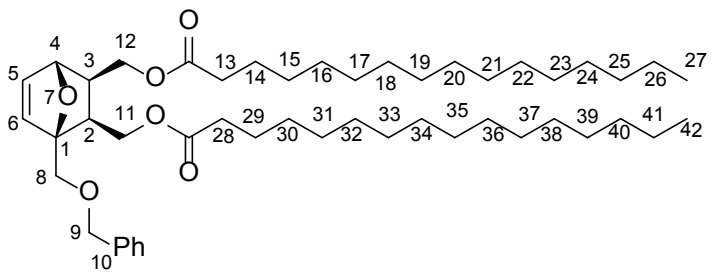
Synthesis of the target molecules started with cycloaddition of *O*-benzyl protected furfuryl alcohol with maleic anhydride. By this method, we were able to prepare a compound with one head group and two lipophilic chains as shown in Scheme 1. Towards this, the anhydride **(±)-3** was first reduced using lithium aluminium hydride to get the diol **(±)-4** and then acylated with palmitoyl chloride. Treatment of resulting diesters **(±)-5** with OsO_4 led to the formation of *cis*-dihydroxylated product **(±)-6** which on hydrogenolysis in presence of H_2-Pd/C afforded the amphiphile **(±)-7** in 71% yield.



Scheme 1. Synthesis of dialkyl lipids **(±)-7.1 & 7.2**

Experimental Procedure:

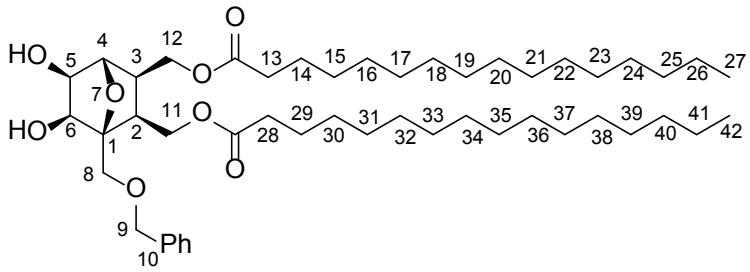
Preparation of ((1RS,2SR,4RS)-1-(benzyloxymethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-diyl)bis(methylene) dipalmitate ((±)-5)



To a stirred solution of the alcohol **(±)-4** (1.0 eq) and Et_3N (3.0 eq) in dry dichloromethane was added palmitoyl chloride (2.2 eq) at 0 °C

under N_2 atmosphere. The reaction mixture was warmed to room temperature and allowed to stir for 45mins. After completion of the reaction, the mixture was washed with water and extracted with dichloromethane. The organic layer was dried using sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using 10-20% EtOAc/Hexane. Colorless solid; Yield = 49%; R_f (20% EtOAc/Hexane), 0.50; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33-7.28 (m, 5H, 10-**H**), 6.34-6.35 (m, 2H, 5-**H**, **6-H**), 4.82 (s, 1H, 4-**H**), 4.69 (d, 1H, *J* = 12.0 Hz, 9-$\mathbf{H_a}$), 4.55 (d, 1H, *J* = 12.4 Hz, 9-$\mathbf{H_b}$), 4.39 (m, 1H, 11-$\mathbf{H_a}$), 4.17 (dd, 1H, *J* = 6.8, 11.6 Hz, 12-$\mathbf{H_a}$), 4.11 (dd, 1H, *J* = 6.0, 11.2 Hz, 12-$\mathbf{H_b}$), 3.97 (t, 1H, *J* = 10.0, 11-$\mathbf{H_b}$), 3.92 (d, 1H *J* = 10.8 Hz, 8-$\mathbf{H_a}$), 3.75 (d, 1H, *J* = 10.8 Hz, 8-$\mathbf{H_b}$), 2.32 (t, 2H, *J* = 7.2 Hz, 28-**H**), 2.24 (t, 2H, *J* = 7.6 Hz, 13-**H**), 2.12-2.07 (m, 2H, 2-**H**, 3-**H**), 1.65-1.54 (m, 4H, 14-**H**, 29-**H**), 1.25 (bs, 48H, 15-26-**H**, 30-41-**H**), 0.88 (t, 6H, *J* = 6.4 Hz, 27-**H**, 42-**H**); ^{13}C NMR ($CDCl_3$,100Hz): δ 173.7, 173.4, 137.9, 137.5, 135.6, 128.5 (2), 128.0 (2), 127.9, 90.0, 80.5, 73.8, 67.8, 63.7, 62.0, 41.4, 40.8, 34.4, 32.0 (2), 29.8 (9), 29.77 (2), 29.73 (2), 29.60 (2), 29.47 (2), 29.38 (2), 29.25 (2), 25.1, 24.9, 22.8 (2), 14.2 (2); IR (neat): 3055, 2926, 2857, 1734, 1458, 1265, 1172, 1105, 738 cm^{-1}.

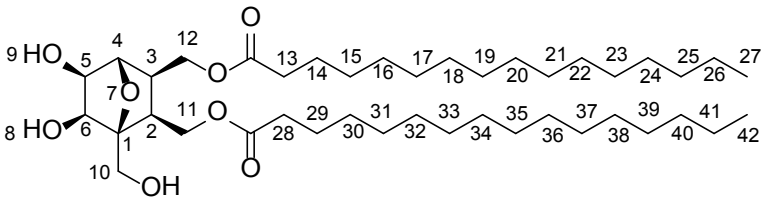
Preparation of ((1RS,2SR,4SR,5RS,6SR)-1-(benzyloxymethyl)-5,6-dihydroxy-7-oxabicyclo[2.2.1]heptane-2,3-diyl)bis(methylene) dipalmitate ((±)-6)



To a stirred solution containing a mixture of the alkene **((±)-5)** 1.0 eq), N-Methyl morpholine N-Oxide (2.4 eq) and pyridine (30 uL for 100 mg of alkene) in ^{t}BuOH-H_2O (3:1) was added osmium tetraoxide (0.01eq, 0.02M solution) and it was heated at 80 ^{o}C for 5-6 h. After completion of the reaction, the mixture was cooled to room temperature, treated with 15% aq. Na_2SO_3 solution (4 mL), stirred for 5-10 minutes and water (8 mL) was added to it. All the volatiles were removed under reduced pressure and the resulting residue was extracted with ethyl acetate. The organic layer was dried using sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using Hexane-EtOAc solvent system. Colorless solid; Yield = 77%; R_f (40% EtOAc-Hexane), 0.35; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.31 (m, 5H, 10-**H**), 4.65 (d, 1H, *J* = 11.6 Hz, 9-$\mathbf{H_a}$), 4.58 (d, 1H, *J* = 12.0 Hz, 9-$\mathbf{H_b}$), 4.26 (s, 1H, 4-**H**), 4.25 (dd, 1H, 11-$\mathbf{H_a}$, merged with 4-**H**), 4.18

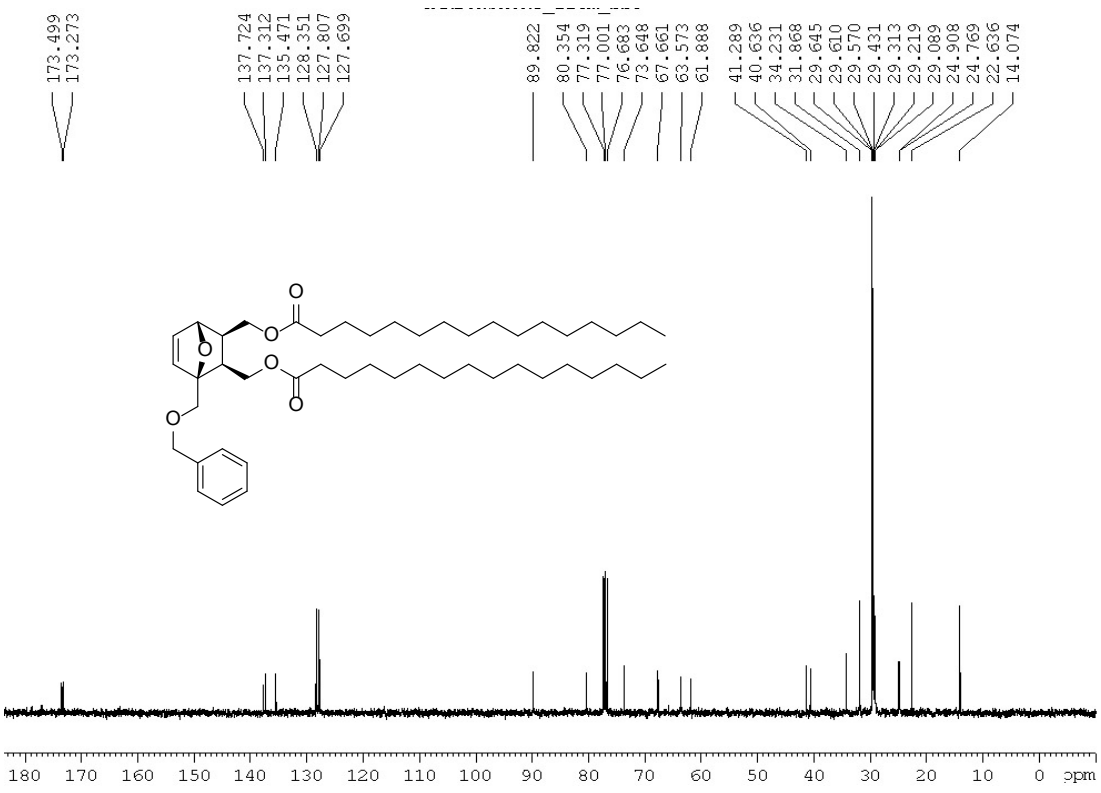
(dd, 1H, *J* = 7.2, 11.6 Hz, 12-**H$_a$**), 4.04-3.99 (m, 2H, **-OH**, 12-**H$_b$**), 3.94 (m, 1H, 11-**H$_b$**), 3.92 (s, 2H, 5-**H**, 6-**H**), 3.93-3.87 (m, 2H, 8-**H**), 3.28 (d, 1H, *J* = 5.6 Hz, **-OH**), 2.30 (t, 2H, *J* = 7.2 Hz, 28-**H**), 2.25 (t, 2H, *J* = 7.2 Hz, 13-**H**), 2.22-2.17 (m, 1H, 3-**H**), 2.14-2.07 (m, 1H, 2-**H**) 1.63-1.56 (bs, 4H, 14-**H**, 29-**H**), 1.26 (bs, 48H, 15-26-**H**, 30-41-**H**), 0.88 (t, 6H, *J* = 6.8 Hz, 27-**H**, 42-**H**); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.6, 173.3, 136.9, 128.6 (2C), 128.2, 128.0 (2C), 86.6, 84.1, 75.7, 74.3, 73.9, 66.8, 61.9, 60.7, 42.0, 40.9, 34.2 (2C), 31.9 (2C), 29.7 (8C), 29.6 (4C), 29.5 (2C), 29.3 (2C), 29.2 (2C), 29.1 (2C), 24.9, 24.8, 22.7 (2C), 14.1 (2C); IR (neat): 3455, 3055, 2926, 2857, 1734, 1458, 1265, 1172, 1105, 996, 738 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{48}H_{82}O_8$ $(M+Na)^+$ 809.5907, found $(M+Na)^+$ 809.5906.

Preparation of ((1RS,2SR,4SR,5RS,6SR)-5,6-dihydroxy-1-(hydroxymethyl)-7-oxabicyclo[2.2.1]heptane-2,3-diyl)bis(methylene) dipalmitate ((±)-7)

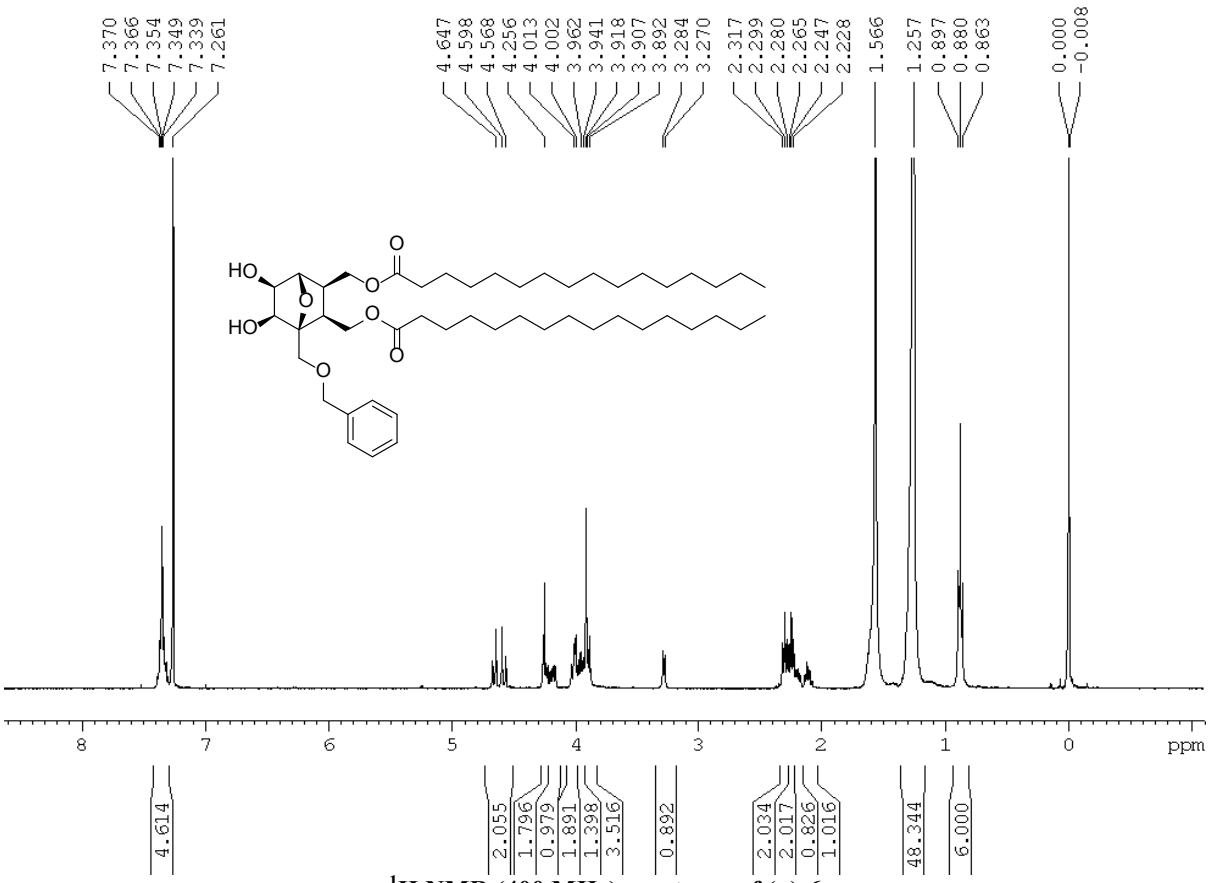


A mixture of the benzyl ether **((±)-6)** and 10% Pd/C (20% w/w) in $CHCl_3$ was stirred under hydrogen atmosphere (H_2 balloon) at room temperature for 5 h. After completion of the reaction, the resulting mixture was filtered through a celite bed and the solvent was evaporated under reduced pressure. The resulting solid was purified by column chromatography using EtOAc-Hexanes as solvent system in a gradient mode. Colorless solid; Yield = 72%; R_f (EtOAc), 0.60; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.52 (bs, 1H, **-OH**), 4.24 (s, 1H, 4-**H**), 4.20 (dd, 1H, *J* = 5.2, 10.8 Hz, 12-**H$_a$**), 4.16-4.03 (m, 4H, 10-**H**, 11-**H**), 4.01-3.90 (m, 3H, 5-**H**, 6-**H**, 12-**H$_b$**), 3.75 (bs, 1H, **-OH**), 3.40 (bs, 1H, **-OH**), 2.36-2.28 (m, 4H, 13-**H**, 28-**H**), 2.23 (ddd, 1H, *J* = 5.6, 9.6, 9.6 Hz, 3-**H**), 2.16-2.09 (m, 1H, 2-**H**), 1.65-1.56 (m, 4H, 14-**H**, 29-**H**), 1.26 (bs, 48H, 15-26-**H**, 30-41-**H**), 0.88 (t, 6H, *J* = 6.4 Hz, 27-**H**, 42-**H**); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.6, 173.3, 87.7, 83.5, 76.1, 74.0, 61.8, 60.6, 59.9, 41.9, 40.9, 34.2 (2C), 31.9 (2C), 29.73 (8C), 29.69 (4C), 29.5 (2C), 29.4 (2C), 29.3 (2C), 29.2 (2C), 24.92, 24.85, 22.7 (2C), 14.2 (2C); IR (neat): 3338, 2920, 2852, 1730, 1462, 1174, 1020, 826, 724 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{41}H_{76}O_8Na$ $(M+Na)^+$ 719.5438, found $(M+Na)^+$ 719.5430.

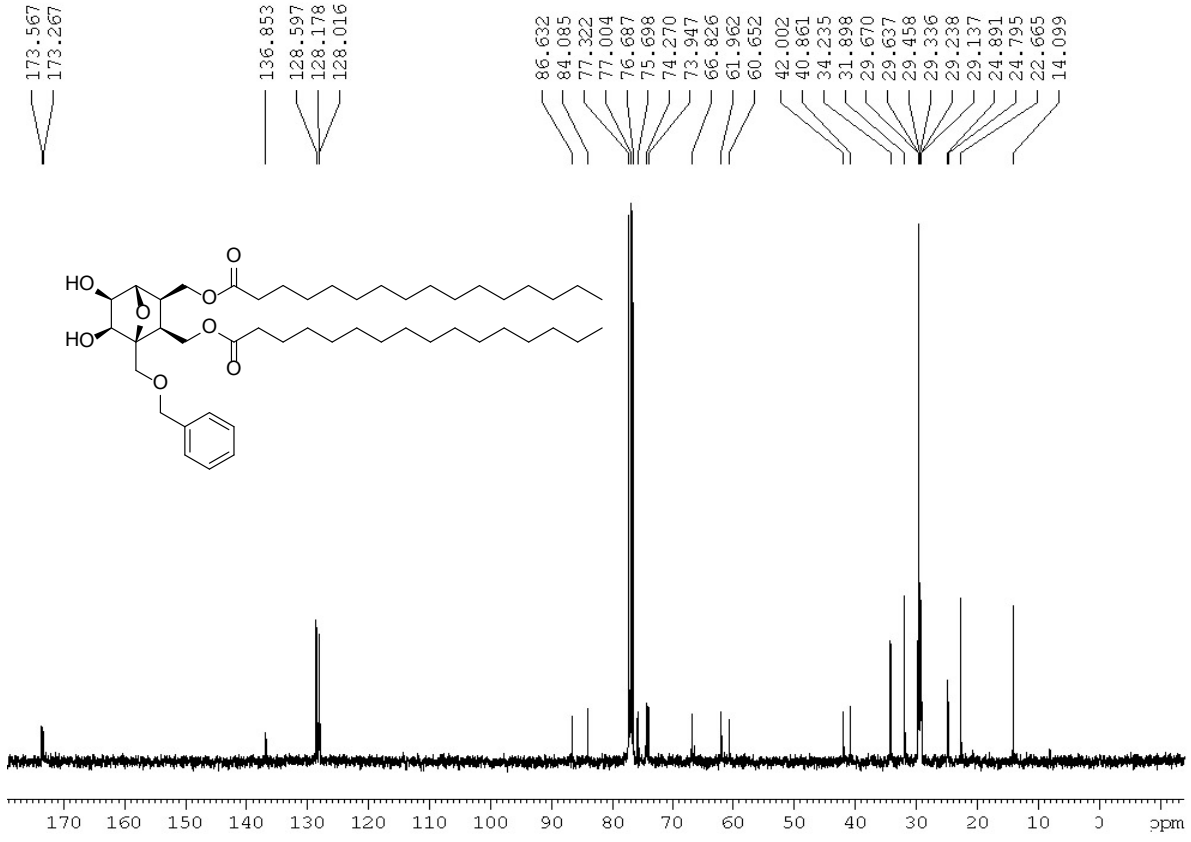
^{1}H NMR (400 MHz) spectrum of (±)-5



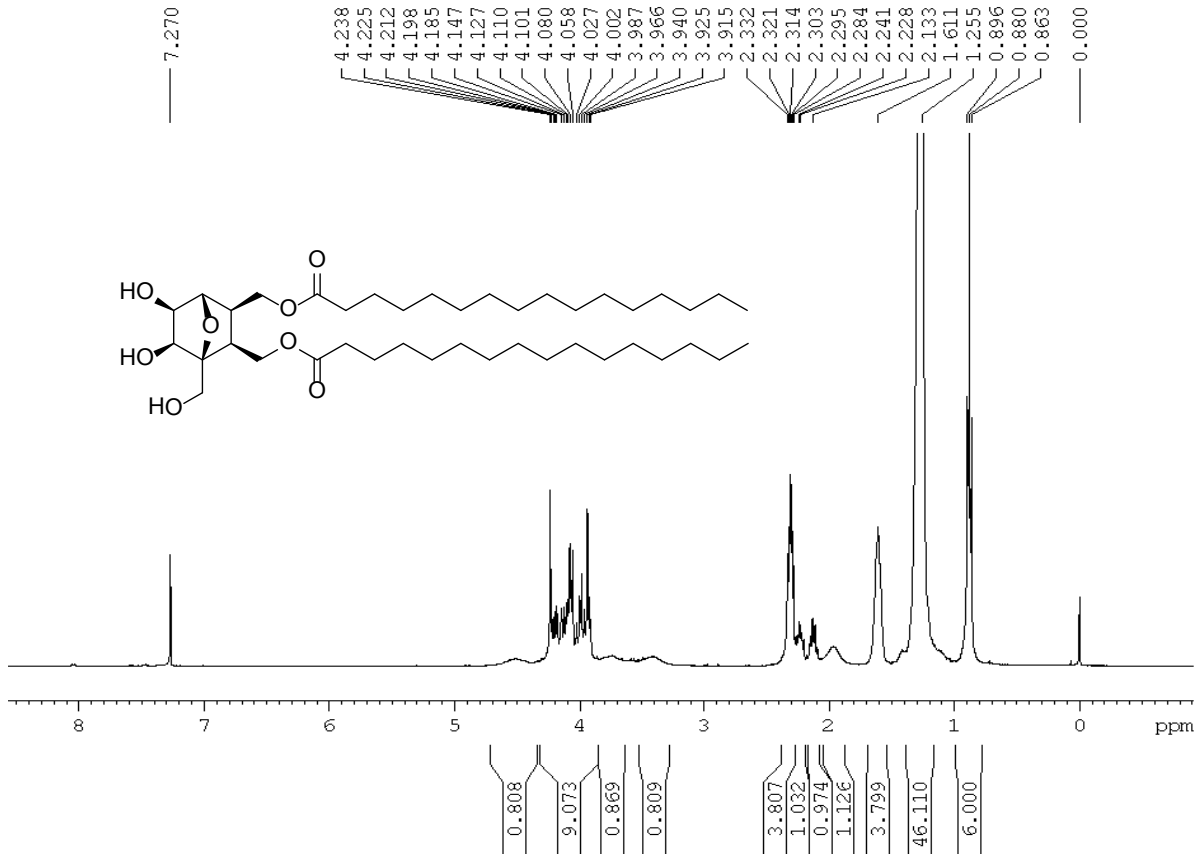
^{13}C NMR (100 MHz) spectrum of (±)-5



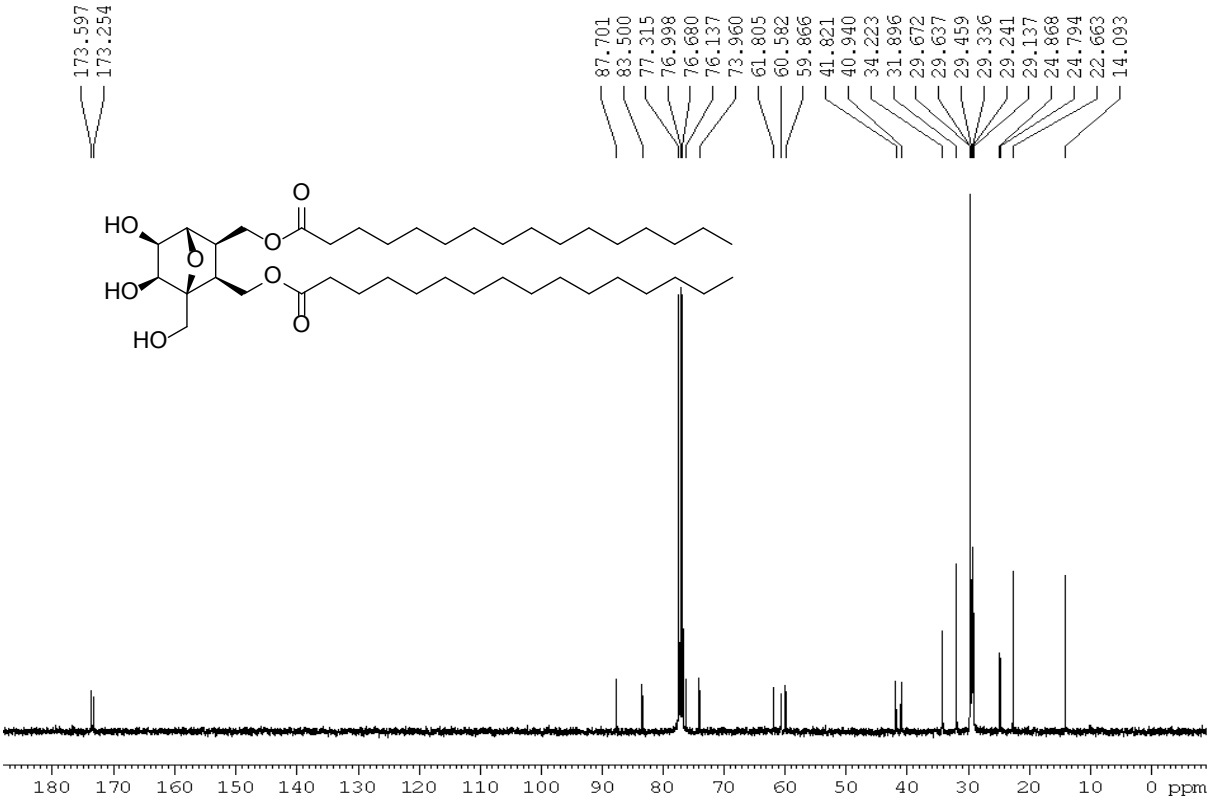
^{1}H NMR (400 MHz) spectrum of (±)-6



^{13}C NMR (100 MHz) spectrum of (±)-6



^{1}H NMR (400 MHz) spectrum of (±)-7



^{13}C NMR (100 MHz) spectrum of (±)-7

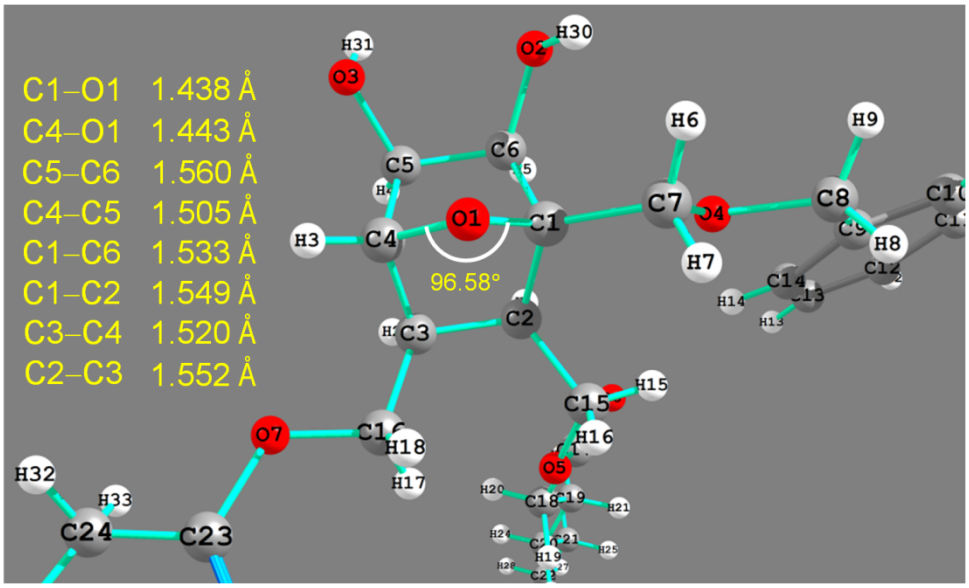


Figure S1. Geometrical parameters for the Oxanorbornane head.

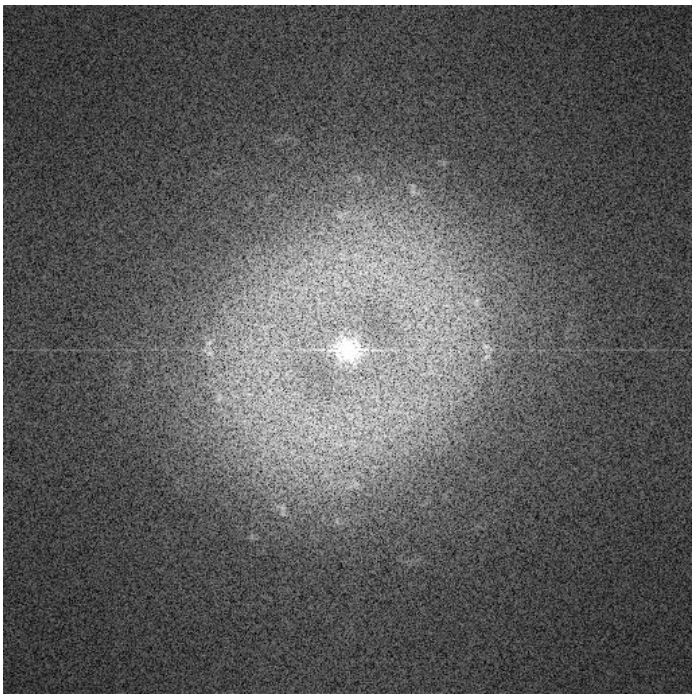
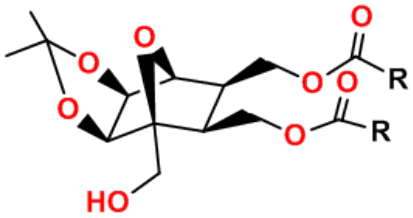
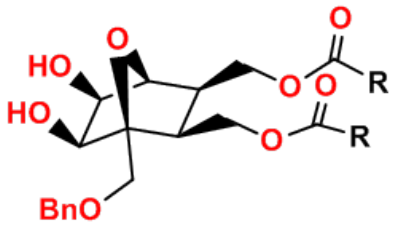


Figure S2. Selective Area Electron Diffraction (SAED) pattern of the surface micelles deposited by Langmuir Schaeffer method at 40 mN/m.



$R = C_{15}H_{31}$

Figure S3a. Chemical Structure of ketal protected 1a.



$R = C_{15}H_{31}$

Figure S3b. Chemical Structure of Benzyl protected 1a.

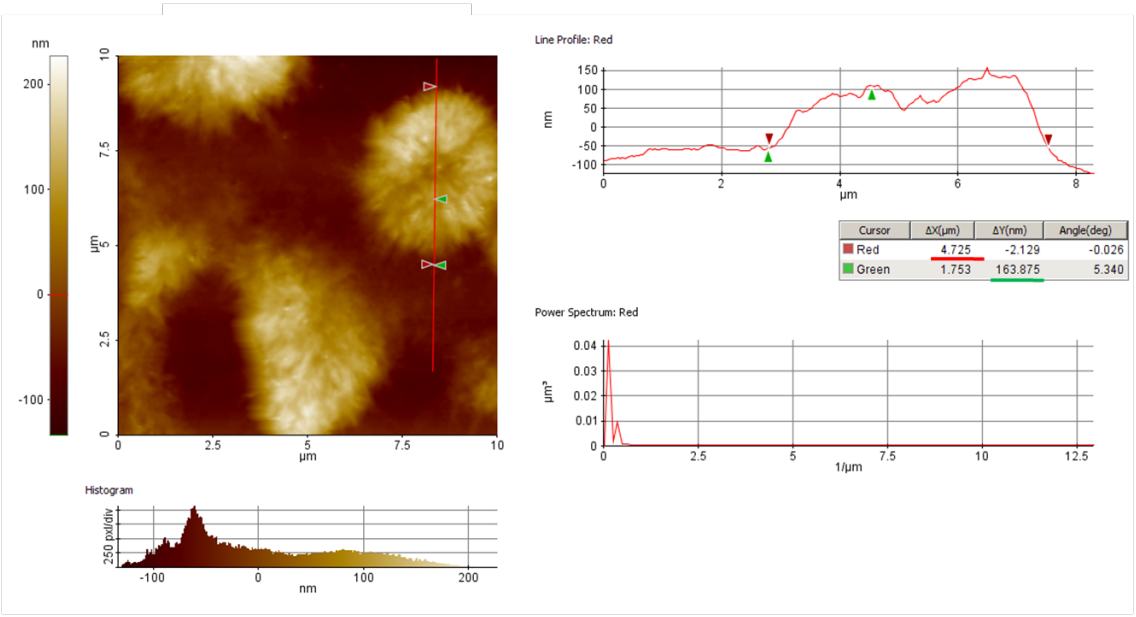
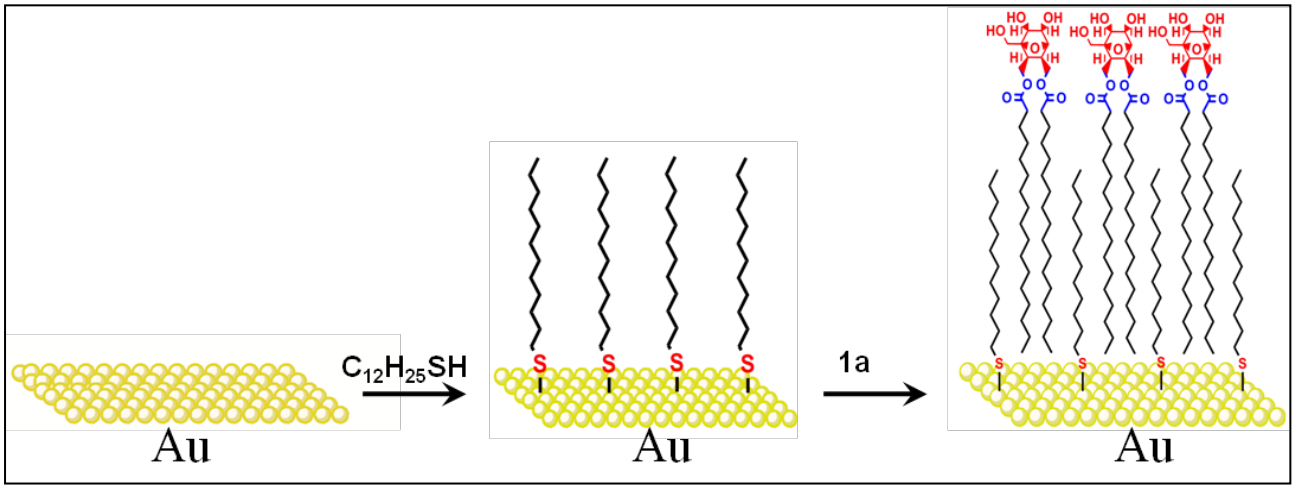
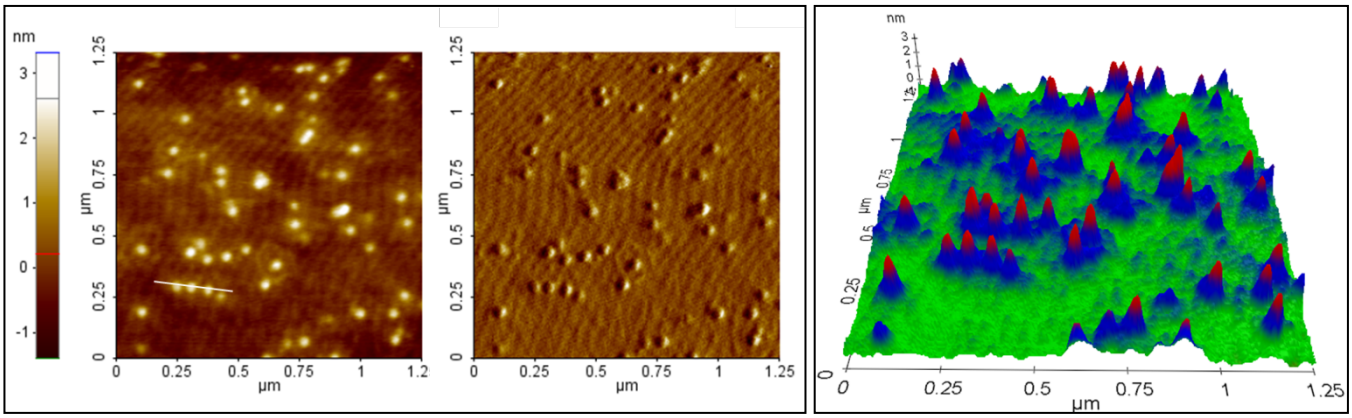
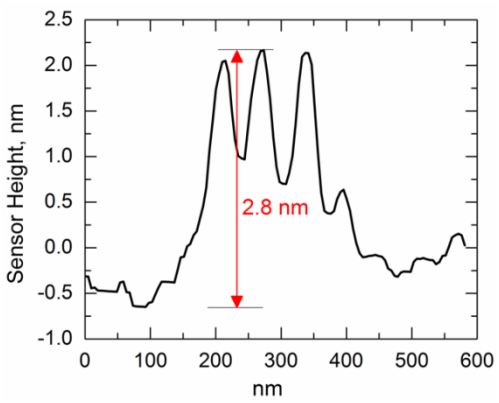


Figure S4. 3-D micro flowers formed by 1mM of benzyl protected 1a in $CHCl_3$ after 3 days; non-contact imaging was done at a scan rate of 1Hz. In the line profile, the width and height of the microflower of interest is underlined with red and green colored lines.







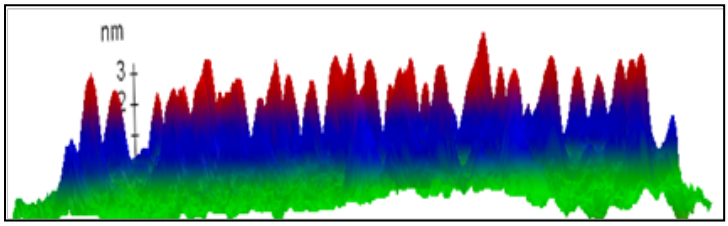


Figure S5. Embedding 1a onto dodecanethiol chemisorbed Au(111) surface. The electrode was fabricated in $CHCl_3$ and CH_3OH (1/4, v/v) solution. AFM images and line profile shows the sensor height.

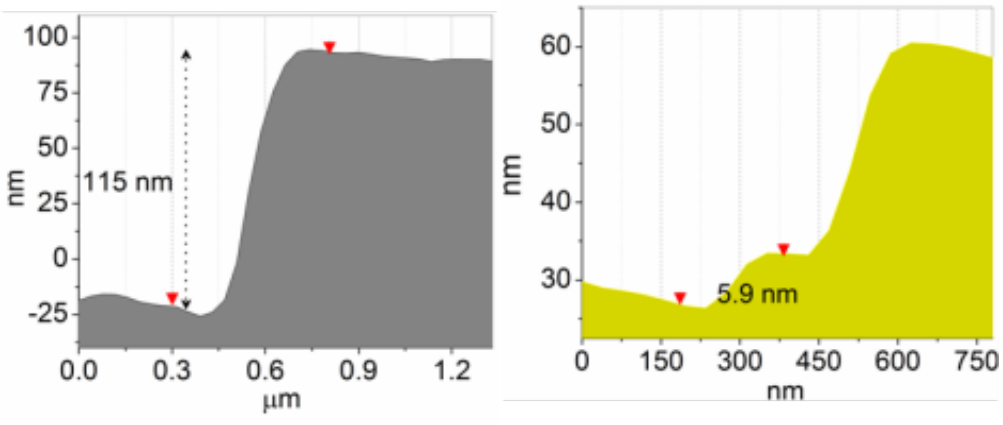


Figure S6. Line profiles indicate the vertical dimensions of the square and rectangular sheets. 5.9 nm corresponds to 1a bilayer height.

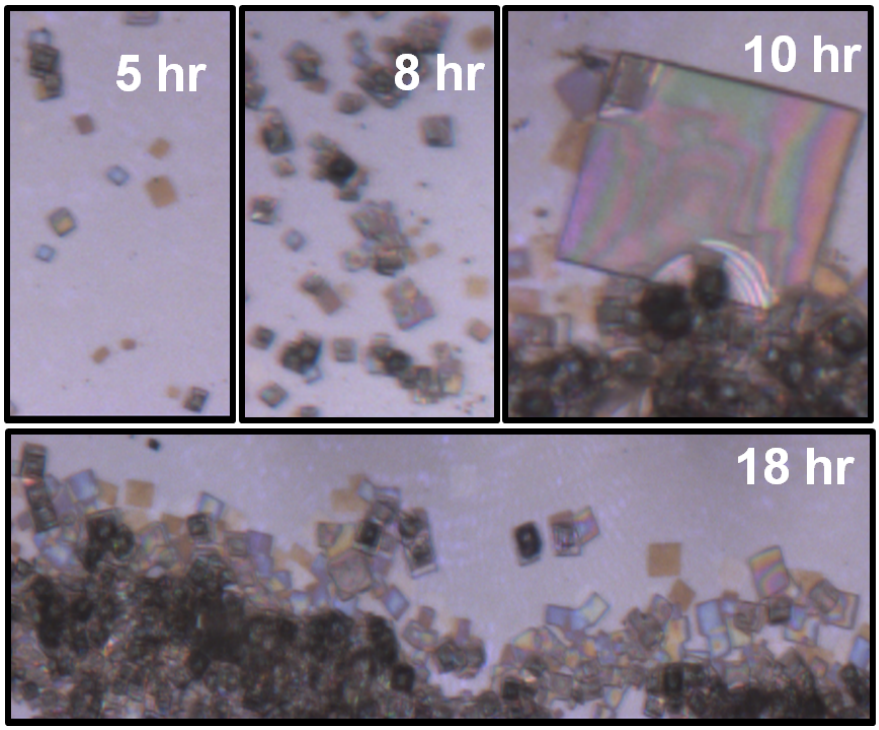


Figure S7. Single crystalline square nanosheets grown on ITO substrates at different incubation times in $CH_3OH/CHCl_3$ (1/1 v/v). Different contrasts (from light to dark colour) indicate increasing heights of the nanosheets.

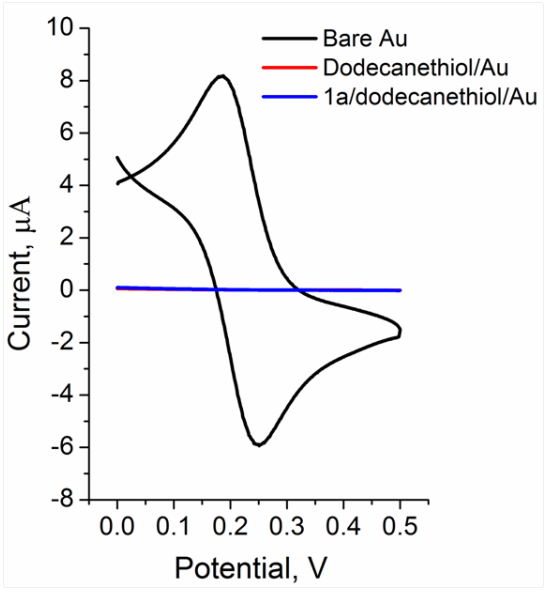


Figure S8. Cyclic Voltammograms of 1mM $Fe(CN)_6^{4-/3-}$ in 0.01M TRIS buffer (pH 7.4) containing 0.1M KCl as supporting electrolyte at bare Au electrode (in black), dodecanethiol-SAM modified Au electrode (in red) and at 1a/SAM/Au electrode (in blue).

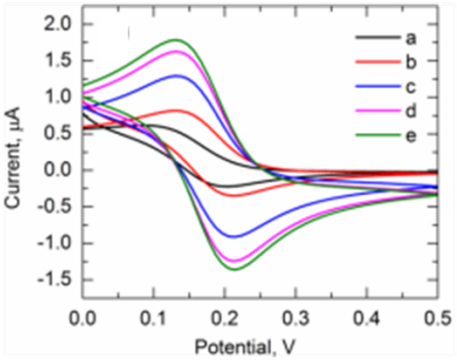


Figure S9. CV response of 1mM $Fe(CN)_6^{4-/3-}$ buffered solutions of pH 7.4 with 0.1M KCl as supporting electrolyte containing the same concentrations of Li^+ described for impedance measurements.

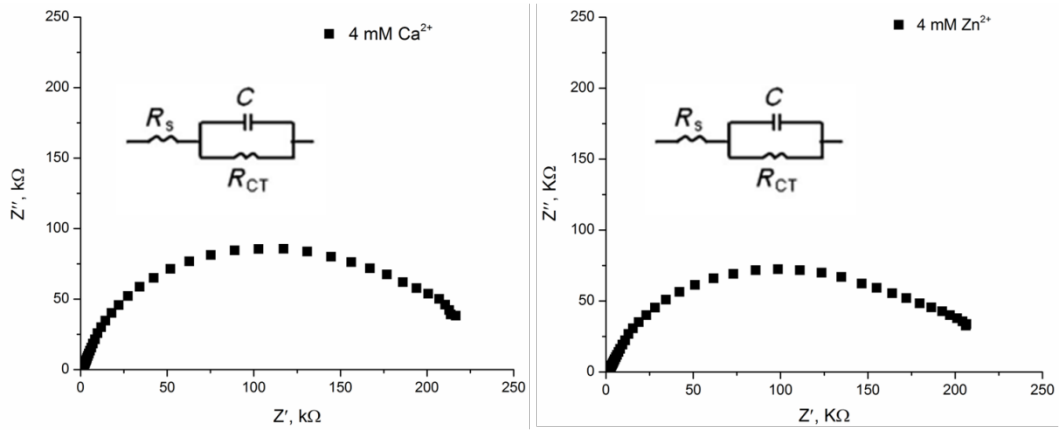


Figure S10. Impedance response of $Fe(CN)_6^{4-/3-}$ at the 1a/SAM/Au electrode in the presence of 4 mM Ca^{2+} and Zn^{2+} ions. Plots were recorded in 0.01M TRIS buffer (pH 7.4) containing 1mM $Fe(CN)_6^{4-/3-}$ as internal standard and 0.1M KCl as the supporting electrolyte.

Ab-initio Molecular dynamics (Atom-centered density matrix propagation, ADMP)

Cartesian Coordinates at 0 fs

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.186316	0.738659	0.517121
2	6	0	1.353201	1.614168	-0.064122
3	1	0	1.031853	2.166019	-0.921974
4	6	0	2.393508	0.501373	-0.456056
5	1	0	2.652167	0.560668	-1.488868
6	6	0	1.582015	-0.777025	-0.154798
7	1	0	2.179646	-1.665875	0.019335
8	6	0	0.452091	-0.944670	-1.192051
9	1	0	0.778102	-0.780286	-2.216579
10	6	0	-0.564527	0.141649	-0.718278
11	1	0	-0.759309	0.887411	-1.490867
12	6	0	-0.744806	1.298658	1.594088
13	1	0	-1.027877	0.480088	2.262315
14	1	0	-0.257891	2.075284	2.194598

15	8	0	0.852850	-0.431514	1.035605
16	8	0	-1.817122	-0.470107	-0.343736
17	8	0	-0.171903	-2.254716	-1.108522
18	8	0	-1.902712	1.831611	0.925539
19	1	0	-2.381069	2.442802	1.509840
20	1	0	-2.356857	0.261569	0.033244
21	3	0	-1.800525	-2.291064	-0.241019
22	1	0	0.418873	-2.916244	-1.499365
23	1	0	3.269742	0.558632	0.160552
24	1	0	1.756764	2.269579	0.684233

Cartesian Coordinates at 50 fs

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.251035	0.766693	0.500163
2	6	0	1.477266	1.600708	-0.000312
3	1	0	1.187117	2.493578	-0.664571
4	6	0	2.385570	0.465833	-0.470764
5	1	0	2.959386	0.335057	-1.450164
6	6	0	1.585598	-0.755976	-0.093161
7	1	0	2.167373	-1.732375	0.028585
8	6	0	0.453788	-0.960483	-1.226121
9	1	0	0.893951	-0.618752	-2.238046
10	6	0	-0.631008	0.154864	-0.681166
11	1	0	-0.913028	0.948087	-1.471030
12	6	0	-0.681242	1.529386	1.536388
13	1	0	-0.796951	0.940007	2.468552
14	1	0	-0.107888	2.473588	1.802291
15	8	0	0.849553	-0.379833	1.072293
16	8	0	-1.800792	-0.623555	-0.380544
17	8	0	-0.214395	-2.222128	-1.271479
18	8	0	-1.978838	1.797048	0.988624
19	1	0	-2.727481	2.101464	1.622399
20	1	0	-2.417145	0.067899	0.048464

21	3	0	-1.956937	-2.494463	-0.202329
22	1	0	0.452213	-2.948365	-1.187789
23	1	0	3.298408	0.513458	0.216914
24	1	0	1.891340	2.111139	0.922622

Cartesian Coordinates at 100 fs

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.171950	0.832822	0.441156
2	6	0	1.400246	1.581245	-0.153588
3	1	0	1.229249	2.103172	-1.035763
4	6	0	2.400093	0.409131	-0.390073
5	1	0	2.912000	0.457233	-1.302979
6	6	0	1.521161	-0.840559	-0.103480
7	1	0	1.879954	-1.826846	-0.047093
8	6	0	0.504327	-0.949102	-1.194020
9	1	0	0.867739	-0.653929	-2.209427
10	6	0	-0.545003	0.206131	-0.722215
11	1	0	-0.674528	0.734419	-1.613320
12	6	0	-0.676136	1.491809	1.515972
13	1	0	-0.772238	0.817238	2.364089
14	1	0	-0.153153	2.371762	1.781831
15	8	0	0.682086	-0.478029	1.029813
16	8	0	-1.764313	-0.388756	-0.287864
17	8	0	-0.091309	-2.235255	-1.220767
18	8	0	-2.014005	1.724688	1.061542
19	1	0	-2.570849	1.994675	1.729302
20	1	0	-2.232002	0.389813	0.240702
21	3	0	-1.710560	-2.471905	-0.114056
22	1	0	0.271782	-2.637258	-2.009597
23	1	0	3.169964	0.451835	0.335232
24	1	0	1.694184	2.342457	0.531246

Cartesian Coordinates at 150 fs

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.189913	0.784603	0.529262
2	6	0	1.389975	1.566498	-0.082380
3	1	0	1.171607	2.113236	-1.108722
4	6	0	2.375063	0.411305	-0.354823
5	1	0	2.738292	0.495883	-1.459805
6	6	0	1.575310	-0.794370	-0.067153
7	1	0	2.117502	-1.802493	0.093803
8	6	0	0.447365	-0.925303	-1.168746
9	1	0	0.775293	-0.563704	-2.132886
10	6	0	-0.586642	0.140780	-0.733261
11	1	0	-0.651332	0.854424	-1.647226
12	6	0	-0.619264	1.489612	1.518922
13	1	0	-0.803742	0.797279	2.341285
14	1	0	-0.094593	2.443214	1.920488
15	8	0	0.783722	-0.433544	1.007270
16	8	0	-1.843172	-0.507530	-0.551195
17	8	0	-0.092214	-2.198981	-1.262007
18	8	0	-1.987605	1.738201	1.031616
19	1	0	-2.486742	2.100722	1.879097
20	1	0	-2.374773	0.268093	-0.108008
21	3	0	-1.648500	-2.419596	0.243582
22	1	0	-0.832354	-2.057641	-1.920505
23	1	0	3.217613	0.323070	0.423392
24	1	0	1.705711	2.291996	0.706393

Cartesian Coordinates at 200 fs

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	0.181944	0.790532	0.464135
2	6	0	1.522447	1.606252	0.142691
3	1	0	1.351759	2.431649	-0.449701
4	6	0	2.395000	0.461216	-0.436304
5	1	0	2.637484	0.671127	-1.446205
6	6	0	1.522749	-0.863069	-0.188450
7	1	0	2.044496	-1.757607	-0.199724
8	6	0	0.440858	-0.951069	-1.271397
9	1	0	0.836687	-0.836284	-2.316577
10	6	0	-0.563327	0.210391	-0.792573
11	1	0	-0.803144	1.007464	-1.433411
12	6	0	-0.788441	1.327483	1.477781
13	1	0	-0.901099	0.583833	2.314820
14	1	0	-0.314690	2.167209	1.908400
15	8	0	0.754845	-0.481373	0.982712
16	8	0	-1.820474	-0.441176	-0.422088
17	8	0	-0.187197	-2.262156	-1.149457
18	8	0	-2.015655	1.804051	0.931745
19	1	0	-2.620847	2.001312	1.591076
20	1	0	-2.322805	0.376851	0.005024
21	3	0	-1.249998	-2.171990	0.361426
22	1	0	-0.469602	-2.522554	-2.016765
23	1	0	3.255514	0.243436	0.132991
24	1	0	1.785507	1.925619	1.144862

Cartesian Coordinates at 250 fs

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.151604	0.650150	0.569635
2	6	0	1.324098	1.562557	0.099446
3	1	0	0.752901	2.357053	-0.554532
4	6	0	2.287727	0.517710	-0.401919
5	1	0	2.643321	0.552257	-1.496946

6	6	0	1.547379	-0.811911	-0.208774
7	1	0	2.247438	-1.723649	-0.299071
8	6	0	0.446903	-0.914479	-1.351202
9	1	0	0.706297	-0.843019	-2.414904
10	6	0	-0.540039	0.224757	-0.833060
11	1	0	-0.764793	1.196989	-1.435671
12	6	0	-0.804357	1.197206	1.560693
13	1	0	-1.155850	0.400580	2.161850
14	1	0	-0.340704	1.919377	2.318123
15	8	0	0.734059	-0.638300	0.987327
16	8	0	-1.769873	-0.399506	-0.543621
17	8	0	-0.089572	-2.205952	-1.194237
18	8	0	-1.848169	1.883303	0.826926
19	1	0	-2.477055	2.395768	1.444280
20	1	0	-2.316719	0.361917	-0.155062
21	3	0	-1.248658	-2.048154	0.947290
22	1	0	-0.942954	-2.276695	-1.733415
23	1	0	3.283550	0.476002	0.130850
24	1	0	1.701034	2.147277	0.956979

Cartesian Coordinates at 300 fs

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.051119	0.646222	0.516340
2	6	0	1.333817	1.517500	0.160631
3	1	0	1.108683	2.217251	-0.632053
4	6	0	2.351838	0.514122	-0.349959
5	1	0	2.660883	0.768859	-1.369734
6	6	0	1.515694	-0.813987	-0.212688
7	1	0	2.024103	-1.724842	-0.171042
8	6	0	0.414061	-0.889886	-1.279937
9	1	0	0.668247	-0.781926	-2.362192
10	6	0	-0.581506	0.175609	-0.861080
11	1	0	-0.705296	0.873427	-1.656621

12	**6**	**0**	**-0.864426**	**1.178170**	**1.493780**
13	**1**	**0**	**-1.445911**	**0.220627**	**1.806169**
14	**1**	**0**	**-0.358416**	**1.579054**	**2.344607**
15	**8**	**0**	**0.745906**	**-0.560316**	**0.981985**
16	**8**	**0**	**-1.855350**	**-0.488757**	**-0.612195**
17	**8**	**0**	**-0.165103**	**-2.238506**	**-1.144020**
18	**8**	**0**	**-1.766735**	**2.099215**	**0.911494**
19	**1**	**0**	**-2.306752**	**2.407487**	**1.650936**
20	**1**	**0**	**-2.445752**	**0.161302**	**-0.329615**
21	**3**	**0**	**-0.720591**	**-2.130828**	**0.737559**
22	**1**	**0**	**-1.040049**	**-2.247464**	**-1.489658**
23	**1**	**0**	**3.276819**	**0.362019**	**0.191351**
24	**1**	**0**	**1.593288**	**2.142121**	**1.050151**

Figure S11. ADMP Potential energy evolution with time for "1a-lithium" tridentate complex calculated at b3lyp/6-31G(d) level of theory. Time evolution of the Lithium ion migration from bidentate to tridentate is given in the form of molecular geometries as well as cartesian coordinates.

Molecular structure and Coordinates for SDS devoid of an alkyl chain

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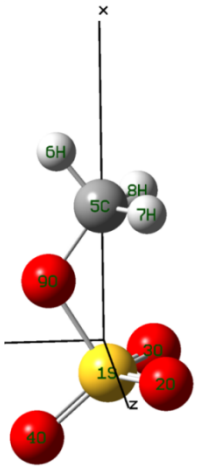
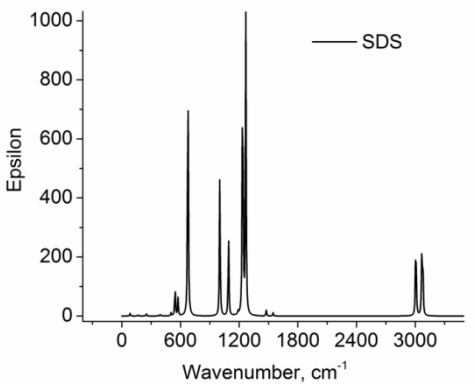
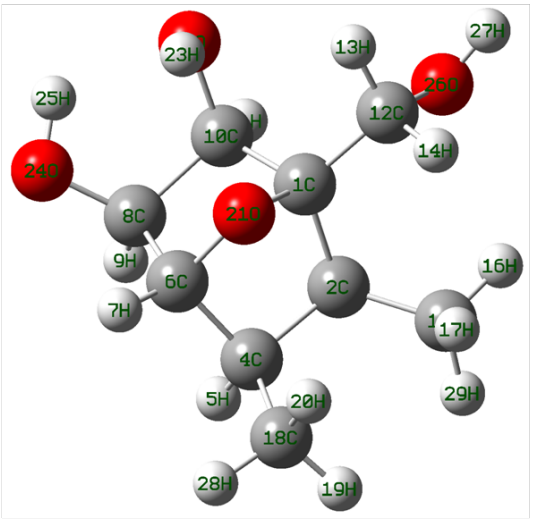
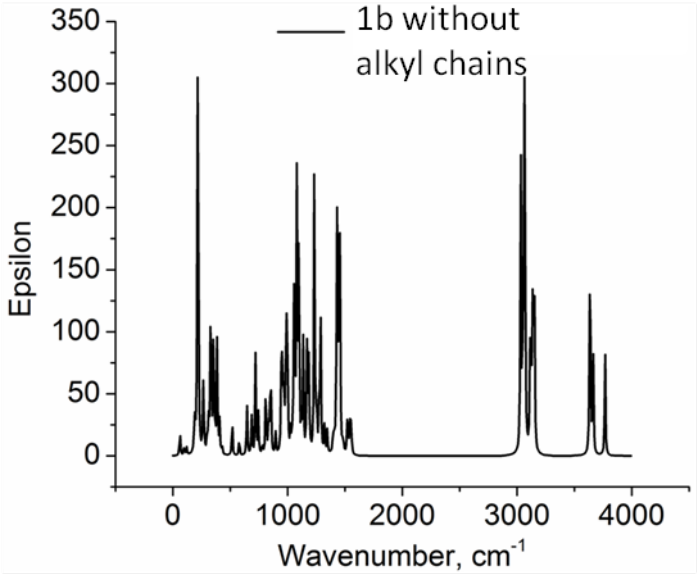
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.516579	-0.054946	0.000021
2	8	0	-0.449488	-0.855695	1.245278
3	8	0	-0.449419	-0.856126	-1.244990
4	8	0	-1.496968	1.044971	-0.000253
5	6	0	2.100307	0.016271	-0.000043
6	1	0	2.969948	0.686604	-0.000057
7	1	0	2.138620	-0.623964	0.892687
8	1	0	2.138660	-0.623926	-0.892782
9	8	0	0.947898	0.834698	-0.000025





Molecular structure and Coordinates for 1b devoid of alkyl chains

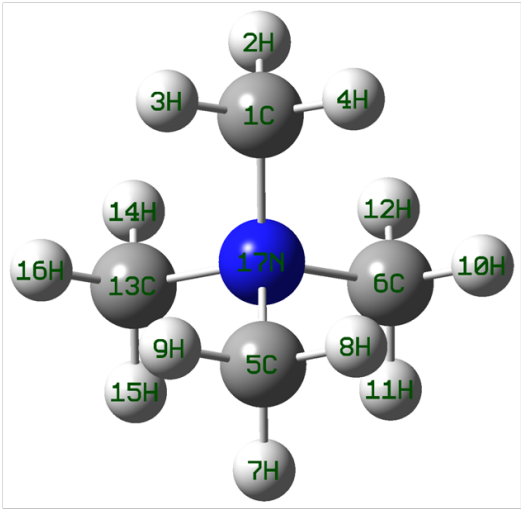


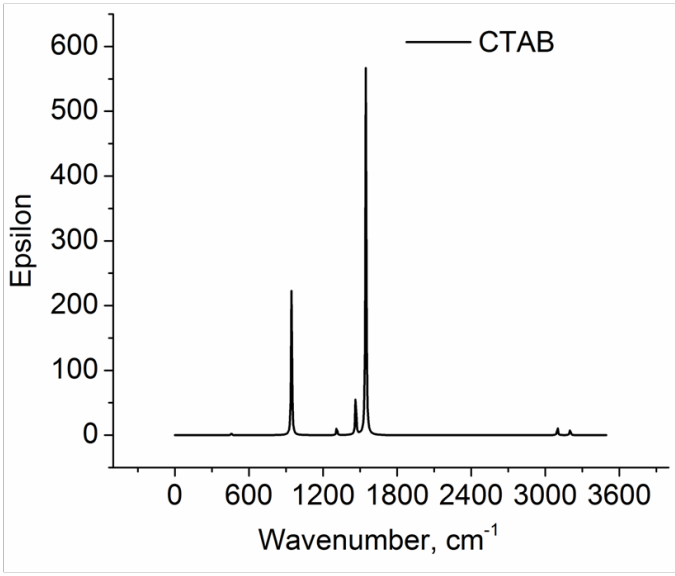


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.105624	0.626266	0.158644
2	6	0	1.221782	-0.052140	-0.709767
3	1	0	0.994436	0.134370	-1.766477
4	6	0	0.975366	-1.576565	-0.393367
5	1	0	0.857343	-2.140318	-1.326789
6	6	0	-0.366775	-1.480380	0.352394
7	1	0	-0.648864	-2.341128	0.960348
8	6	0	-1.474187	-1.014198	-0.622825
9	1	0	-1.307419	-1.423135	-1.628831
10	6	0	-1.246997	0.544265	-0.589196
11	1	0	-1.249799	1.025584	-1.567642
12	6	0	0.421078	1.985797	0.756106
13	1	0	-0.416702	2.306059	1.388539
14	1	0	1.315023	1.909574	1.390632
15	6	0	2.645417	0.454802	-0.457754

16	1	0	2.714575	1.518896	-0.700349
17	1	0	2.957245	0.316872	0.582640
18	6	0	2.043289	-2.265469	0.462876
19	1	0	3.027166	-2.249639	-0.017074
20	1	0	2.132833	-1.787743	1.443707
21	8	0	-0.152578	-0.329492	1.215427
22	8	0	-2.292411	1.154941	0.165797
23	1	0	-2.153965	0.843942	1.080736
24	8	0	-2.765805	-1.372509	-0.181880
25	1	0	-3.250573	-0.530878	-0.086536
26	8	0	0.619507	2.884636	-0.331820
27	1	0	0.679289	3.781113	0.029720
28	1	0	1.771839	-3.315441	0.624903
29	1	0	3.360280	-0.083002	-1.090392

Molecular structure and Coordinates for CTAB devoid of an alkyl chain

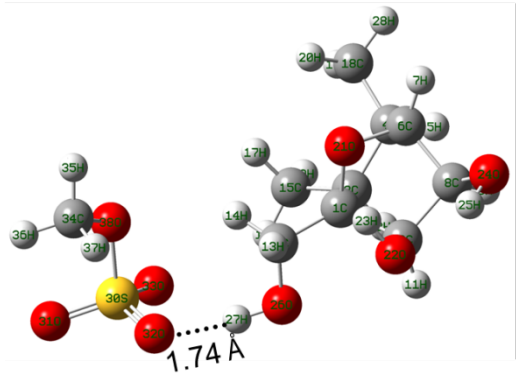


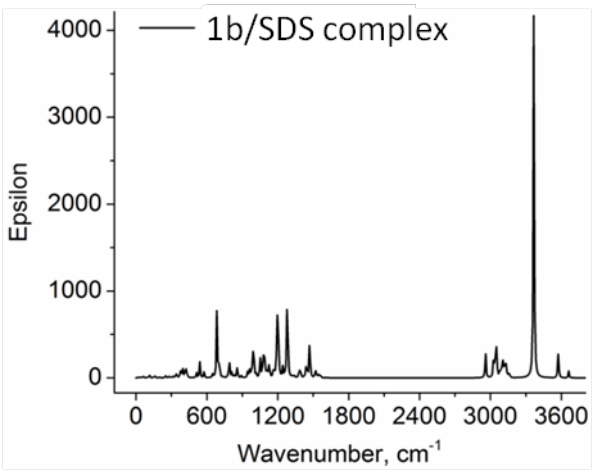


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.871473	0.871473	0.871473
2	1	0	1.496821	1.496821	0.232609

3	1	0	0.232609	1.496821	1.496821
4	1	0	1.496821	0.232609	1.496821
5	6	0	-0.871473	-0.871473	0.871473
6	6	0	0.871473	-0.871473	-0.871473
7	1	0	-1.496821	-1.496821	0.232609
8	1	0	-0.232609	-1.496821	1.496821
9	1	0	-1.496821	-0.232609	1.496821
10	1	0	1.496821	-1.496821	-0.232609
11	1	0	0.232609	-1.496821	-1.496821
12	1	0	1.496821	-0.232609	-1.496821
13	6	0	-0.871473	0.871473	-0.871473
14	1	0	-0.232609	1.496821	-1.496821
15	1	0	-1.496821	0.232609	-1.496821
16	1	0	-1.496821	1.496821	-0.232609
17	7	0	0.000000	0.000000	0.000000

Molecular structure and Coordinates for 1b/SDS devoid of an alkyl chain



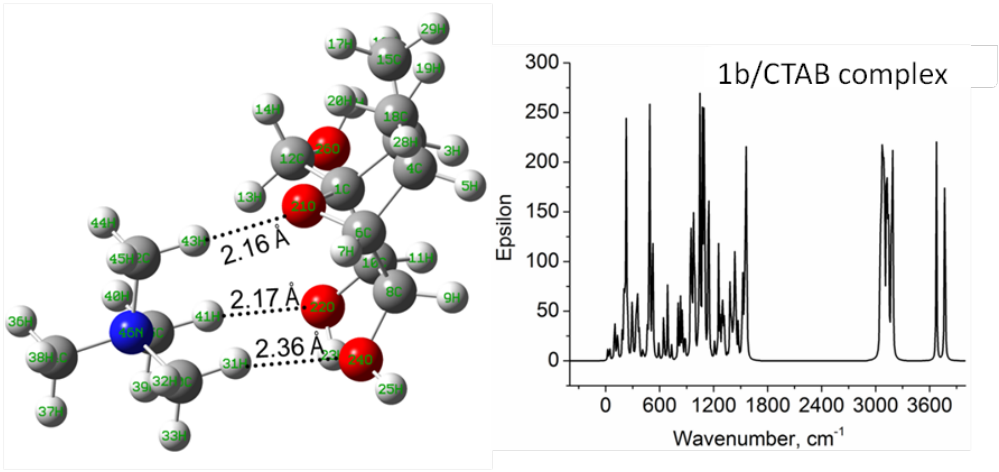


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.476576	-0.292499	-0.034064

2	6	0	1.477324	1.022117	-0.889775
3	1	0	1.717676	0.750077	-1.925506
4	6	0	2.703124	1.798244	-0.273696
5	1	0	3.394555	2.111900	-1.067279
6	6	0	3.325241	0.675955	0.574305
7	1	0	4.035653	0.983344	1.345092
8	6	0	3.862945	-0.437051	-0.360629
9	1	0	4.245482	-0.007414	-1.296003
10	6	0	2.543582	-1.262631	-0.596316
11	1	0	2.370889	-1.570995	-1.627415
12	6	0	0.124065	-0.926843	0.249227
13	1	0	0.256093	-1.747867	0.976778
14	1	0	-0.538945	-0.190061	0.718480
15	6	0	0.152729	1.790168	-0.921482
16	1	0	-0.644364	1.184681	-1.358210
17	1	0	-0.179862	2.094896	0.075433
18	6	0	2.359278	3.019368	0.585297
19	1	0	1.819850	3.782081	0.014535
20	1	0	1.738475	2.733739	1.440045
21	8	0	2.156926	0.085914	1.199016
22	8	0	2.617370	-2.458250	0.188539
23	1	0	2.400193	-2.167466	1.094387
24	8	0	4.884045	-1.224235	0.218150
25	1	0	4.443299	-2.079779	0.398910
26	8	0	-0.383710	-1.391870	-0.979004
27	1	0	-1.371081	-1.408735	-0.892696
28	1	0	3.278435	3.478631	0.972715
29	1	0	0.257881	2.698519	-1.528183
30	16	0	-3.736353	-0.062133	-0.377517
31	8	0	-5.197698	-0.163998	-0.213486
32	8	0	-3.054614	-1.393929	-0.451307
33	8	0	-3.240321	0.933620	-1.339054
34	6	0	-3.577097	-0.139835	2.234920
35	1	0	-3.147488	0.377781	3.099682

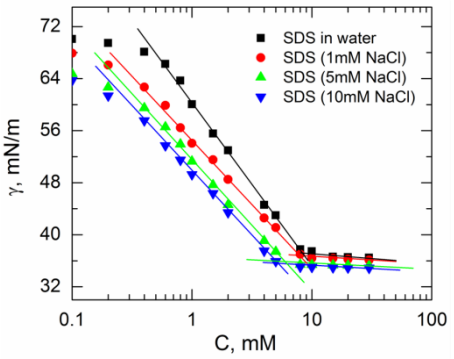
36	1	0	-4.670239	-0.160157	2.323228
37	1	0	-3.201081	-1.170873	2.204726
38	8	0	-3.170794	0.590233	1.085251

Molecular structure and Coordinates for 1b/CTAB devoid of alkyl chains



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.323292	0.637488	0.137816
2	6	0	-2.810291	0.210044	-0.120319
3	1	0	-3.388549	0.374046	0.796433
4	6	0	-2.654544	-1.342341	-0.361090
5	1	0	-3.268545	-1.895446	0.359693
6	6	0	-1.156219	-1.520973	-0.044804
7	1	0	-0.687611	-2.414159	-0.464021
8	6	0	-0.919509	-1.328012	1.466815
9	1	0	-1.704904	-1.796721	2.067642
10	6	0	-0.946831	0.238282	1.586522
11	1	0	-1.681891	0.594818	2.315947
12	6	0	-0.922027	2.056935	-0.249408
13	1	0	0.153022	2.176527	-0.097551
14	1	0	-1.131888	2.229527	-1.312970

15	6	0	-3.517273	0.965777	-1.251069
16	1	0	-3.640777	2.027568	-1.008876
17	1	0	-2.978211	0.898770	-2.200636
18	6	0	-2.986809	-1.852220	-1.767955
19	1	0	-4.025755	-1.648400	-2.042152
20	1	0	-2.338628	-1.396329	-2.523167
21	8	0	-0.564936	-0.337946	-0.630057
22	8	0	0.341805	0.732360	1.919153
23	1	0	0.738750	0.049742	2.490000
24	8	0	0.364748	-1.796400	1.905937
25	1	0	0.250686	-2.666235	2.317090
26	8	0	-1.547171	3.016140	0.587656
27	1	0	-2.427867	3.211922	0.234874
28	1	0	-2.845181	-2.938084	-1.814211
29	1	0	-4.523583	0.566703	-1.409783
30	6	0	3.282590	-1.259275	0.193442
31	1	0	2.261151	-1.320873	0.575325
32	1	0	3.488157	-2.090290	-0.483787
33	1	0	3.996577	-1.270430	1.019182
34	6	0	4.855860	0.136802	-1.089382
35	6	0	3.160363	1.191643	0.355123
36	1	0	4.959970	1.074435	-1.637607
37	1	0	5.549526	0.118998	-0.247343
38	1	0	5.052470	-0.706604	-1.753269
39	1	0	3.890993	1.177633	1.166268
40	1	0	3.257662	2.119003	-0.212041
41	1	0	2.147242	1.084622	0.753072
42	6	0	2.476307	0.053946	-1.722124
43	1	0	1.459760	-0.048842	-1.332858
44	1	0	2.592967	1.000101	-2.253566
45	1	0	2.715406	-0.776198	-2.389510
46	7	0	3.449076	0.031770	-0.567870

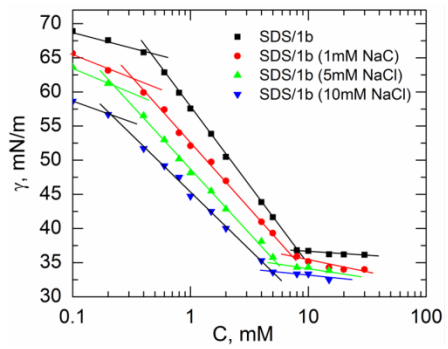


CMC $_{SDS\ in\ water}$ = 8.1 mM

CMC $_{SDS/1mM\ NaCl}$ = 7.8 mM

CMC $_{SDS/5\ mM\ NaCl}$ = 5.9 mM

CMC $_{SDS/10\ mM\ NaCl}$ = 5.2 mM

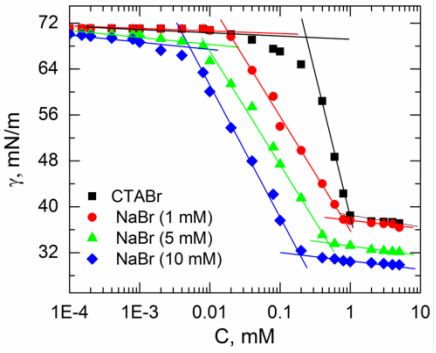


CMC $_{SDS\ /1b}$ = 8.0 mM

CMC $_{SDS/1b\ (1mM\ NaCl\ )}$ = 7.3 mM

CMC $_{SDS/1b\ (5\ mM\ NaCl)}$ = 5.4 mM

CMC $_{SDS/1b\ (10\ mM\ NaCl)}$ = 4.8 mM

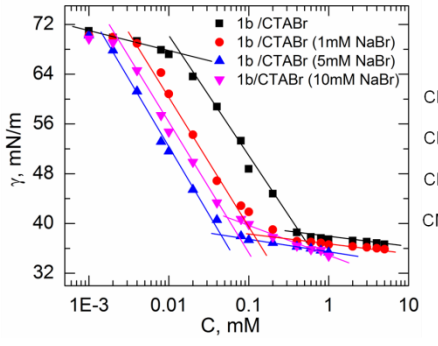


CMC $_{CTABr\ \ in\ water}$ = 0.98 mM

CMC $_{CTABr/1mM\ NaCl}$ = 0.77 mM

CMC $_{CTABr/5\ mM\ NaCl}$ = 0.48 mM

CMC $_{CTABr/10\ mM\ NaCl}$ = 0.19 mM



CMC $_{CTABr\ /1b}$ = 0.43 mM

CMC $_{CTABr/1b\ (1mM\ NaBr)}$ = 0.11 mM

CMC $_{CTABr/1b\ (5\ mM\ NaBr)}$ = 0.05 mM

CMC $_{CTABr/1b\ (10\ mM\ NaBr)}$ = 0.04 mM

Figure S12. Surface tension plots of pure surfactants as well as their association complexes with 1b.

Additional Images of 0-D Surface Micelles:

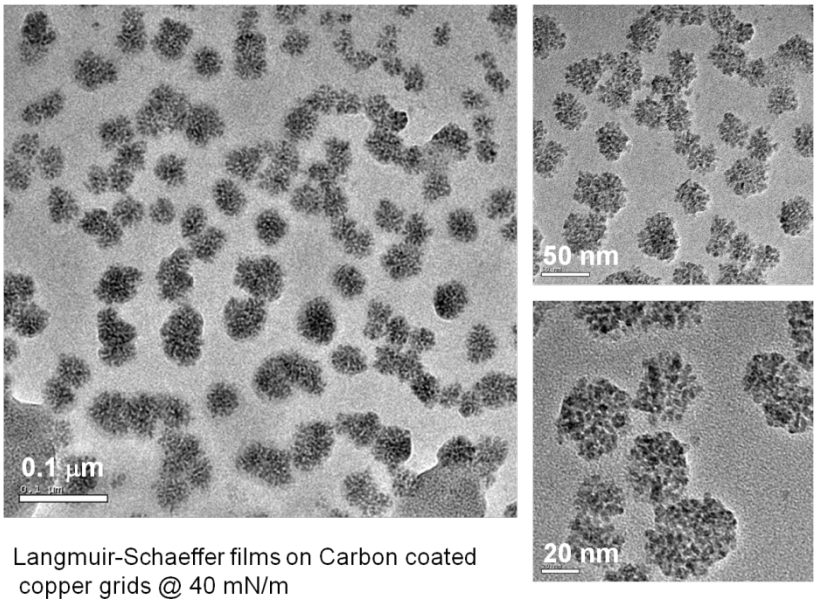


Figure A1. Transmission Electron Micrograph of a Langmuir Schaeffer film deposited on a carbon coated copper grid at 40 mN/m by horizontal deposition technique.

0-D Reverse micelles:

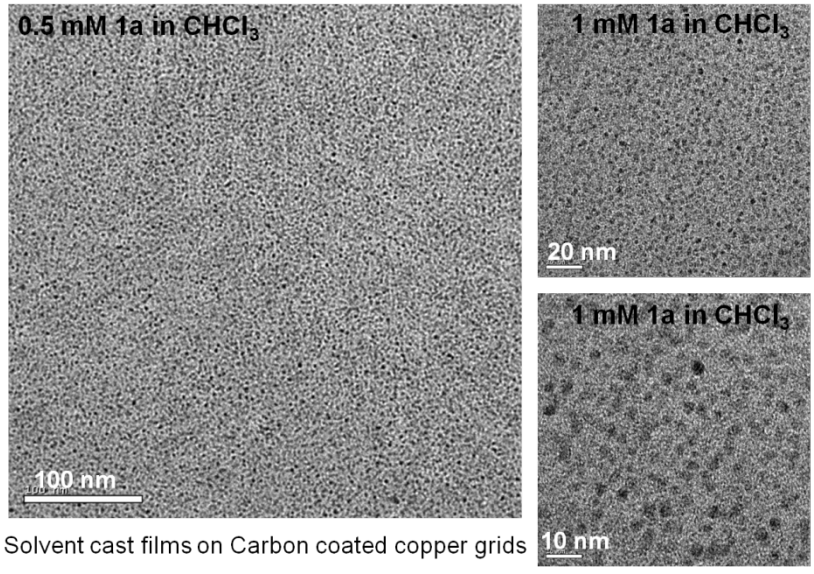
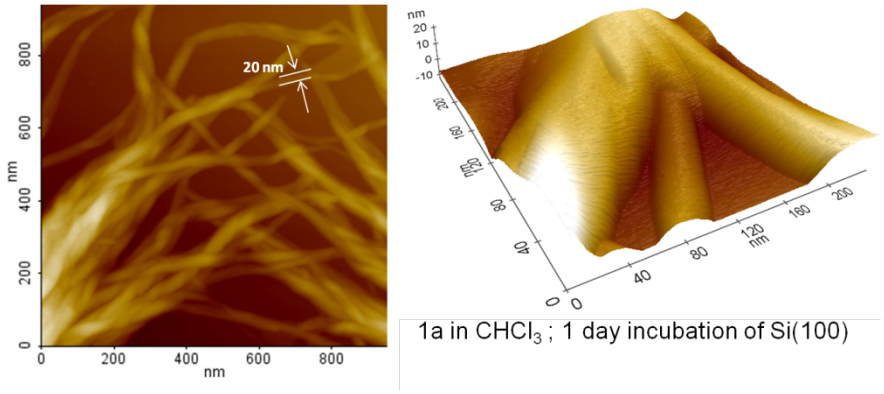
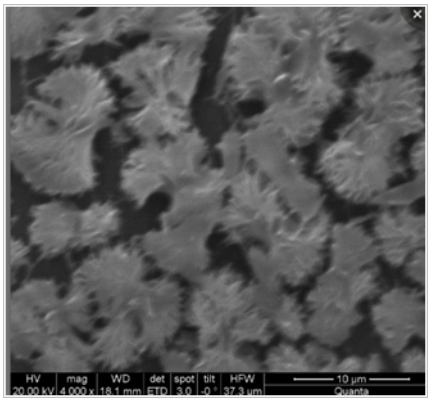


Figure A2. Transmission electron micrographs of freshly prepared 0.5 mM and 1mM 1a solution in chloroform drop casted onto a carbon-coated copper grid.

1-D Nanofibers:





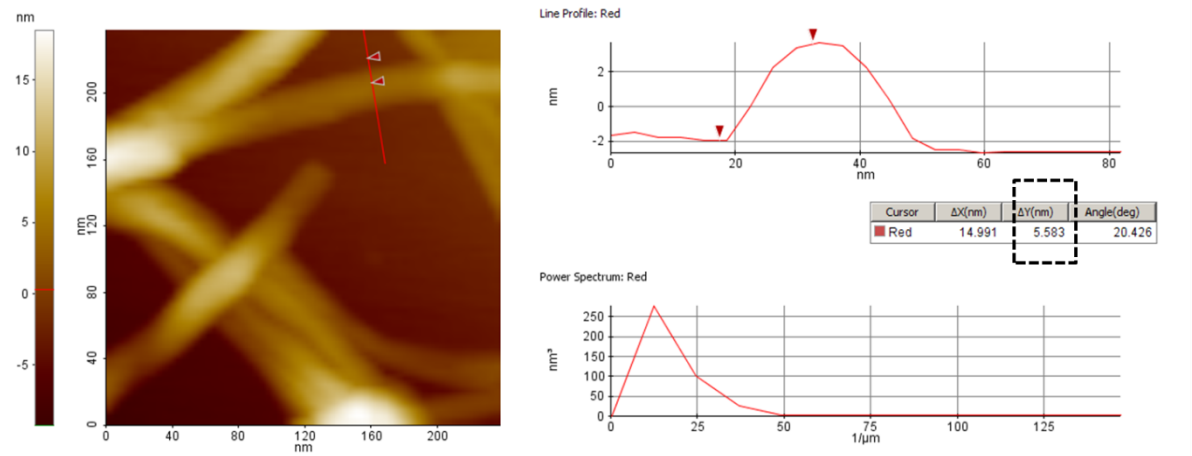


Figure A3. Non contact mode AFM images of 1-D nanofibers of 1a after 1 day incubation in chloroform solution. The line profile indicates the height/thickness of the nanofiber as ~ 5.5 nm. Scanning Electron Micrograph of 1-D nanofibers which are partially converted to 3-D microflowers. For SEM, the sampling is done on a Silicon (100) substrate. Prior to that the substrate is treated with pirahna solution and subsequently with water to make it hydrophilic.

3-D micro flowers:

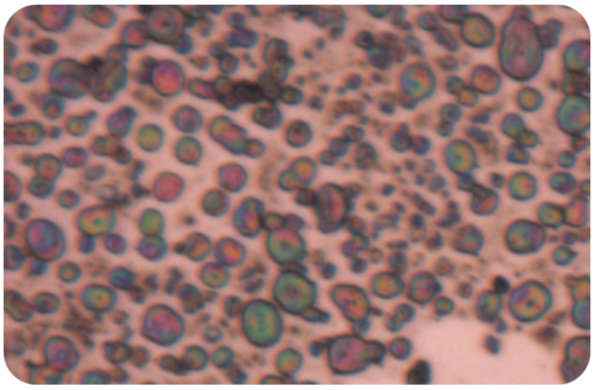


Figure A4. Optical Micrograph of 3-D microflowers imaged after incubating the Silicon (100) substrate for a period of 36 hours. The concentration of 1a used is 1mM in chloroform solution.

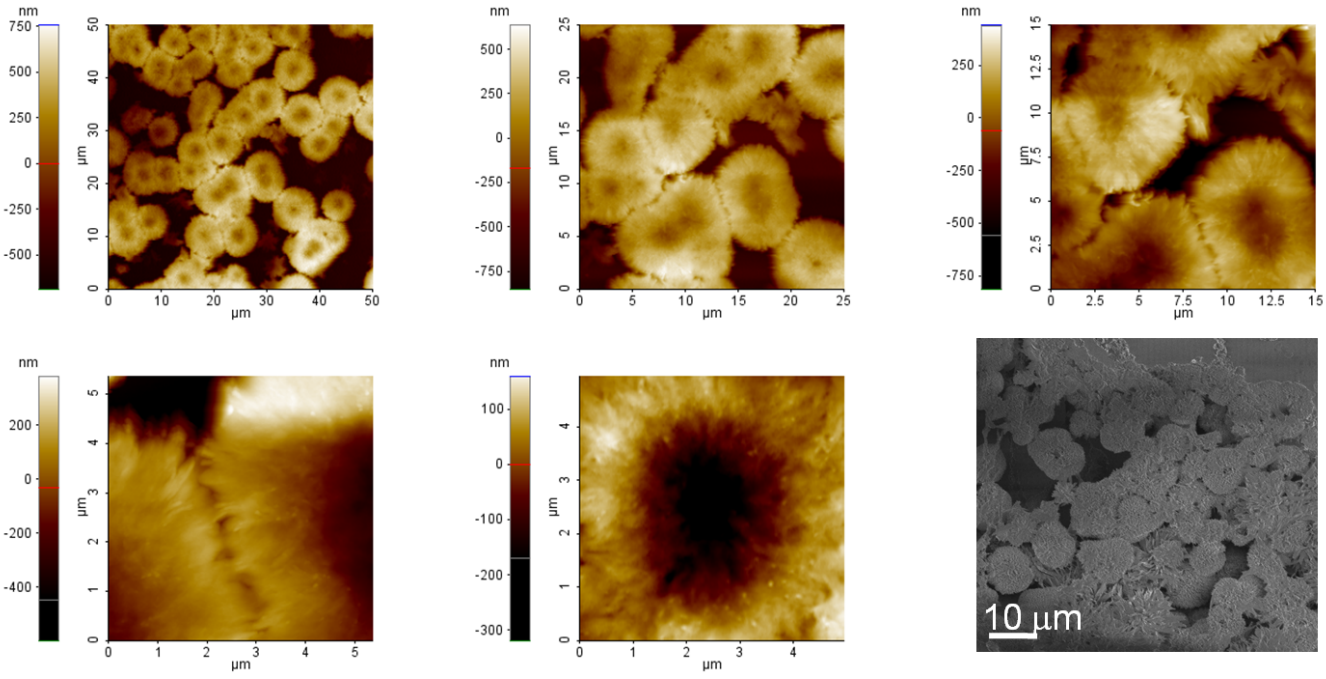


Figure A5: High-resolution AFM images of 3-D microflowers imaged using super-sharp Single crystal silicon probes (radius of curvature (ROC) < 5nm). The concentration of 1a used is 1mM in chloroform solution. All the images were procured at a scan rate of 1Hz. The SEM image was done for the sample that is subjected to AFM imaging. Note that the SEM samples were not coated with gold.

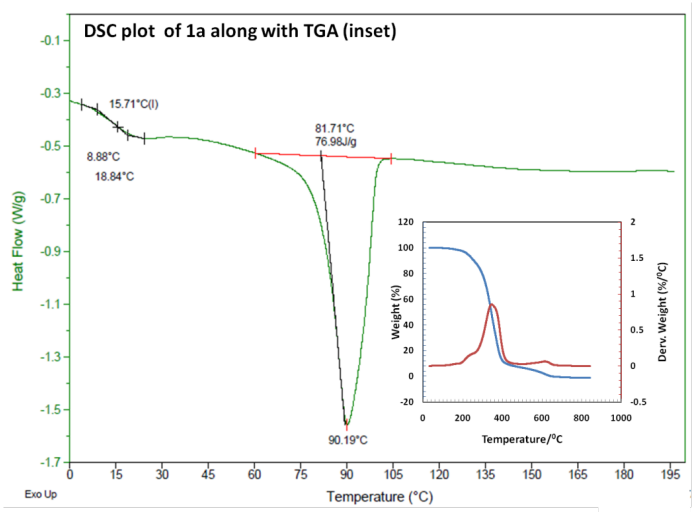
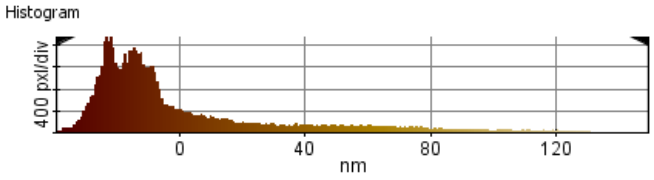


Fig. A6 Differential Scanning Calorimetric (DSC) and Thermo-gravimetric analysis (inset) of 1a powder showing phase transition points and decomposition temperature ranges.

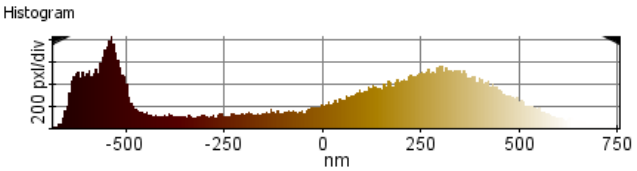
Roughness Statistical parameters along with histogram for 1-D nanofibers in Fig.3 (b):



Minimum (nm)	-39.495
Maximum (nm)	149.714
Mid (nm)	55.110
Mean (nm)	0.312
R_{pv} (nm)	189.209
R_q (nm)	32.837
R_a (nm)	24.373
R_z (nm)	185.603
R_{sk} (nm)	-1.754
R_{ku} (nm)	5.576

R_{pv} = peak-to-valley, R_q = standard deviation of the height value, R_a = Roughness average, R_{sk} = skewness, R_{ku} = kurtosis

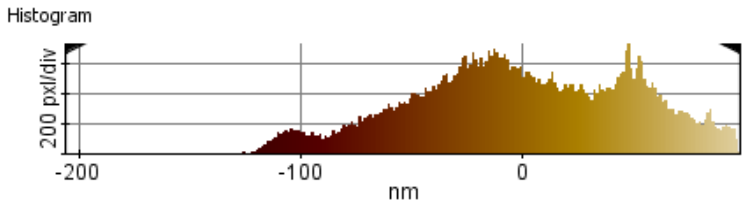
Roughness Statistical parameters along with histogram for 3-D microflowers in Fig.3 (c):



Minimum (nm)	-687.457
Maximum (nm)	756.290
Mid (nm)	34.416
Mean (nm)	-1.266
R_{pv} (nm)	1443.747
R_q (nm)	394.744
R_a (nm)	349.389
R_z (nm)	1431.694
R_{sk} (nm)	0.343
R_{ku} (nm)	1.675

R_{pv} = peak-to-valley, R_q = standard deviation of the height value, R_a = Roughness average, R_{sk} = skewness, R_{ku} = kurtosis

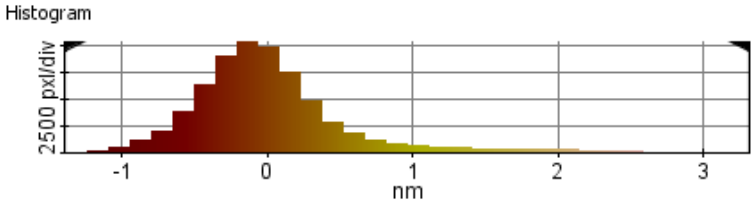
Roughness Statistical parameters along with histogram for 2-D sheets in Fig.4 (d):



Minimum (nm)	-206.098
Maximum (nm)	98.196
Mid (nm)	-53.951
Mean (nm)	-0.762
R_{pv} (nm)	304.293
R_q (nm)	49.051

R_a (nm)	40.592
R_z (nm)	237.904
R_{sk} (nm)	0.159
R_{ku} (nm)	2.346

Roughness Statistical parameters along with histogram for Lithium ion sensor in Fig.4 (c):



Minimum (nm)	-1.396
Maximum (nm)	3.316
Mid (nm)	0.960
Mean (nm)	-0.007
R_{pv} (nm)	4.713
R_q (nm)	0.522
R_a (nm)	0.365
R_z (nm)	4.442
R_{sk} (nm)	-1.556
R_{ku} (nm)	7.305

R_{pv} = peak-to-valley, R_q = standard deviation of the height value, R_a = Roughness average, R_{sk} = skewness, R_{ku} = kurtosis