Supporting information

Entangled Uranyl Organic Frameworks with (10,3)-*b* Topology and Polythreading Network: Structure, Luminescence and Computational Investigation

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Table S1. Selected bond lengths (Å) and angles (°) for compound **1**

U(1)-O(16)	1.752(7)	U(2)-O(1)	1.719(9)
U(1)-O(15)	1.767(7)	U(2)-O(2)	1.744(8)
U(1)-O(9)	2.440(6)	U(2)-O(3)	2.420(9)
U(1)-O(10)	2.452(6)	U(2)-O(8)	2.475(7)
U(1)-O(11)#1	2.503(6)	U(2)-O(4)	2.446(6)
U(1)-O(12)#1	2.465(6)	U(2)-O(5)	2.507(7)
U(1)-O(13)#2	2.435(7)	U(2)-O(6)#3	2.459(6)
U(1)-O(14)#2	2.482(6)	U(2)-O(7)#3	2.434(7)
O(16)-U(1)-O(15)	179.3(3)	O(1)-U(2)-O(2)	179.9(4)
O(16)-U(1)-O(12)#1	90.5(3)	O(1)-U(2)-O(3)	93.5(5)
O(15)-U(1)-O(12)#1	89.9(3)	O(2)-U(2)-O(3)	86.6(4)
O(16)-U(1)-O(13)#2	91.9(3)	O(1)-U(2)-O(7)#3	92.3(4)
O(15)-U(1)-O(13)#2	87.7(3)	O(2)-U(2)-O(7)#3	87.6(3)
O(12)#1-U(1)-O(13)#2	64.9(2)	O(3)-U(2)-O(7)#3	170.6(3)
O(16)-U(1)-O(9)	92.0(3)	O(1)-U(2)-O(4)	92.1(3)
O(15)-U(1)-O(9)	87.6(3)	O(2)-U(2)-O(4)	88.0(3))
O(12)#1-U(1)-O(9)	170.7(2)	O(3)-U(2)-O(4)	65.8(2)
O(13)#2-U(1)-O(9)	123.0(2)	O(7)#3-U(2)-O(4)	121.3(2)
O(16)-U(1)-O(10)	94.4(3)	O(1)-U(2)-O(6)#3	92.3(3)
O(15)-U(1)-O(10)	85.8(3)	O(2)-U(2)-O(6)#3	87.6(3)
O(12)#1-U(1)-O(10)	117.4(2)	O(3)-U(2)-O(6)#3	119.0(2)
O(13)#2-U(1)-O(10)	173.0(3)	O(7)#3-U(2)-O(6)#3	53.4(2)
O(9)-U(1)-O(10)	53.5(2)	O(4)-U(2)-O(6)#3	173.3(2)
O(16)-U(1)-O(14)#2	90.0(4)	O(1)-U(2)-O(8)	88.3(4)
O(15)-U(1)-O(14)#2	89.4(3)	O(2)-U(2)-O(8)	91.7(3)
O(12)#1-U(1)-O(14)#2	118.8(2)	O(3)-U(2)-O(8)	52.7(2)
O(13)#2-U(1)-O(14)#2	53.0(2)	O(7)#3-U(2)-O(8)	120.2(2)
O(9)-U(1)-O(14)#2	70.1(2)	O(4)-U(2)-O(8)	118.4(2)
O(10)-U(1)-O(14)#2	123.5(2)	O(6)#3-U(2)-O(8)	66.9(3)
O(16)-U(1)-O(11)#1	87.1(3)	O(1)-U(2)-O(5)	85.0(4)
O(15)-U(1)-O(11)#1	93.5(3)	O(2)-U(2)-O(5)	94.6(3)
O(12)#1-U(1)-O(11)#1	52.0(2)	O(3)-U(2)-O(5)	118.6(3)
O(13)#2-U(1)-O(11)#1	117.8(2)	O(7)#3-U(2)-O(5)	69.3(2)
O(9)-U(1)-O(11)#1	119.3(2)	O(4)-U(2)-O(5)	52.9(3)
O(10)-U(1)-O(11)#1	66.1(2)	O(6)#3-U(2)-O(5)	122.5(2)
O(14)#2-U(1)-O(11)#1	170.2(2)	O(8)-U(2)-O(5)	168.8(2)

Symmetry code: #1 x+1,y-1,z; #2 x+1,y,z-1; #3 x,y+1,z

Table S2. Selected bond lengths (Å) and angles (°) for compound **2**

U(1)-O(1)	1.771(5)	U(1)-O(2)	1.773(5)
U(1)-O(3)#1	2.310(5)	U(1)-O(6)#2	2.330(5)
U(1)-O(4)	2.440(5)	U(1)-O(1W)	2.457(5)

U(1)-O(5)	2.484(5)	U(2)-O(7)	1.795(5)
U(2)-O(8)#3	2.441(5)	U(2)-O(9)	2.462(6)
U(2)-O(2W)	2.476(6)		
O(1)-U(1)-O(2)	179.3(2)	O(6)#2-U(1)-O(1W)	75.46(17)
O(2)-U(1)-O(3)#1	91.6(2)	O(4)-U(1)-O(1W)	122.57(16)
O(1)-U(1)-O(3)#1	88.4(2)	O(7)#3-U(2)-O(7)	180.000(2)
O(2)-U(1)-O(6)#2	90.5(2)	O(7)#3-U(2)-O(8)#3	91.3(2)
O(1)-U(1)-O(6)#2	90.1(2)	O(7)-U(2)-O(8)#3	88.7(2)
O(3)#1-U(1)-O(6)#2	85.04(17)	O(8)#3-U(2)-O(8)	180.0(2)
O(2)-U(1)-O(4)	90.7(2)	O(7)#3-U(2)-O(9)#3	87.8(2)
O(1)-U(1)-O(4)	88.8(2)	O(7)-U(2)-O(9)#3	92.2(2)
O(3)#1-U(1)-O(4)	76.89(17)	O(8)#3-U(2)-O(9)#3	53.20(18)
O(6)#2-U(1)-O(4)	161.92(17)	O(8)-U(2)-O(9)#3	126.80(18)
O(1)-U(1)-O(5)	87.5(2)	O(9)#3-U(2)-O(9)	180.0(2)
O(2)-U(1)-O(5)	92.1(2)	O(7)#3-U(2)-O(2W)	88.8(2)
O(4)-U(1)-O(5)	53.21(16)	O(7)-U(2)-O(2W)	91.2(2)
O(3)#1-U(1)-O(5)	129.99(16)	O(8)#3-U(2)-O(2W)	63.97(18)
O(6)#2-U(1)-O(5)	144.76(17)	O(8)-U(2)-O(2W)	116.03(18)
O(2)-U(1)-O(1W)	90.7(2)	O(9)#3-U(2)-O(2W)	116.94(18)
O(1)-U(1)-O(1W)	89.5(2)	O(9)-U(2)-O(2W)	63.06(18)
O(3)#1-U(1)-O(1W)	160.39(17)	O(2W)-U(2)-O(2W)#3	180.0(3)

Symmetry code: #1 x,-y+3/2,z-1/2; #2 -x+3,y-1/2,-z+1/2; #3 x,-y+2,-z

Table S3. Optimized geometry parameters and bond orders (in parentheses) for $[UO_2\{(OOC)(C_6H_4)(SiR_3)\}_3]^-$ (R = H (**3a**) and Me (**3b**)) in the gas phase, compared with experimental values of **1** and **2**. (Bond lengths in Å and angles in degree)

	3a	**3b**	Expt. (**1**)	Expt. (**2**)
U=O	1.806 (2.37)	1.807 (2.37)	1.762	1.776
U-O_{eq}	2.502 (0.48)	2.501 (0.49)	2.459	2.461
U-C	2.864	2.865	2.839	2.835
O_{eq}-C	1.270(1.60)	1.270 (1.60)	1.267	1.269
C-C	1.507(1.00)	1.507 (1.00)	1.482	1.467
O=U=O	180.0	180.0	179.4	179.5
O=U-O_{eq1}	90.0	90.0	90.9	91.5
O=U-O_{eq2}	92.9	90.0	89.5	88.5
O=U-C	90.0	90.0	91.7	90.3
O_{eq1}-U-O_{eq2}	52.6	52.6	53.5	53.2
O_{eq1}-C-O_{eq2}	121.5	121.3	121.1	119.9

Table S4. Calculated absorptions of **3a** in the THF solution at the TD-PBE/TZP/ZORA/COSMO level.

λ (nm) [a]		λ (nm) [b]	E (eV) [b]	*f* [c]	Configurations [d]	Weight > 0.1	Expt.
Band I	443	443	2.80	0.017	94→101	0.6580	407~449
					95→102	0.2697	
Band II	354	354	3.50	0.079	98→103	0.5890	330
					87→101	0.1369	
		354	3.50	0.078	97→103	0.5787	
					87→102	0.1339	
		336	3.69	0.031	87→101	0.5935	
					97→103	0.1470	
		336	3.69	0.031	87→102	0.5942	
					98→103	0.1488	
Band III	309	311	3.99	0.042	83→100	0.4472	293
					82→100	0.2374	
					89→103	0.1665	
					88→103	0.1181	
		311	3.99	0.043	82→100	0.4238	
					83→100	0.2570	
					88→103	0.1489	
					89→103	0.1385	
		309	4.01	0.192	89→103	0.6404	
					82→100	0.2974	
		309	4.01	0.201	88→103	0.6791	
					83→100	0.2623	
Band IV	267	272	4.57	0.087	98→108	0.3650	243
		272	4.57	0.085	98→107	0.3666	
					97→108	0.3505	
		267	4.64	0.332	87→105	0.4969	
					99→105	0.1050	
		267	4.64	0.315	87→106	0.4690	

[a] The simulated absorption peak (nm).

[b] Calculated absorption transitions in nm and eV.

[c] Oscillator strength (*f*).

[d] Orbitals 99 and 100 correspond to HOMO and LUMO, respectively.

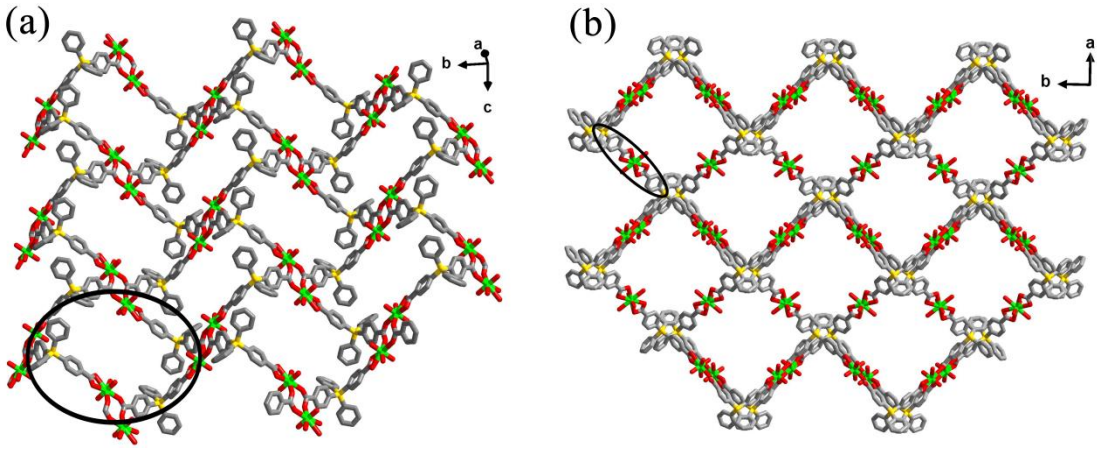

Figure S1 (a) Dimers uranyl units in compound **2** are linked by L ligands constituting a loop (highlight). The loops are linked forming the sheet (a), which are pillared by the linear $UO_2(COOR)_2(H_2O)_2$ unit (highlight) to give rise to the 3D framework (b). Hydrogen atoms are omitted for clarity

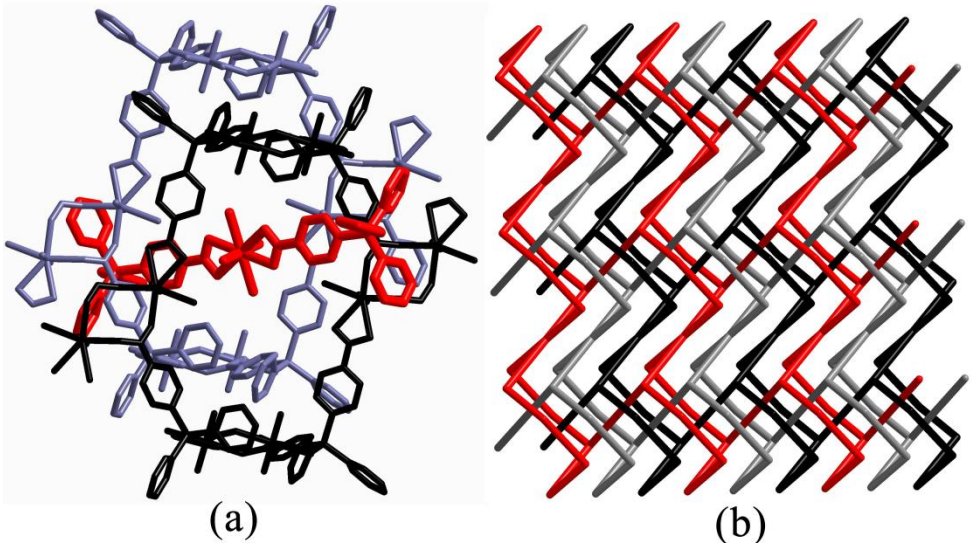

Figure S2 (a) The entangled motif of compound **2**. (b) Schematic view of the 3D polythreading nets of compound **2**

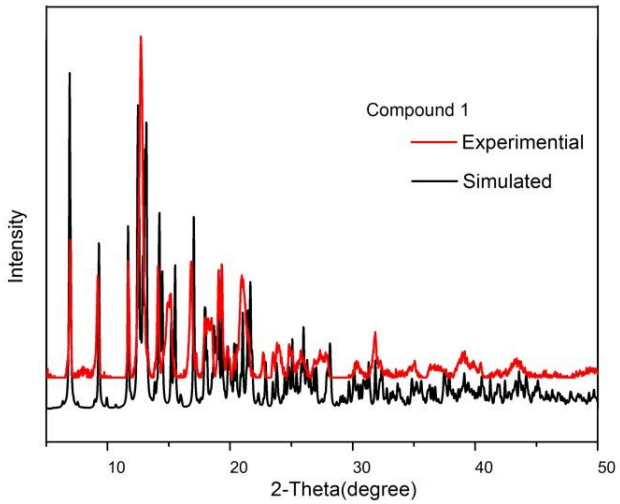

Figure S3. Simulated and experimental XRD patterns of compound **1**.

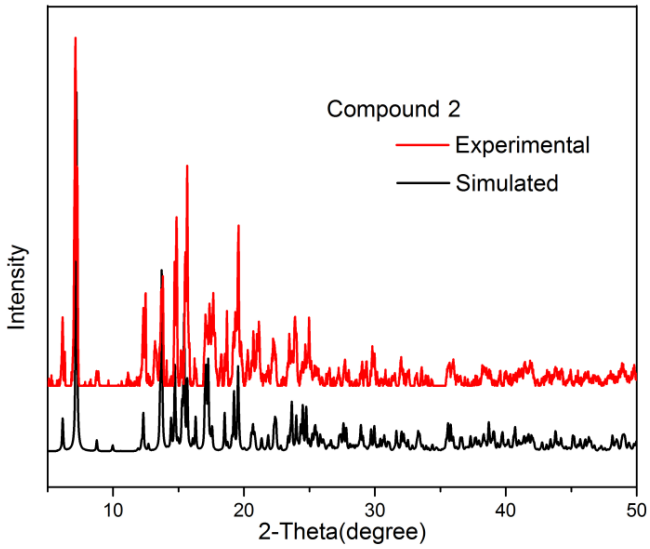

Figure S4. Simulated and experimental XRD patterns of compound **2**.

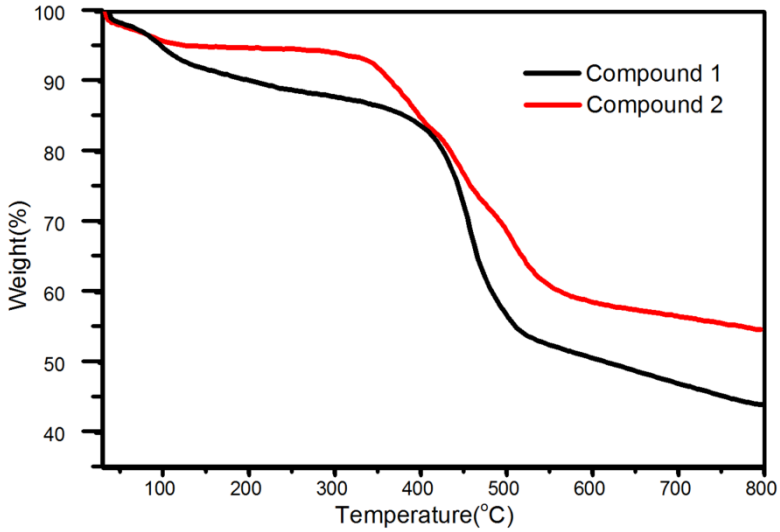

Figure S5. TG curve for compounds **1** and **2**.

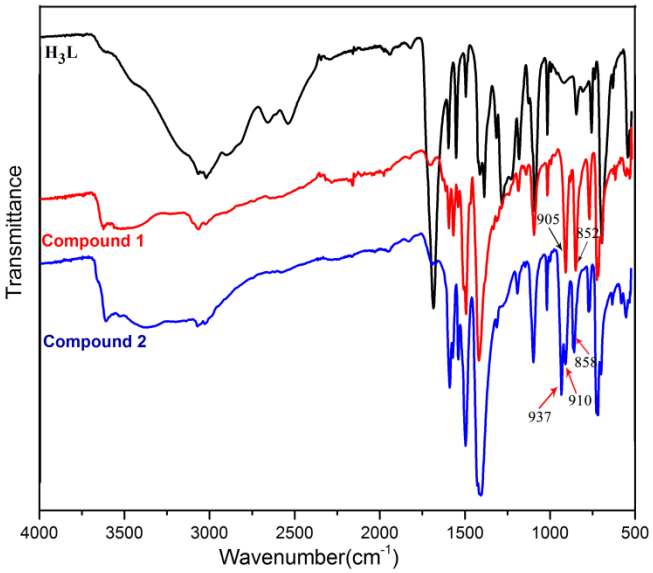

Figure S6. FT-IR spectra of and H_3L ligand as well as compounds **1** and **2**.

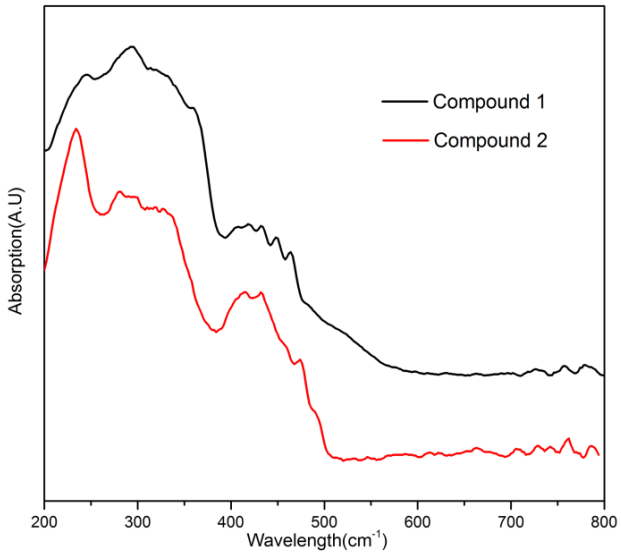

Figure S7. Solid state absorption spectra of compounds **1** and **2**

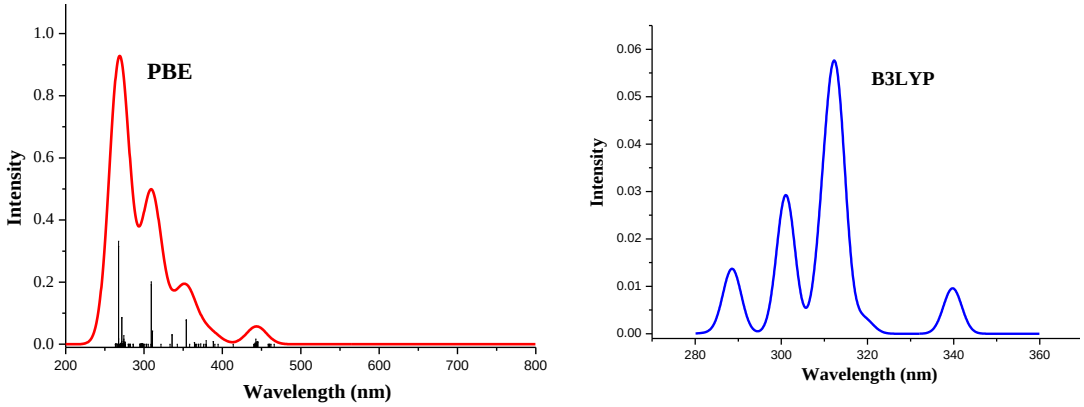

Figure S8. Simulated absorption spectra in THF for **3a** under the TD-DFT calculations with the PBE (left) and B3LYP (right) functionals.

Optimized geometry of **3a**

U 0.05383233 3.67454521 10.42498314
O 0.97341496 5.22744458 10.49356051
O -0.86562593 2.12155424 10.35657018
O -1.83818515 4.84657834 9.28251230
O -1.91259361 4.79097340 11.49576772
C -2.40917316 5.13578376 10.37916269
C -3.70422294 5.90633495 10.35487907
C -4.35052864 6.23394235 11.55228555
C -4.26864587 6.29513969 9.13458840
C -5.54871048 6.94543489 11.52915947
C -5.46682782 7.00665213 9.11254405
C -6.12676224 7.34640815 10.30926591
H -3.88788902 5.91291673 12.48947414
H -3.74314572 6.02098413 8.21583630
H -6.04591467 7.18959257 12.47439586
H -5.89936954 7.29916304 8.14939477
Si -7.72329312 8.34667611 10.28041900
H -7.46217101 9.82927233 10.32659593
H -8.58255317 8.00664220 11.46667441
H -8.49973433 8.06819808 9.02313235
O 1.79641201 2.57753652 11.84557520
O 0.11197689 3.53197978 12.92209764
C 1.20353412 2.88334130 12.92602571
C 1.80950454 2.46803856 14.24202169
C 1.17282536 2.79523433 15.44429226
C 3.01111396 1.75022328 14.26771269
C 1.73350530 2.40998339 16.66110965
C 3.57056657 1.36547505 15.48439638
C 2.94297571 1.69043597 16.70275218
H 0.23371023 3.35274041 15.39240839
H 3.48305998 1.50573060 13.31226499
H 1.22155630 2.66875456 17.59430172
H 4.50898156 0.79973985 15.48755353
Si 3.72370828 1.20593327 18.34774474
H 4.36229487 -0.15296747 18.25941257
H 2.68386930 1.18255824 19.43333801
H 4.79828681 2.17358332 18.76863962
O 1.89146009 2.65111450 9.06991461
O 0.27479629 3.65173978 7.93323183
C 1.36846095 3.00763964 7.96913457
C 2.06099592 2.65816148 6.67694623
C 1.50024263 3.03858946 5.45282998

C 3.27075019 1.95374001 6.69545936
C 2.14201878 2.71588359 4.25797611
C 3.91151684 1.63212050 5.50086536
C 3.35759426 2.00566428 4.26079683
H 0.55692200 3.59113670 5.47013478
H 3.68615420 1.67337890 7.66717280
H 1.69396123 3.02406976 3.30715951
H 4.86051032 1.08509547 5.53247548
Si 4.20771068 1.53480548 2.64652523
H 5.69994884 1.68631621 2.75931818
H 3.71679411 2.40743821 1.52502852
H 3.93690848 0.10386510 2.26272259

Optimized geometry of **3b**

U 0.15344356 3.80225111 10.44979275
O 1.08977249 5.34682341 10.49545393
O -0.78283577 2.25765598 10.40419848
O -1.73509118 4.97889423 9.30764204
O -1.79430709 4.94836495 11.52131928
C -2.29767060 5.28463535 10.40461752
C -3.58815493 6.06149743 10.38108115
C -4.22485188 6.40774041 11.57914499
C -4.16037306 6.44233213 9.16285864
C -5.41845835 7.12592162 11.55376045
C -5.35568487 7.16128704 9.14350762
C -6.01192303 7.51947137 10.33673938
H -3.75607091 6.09736726 12.51700507
H -3.64244530 6.15870987 8.24248044
H -5.89965568 7.38607637 12.50426957
H -5.78651106 7.44894708 8.17862132
Si -7.63593737 8.49716771 10.34318266
C -7.38911074 10.14348714 11.26740159
C -8.98530921 7.49252225 11.23488373
C -8.20027927 8.85883649 8.56380427
H -7.04777385 9.96737330 12.30085599
H -6.62763172 10.76076979 10.76317080
H -8.32964561 10.71860419 11.31066248
H -9.16752121 6.53851074 10.71358669
H -8.68325127 7.25753877 12.26885246

H -9.93450504 8.05346510 11.27509466
H -9.14633124 9.42601413 8.57376872
H -7.45205122 9.45834155 8.01959065
H -8.36977743 7.92688053 7.99976573
O 1.89523341 2.70506970 11.87008948
O 0.22751646 3.68648669 12.94727487
C 1.31429550 3.02908382 12.95222779
C 1.92731056 2.62613176 14.26800588
C 1.30543718 2.97341759 15.47183296
C 3.12521138 1.90163481 14.29560428
C 1.87549859 2.60036688 16.68916659
C 3.69002980 1.53179143 15.51434807
C 3.07954520 1.87200241 16.73901316
H 0.37103802 3.53921286 15.42133548
H 3.59020298 1.64347274 13.34019275
H 1.37188402 2.88270069 17.61976884
H 4.62892158 0.96506356 15.51209472
Si 3.88053807 1.35336747 18.37692838
C 4.04415374 -0.54256716 18.43905524
C 2.82495142 1.93725603 19.84675230
C 5.61772784 2.12118454 18.51122419
H 3.05199106 -1.01995354 18.38604801
H 4.64114661 -0.91445022 17.59003823
H 4.53653242 -0.86693053 19.37155369
H 3.29375809 1.62887652 20.79645403
H 2.72638281 3.03525551 19.85862421
H 1.81266246 1.50197594 19.81156864
H 6.11788104 1.80968801 19.44395017
H 6.25130324 1.81194574 17.66358131
H 5.55701555 3.22177842 18.50043124
O 1.96928647 2.74297179 9.09452524
O 0.35947825 3.75307089 7.95750943
C 1.44571208 3.09563981 7.99227342
C 2.12744996 2.72761548 6.70029833
C 1.56974440 3.10767257 5.47511913
C 3.32523641 2.00259154 6.71641891
C 2.20322204 2.76666612 4.27994354
C 3.95336783 1.66453164 5.51962428
C 3.40815329 2.03806208 4.27404660
H 0.63385655 3.67301684 5.49143304
H 3.73917116 1.71823998 7.68774805
H 1.74937627 3.07453631 3.33199293
H 4.89063754 1.09632161 5.55618736
Si 4.29205702 1.55890472 2.66706019

C 6.04797148 2.29506071 2.65754959
C 3.33323810 2.21286134 1.16088715
C 4.42390248 -0.33692907 2.54901167
H 6.62799183 1.94190923 3.52608294
H 6.59279700 2.00730877 1.74235734
H 6.00776241 3.39557917 2.70617177
H 3.85324290 1.93202752 0.22946107
H 2.31486677 1.79256061 1.11979734
H 3.25044508 3.31196165 1.18444468
H 3.42139090 -0.79495927 2.53174245
H 4.96058606 -0.64060447 1.63416393
H 4.96590929 -0.74848274 3.41640668