Supporting Information

Bi_4TaO_8Cl Nano-Photocatalyst: Influence of Local, Average and Band Structure

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Table S1. Atomic coordinates and isotropic thermal parameters obtained from Rietveld refinement for nano-Bi_4TaO_8Cl.

Atoms	Site	x	y	z	Occupancy	U $(Å)^2$
Ta (1)	4a	-0.003(1)	0.291(1)	0.259(1)	0.99(1)	0.013(1)
Bi (1)	4a	-0.006(1)	0.836(4)	0.155(2)	0.98(1)	0.009(1)
Bi (2)	4a	0.009(1)	0.231(1)	0.432(1)	0.98(1)	0.027(2)
Bi (3)	4a	-0.006(3)	0.751(1)	0.338(1)	0.99(1)	0.010(2)
Bi (4)	4a	0.018(1)	0.275(1)	0.071(1)	0.99(1)	0.010(1)
Cl (1)	4a	0.5160(7)	0.238(4)	0.006(5)	0.99(1)	0.017(3)
O (1)	4a	0.724(6)	0.481(1)	0.397(2)	0.99(1)	0.025(2)
O (2)	4a	0.257(2)	0.485(1)	0.394(1)	0.99(1)	0.011(2)
O (3)	4a	0.768(1)	0.003(3)	0.395(3)	0.99(1)	0.010(1)
O (4)	4a	0.269(1)	0.006(1)	0.395(2)	0.99(1)	0.035(1)
O (5)	4a	0.483(1)	0.669(1)	0.299(1)	0.99(1)	0.017(1)
O (6)	4a	0.583(1)	0.726(1)	0.187(2)	0.99(1)	0.012(1)
O (7)	4a	0.213(2)	-0.007(3)	0.239(1)	0.99(1)	0.043(1)
O (8)	4a	0.822(1)	-0.019(1)	0.264(1)	0.97(1)	0.013(1)

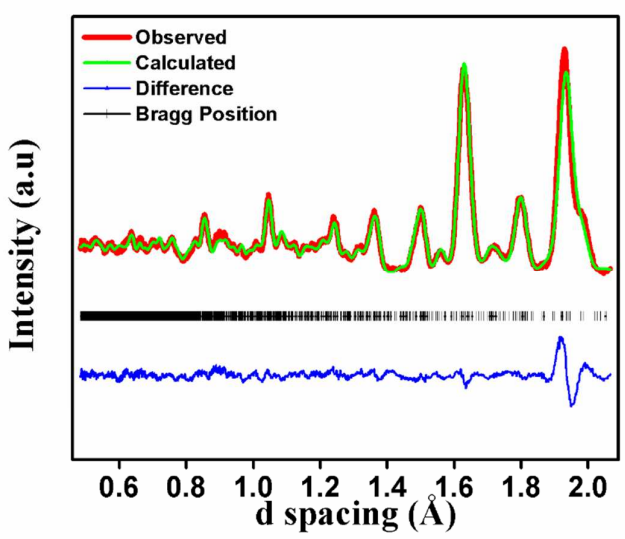

Figure S1. Observed, Calculated and Difference plot obtained from Rietveld refinement of TOF neutron diffraction data of bulk-Bi_4TaO_8Cl.

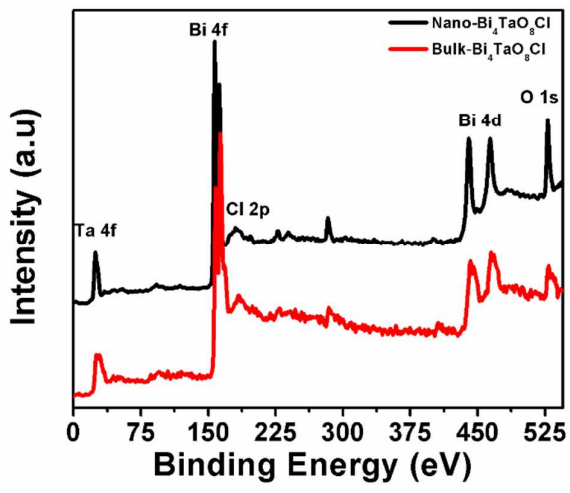

Figure S2. XPS of nano and bulk-Bi_4TaO_8Cl.

Table S2. Surface and bulk composition of nano-Bi_4TaO_8Cl obtained from XPS.

	Calculated	**Nano-Bi_4TaO_8Cl**	**Bulk-Bi_4TaO_8Cl**
Bi/O	0.5	0.7	0.59
Ta/O	0.125	0.101	0.113
Cl/O	0.125	0.114	0.119

Table S3. Atomic coordinates and isotropic thermal parameters obtained from Rietveld refinement for bulk-Bi_4TaO_8Cl.

.Atoms	Site	x	y	z	Occupancy	U $(Å)^2$
Ta (1)	4a	0.030(1)	0.241(1)	0.245(1)	0.98(1)	0.010(3)
Bi (1)	4a	0.0059(1)	0.832(4)	0.157(2)	0.98(1)	0.012(1)
Bi (2)	4a	-0.003(1)	0.269(1)	0.431(1)	0.99(1)	0.004(2)
Bi (3)	4a	0.023(3)	0.763(1)	0.431(1)	0.99(1)	0.018(2)
Bi (4)	4a	0.021(1)	0.262(1)	0.067(1)	0.99(1)	0.011(2)
Cl (1)	4a	0.498(7)	0.243(4)	-0.002(5)	0.99(1)	0.017(3)
O (1)	4a	0.753(6)	0.522(1)	0.392(2)	0.99(1)	0.007(3)
O (2)	4a	0.256(2)	0.502(1)	0.394(1)	0.99(1)	0.001(1)
O (3)	4a	0.760(1)	0.020(3)	0.395(3)	0.97(1)	0.011(2)
O (4)	4a	0.267(1)	0.008(1)	0.395(2)	0.99(1)	0.002(1)
O (5)	4a	0.427(1)	0.697(1)	0.319(1)	0.99(1)	0.017(1)
O (6)	4a	0.594(1)	0.724(1)	0.187(2)	0.99(1)	0.016(3)
O (7)	4a	0.314(2)	0.043(3)	0.240(1)	0.98(1)	0.017(1)
O (8)	4a	0.794(1)	-0.051(1)	0.260(1)	0.99(1)	0.036(2)

Table S4. Selected bond distances of Bi_4TaO_8Cl.

Bond Type	A-bulk Bi_4TaO_8Cl	A-nano Bi_4TaO_8Cl	L-bulk Bi_4TaO_8Cl	L-nano Bi_4TaO_8Cl	Bond Type	A-bulk Bi_4TaO_8Cl	A-nano Bi_4TaO_8Cl	L-bulk Bi_4TaO_8Cl	L-nano Bi_4TaO_8Cl
Ta-O(5)	1.97(1)	1.81(1)	2.08(1)	1.79(1)	Bi(1)-O(1)	2.21(2)	2.09(1)	2.24(1)	2.09(1)
Ta-O(6)	1.99(1)	1.69(1)	1.86(1)	1.80(1)	Bi(1)-O(2)	2.20(2)	2.12(1)	2.22(1)	2.09(1)
Ta-O(7)	1.89(5)	1.90(1)	2.07(1)	1.99(1)	Bi(1)-O(3)	2.67(1)	2.76(1)	2.68(1)	2.74(1)
	2.07(4)	2.08(1)	1.93(1)	2.00(1)	Bi(1)-O(4)	2.66(2)	2.61(1)	2.67(1)	2.57(1)
Ta-O(8)	2.10(1)	2.16(1)	2.04(1)	2.21(1)	Bi(1)-O(5)	2.16(1)	2.23(1)	2.70(1)	2.22(1)
	1.85(4)	1.94(1)	1.93(1)	1.79(1)	Bi(1)-O(6)	2.47(2)	2.49(1)	2.43(1)	2.45(1)
					Bi(1)-O(7)	3.18(2)	2.82 (1)	2.72(1)	2.79(1)
					Bi(1)-O(8)	3.26(3)	3.36(1)	3.59(1)	3.38(1)
Bi(2)-O(1)	2.21(1)	2.29(1)	2.18(1)	2.15(1)	Bi(3)-O(1)	2.45(1)	2.69(1)	2.71(1)	2.67(1)
Bi(2)-O(2)	2.17(1)	2.22(1)	2.22(1)	2.28(1)	Bi(3)-O(2)	2.44(1)	2.61(1)	2.43(1)	2.52(1)
Bi(2)-O(3)	2.14(1)	2.09(1)	2.35(1)	2.31(1)	Bi(3)-O(3)	2.52(1)	2.48(1)	2.38(1)	2.65(1)
Bi(2)-O(4)	2.29(4)	2.15(1)	2.17(1)	2.18(1)	Bi(3)-O(4)	2.43(2)	2.63(1)	2.34(1)	2.45(1)
Bi(2)-Cl(1)	3.31(2)	3.23(1)	3.31(1)	2.98(6)	Bi(3)-O(5)	2.32(1)	2.92(1)	2.22(1)	2.00(1)
	3.34(2)	3.29(1)	3.31(1)	3.41(1)	Bi(3)-O(6)	2.66(1)	2.72(1)	2.80(1)	2.82(1)
	3.36(1)	3.44(1)	3.35(1)	3.57(1)	Bi(3)-O(7)	2.88(2)	3.02(1)	3.06(1)	3.11(1)
	3.54(1)	3.50(1)	3.37(1)	3.97(1)	Bi(3)-O(8)	2.85(1)	2.63(1)	3.09(1)	3.14(1)
Bi(4)-O(1)	2.16(4)	2.16(1)	2.26(1)	2.33(1)					
Bi(4)-O(2)	2.30(2)	2.35(1)	2.36(1)	2.26(1)					
Bi(4)-O(3)	2.20(2)	2.09(1)	2.08(1)	2.09(1)					
Bi(4)-O(4)	2.22(1)	2.093(1)	2.18(1)	2.19(1)					
Bi(4)-Cl(1)	3.28(1)	3.32(1)	3.41(1)	2.81(10)					
	3.31(1)	3.33(1)	3.46(1)	3.48(1)					
	3.36(1)	3.45(1)	3.51(1)	3.65(1)					
	3.48(1)	3.56(1)	3.52(1)	3.99(1)					

Table S5. Atomic coordinates and isotropic thermal parameters obtained from PDF refinement for nano-Bi_4TaO_8Cl.

Atoms	Site	x	Y	Z	Occupancy	U $(Å)^2$
Ta (1)	4a	0.009 (3)	0.287 (6)	0.259 (1)	0.99(1)	0.008 (3)
Bi (1)	4a	0.0	0.844 (1)	0.155 (7)	0.99(1)	0.020 (2)
Bi (2)	4a	0.003 (2)	0.231 (2)	0.432 (1)	0.98(1)	0.021 (2)
Bi (3)	4a	0.015 (6)	0.752 (7)	0.337 (1)	0.99(1)	0.016 (1)
Bi (4)	4a	0.012 (1)	0.276 (1)	0.071 (2)	0.99(1)	0.009 (4)
Cl (1)	4a	0.516 (2)	0.232 (1)	0.002 (2)	0.97(2)	0.017 (1)
O (1)	4a	0.721 (1)	0.481 (1)	0.399 (1)	0.99(1)	0.010 (1)
O (2)	4a	0.255 (5)	0.485 (1)	0.395 (3)	0.99(1)	0.009 (3)
O (3)	4a	0.765 (2)	0.001 (5)	0.394 (1)	0.96(1)	0.020 (2)
O (4)	4a	0.272 (3)	0.026 (6)	0.395 (1)	0.98(1)	0.039 (1)
O (5)	4a	0.480 (4)	0.665 (6)	0.298 (4)	0.99(1)	0.036 (1)
O (6)	4a	0.607 (5)	0.736 (5)	0.180(2)	0.99(1)	0.021 (1)
O (7)	4a	0.213 (1)	0.006 (4)	0.238 (3)	0.99(1)	0.039 (1)
O (8)	4a	0.824 (3)	0.016 (3)	0.263 (2)	0.99(1)	0.036 (1)

Table S6. Atomic coordinates and isotropic thermal parameters obtained from PDF refinement for bulk-Bi_4TaO_8Cl.

Atoms	Site	x	y	Z	Occupancy	U $(Å)^2$
Ta (1)	4a	0.006 (3)	0.258 (6)	0.253 (1)	0.99(1)	0.008 (3)
Bi (1)	4a	0.0	0.659 (1)	0.154 (7)	0.99(1)	0.020 (2)
Bi (2)	4a	0.009 (2)	0.239 (2)	0.431 (1)	0.98(1)	0.021 (2)
Bi (3)	4a	-0.003 (6)	0.760 (7)	0.342 (1)	0.98(1)	0.016 (1)
Bi (4)	4a	0.026 (1)	0.248 (1)	0.066 (2)	0.99(1)	0.009 (4)
Cl (1)	4a	0.555 (2)	0.246 (1)	0.001 (2)	0.99(1)	0.017 (1)
O (1)	4a	0.772 (1)	0.479 (1)	0.391 (1)	0.97(1)	0.010 (1)
O (2)	4a	0.265 (5)	0.006 (1)	0.395 (3)	0.99(1)	0.009 (3)
O (3)	4a	0.774 (2)	0.004 (5)	0.394 (1)	0.99(1)	0.020 (2)
O (4)	4a	0.265 (3)	0.005 (6)	0.395 (1)	0.99(1)	0.039 (1)
O (5)	4a	0.435 (4)	0.785 (6)	0.318 (4)	0.97(1)	0.036 (1)
O (6)	4a	0.617 (5)	0.798 (5)	0.187 (2)	0.99(1)	0.021 (1)
O (7)	4a	0.285 (1)	0.0515 (4)	0.239 (3)	0.99(1)	0.039 (1)
O (8)	4a	0.779 (3)	0.044 (3)	0.263 (2)	0.99(1)	0.036 (1)

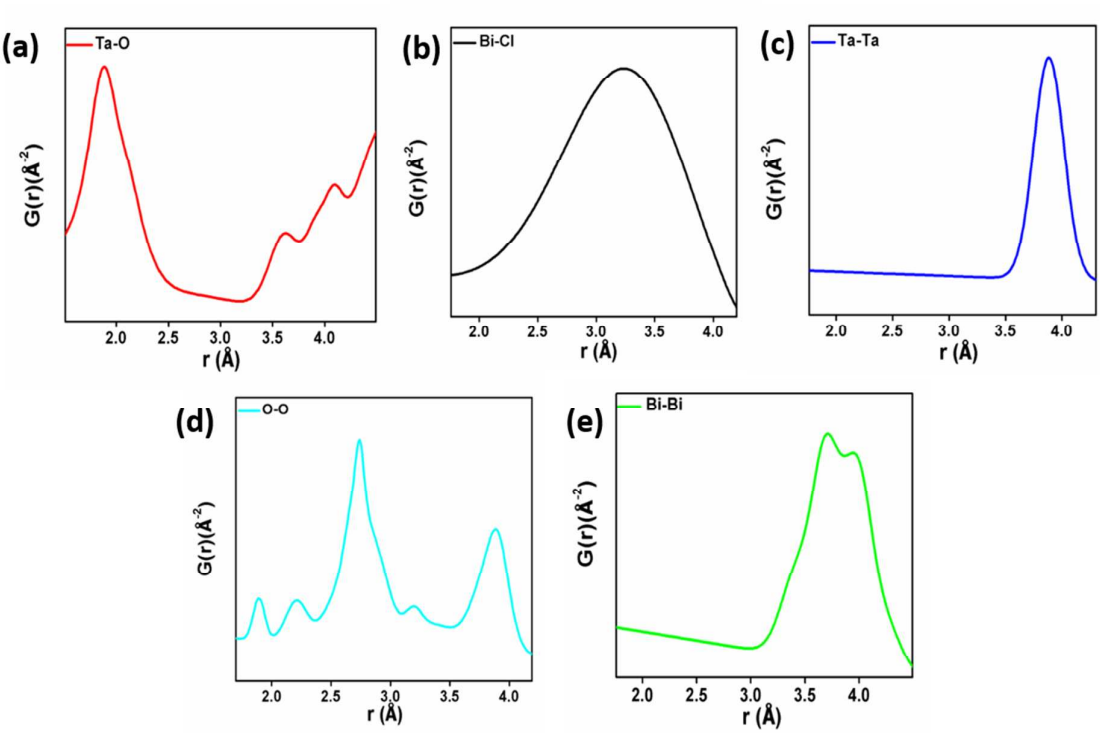

Figure S3. Partial PDF of nano-Bi_4TaO_8Cl showing (a) Ta-O, (b) Bi-Cl, (c) Ta-Ta, (d) O-O and (e) Bi-Bi coordianation spheres.

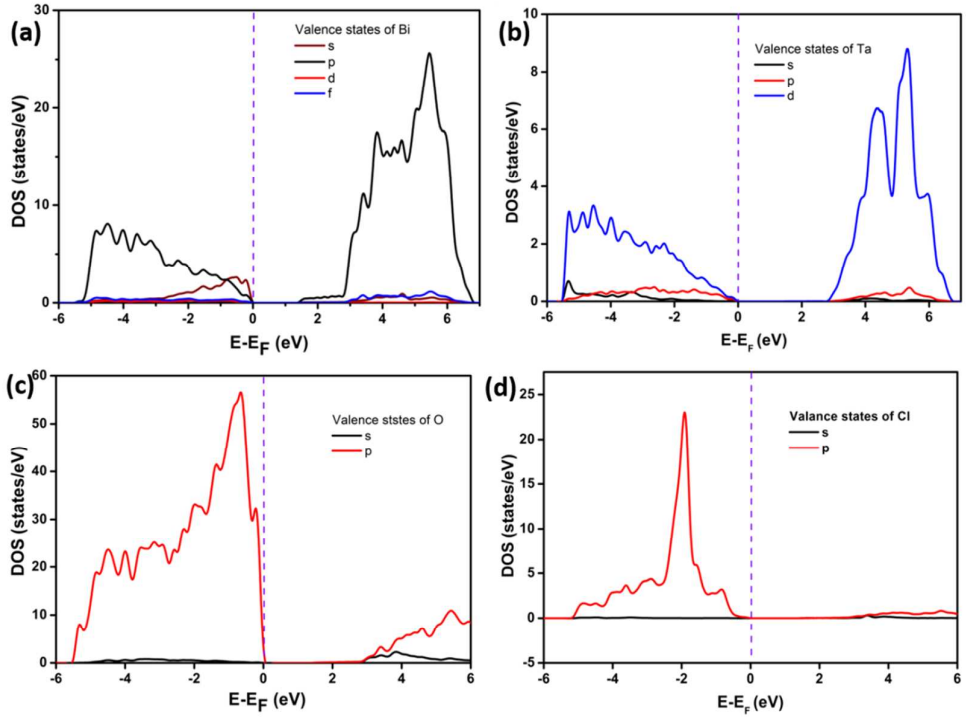

Figure S4. Density of states (DOS) for nano-Bi_4TaO_8Cl (a) Bi, (b) Ta (c) O (d) Cl.

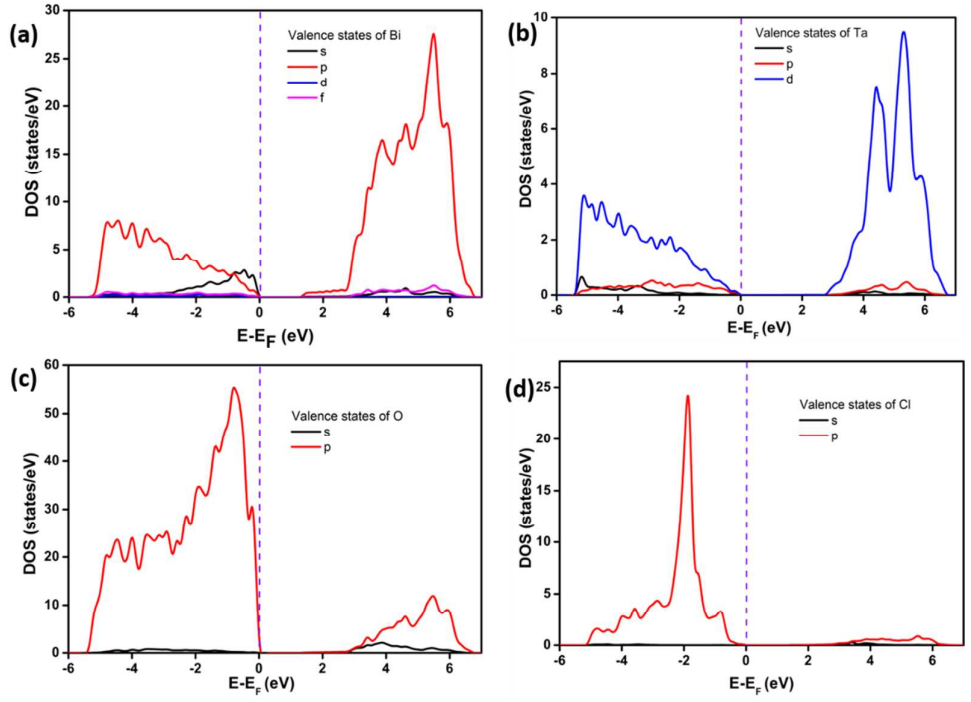

Figure S5. Density of states (DOS) for bulk-Bi_4TaO_8Cl (a) Bi, (b) Ta (c) O (d) Cl.

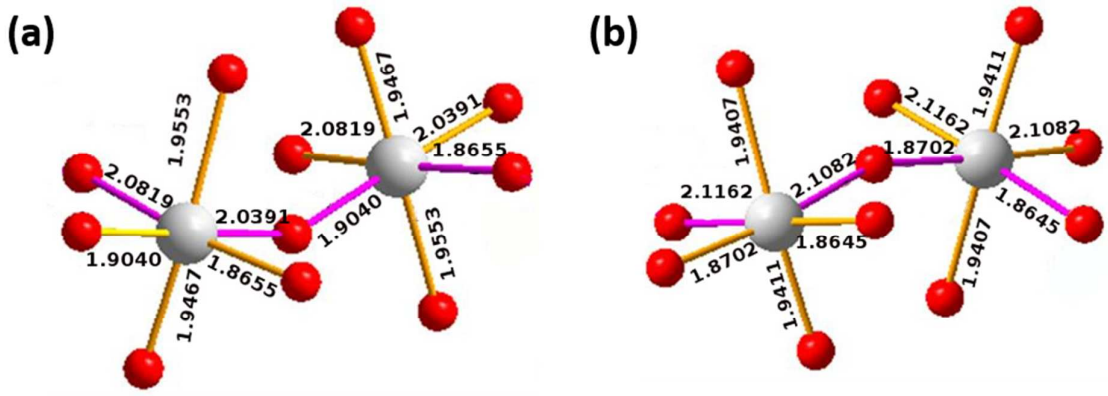

Figure S6. Ta-O bond distances in (a) nano-Bi_4TaO_8Cl and (b) bulk-Bi_4TaO_8Cl.

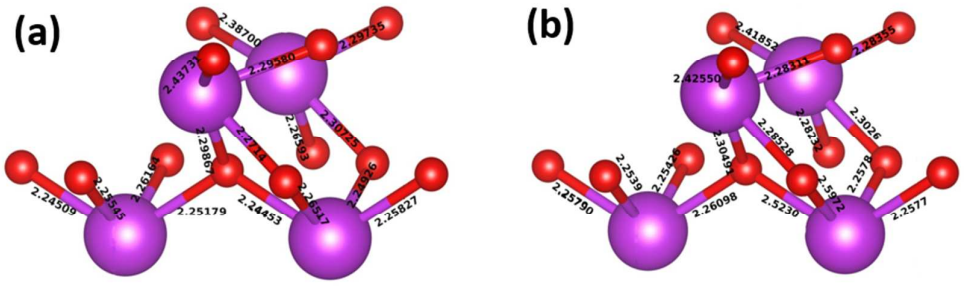

Figure S7. Bi-O bond distances in (a) nano-Bi_4TaO_8Cl and (b) bulk-Bi_4TaO_8Cl.

Table S7. Relaxed atomic coordinates of nano-Bi_4TaO_8Cl.

	x	y	z
Ta1	1.013118	0.253099	0.24995
Ta2	0.513118	0.746901	0.75005
Ta3	1.013118	0.246901	0.74995
Ta4	0.513118	0.7531	0.25005
Bi1	1.008696	0.815883	0.159417
Bi2	0.508696	0.184117	0.840582
Bi3	1.008696	0.684117	0.659418
Bi4	0.508696	0.315883	0.340582
Bi5	0.013924	0.251447	0.434313
Bi6	0.513924	0.748553	0.565687
Bi7	0.013924	0.248553	0.934313
Bi8	0.513924	0.751448	0.065687
Bi9	1.017138	0.815829	0.340553
Bi10	0.517138	0.184171	0.659447
Bi11	1.017138	0.684171	0.840553
Bi12	0.517138	0.315829	0.159447
Bi13	0.013671	0.251676	0.06551
Bi14	0.513671	0.748324	0.93449
Bi15	0.013671	0.248324	0.56551
Bi16	0.513671	0.751676	0.43449
Cl1	0.503417	0.250173	-0.000013
Cl2	0.003417	0.749827	1.000013
Cl3	0.503417	0.249827	0.499987
Cl4	0.003417	0.750173	0.500014
O1	0.761391	0.502142	0.393882
O2	0.261391	0.497858	0.606118
O3	0.761391	-0.002142	0.893882
O4	0.261391	1.002142	0.106118
O5	0.262086	0.500628	0.393687
O6	0.762086	0.499372	0.606313
O7	0.262086	-0.000628	0.893687
O8	0.762086	1.000628	0.106313
O9	0.762617	0.001966	0.394003

O10	0.262617	0.998034	0.605998
O11	0.762617	0.498034	0.894002
O12	0.262617	0.501966	0.105997
O13	0.262825	0.000607	0.393523
O14	0.762825	0.999393	0.606477
O15	0.262825	0.499393	0.893523
O16	0.762825	0.500607	0.106477
O17	0.417952	0.704946	0.314898
O18	0.917952	0.295054	0.685102
O19	0.417952	0.795054	0.814898
O20	0.917952	0.204946	0.185102
O21	0.59664	0.708171	0.184855
O22	0.09664	0.291829	0.815145
O23	0.59664	0.791829	0.684855
O24	0.09664	0.208171	0.315145
O25	0.251995	0.973806	0.236527
O26	0.751995	0.026194	0.763473
O27	0.251995	0.526194	0.736527
O28	0.751995	0.473806	0.263473
O29	0.75993	0.977515	0.264548
O30	0.25993	0.022485	0.735452
O31	0.75993	0.522485	0.764548
O32	0.25993	0.477516	0.235452

Table S8. Relaxed atomic coordinates of bulk-Bi_4TaO_8Cl.

	x	y	z
Ta1	1.015825	0.252522	0.249932
Ta2	0.515825	0.747477	0.750068
Ta3	1.015825	0.247478	0.749932
Ta4	0.515825	0.752522	0.250068
Bi1	1.012702	0.811899	0.159422
Bi2	0.512702	0.188101	0.840578
Bi3	1.012702	0.688101	0.659422
Bi4	0.512702	0.311899	0.340578
Bi5	0.015473	0.249827	0.434039
Bi6	0.515473	0.750173	0.565961
Bi7	0.015473	0.250173	0.934039
Bi8	0.515473	0.749827	0.065961
Bi9	0.019425	0.812549	0.340633
Bi10	0.519424	0.187451	0.659367
Bi11	0.019425	0.687451	0.840633
Bi12	0.519424	0.312549	0.159367
Bi13	0.016959	0.249796	0.065897
Bi14	0.516959	0.750204	0.934103
Bi15	0.016959	0.250204	0.565897
Bi16	0.516959	0.749796	0.434103
Cl1	0.512259	0.249632	1
Cl2	0.012259	0.750368	0.000001

Cl3	0.512259	0.250368	0.499999
Cl4	0.012259	0.749632	0.5
O1	0.76597	0.501004	0.393623
O2	0.26597	0.498996	0.606377
O3	0.76597	0.998996	0.893623
O4	0.26597	0.001004	0.106377
O5	0.266022	0.499329	0.393933
O6	0.766022	0.500671	0.606067
O7	0.266022	0.000671	0.893933
O8	0.766022	0.999329	0.106067
O9	0.765992	0.000477	0.393681
O10	0.265992	0.999523	0.606319
O11	0.765992	0.499523	0.893681
O12	0.265992	0.500477	0.106319
O13	0.266125	-0.000446	0.393885
O14	0.766126	1.000446	0.606115
O15	0.266125	0.500446	0.893885
O16	0.766126	0.499554	0.106115
O17	0.422743	0.693149	0.314329
O18	0.922743	0.306851	0.685671
O19	0.422743	0.806851	0.814329
O20	0.922743	0.193149	0.185671
O21	0.607371	0.694236	0.185675
O22	0.107371	0.305764	0.814325
O23	0.607371	0.805764	0.685675
O24	0.107371	0.194236	0.314325
O25	0.257276	-0.037241	0.23586
O26	0.757276	1.037241	0.76414
O27	0.257276	0.537241	0.73586
O28	0.757276	0.462759	0.26414
O29	0.770858	0.964609	0.264651
O30	0.270858	0.035391	0.735349
O31	0.770858	0.535391	0.764651
O32	0.270858	0.464609	0.235349