Supporting Information

Investigating the Stable Structures of Yttrium Oxide Clusters: Y_n Clusters as Promising Candidates for O_2 Dissociation

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This Supporting Information contains the following:

Table S1. Cartesian coordinates (x, y, z) of the ground state structures of the Y_nO_2 (n = 2–8) clusters.
Table S2. Vibrational frequencies of neutral and cation clusters of Y_nO_2 (n=2-8).
Table S3. Bader charge analysis of Y_nO_2 (n =2 to 8) of the structural isomers presented in Fig 5 in the manuscript.
Fig. S1. Additional geometric structural isomers of Y_nO_2 (n = 2 – 8) clusters arranged in the increasing order of energy. The spin states, and DFT calculated relative energies in eV are provided. The blue and red spheres denote yttrium and oxygen atoms, respectively.
Fig. S2. (a) Some of the initial input geometries and the resultant converged geometry for Y_2O_2 (2a). **(b)** Initial input geometries converging into 3b structure of Y_3O_2, and **(c)** Initial input geometries converging into 3a structure of Y_3O_2.
Figs. S3 to S8. Photoionization spectra (simulated and experimental) of Y_nO_2 (n = 4–8) and Y_3O_3.
Fig. S9. Experimental PI spectra of Y_nO_m (n = 4–5, m = 3–4)
Fig. S10. Lowest geometric structural isomers of Y_nO_3 (n = 3 – 5) clusters arranged in the increasing order of energy.
Fig. S11. Lowest geometric structural isomers of Y_nO_4 (n = 4 – 5) clusters arranged in the increasing order of energy.
Fig. S12. Molecular orbitals (MOs) of Y_3O_m (m = 1–3) clusters.
Fig. S13. Average binding energy of Y_nO_2 (n=1-8) cluster
Fig. S14. DOS/PDOS of Y_nO_2 (n = 1-6) along with the DOS/PDOS of isolated Y and O_2.

Table S1. Cartesian coordinates (x, y, z) of the ground state structures of the Y_nO_2 (n = 2–8) clusters.

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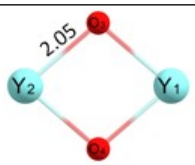
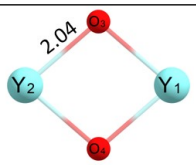
<tr><th colspan="4">Neutral</th><th colspan="4">Cation</th></tr>
<tr><td colspan="8">Y_2O_2</td></tr>
<tr><td colspan="4"> 
</td><td colspan="4"> 
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<tr><td>Atom</td><td>x</td><td>y</td><td>z</td><td>Atom</td><td>x</td><td>y</td><td>z</td></tr>
<tr><td>Y</td><td>-0.237120805</td><td>0.561027786</td><td>0.972872329</td><td>Y</td><td>-0.238782425</td><td>0.564472807</td><td>0.978920195</td></tr>
<tr><td>Y</td><td>0.425753499</td><td>-1.052488285</td><td>-1.588644730</td><td>Y</td><td>0.427371902</td><td>-1.056263378</td><td>-1.594687285</td></tr>
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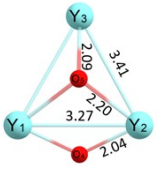
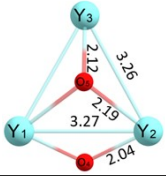
<tr><td colspan="4"> 
</td><td colspan="4"> 
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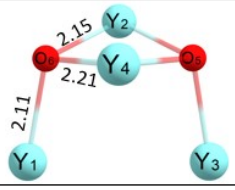
Y_4O_2



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Y	1.979525559	0.087735070	-1.109789903
Y	-0.016772996	-1.585831166	1.049165869
O	1.438679366	0.082671047	0.937531872
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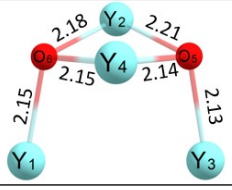
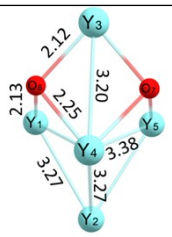


Y	-1.472924231	0.064378317	-1.366078231
Y	0.260704559	1.695444696	1.468148935
Y	1.835546318	0.290733882	-1.135962065
Y	-0.109051350	-1.560318757	1.130193651
O	1.433090965	-0.032990212	0.951174614
O	-1.205149377	0.321177620	0.736896015

Y_5O_2



Y	0.637104669	1.563735775	0.943875808
Y	1.738305012	0.812998368	-2.041030581
Y	-1.877398699	-0.941258384	1.692035315
Y	-1.367645639	0.067936389	-1.298527586
Y	1.207231075	-1.708976690	-0.015980534
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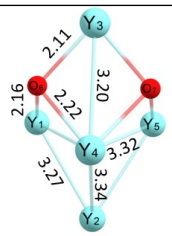
O	-0.922567595	-1.732083742	-0.029783236



Y	0.566220568	1.557013996	0.932515153
Y	1.845913644	0.823413294	-1.985558348
Y	-1.663789592	-0.933679404	1.814522657
Y	-1.352172799	0.081273615	-1.344348232
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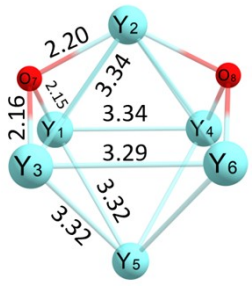
O	-1.029422703	-1.706643313	-0.044240909

Y_6O_2



Y	1.084452487	-2.053721799	-0.015186085
Y	1.418498249	0.813868578	1.682182098
Y	1.394447955	0.795121452	-1.653764597
Y	-1.516658545	-0.773583708	1.652934837
Y	-1.518518997	-0.796680966	-1.661760031
Y	-1.162165764	2.045801229	0.001392909
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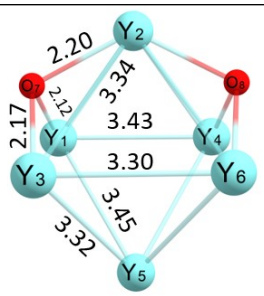
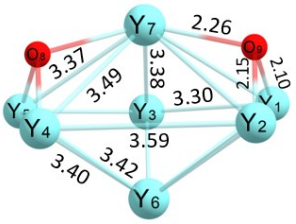
O	-0.731081377	1.212551301	1.963519239

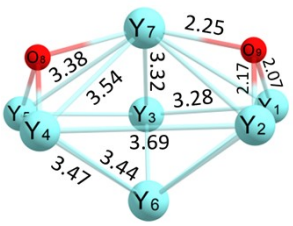


Y	1.145874426	-2.075086024	0.007278657
Y	1.412712234	0.812887368	1.674263725
Y	1.390961310	0.789552722	-1.659141740
Y	-1.528640825	-0.760995403	1.712782708
Y	-1.540358080	-0.760517780	-1.724895094
Y	-1.170574732	2.047827657	0.002213484
O	2.296499487	-0.291475275	-0.012515826
O	-0.736112136	1.201720935	1.961101195

Y_7O_2



Y	-0.659620331	-2.164720296	-1.756976892
Y	-0.816755410	-2.257171234	1.674601625



Y	-0.667310877	-2.161051283	-1.736611227
Y	-0.839345514	-2.301257115	1.636660778

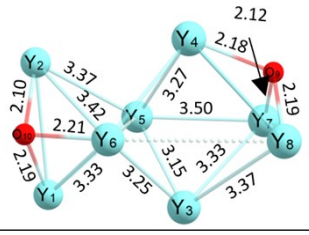
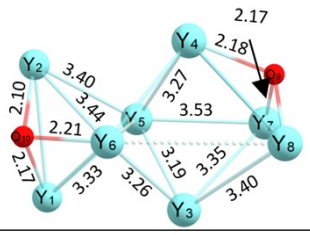
Y	0.094043489	0.920117696	-2.672990514	Y	0.107241897	0.899270683	-2.636344844
Y	0.225411039	0.992610759	2.781591540	Y	0.256195896	1.042647931	2.767755122
Y	0.915145438	2.802274344	-0.084362502	Y	0.886966490	2.793965244	-0.056946101
Y	-1.684825636	0.581686989	0.014223474	Y	-1.769385622	0.612971084	-0.017838149
Y	1.663051113	-0.485541756	-0.033982920	Y	1.712013778	-0.490087053	-0.074004463
O	1.666877975	1.335691851	1.279840080	O	1.692697398	1.304724446	1.288938391
O	0.495088739	-2.420947187	0.041253727	O	0.519342971	-2.397182771	0.071588110
Y_8O_2							
							
Y	-1.338917126	-2.542163663	1.611810290	Y	-1.355427726	-2.556621838	1.590677743
Y	-1.282027521	-2.498085885	-1.736771028	Y	-1.292259920	-2.497146742	-1.759851611
Y	0.250129394	0.495164361	2.177831765	Y	0.256185174	0.512648891	2.193498268
Y	0.472115577	0.944343476	-1.940914940	Y	0.460903343	0.912921617	-1.909401420
Y	1.404237028	-1.498505075	0.028936894	Y	1.427995902	-1.528852085	0.041140561
Y	-2.190936129	0.268969516	0.049032420	Y	-2.197288950	0.282418235	0.061472351
Y	2.797631443	1.689689331	0.401467217	Y	2.807440634	1.706562949	0.376863746
Y	-0.026034078	3.391505051	0.464724116	Y	-0.033 212776	3.418223850	0.451301077
O	1.371501044	2.663978043	-0.953783415	O	1.362030109	2.655742936	-0.937831873
O	-2.511326159	-1.912846851	-0.132228823	O	-2.489992317	-1.903849509	-0.137764346

Table S2. Vibrational frequencies of neutral and cation clusters of Y_nO_2 (n=2-8) of the lowest-energy structures provided in Table S1.

Mode	Symmetry	ω (cm^{-1})		Symmetry	ω (cm^{-1})
	Y_2O_2			$Y_2O_2^+$	
ν_1	a	7.033		a	0.012
ν_2	a	0.081		a	0.006
ν_3	a	0.049		a	0.002
ν_4	a	0.007		a	12.799
ν_5	a	3.828		a	28.534
ν_6	a	6.391		a	77.514
ν_7	a	121.596		a	160.502
ν_8	a	262.036		a	276.261
ν_9	a	446.258		a	437.646
ν_{10}	a	541.763		a	477.857
ν_{11}	a	559.923		a	546.215
ν_{12}	a	625.244		a	627.395
	Y_3O_2			$Y_3O_2^+$	
ν_1	a	3.289		a	6.052
ν_2	a	1.850		a	1.712
ν_3	a	0.651		a	0.368
ν_4	a	0.145		a	0.107
ν_5	a	0.084		a	0.027
ν_6	a	0.028		a	0.820
ν_7	a	17.131		a	20.905
ν_8	a	58.945		a	48.054
ν_9	a	76.202		a	63.142
ν_{10}	a	88.130		a	96.958

v_{11}	a	145.671		a	135.858
v_{12}	a	240.183		a	444.782
v_{13}	a	279.562		a	465.370
v_{14}	a	779.279		a	694.022
v_{15}	a	846.849		a	740.652
	Y_4O_2			$Y_4O_2^+$	
v_1	a	9.385		a	8.416
v_2	a	8.430		a	7.206
v_3	a	0.845		a	0.181
v_4	a	0.289		a	0.099
v_5	a	0.145		a	0.083
v_6	a	0.094		a	2.706
v_7	a	89.867		a	75.550
v_8	a	105.644		a	77.930
v_9	a	113.040		a	88.585
v_{10}	a	123.819		a	99.040
v_{11}	a	134.700		a	115.960
v_{12}	a	138.979		a	139.925
v_{13}	a	173.058		a	142.215
v_{14}	a	213.339		a	161.490
v_{15}	a	531.429		a	484.405
v_{16}	a	547.079		a	499.369
v_{17}	a	578.387		a	621.064
v_{18}	a	578.758		a	623.503
	Y_5O_2			$Y_5O_2^+$	
v_1	a	19.780		a	19.652
v_2	a	8.425		a	12.566
v_3	a	4.125		a	3.769
v_4	a	0.333		a	0.130
v_5	a	0.118		a	0.099
v_6	a	0.075		a	0.044
v_7	a	61.888		a	68.598
v_8	a	80.848		a	80.254
v_9	a	97.326		a	102.152
v_{10}	a	109.652		a	121.918
v_{11}	a	122.809		a	128.176
v_{12}	a	136.470		a	137.168
v_{13}	a	157.106		a	150.907
v_{14}	a	163.988		a	162.618
v_{15}	a	232.200		a	224.516
v_{16}	a	280.496		a	324.893
v_{17}	a	357.824		a	376.975
v_{18}	a	397.685		a	402.737
v_{19}	a	421.982		a	410.032
v_{20}	a	462.765		a	440.189
v_{21}	a	534.094		a	543.001
	Y_6O_2			$Y_6O_2^+$	
v_1	a	7.622		a	10.209
v_2	a	6.941		a	6.391
v_3	a	5.201		a	3.710
v_4	a	0.570		a	0.409
v_5	a	0.135		a	0.225
v_6	a	0.078		a	0.045
v_7	a	93.186		a	84.885
v_8	a	98.761		a	98.882
v_9	a	108.199		a	100.085
v_{10}	a	117.846		a	112.632
v_{11}	a	130.041		a	117.608
v_{12}	a	132.685		a	124.870
v_{13}	a	147.201		a	141.286

ν_{14}	a	157.199		a	145.709
ν_{15}	a	161.409		a	155.771
ν_{16}	a	177.123		a	176.399
ν_{17}	a	181.836		a	190.213
ν_{18}	a	242.481		a	243.996
ν_{19}	a	334.887		a	352.429
ν_{20}	a	405.637		a	415.322
ν_{21}	a	410.905		a	428.573
ν_{22}	a	460.784		a	466.683
ν_{23}	a	480.196		a	489.343
ν_{24}	a	516.829		a	521.048
	Y_7O_2			$Y_7O_2^+$	
ν_1	a	13.119		a	13.375
ν_2	a	7.753		a	6.698
ν_3	a	7.064		a	5.422
ν_4	a	0.815		a	0.763
ν_5	a	0.339		a	0.557
ν_6	a	0.117		a	0.201
ν_7	a	68.862		a	62.648
ν_8	a	75.025		a	78.023
ν_9	a	81.401		a	83.576
ν_{10}	a	86.524		a	96.191
ν_{11}	a	101.543		a	105.982
ν_{12}	a	110.080		a	113.131
ν_{13}	a	112.283		a	117.074
ν_{14}	a	119.481		a	122.690
ν_{15}	a	121.498		a	130.863
ν_{16}	a	129.084		a	132.076
ν_{17}	a	136.689		a	136.185
ν_{18}	a	141.587		a	150.427
ν_{19}	a	158.529		a	153.657
ν_{20}	a	172.008		a	175.956
ν_{21}	a	190.673		a	193.137
ν_{22}	a	322.985		a	326.083
ν_{23}	a	376.227		a	364.615
ν_{24}	a	411.268		a	412.151
ν_{25}	a	427.004		a	414.194
ν_{26}	a	480.641		a	516.943
ν_{27}	a	499.812		a	531.077
	Y_8O_2			$Y_8O_2^+$	
ν_1	a	7.894		a	8.169
ν_2	a	7.000		a	6.922
ν_3	a	4.518		a	2.804
ν_4	a	0.635		a	0.832
ν_5	a	0.314		a	0.381
ν_6	a	0.274		a	0.144
ν_7	a	53.668		a	60.417
ν_8	a	62.759		a	62.438
ν_9	a	71.586		a	71.895
ν_{10}	a	78.897		a	79.521
ν_{11}	a	83.779		a	81.311
ν_{12}	a	101.931		a	102.592
ν_{13}	a	106.532		a	104.147
ν_{14}	a	109.079		a	109.379
ν_{15}	a	113.256		a	114.602
ν_{16}	a	123.566		a	122.947
ν_{17}	a	130.247		a	129.196
ν_{18}	a	133.558		a	130.162
ν_{19}	a	140.975		a	138.371
ν_{20}	a	148.228		a	144.304

v_{21}	a	150.243		a	149.723
v_{22}	a	153.410		a	152.633
v_{23}	a	196.968		a	192.643
v_{24}	a	203.449		a	195.951
v_{25}	a	344.640		a	361.623
v_{26}	a	359.430		a	376.415
v_{27}	a	413.369		a	416.538
v_{28}	a	420.615		a	425.760
v_{29}	a	479.172		a	481.640
v_{30}	a	483.168		a	486.479

Table S3. Bader charge analysis of Y_nO_2 (n =2 to 8) of the structural isomers presented in Fig 5 in the manuscript.

Y O_2: n=2 to 8 and BC indicate Bader Charge in Coulomb													
n=2		n=3		n=4		n=5		n=6		n=7		n=8	
BC		BC		BC		BC		BC		BC		BC	
Y1	0.618	Y1	0.707	Y1	0.056	Y1	0.448	Y1	0.454	Y1	0.441	Y1	0.375
Y2	0.713	Y2	0.735	Y2	-0.052	Y2	0.054	Y2	0.459	Y2	0.399	Y2	0.322
O1	-0.708	Y3	1.204	Y3	0.631	Y3	0.975	Y3	0.456	Y3	-0.239	Y3	0.127
O2	-0.623	O1	-1.321	Y4	0.638	Y4	0.8435	Y4	0.453	Y4	0.384	Y4	0.584
		O2	-1.324	O1	-0.710	Y5	0.461	Y5	0.492	Y5	0.446	Y5	0.136
				O2	-0.563	O1	-1.390	Y6	0.490	Y6	0.350	Y6	0.580
						O2	-1.385	O1	-1.402	Y7	1.067	Y7	0.385
								O2	-1.403	O1	-1.425	Y8	0.311
										O2	-1.423	O1	-1.411
												O2	-1.409

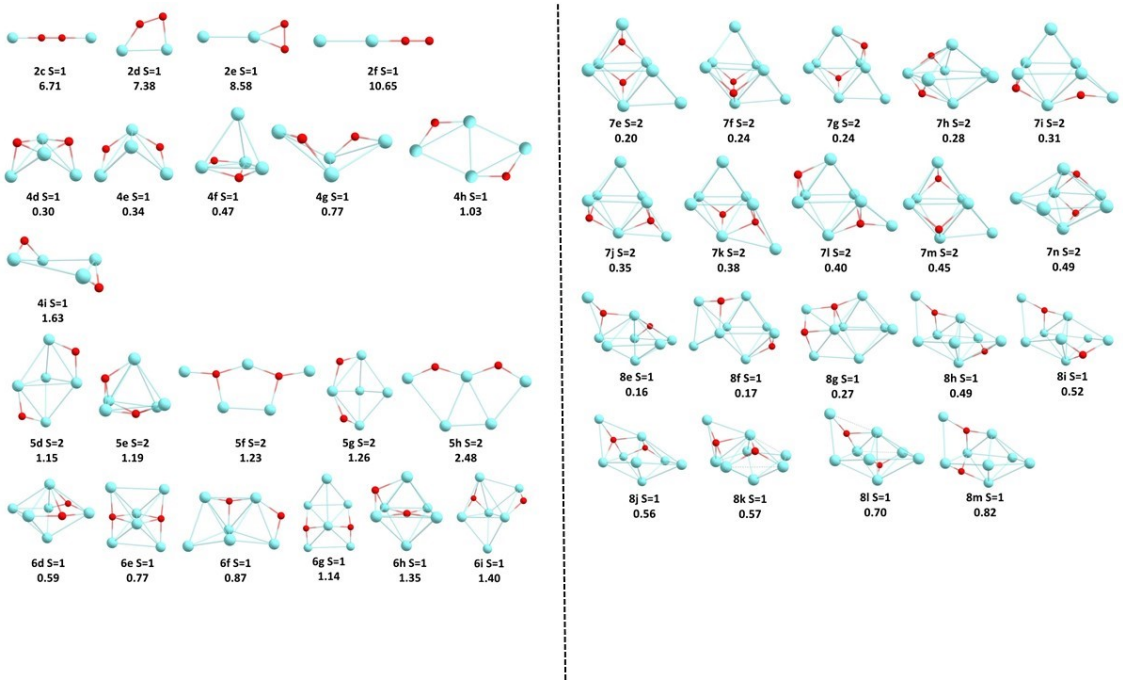


Fig. S1. Additional geometric structural isomers of Y_nO_2 (n = 2 – 8) clusters arranged in the increasing order of energy. The spin states, and DFT calculated relative energies in eV are provided. The blue and red spheres denote yttrium and oxygen atoms, respectively.

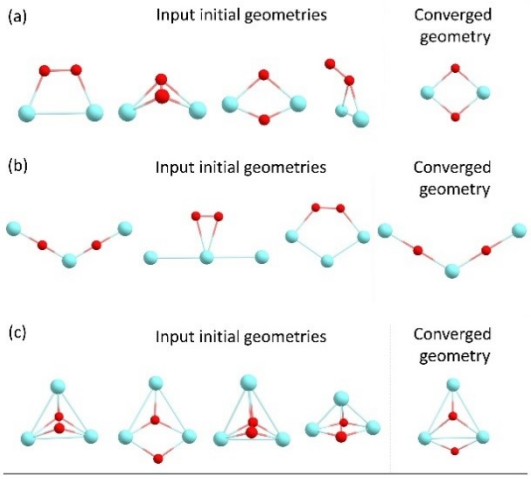


Fig. S2. (a) Some of the initial input geometries and the resultant converged geometry for Y_2O_2 (2a). **(b)** Initial input geometries converging into 3b structure of Y_3O_2, and **(c)** Initial input geometries converging into 3a structure of Y_3O_2.

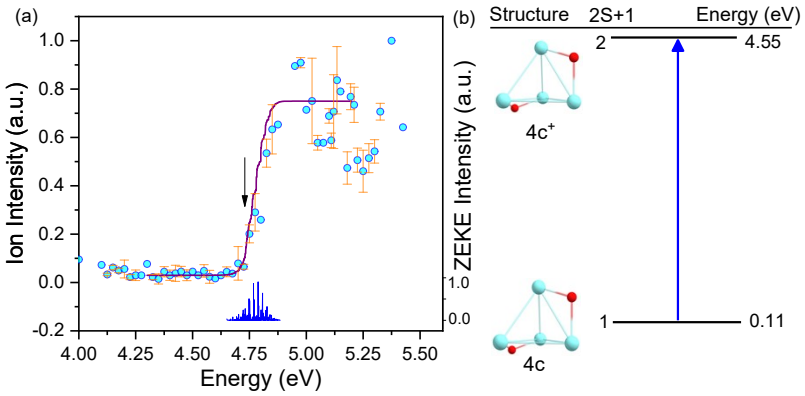


Fig. S3. (a) The simulated PI spectrum of Y_4O_2 (violet solid line) is overlaid against the experimental spectrum (blue spheres). The calculated ZEKE spectrum for the 1→2 ionization process of 4c is shown below the PI spectrum in blue. The AIE is labelled with a solid black arrow. (b) DFT calculated the lowest-energy geometric structures and energy levels of the neutral and cation clusters of Y_4O_2.

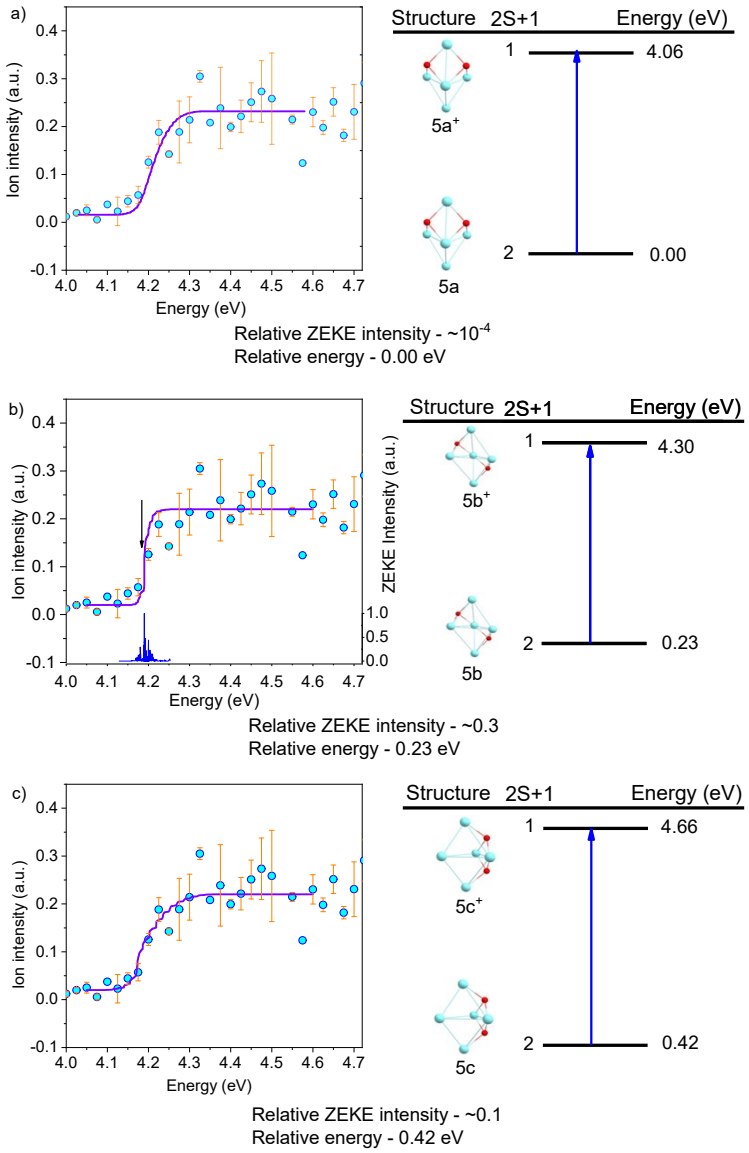


Fig. S4. Left Panel a to c presents the simulated PI spectra of Y_5O_2 (violet line) overlaid against the experimental spectrum (blue spheres) for the isomers 5a to 5c, respectively. The calculated ZEKE spectrum for the 2→1 ionization process for the 5b isomer is shown below the PI spectrum in blue. The AIE is labelled with a solid black arrow. Right Panels in from a to c show the ionization processes contributing to the calculated PI spectrum of respective isomers.

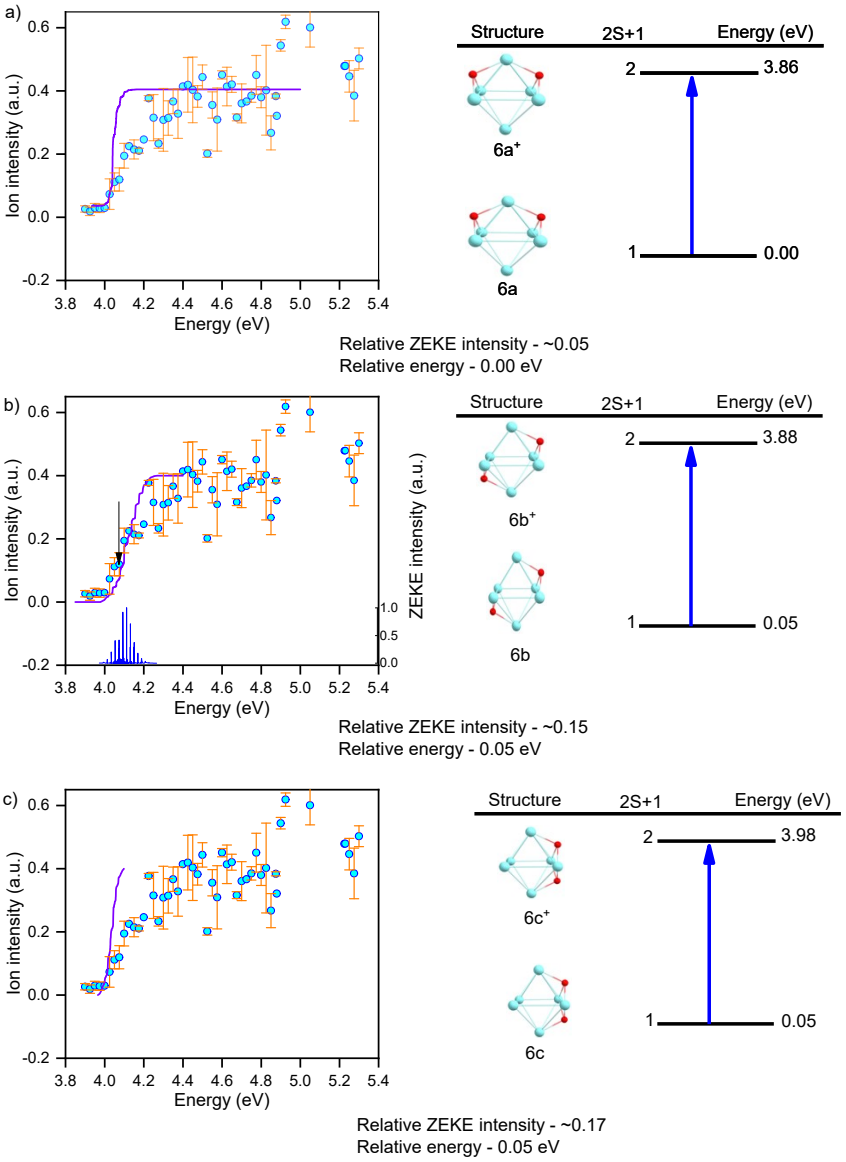


Fig. S5. Left Panel a to c presents the simulated PI spectra of Y_6O_2 (violet line) overlaid against the experimental spectrum (blue spheres) for the isomers 6a to 6c, respectively. The calculated ZEKE spectra for the 1→2 ionization process for the 6b isomer contributing to the PI spectrum is shown below the PI spectra in blue. The AIE is labelled with a solid black arrow. Right Panels in from a to c show the ionization processes contributing to the calculated PI spectrum of respective isomers.

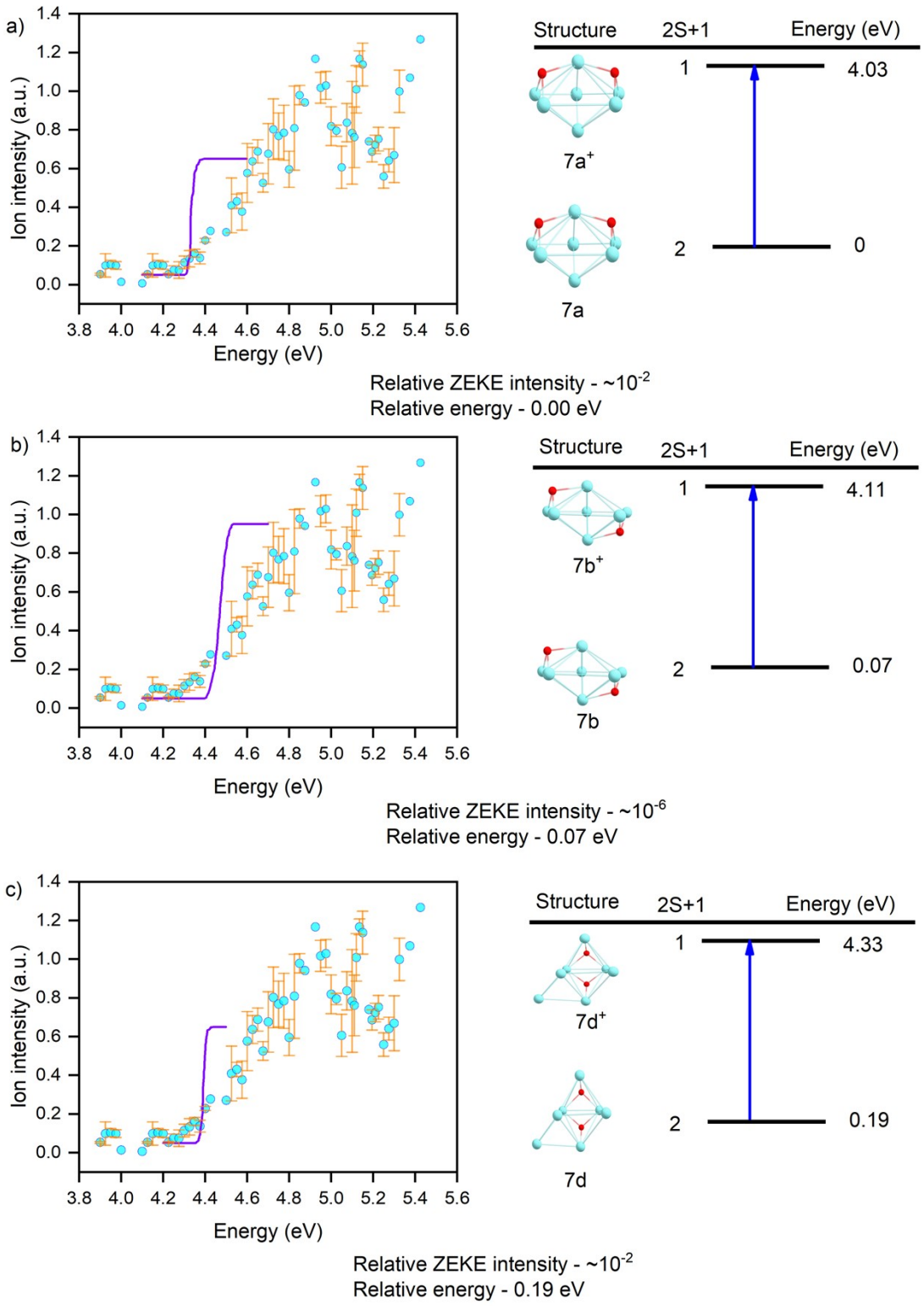


Fig. S6. Left Panel a to c presents the simulated PI spectra of Y_7O_2 (violet line) overlaid against the experimental spectrum (blue spheres) for the isomers 7a, 7b, and 7d, respectively. The ZEKE spectrum could not be generated somehow for the isomer 7c at 0.18 eV. Right Panels from a to c show the ionization processes contributing to the calculated PI spectrum of respective isomers.

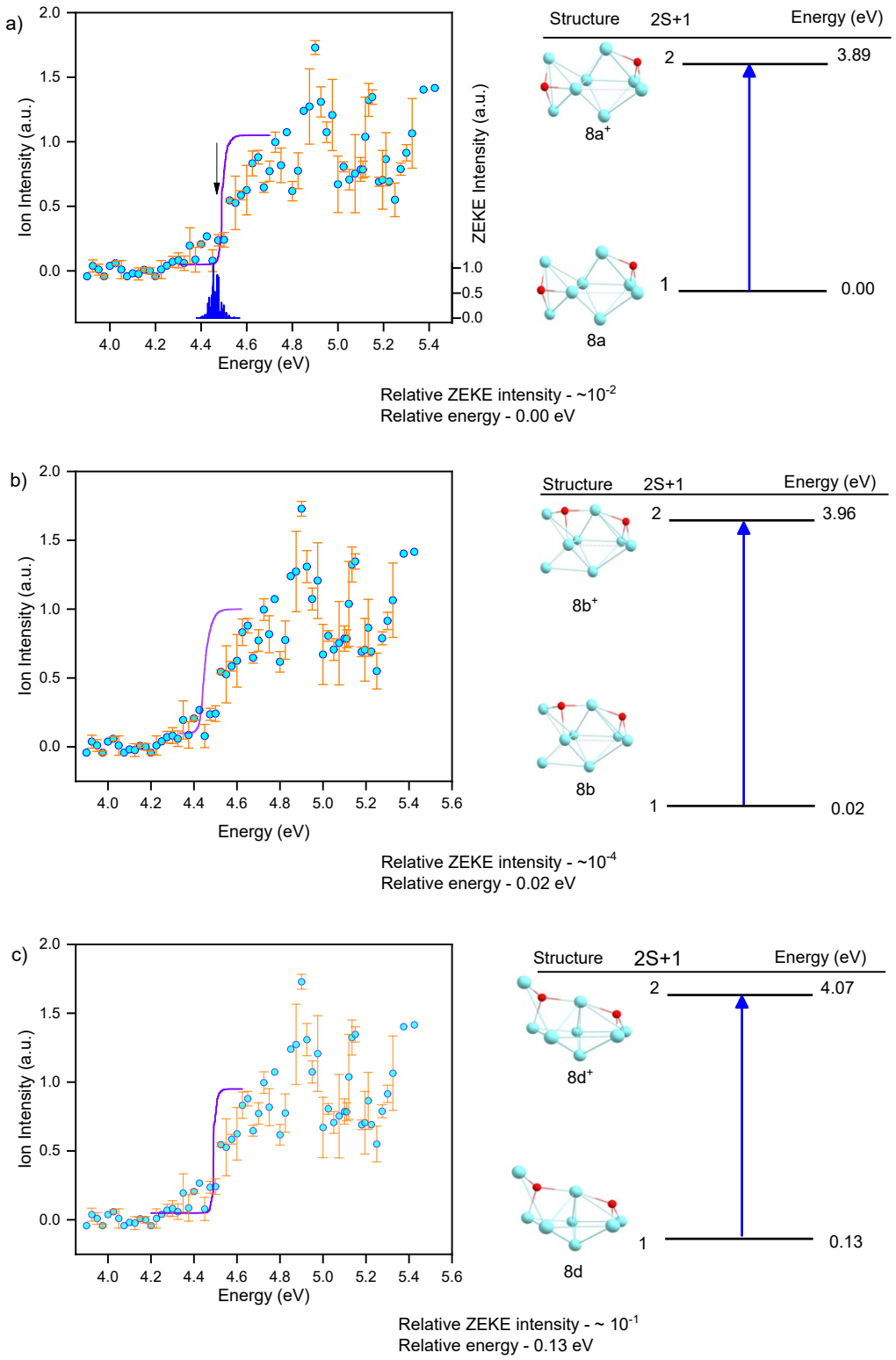


Fig. S7. Left Panel a to c presents the simulated PI spectra of Y_8O_2 (violet line) overlaid against the experimental spectrum (blue spheres) for the isomers 8a, 8b, and 8c, respectively. The ZEKE spectrum could not be generated somehow for the isomer 8c at 0.09 eV. The calculated ZEKE spectrum for the 1→2 ionization process for the 8a isomer is shown below the PI spectrum in blue. The AIE is labelled with a solid black arrow. Right Panels from a to c show the ionization processes contributing to the calculated PI spectrum of respective isomers.

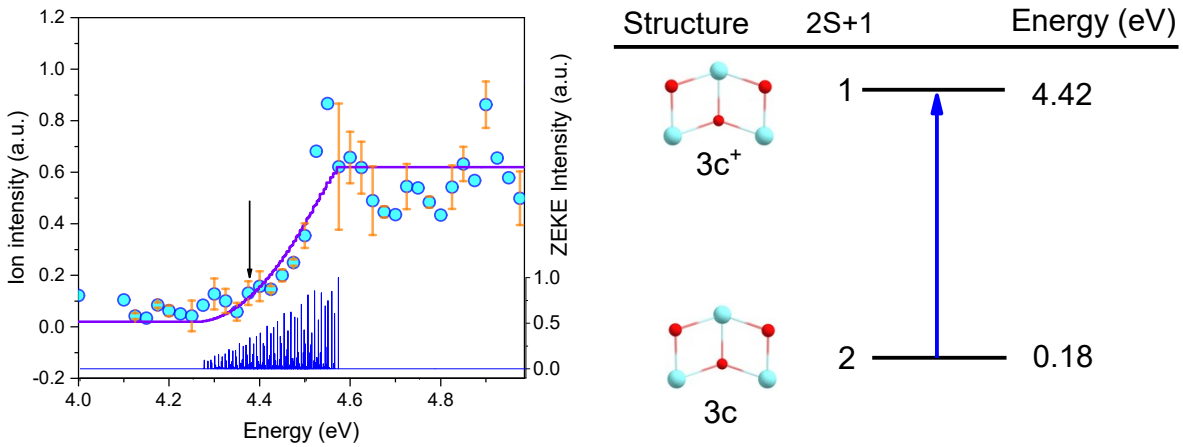


Fig. S8. (a) The simulated PI spectrum of Y_3O_3 (violet solid line) is overlaid against the experimental spectrum (blue spheres). The black arrow denotes the experimentally corrected adiabatic ionization energy. (b) DFT calculated the lowest-energy geometric structures and energy levels of the neutral and cation clusters of Y_3O_3.

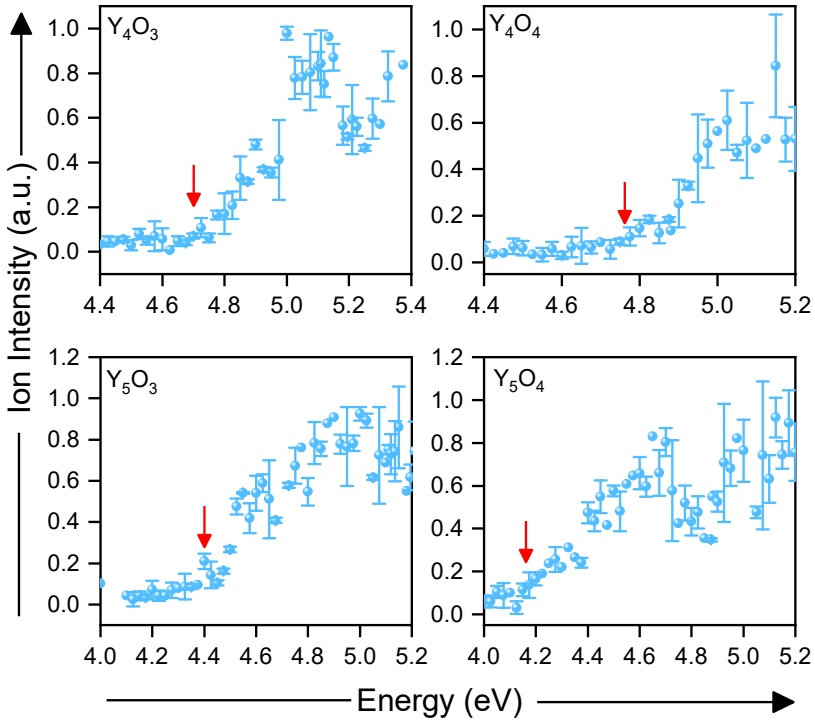


Fig. S9. Experimental PI spectrum of Y_nO_m (n = 4–5, m = 3–4). Red arrow marks the threshold ionization energy (TIE).

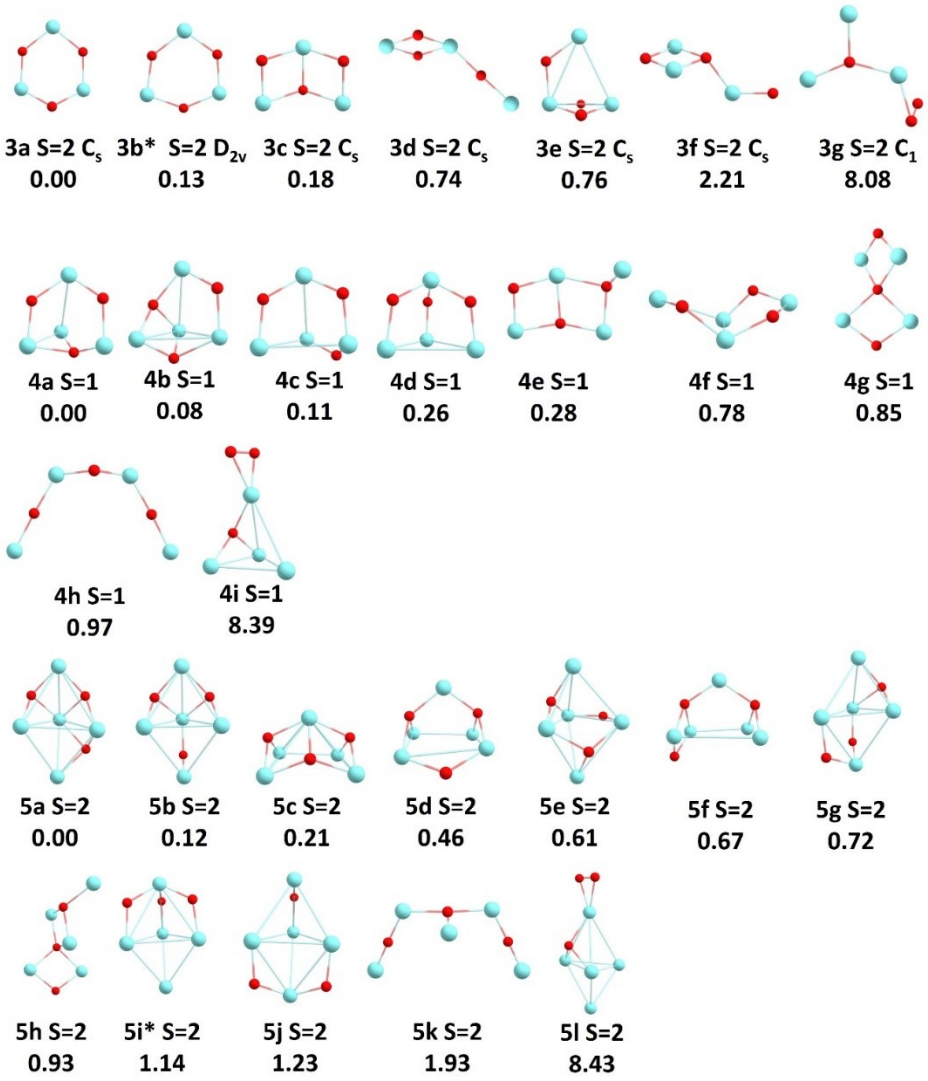


Fig. S10. Lowest geometric structural isomers of Y_nO_3 (n = 3 – 5) clusters arranged in the increasing order of energy. The point group symmetry, spin states, and DFT calculated relative energies in eV are provided. The blue and red spheres denote yttrium and oxygen atoms, respectively.

(*Geometric structures marked with an asterisk are reported to be the ground states Y_nO_3(n=3-5) in the following publication- **Zhi Yang and Shi-Jie Xiong 2009 J. Phys. B: At. Mol. Opt. Phys. 42 245101)**

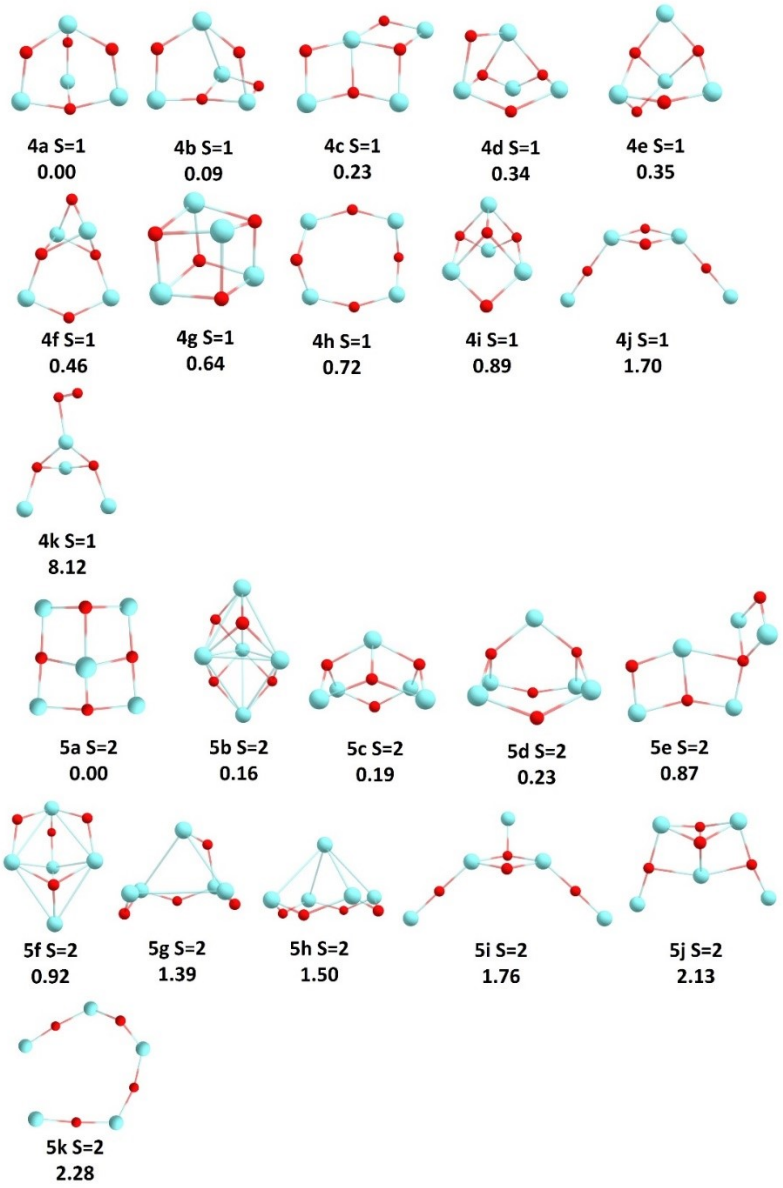
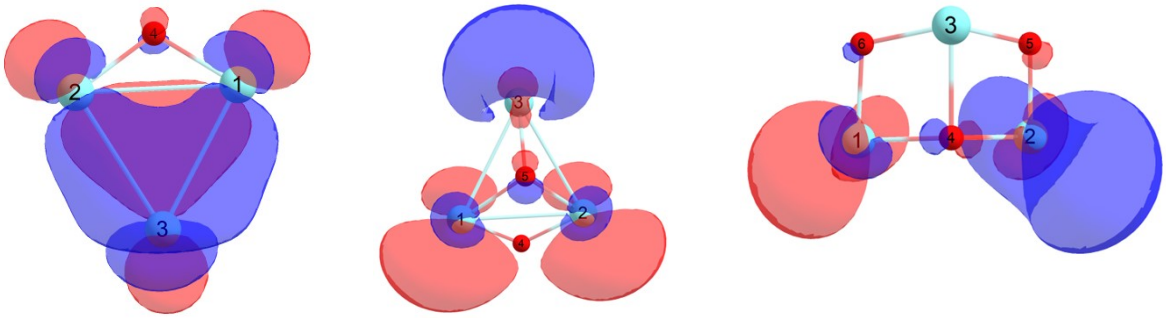


Fig. S11. Lowest geometric structural isomers of Y_nO_4 (n = 4 – 5) clusters arranged in the increasing order of energy. The spin states, and DFT calculated relative energies in eV are provided. The blue and red spheres denote yttrium and oxygen atoms, respectively.



Y_3O Y_3O_2 Y_3O_3

Fig. S12. Molecular orbitals (MOs) of Y_3O_m (m = 1–3) clusters.

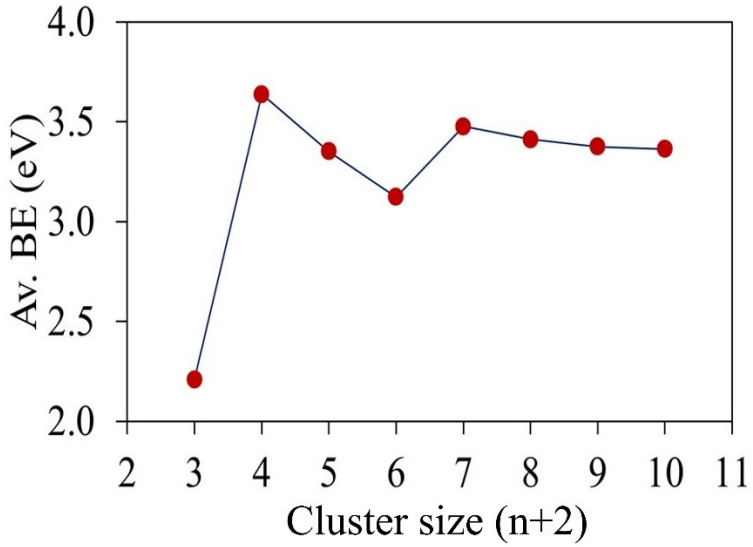


Fig. S13. Average binding energy of Y_nO_2 (n=1-8) clusters.

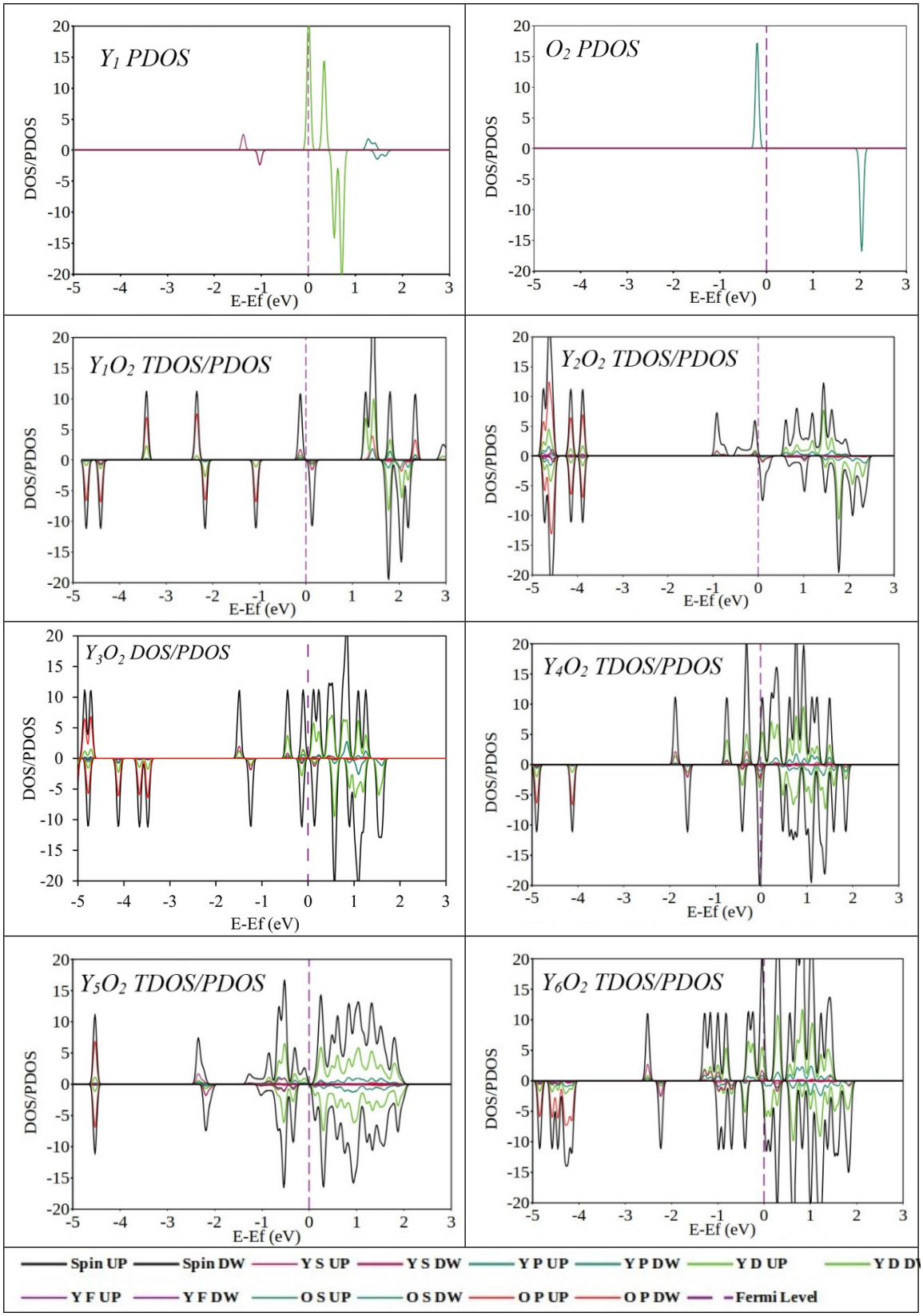


Fig. S14. DOS/PDOS of Y_nO_2 (n=1-6) clusters presented in Fig 5 in the manuscript along with the DOS/PDOS of isolated Y and O_2.