

Supporting Information

Compositions and Isomer Separation of Palladium Oxide Cluster Cations Studied by Ion Mobility Mass Spectrometry

M. Abdul Latif,^{1,2} Jenna W. J. Wu,¹ Toshiaki Nagata,¹ Motoyoshi Nakano,^{1,3} Keijiro Ohshima,¹

and Fuminori Misaizu^{1*}

*1. Department of Chemistry, Graduate School of Science, Tohoku University, 6–3 Aoba,
Aramaki, Aoba-ku, Sendai 980–8578, Japan*

*2. Department of Chemistry, Faculty of Science, Begum Rokeya University, Rangpur-5400,
Bangladesh*

*3. Institute for Excellence in Higher Education, Tohoku University, 41 Kawauchi, Aoba-ku,
Sendai, 980-8576, Japan*

* Corresponding author. Tel.: +81 22 795 6577, Fax: +81 22 795 6580

E-mail address: misaizu@m.tohoku.ac.jp (F. Misaizu)

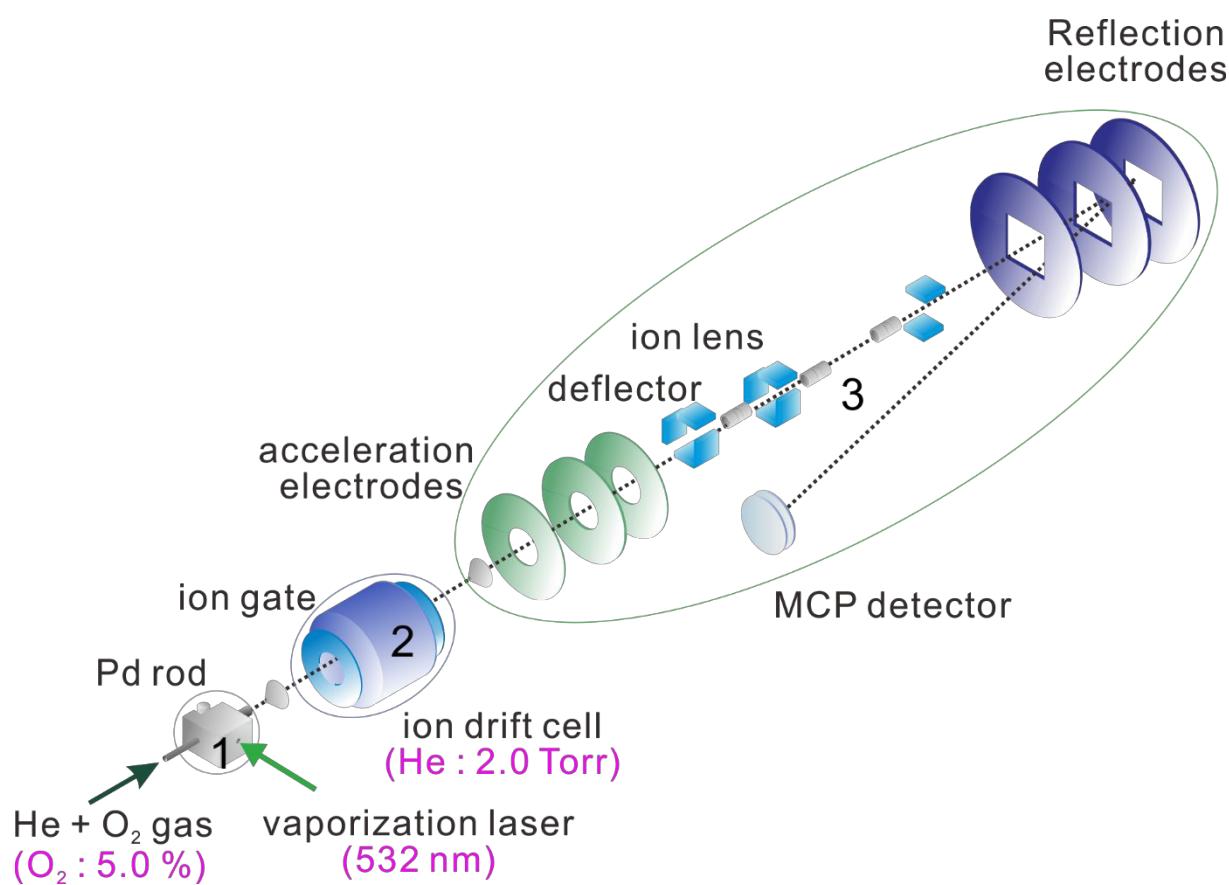


Figure S1. Brief illustration of a home-built experimental apparatus used for cluster studies in ion mobility mass spectrometry. It includes: 1. Cluster ion source, where cluster is generated by laser vaporization and supersonic jet. 2. The generated cluster ion passes through the ion-drift cell, where ion mobility spectrometry is taken place, and structural separation is achieved. 3. The cluster ion enters the reflectron type mass spectrometer, where mass separation is achieved.

Cartesian coordinates and natural charges of all assigned geometries, optimized at B3LYP/SDD (Pd) and cc-pVDZ (O) level of Gaussian 09

$\text{Pd}_3\text{O}^+(\Delta E = 0.4 \text{ eV})$

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	0.745236	0.000000	0.208499	0.24425
Pd	0.123772	0.000002	2.801938	0.65154
Pd	-0.596587	0.000001	6.438598	0.64041
O	0.343216	-0.000002	4.742413	-0.53620

$\text{Pd}_3\text{O}_2^+(\Delta E = 0 \text{ eV})$

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
O	0.213554	-0.202515	0.234337	-0.65298
Pd	1.719687	-0.150240	0.193395	0.80236
O	3.606102	-0.251918	0.213129	-0.67938
Pd	4.997584	-0.519475	-1.113491	0.75813
Pd	-1.572009	1.121322	0.475620	0.77187

$\text{Pd}_3\text{O}_3^+(\Delta E = 0 \text{ eV})$

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	-0.031784	0.195130	0.193065	0.61180
Pd	-0.420285	-0.722513	2.853736	0.59965
Pd	2.986526	0.260108	1.688061	0.75499
O	2.810165	0.948644	-0.272429	-0.10610
O	1.713447	0.891316	-0.871301	-0.09371
O	1.095368	-0.330683	1.693606	-0.76663

$\text{Pd}_3\text{O}_3^+(\Delta E = 0.1 \text{ eV})$

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
O	-0.903915	0.205126	-0.826448	-0.39968
Pd	-2.867980	0.396240	-0.589737	0.71692
Pd	-0.190896	-0.617997	-2.480205	-0.00577
O	1.694289	-0.240727	2.210186	-0.00228
O	2.896431	-0.079765	2.047360	0.02047
Pd	0.347681	-0.055427	0.684212	0.67034

Pd₃O₄⁺ ($\Delta E = 0$ eV)

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	-0.041025	-0.103993	-0.067284	0.64188
Pd	2.325355	1.403319	-0.030172	0.65483
Pd	-0.083080	2.578946	0.020082	0.76694
O	1.626751	-1.289714	-0.120647	-0.12115
O	2.700094	-0.580034	-0.108615	-0.11888
O	-1.456307	1.210037	-0.015453	-0.40468
O	1.753385	3.225682	0.034398	-0.41894

Pd₃O₄⁺ ($\Delta E = 0.9$ eV)

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	-1.418412	-0.391333	-0.471037	1.02359
O	-1.353119	-0.322984	1.419975	-0.49196
Pd	0.649189	-0.559251	1.687650	1.03039
O	1.342301	0.967853	0.747427	-0.50003
Pd	1.266495	0.560508	-1.269005	0.99727
O	-0.728697	0.711865	-1.837220	-0.47661
O	0.339479	-1.261670	-0.368729	-0.58264

Pd₃O₅⁺ ($\Delta E = 0$ eV)

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	-0.070554	-0.047765	-0.144348	0.51458
Pd	-0.021323	-0.038592	2.684444	0.67416
Pd	2.384825	0.047589	1.255633	0.67367
O	-1.890833	-0.114308	0.734616	-0.10466
O	-1.896219	-0.110983	2.012048	-0.10102
O	1.572907	0.011280	-1.322283	-0.10455
O	1.849208	0.032429	3.096256	-0.45107
O	2.694557	0.054183	-0.712330	-0.10111

Pd₃O₅⁺ ($\Delta E = 4.6$ eV)

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
O	-0.102748	-0.193264	0.204740	-0.44807
Pd	1.753258	-0.146288	-0.475662	1.01787
Pd	-0.229536	1.812134	0.035814	1.03726
O	3.280027	1.140429	-0.217537	-0.43115
O	0.753802	3.784697	-0.221724	-0.31643
Pd	2.419733	2.842248	0.306109	0.96614
O	0.861475	1.282879	-1.465807	-0.41509
O	1.119381	1.932294	1.404836	-0.41053

$\text{Pd}_3\text{O}_6^+(\Delta E = 0.4 \text{ eV})$

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
O	-0.393590	0.130401	-0.479327	-0.12817
O	0.651457	-0.796703	3.515461	-0.12803
O	3.609854	-0.104429	-0.020738	-0.10140
Pd	1.633431	0.026025	-0.211278	0.50169
O	3.926425	-0.365824	1.193507	-0.10092
O	-0.239570	-1.563873	3.029672	-0.07798
O	-1.034607	-0.852107	0.014513	-0.07880
Pd	0.280243	-2.205630	1.044159	0.61061
Pd	2.292087	-0.542967	2.313501	0.50299

$\text{Pd}_4\text{O}_2^+(\Delta E = 0.1 \text{ eV})$

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	0.033364	-0.069048	-0.039309	0.40531
Pd	-0.127126	-0.121964	2.567872	0.51470
Pd	2.189744	0.091350	1.416187	0.48113
Pd	0.883729	-2.149357	1.291273	0.51460
O	-2.829336	-0.907768	-0.990912	-0.46924
O	-1.845002	-0.256872	-1.258778	-0.44650

$\text{Pd}_4\text{O}_3^+(\Delta E = 0 \text{ eV})$

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	-0.109775	-0.064569	-0.060527	0.84774
O	0.093712	0.089923	1.868548	-0.53297
O	1.684477	0.108970	-0.808654	-0.55001
Pd	3.101360	-0.070103	0.436373	0.69849
O	3.878183	-0.125195	2.286677	-0.89547
Pd	1.859401	-0.070913	2.537915	0.69277
Pd	5.600715	0.131887	3.239668	0.73945

$\text{Pd}_4\text{O}_3^+(\Delta E = 0.7 \text{ eV})$

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	-0.031998	0.052521	-0.069520	0.35065
Pd	-0.116157	0.055667	2.600251	0.66940
Pd	2.262287	0.049674	1.300453	0.64075
Pd	0.701719	-2.166495	1.219796	0.66974
O	1.360589	1.299494	2.532326	-0.44020
O	2.500927	-1.791823	0.629851	-0.44158
O	-0.701714	-1.790387	2.507102	-0.44877

Pd₄O₄⁺ ($\Delta E = 0.5$ eV)

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	-0.056963	-0.000098	-0.105686	0.75629
Pd	-0.055315	0.000093	2.813286	0.80081
Pd	2.744980	-0.000103	-0.109736	0.75628
Pd	2.753804	0.000092	2.808868	0.80117
O	3.966025	-0.000166	1.367234	-0.53473
O	1.342597	0.000276	-1.422560	-0.46586
O	1.351413	0.000077	4.074204	-0.57975
O	-1.272752	-0.000170	1.375315	-0.53420

Pd₄O₄⁺ ($\Delta E = 0.9$ eV)

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	0.130029	0.311540	0.321146	0.61216
Pd	0.629353	-2.435086	-0.248458	0.27380
Pd	2.476538	-0.492028	-0.501935	0.05622
Pd	0.527327	-0.570536	-2.359169	0.27379
O	0.936028	-3.283359	-2.036820	-0.00418
O	0.890209	-2.433361	-2.996734	-0.00421
O	0.127721	-1.354093	1.244868	-0.10396
O	-0.003987	1.019739	-1.441360	-0.10362

Pd₄O₅⁺ ($\Delta E = 0$ eV)

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	-0.076812	-0.081274	-0.057264	0.57851
Pd	-0.088722	-0.050603	2.893314	0.48424
Pd	2.126152	0.041696	1.417124	0.28760
Pd	0.942459	-2.331452	1.343398	0.57732
O	0.614051	-1.609211	3.976928	-0.12205
O	1.067570	-2.621721	3.321797	-0.12005
O	-0.858766	1.588481	1.988555	-0.12187
O	0.628903	-1.820312	-0.485440	-0.44353
O	-0.864881	1.599587	0.700439	-0.12018

Pd₄O₅⁺ ($\Delta E = 0.2$ eV)

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
O	0.053150	0.121640	-0.062560	-0.51852
Pd	-0.132250	0.041831	1.837374	0.61230
Pd	1.317405	0.020119	-1.461339	0.75778
Pd	2.212631	-0.182973	2.942222	0.62941
O	3.620915	-0.262733	1.666006	-0.55348
O	3.128060	-0.164318	-2.080223	-0.44768

Pd	3.584939	-0.225801	-0.234170	0.75425
O	0.815673	-0.141306	4.373222	-0.11360
O	-0.340084	-0.039570	3.818207	-0.12046

$\text{Pd}_4\text{O}_6^+ (\Delta E = 0 \text{ eV})$

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	-0.134570	0.009030	-0.149404	0.51381
Pd	-0.085957	-0.023330	2.934638	0.52079
Pd	2.043323	-0.034744	1.362238	0.25228
Pd	0.962963	-2.455920	1.361399	0.51348
O	0.601252	-1.563189	4.007777	-0.13669
O	1.042384	-2.577869	3.343965	-0.12927
O	-0.845157	1.608135	2.060403	-0.13663
O	0.488167	-1.521106	-1.256579	-0.13416
O	-0.855083	1.619560	0.770582	-0.12935
O	0.936045	-2.554450	-0.625794	-0.13426

$\text{Pd}_4\text{O}_6^+ (\Delta E = 0.1 \text{ eV})$

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	0.597561	-0.429521	-0.141733	0.62684
Pd	-2.364540	1.579957	0.194334	0.63895
Pd	1.366627	0.997914	-2.124416	0.66006
Pd	-1.624770	3.034525	-1.784531	0.65950
O	0.035990	2.319405	-2.334092	-0.55487
O	-3.839253	2.868276	-0.215718	-0.09977
O	-3.496433	3.528145	-1.266343	-0.13688
O	2.375189	-1.150957	-0.775679	-0.10108
O	2.777457	-0.360951	-1.709447	-0.13609
O	-1.039722	0.271837	0.586444	-0.55666

$\text{Pd}_4\text{O}_7^+ (\Delta E = 0.5 \text{ eV})$

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	-0.145153	-0.115631	-0.164453	0.46450
Pd	-0.084331	0.016013	2.970843	0.51945
Pd	2.055024	0.018104	1.417643	0.43482
Pd	0.898136	-2.431485	1.266882	0.46493
O	0.586643	-1.609320	4.023104	-0.09389
O	0.888814	-2.595891	3.252166	-0.13688
O	-0.890140	1.637888	2.016109	-0.09359
O	0.577131	-1.544296	-1.343254	-0.11534
O	-0.945338	1.472027	0.739982	-0.13687
O	1.042299	-2.565833	-0.711113	-0.11536
O	-0.052271	1.016071	4.565790	-0.19177

Pd₄O₈⁺ ($\Delta E = 0$ eV)

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	0.060307	-0.065330	-0.083312	0.51261
Pd	0.028166	-0.091836	2.797019	0.40497
Pd	2.526571	-0.014406	1.428331	0.46444
Pd	0.808951	-2.353588	1.203591	0.50458
O	-1.308574	-0.599741	1.335357	-0.28090
O	-1.215894	-1.967075	1.368200	-0.22863
O	1.633640	0.284024	-1.262590	-0.11181
O	2.716994	0.165255	-0.572848	-0.13636
O	2.659428	0.033523	3.422705	-0.12231
O	1.556126	0.158998	4.078205	-0.11388
O	-1.301183	0.994970	5.393032	0.13234
O	-1.548430	0.602973	4.276907	-0.02505

Pd₅O₃⁺ ($\Delta E = 0.3$ eV)

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	0.612161	-0.260890	0.802365	0.57066
Pd	-2.427063	1.394777	2.194774	0.74247
Pd	3.200279	0.252012	1.295909	0.59734
Pd	1.296532	1.849907	2.318599	0.57527
O	-0.493914	1.056035	1.848707	-0.84831
O	2.230757	-1.178131	0.346233	-0.48613
Pd	1.864783	1.863268	-0.340441	0.33514
O	3.200651	1.808552	2.506521	-0.48644

Pd₅O₄⁺ ($\Delta E = 0$ eV)

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	-0.145497	-0.132114	-0.128907	0.75476
Pd	-0.173632	-0.188114	2.733186	0.75175
Pd	2.756878	0.004342	-0.089638	0.71313
Pd	2.722807	-0.039231	2.778092	0.71146
Pd	1.200176	1.676832	1.347245	0.12919
O	4.040090	0.028577	1.359572	-0.45999
O	1.309508	-0.129716	-1.355110	-0.51235
O	-1.408926	-0.250160	1.288078	-0.58021
O	1.241989	-0.161199	4.008148	-0.50773

$\text{Pd}_5\text{O}_4^+(\Delta E = 0.4 \text{ eV})$

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
O	-0.128349	0.113462	0.140726	-0.18609
Pd	1.925061	0.009449	-0.015214	0.46750
Pd	0.397790	2.025536	-0.457293	0.31817
O	0.185620	1.537098	2.721528	-0.28923
Pd	3.381177	2.899887	-0.941262	0.42243
O	1.569038	3.464942	-0.872234	-0.28789
Pd	1.862445	1.772566	1.849762	0.31959
O	3.327583	1.452275	0.423179	-0.18850
Pd	-0.784457	0.062015	2.013118	0.42404

$\text{Pd}_5\text{O}_5^+(\Delta E = 0 \text{ eV})$

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	0.112882	0.054726	-0.069779	0.77733
Pd	0.112882	-0.143541	3.000929	0.64185
Pd	2.853057	0.056976	-0.113958	0.74593
Pd	3.078382	-0.126489	2.955380	0.65095
Pd	1.505377	1.630937	1.653390	0.09303
O	4.053142	-0.267668	1.316279	-0.50502
O	1.450443	0.278383	-1.377497	-0.56908
O	-1.007889	-0.317705	1.390493	-0.54451
O	2.226076	0.028429	4.757867	-0.14505
O	0.936756	0.052217	4.792716	-0.14543

$\text{Pd}_5\text{O}_5^+(\Delta E = 0.4 \text{ eV})$

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	-1.721046	-1.171474	-1.242826	1.06711
O	-1.824295	-0.863647	0.923668	-0.20992
O	0.338693	-0.853602	-0.777312	-0.13865
Pd	0.185256	-0.941968	1.209165	0.35846
Pd	0.378185	1.131105	-0.979409	0.35859
Pd	-2.399139	0.997880	0.700732	0.37734
O	2.307974	1.202618	-0.801647	-0.45059
O	-1.645207	1.009830	-1.107200	-0.21512
O	2.110915	-0.959196	1.442677	-0.45558
Pd	3.217800	0.152441	0.437052	0.30836

Pd₅O₆⁺ ($\Delta E = 0$ eV)

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	-0.035954	-0.122635	-0.304742	0.65181
Pd	0.063146	-0.017476	2.993002	0.62260
Pd	2.634549	-0.085262	-0.158324	0.58930
Pd	2.781151	0.002521	3.049472	0.61763
Pd	1.497790	-1.773731	1.503593	0.17726
O	-0.736534	0.523471	1.340774	-0.49218
O	0.740174	-0.577662	4.798982	-0.15434
O	2.034914	-0.506096	4.874862	-0.13614
O	3.534860	0.496330	1.381716	-0.60718
O	1.983891	-0.817803	-1.978045	-0.13069
O	0.691868	-0.800079	-2.029316	-0.13806

Pd₅O₆⁺ ($\Delta E = 0.8$ eV)

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	-0.195242	-0.069926	-0.425109	0.95430
O	1.840417	-0.209862	-0.087817	-0.40894
O	0.321720	1.977140	-0.010120	-0.57676
O	-2.011209	0.221389	-0.913931	-0.58243
Pd	2.056008	1.487651	0.815153	0.88282
Pd	-3.054918	1.573286	-0.114515	0.86098
Pd	-0.322675	2.690354	1.751863	0.80742
Pd	-1.903154	0.083669	2.510098	0.82020
O	-2.154005	1.865554	1.640809	-0.77570
O	1.587272	3.069199	1.971182	-0.43370
O	-0.556973	-0.695350	1.417553	-0.54819

Pd₅O₇⁺ ($\Delta E = 0$ eV)

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	-0.349169	-0.522948	-0.288593	0.48856
Pd	0.495958	0.213729	2.390786	0.27898
Pd	2.929380	-0.095245	-0.078811	0.63312
Pd	2.960325	-0.180656	3.124348	0.53188
Pd	1.479188	-1.881449	1.209865	0.25403
O	-1.846021	-0.428584	1.034521	-0.12537
O	-1.596940	0.040203	2.197814	-0.09952
O	0.574275	-0.118279	4.456713	-0.07163
O	1.782778	-0.383389	4.786749	-0.11839
O	3.921104	0.190479	1.513913	-0.48946
O	2.080653	-0.348156	-1.851987	-0.14122
O	0.820395	-0.586818	-1.933395	-0.14098

$\text{Pd}_5\text{O}_7^+ (\Delta E = 1.8 \text{ eV})$

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	-0.243529	-0.023827	0.657288	0.45320
Pd	2.995978	-0.080025	-0.400293	0.24587
O	1.431568	0.785324	0.180738	-0.57205
O	-0.383991	-1.447637	-0.625950	-0.00792
O	3.413479	-1.238946	1.082496	-0.23046
Pd	0.963056	-2.539205	-1.346218	0.64127
O	2.312472	-3.002859	-2.676353	-0.19385
Pd	3.489355	-3.110449	0.685527	0.74550
O	1.691750	-3.477549	0.173616	-0.12058
Pd	4.104902	-2.589318	-2.277070	0.53700
O	4.216583	-0.775839	-1.754519	-0.39277
O	4.668880	-3.664434	-0.859950	-0.10522

$\text{Pd}_5\text{O}_8^+ (\Delta E = 0 \text{ eV})$

Element	Coordinates (Angstroms)			Charges
	X	Y	Z	
Pd	0.411806	-0.144797	-0.434372	0.36613
Pd	-0.302799	0.214553	2.213751	0.18847
Pd	2.444605	0.068791	1.455942	0.47363
Pd	0.714696	-2.242634	1.178380	0.35661
Pd	-1.891425	-1.661863	1.397753	0.41108
O	2.599829	-2.628411	0.686638	-0.07465
O	3.329828	-1.579406	0.698707	-0.10681
O	-1.213145	-1.006449	-1.376902	-0.09355
O	-1.956143	-1.756107	-0.655095	-0.13169
O	-2.124907	-1.353073	3.396312	-0.11703
O	-1.547733	-0.276797	3.799704	-0.06673
O	1.872276	1.780690	2.388367	-0.13691
O	0.751261	1.798965	3.015619	-0.06855

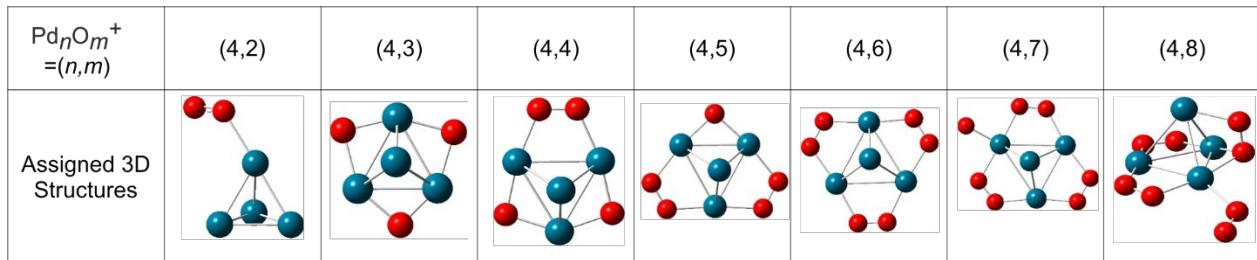


Figure S2. An enlarged figure for all assigned/selected 3D structures of Pd_4O_m^+ ($m = 2-8$) containing Pd_4 -tetrahedral metal-core configuration.

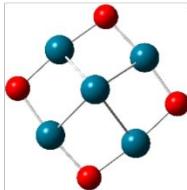
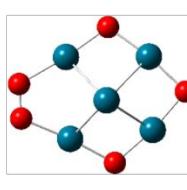
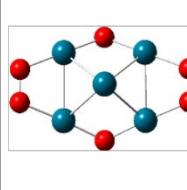
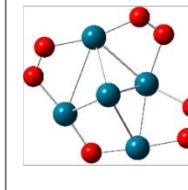
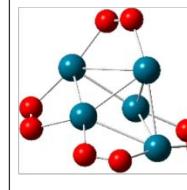
Pd_nO_m^+ $= (n,m)$	(5,4)	(5,5)	(5,6)	(5,7)	(5,8)
Assigned 3D Structures					

Figure S3. An enlarged figure for all assigned/selected 3D structures of Pd_5O_m^+ ($m = 4-8$) containing Pd_5 -square pyramidal metal-core configuration.