Pure and Zn-Doped Pt Clusters Go Flat and Upright on MgO(100)

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Supporting Information

Table S1. Relative energies (in eV) of the lowest energy isomers of Pt_5^- and Pt_4Zn^- in the gas phase calculated with various levels of theory. Showing that the PW-DFT results are reliable and produce results consistent with different levels of theory. Labels are as in the main text. Black – UTPSSh/aug-cc-pvTZ+pp, red – MP2/aug-cc-pvTZ. Note that all structures with relative energies computed were found to have fairly clean single-reference wave functions with the HF Slater contributing 0.9 of higher into the CASSCF(m,n)/LANL2DZ expansions. Thus, single reference methods are reliable.*

	Pt_5	**Pt_5^-**	**Pt_4Zn**	**Pt_4Zn^-**
D_{3h}, 5	0 0	-	-	-
C_s, 3	-	-	0.2329 1.1142	-
C_{4v}, 5	-	0 0	-	-
C_{2v}, 6	-	-	-	0.1146 0.4451
C_{2v}, 5	0.0499 0.9156	-	0 0	-
C_{2v}, 4	-	-	-	0 0
C_{2v}, 2	-	0.1448 0.2998	-	-

* Some isomers do not exist at higher levels of theory. For example, the **C_s, 4** structure of Pt_4Zn^- (from Figure 3, main text) rearranges into structure **C_{2v}, 4** when anything other than PW-DFT is used. For this reason, this species is not reported in Table S1. All other isomers found via GEGA were at least ~1 eV higher in energy than the most stable isomers that reported in this Table, and therefore they were considered not competitive and not of further interest.

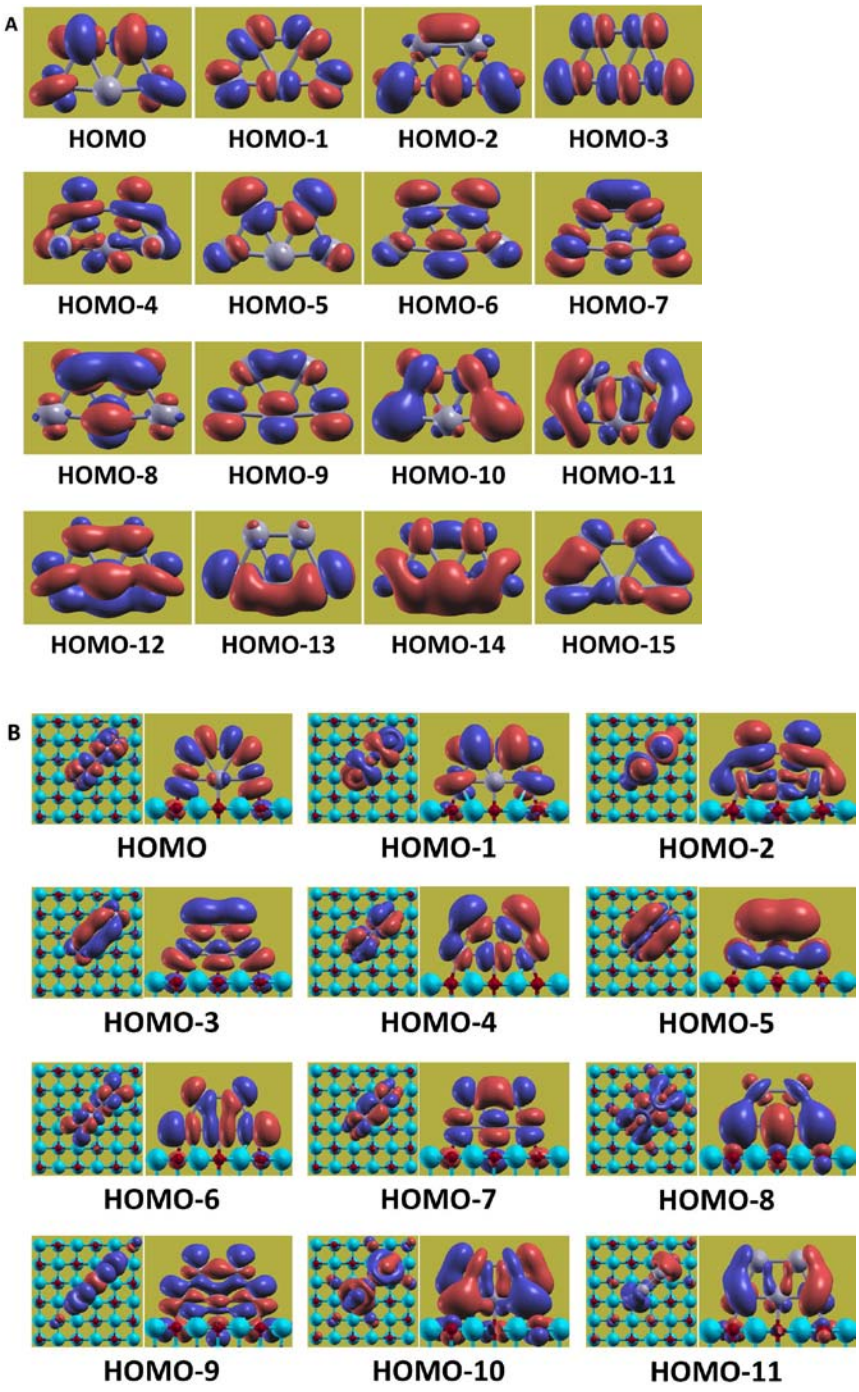

Figure S2. Valence MOs of the Pt_5^- cluster in the gas phase (A) and on MgO(100) (B) – top and side views are shown. The two sets of MOs are strikingly similar, indicating that the surface does not strongly disrupt in the intra-cluster bonding.

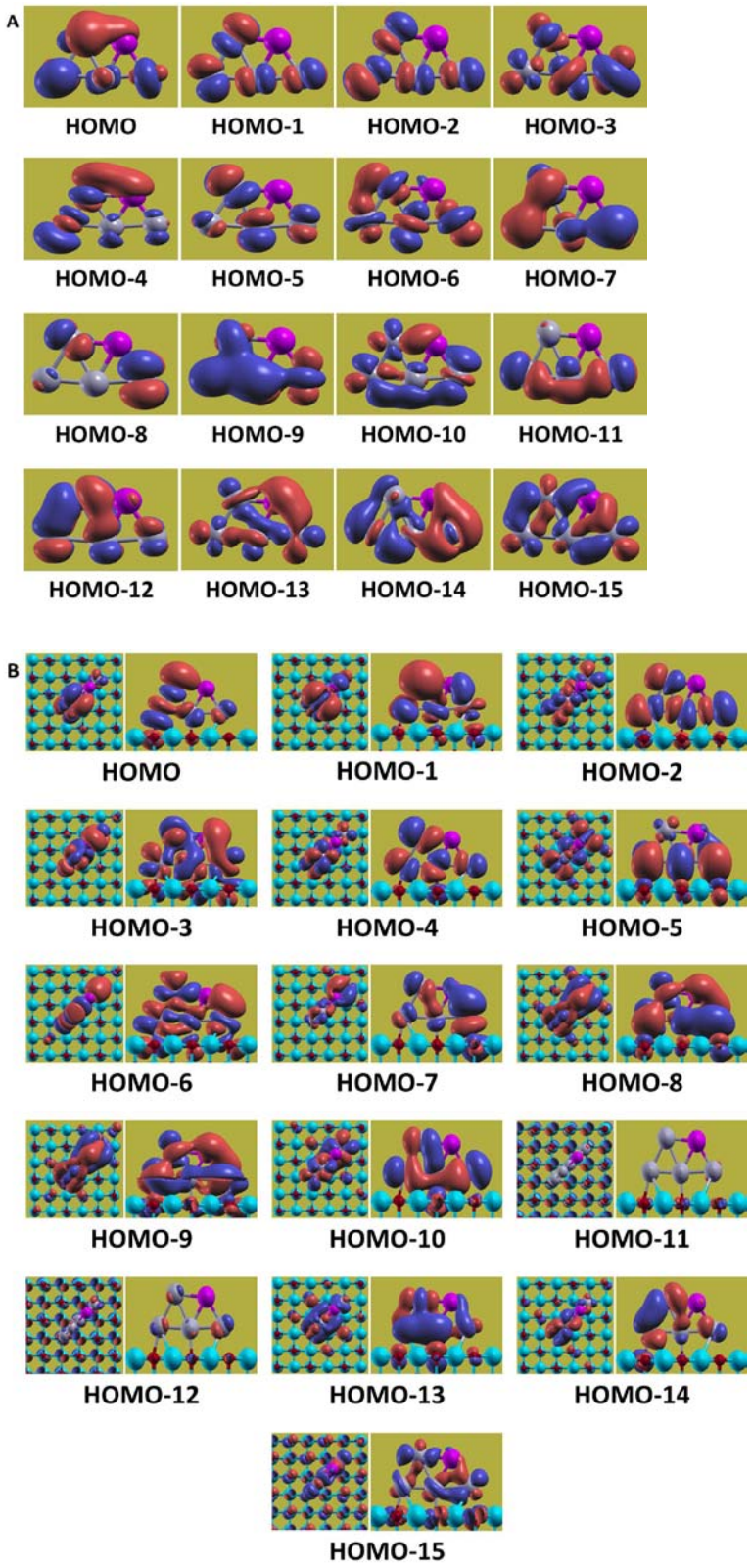

Figure S3. Valence MOs of the Pt_4Zn^- cluster in the gas phase (A) and on MgO(100) (B) – top and side views are shown. Again the two sets of MOs show a strong resemblance, indicating that the surface minimally interferes with intra-cluster bonding.

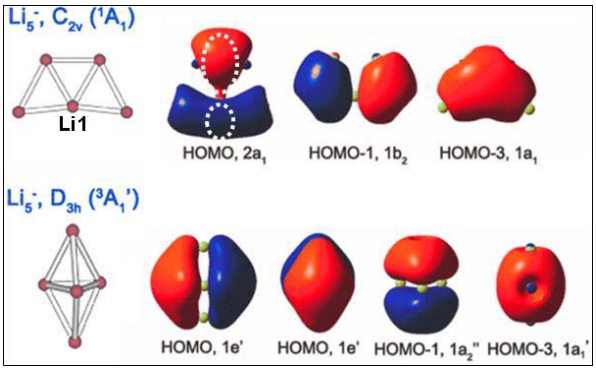

Figure S4. Two of the lowest energy isomers of Li_5^- and their valence MOs. The contribution of the 2p-AO in the flat cluster is outlined with the white dotted line (see refs. 60, 61, main text.