Electronic Supplementary Information

Structure and bonding of [Pd2Sn18]4-: an interesting example of the mutual delocalisation phenomenon

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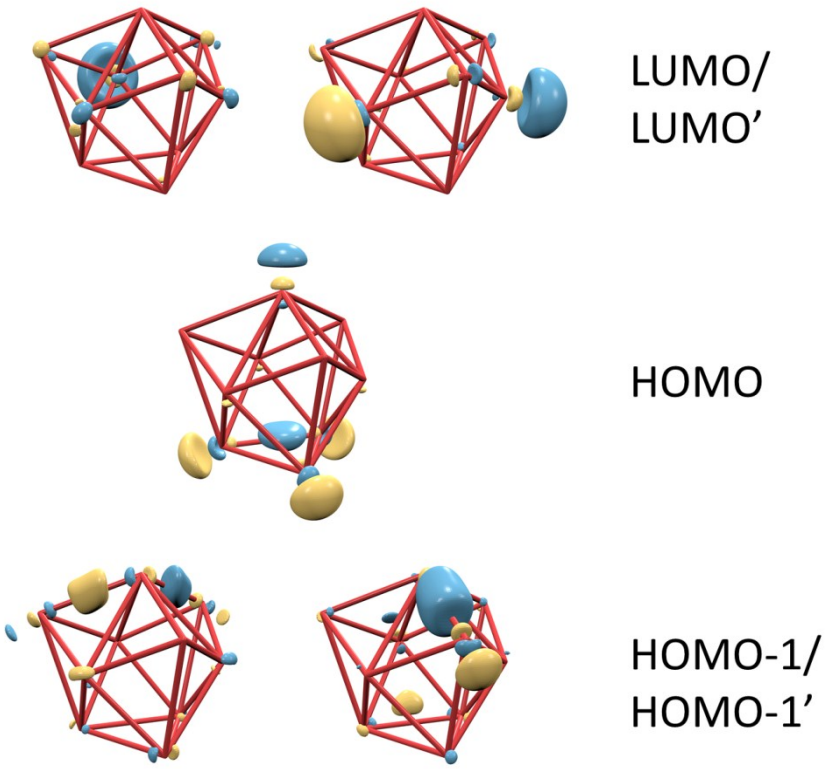

Figure S1. Frontier orbitals of $[Sn_{10}]^0$, note that the LUMOs are degenerated, meaning that a singlet $[Sn_{10}]^{2-}$ as predicted by the Wade-Mingos rule is unlikely.

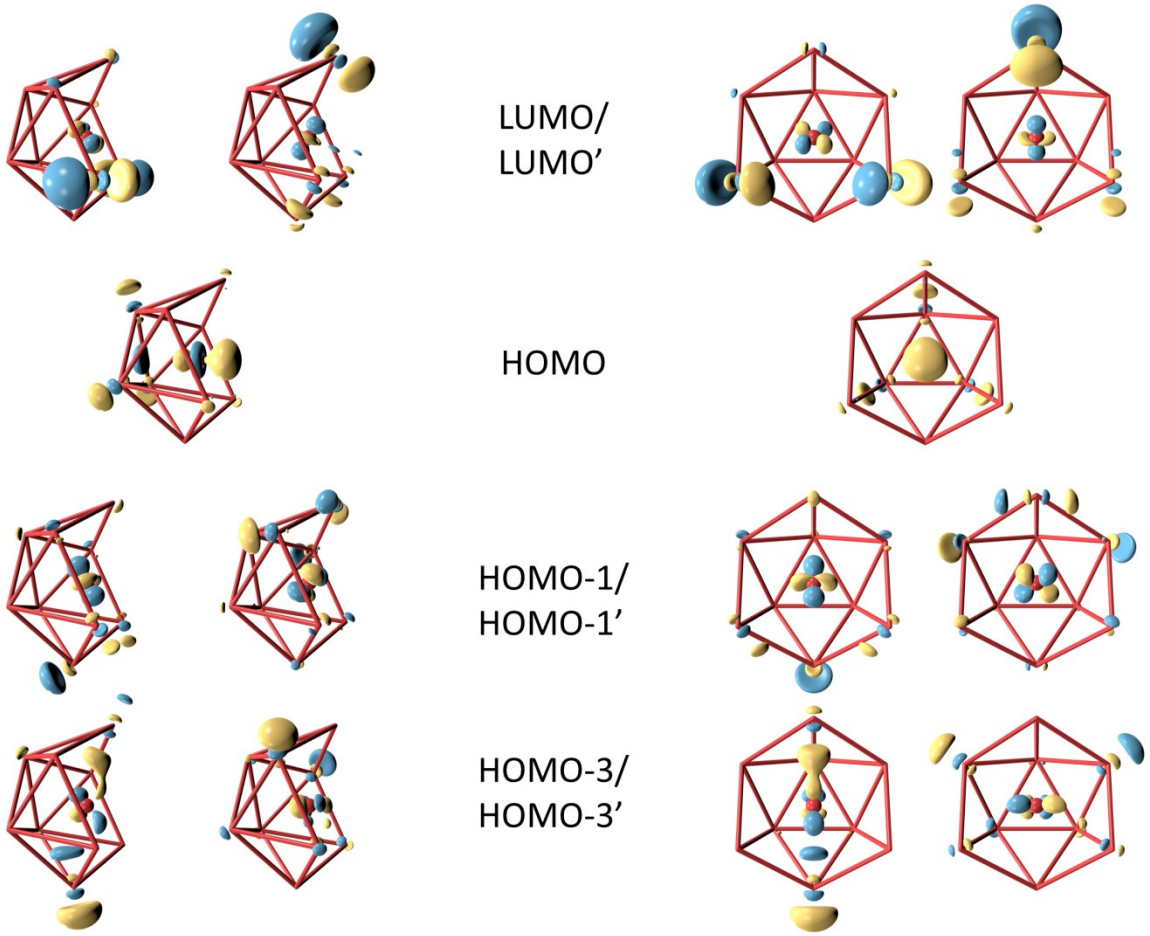

Figure S2. Frontier orbitals of unoptimised *iso-nido*-$[Pd@Sn_9]^{2-}$ fragment based on the optimised geometry of $[Pd_2@Sn_{18}]^{4-}$ same as Fig. 1, with top view included to better illustrate the orbital symmetries.

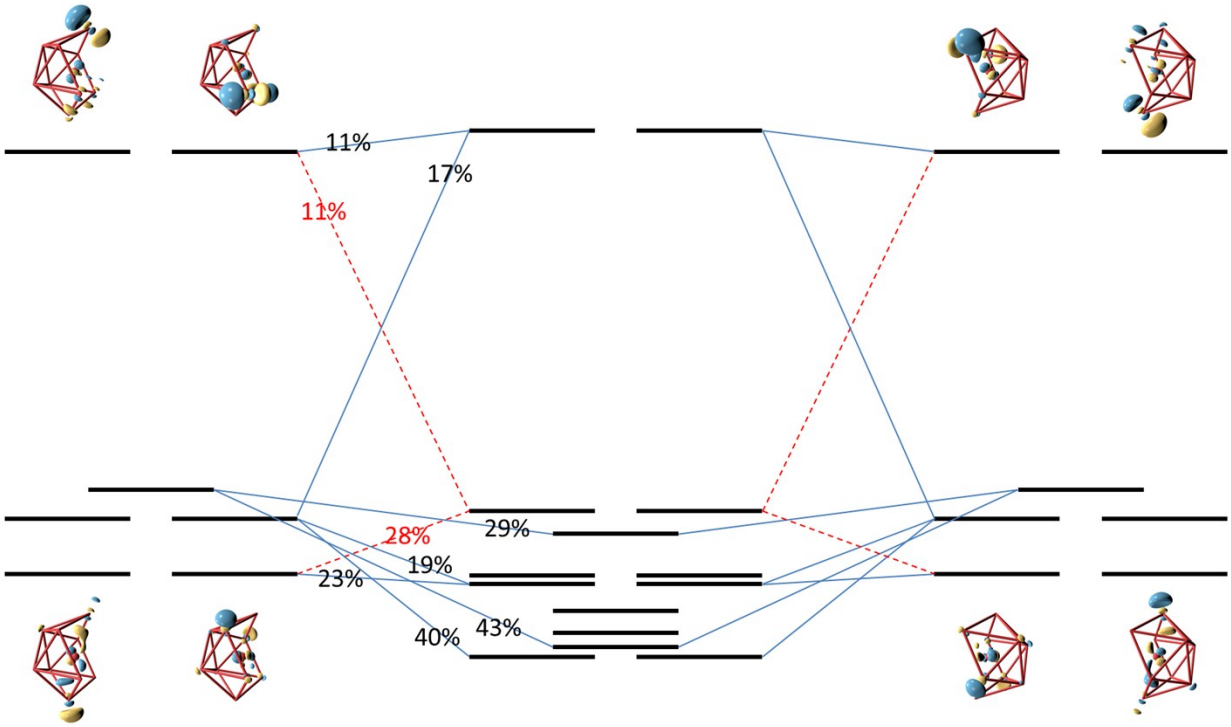

Figure S3. Fragment analysis of $[Pd_2Sn_{18}]^{4-}$. Prominent orbital contributions (> 10%) to and molecular orbitals (HOMO-10/HOMO-10' pair to LUMO/LUMO’ pair) by fragment orbitals (HOMO-3/HOMO-3' pair to LUMO/LUMO' pair) are shown.

Cartesian coordinates of Optimised structures

$[Sn_{10}]^{0}$

Sn	0.000000	1.734107	4.020753
Sn	-1.501781	-0.867053	4.020753
Sn	1.501781	-0.867053	4.020753
Sn	-2.427198	1.401344	2.210079
Sn	0.000000	-2.802687	2.210079
Sn	2.427198	1.401344	2.210079
Sn	0.000000	2.794187	0.897596
Sn	-2.419837	-1.397094	0.897596
Sn	2.419837	-1.397094	0.897596
Sn	0.000000	-1.734107	-4.020753
Sn	1.501781	0.867053	-4.020753
Sn	-1.501781	0.867053	-4.020753
Sn	2.427198	-1.401344	-2.210079
Sn	-2.427198	-1.401344	-2.210079
Sn	0.000000	2.802687	-2.210079
Sn	0.000000	-2.794187	-0.897596
Sn	2.419837	1.397094	-0.897596
Sn	-2.419837	1.397094	-0.897596

$[Pd_2Sn_{18}]^{4-}$ (fragment 1: atom 1-10; fragment 2: atom 11-20)

Pd	0.000000	0.000000	1.806908
Sn	0.000000	1.752016	4.080608
Sn	-1.517290	-0.876008	4.080608
Sn	1.517290	-0.876008	4.080608
Sn	-2.456699	1.418376	2.224405
Sn	0.000000	-2.836751	2.224405
Sn	2.456699	1.418376	2.224405
Sn	0.000000	2.784875	0.904716
Sn	-2.411772	-1.392437	0.904716
Sn	2.411772	-1.392437	0.904716
Pd	0.000000	0.000000	-1.806908
Sn	0.000000	-1.752016	-4.080608
Sn	1.517290	0.876008	-4.080608
Sn	-1.517290	0.876008	-4.080608
Sn	2.456699	-1.418376	-2.224405
Sn	-2.456699	-1.418376	-2.224405
Sn	0.000000	2.836751	-2.224405
Sn	0.000000	-2.784875	-0.904716
Sn	2.411772	1.392437	-0.904716
Sn	-2.411772	1.392437	-0.904716

$[Ni_3Ge_{18}]^{4-}$

Ni	0.000000	0.000000	2.478720
Ge	0.000000	1.539498	4.469541
Ge	-1.333245	-0.769749	4.469541
Ge	1.333245	-0.769749	4.469541
Ge	-2.129875	1.229684	2.770728
Ge	0.000000	-2.459367	2.770728
Ge	2.129875	1.229684	2.770728
Ge	0.000000	2.104344	1.454777
Ge	-1.822416	-1.052172	1.454777
Ge	1.822416	-1.052172	1.454777
Ni	0.000000	0.000000	-2.478720
Ge	0.000000	-1.539498	-4.469541
Ge	1.333245	0.769749	-4.469541
Ge	-1.333245	0.769749	-4.469541
Ge	2.129875	-1.229684	-2.770728
Ge	0.000000	2.459367	-2.770728
Ge	-2.129875	-1.229684	-2.770728
Ge	0.000000	-2.104344	-1.454777
Ge	1.822416	1.052172	-1.454777
Ge	-1.822416	1.052172	-1.454777
Ni	0.000000	0.000000	0.000000

$[Ge_{18}(SiH_3)_6]^0$ (fragment 1: atom 1 to 21; fragment 2: atom 22 to 42)

Ge	1.454191	-4.234767	0.000000
Ge	-0.809336	-4.282247	1.289510
Ge	-0.809336	-4.282247	-1.289510
Ge	0.972707	-2.389495	1.822897
Ge	0.972707	-2.389495	-1.822897
Ge	-2.111295	-2.370291	0.000000
Ge	-1.365949	-1.479558	-2.303210
Ge	2.500347	-1.401750	0.000000
Ge	-1.365949	-1.479558	2.303210
Si	2.184645	-3.073303	3.770148
H	2.607336	-1.881575	4.557703
H	3.403904	-3.835414	3.386354
H	1.334164	-3.930486	4.639925
Si	2.184645	-3.073303	-3.770148
H	2.607336	-1.881575	-4.557703
H	1.334164	-3.930486	-4.639925
H	3.403904	-3.835414	-3.386354
Si	-4.414944	-3.028730	0.000000
H	-5.292953	-1.824928	0.000000
H	-4.732997	-3.835086	1.209934
H	-4.732997	-3.835086	-1.209934
Ge	1.274186	0.842082	0.000000
Ge	-0.920579	0.883518	1.293618
Ge	-0.920579	0.883518	-1.293618
Ge	0.938485	2.611042	2.162917
Ge	-1.376523	3.331271	1.235001
Ge	-1.376523	3.331271	-1.235001
Ge	0.938485	2.611042	-2.162917
Ge	2.233351	3.145415	0.000000
Ge	0.412278	4.831384	0.000000
Si	-2.865534	4.593254	2.588910
H	-2.846201	6.004204	2.126735
H	-2.418757	4.510389	4.001461
H	-4.235781	4.038336	2.457501
Si	-2.865534	4.593254	-2.588910
H	-2.846201	6.004204	-2.126735
H	-4.235781	4.038336	-2.457501
H	-2.418757	4.510389	-4.001461
Si	4.589583	3.423382	0.000000
H	5.227074	2.084167	0.000000
H	4.980563	4.179987	1.215329
H	4.980563	4.179987	-1.215329