Supporting Information for:

Ligand-Free Supermolecules. $[Pd_2@Ge_{18}]^{4-}$ and $[Pd_2@Sn_{18}]^{4-}$ as Single Bonded Zintl-Ions Cluster Based on Pd@Ge$_9$ and Pd@Sn$_9$ Assembled Units

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Content

Figure S1. Isosurface for superatomic shells of *closo*-$[Pd@Sn_{12}]^{2-}$ accounting for the 50 cage and 10 4d-Pd electrons, given by $1S^2 1P^6 1D^{10} 1F^{14} (4d\text{-}Pd)^{10} 2S^2 2P^6 1G^{10}$ shell structure.
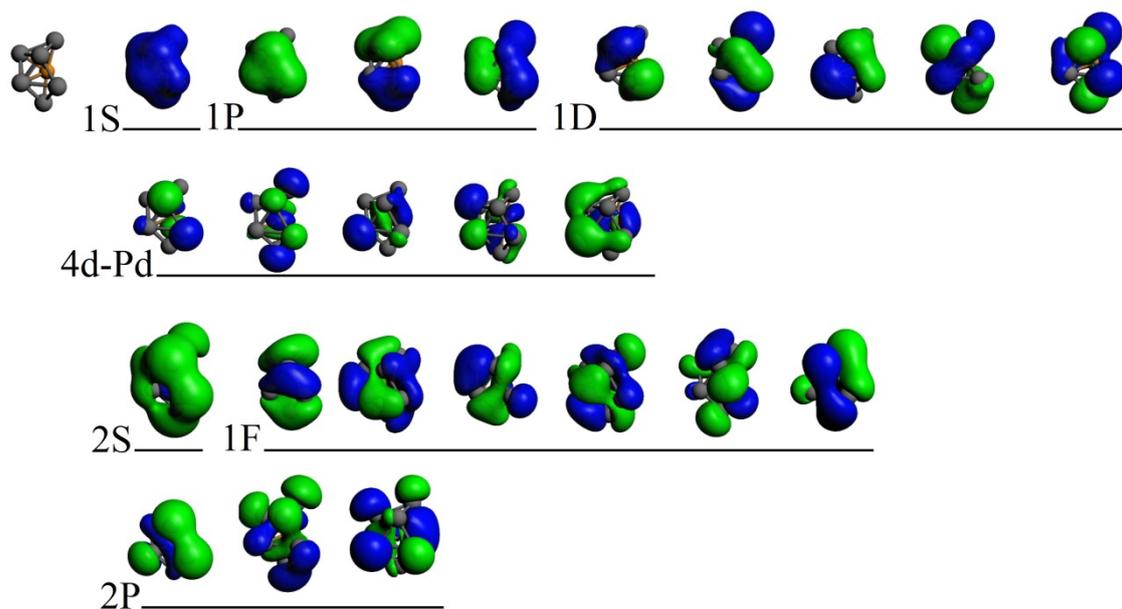
Figure S2. Isosurface for superatomic shells of the $[Pd@Sn_9]^{2-}$ unit at the structure given by the overall $[Pd_2@Sn_{18}]^{4-}$ cluster.

1S+1S   1P+1P   1D+1D

1S-1S   1P-1P   1D-1D

4d-Pd+4d-Pd

4d-Pd-4d-Pd

1F+1F

1F-1F

2S+2S   2P+2P

2S-2S   2P-2P

1G+1G

1G-1G

Figure S3. Isosurface for the bonding or in-phase (+) combinations, and, antibonding or out-of phase combinations (-) between the two $[Pd@Sn_9]^{2-}$ motifs within the $[Pd_2@Sn_{18}]^{4-}$ oblate cluster.

Table S1. Energy decomposition analysis (EDA) for Pd/[Pd@E$_{18}$]$^{4-}$ and Pd/[@E$_{12}$]$^{2-}$ interaction, denoting the individual contribution from relevant deformation density channels. Values in kcal/mol.
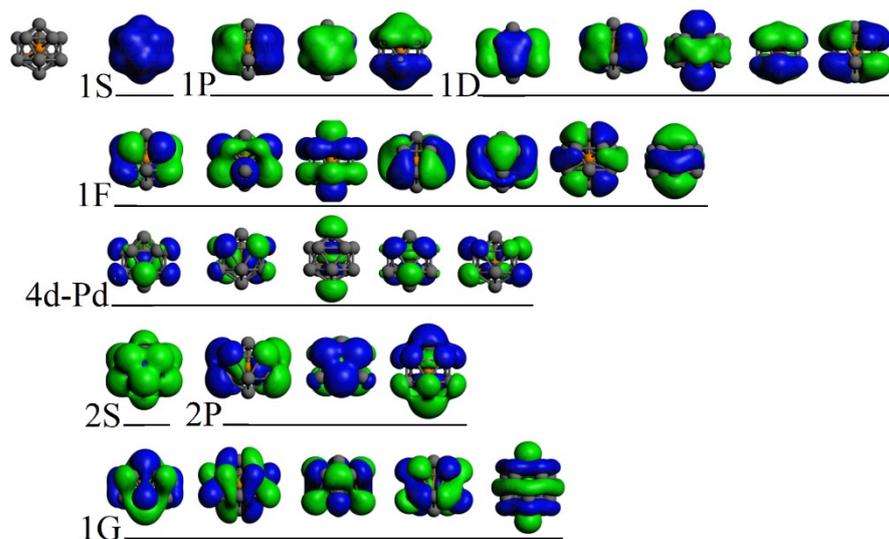
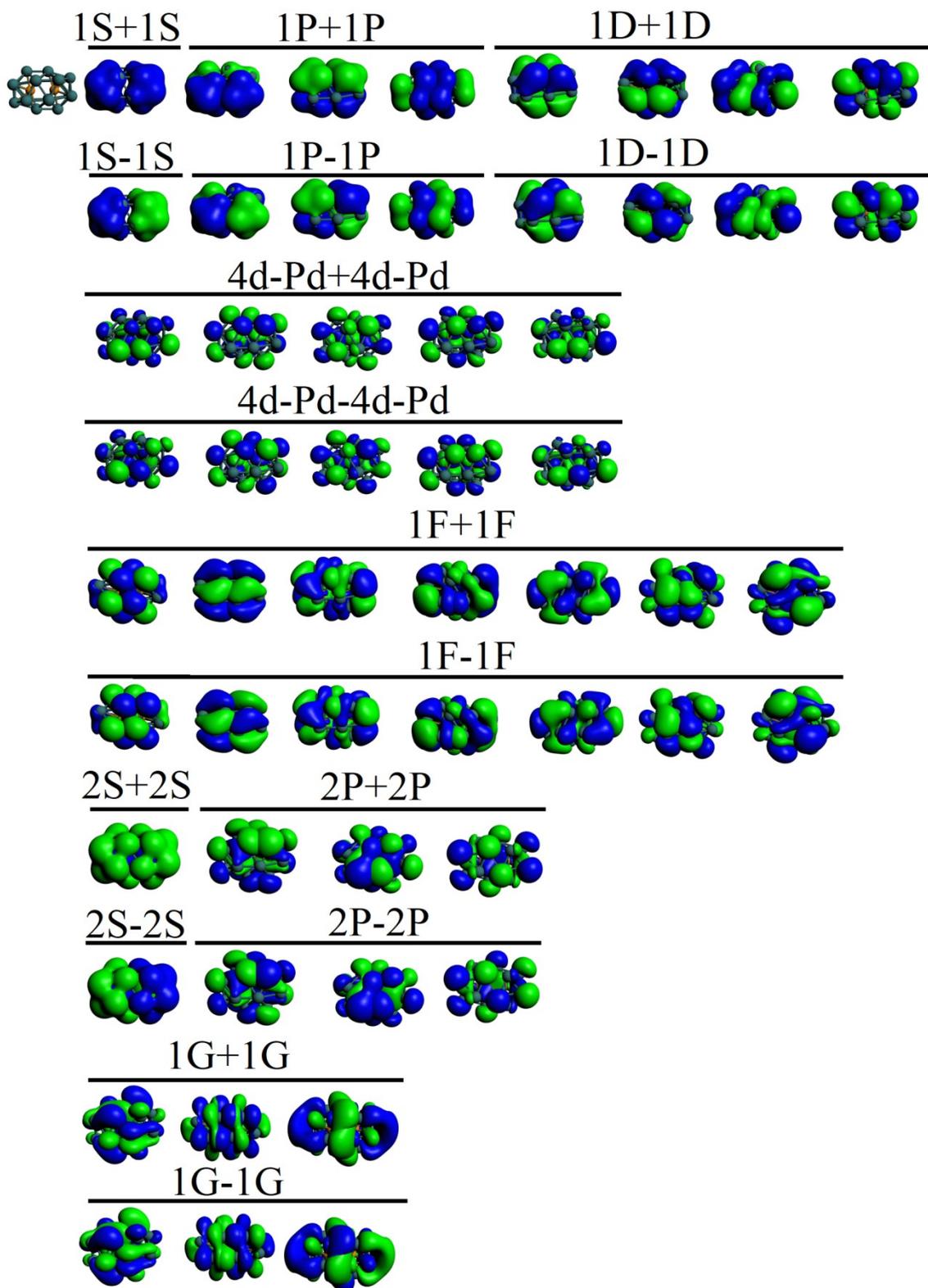|	E=Ge		E=Sn	
Pd/[Pd@E$_{18}$]$^{4-}$				
ΔE_{Pauli}	334.9		278.3	
$\Delta E_{elestat}$	-307.6	68.0%	-277.8	70.2%
ΔE_{orb}	-137.8	30.5%	-109.8	27.7%
ΔE_{disp}	-6.8	1.5%	-8.2	2.1%
ΔE_{int}	-117.3		-117.6	
$\Delta\rho_1$	-31.7	23.0%	-23.9	21.8%
$\Delta\rho_2$	-31.7	23.0%	-23.9	21.8%
$\Delta\rho_3$	-23.4	17.0%	-12.0	10.9%
$\Delta\rho_4$	-18.0	13.1%	-14.0	12.8%
$\Delta\rho_5$	-18.0	13.1%	-12.7	11.6%
$\Delta\rho_6$	-7.2	5.2%	-12.7	11.6%
Endo				
Pd/[E$_{12}$]$^{2-}$				
ΔE_{Pauli}	424.1		303.7	
$\Delta E_{elestat}$	-369.5	69.5%	-293.1	69.5%
ΔE_{orb}	-157.6	29.7%	-122.7	29.1%
ΔE_{disp}	-4.3	0.8%	-6.1	1.4%
ΔE_{int}	-107.3		-118.1	
$\Delta\rho_1$	-32.6	20.7%	-21.4	17.5%
$\Delta\rho_2$	-29.8	18.9%	-19.6	16.0%
$\Delta\rho_3$	-29.8	18.9%	-19.6	16.0%
$\Delta\rho_4$	-27.5	17.5%	-18.3	14.9%
$\Delta\rho_5$	-27.5	17.5%	-18.3	14.9%
$\Delta\rho_6$	-5.0	3.2%	-15.0	12.2%
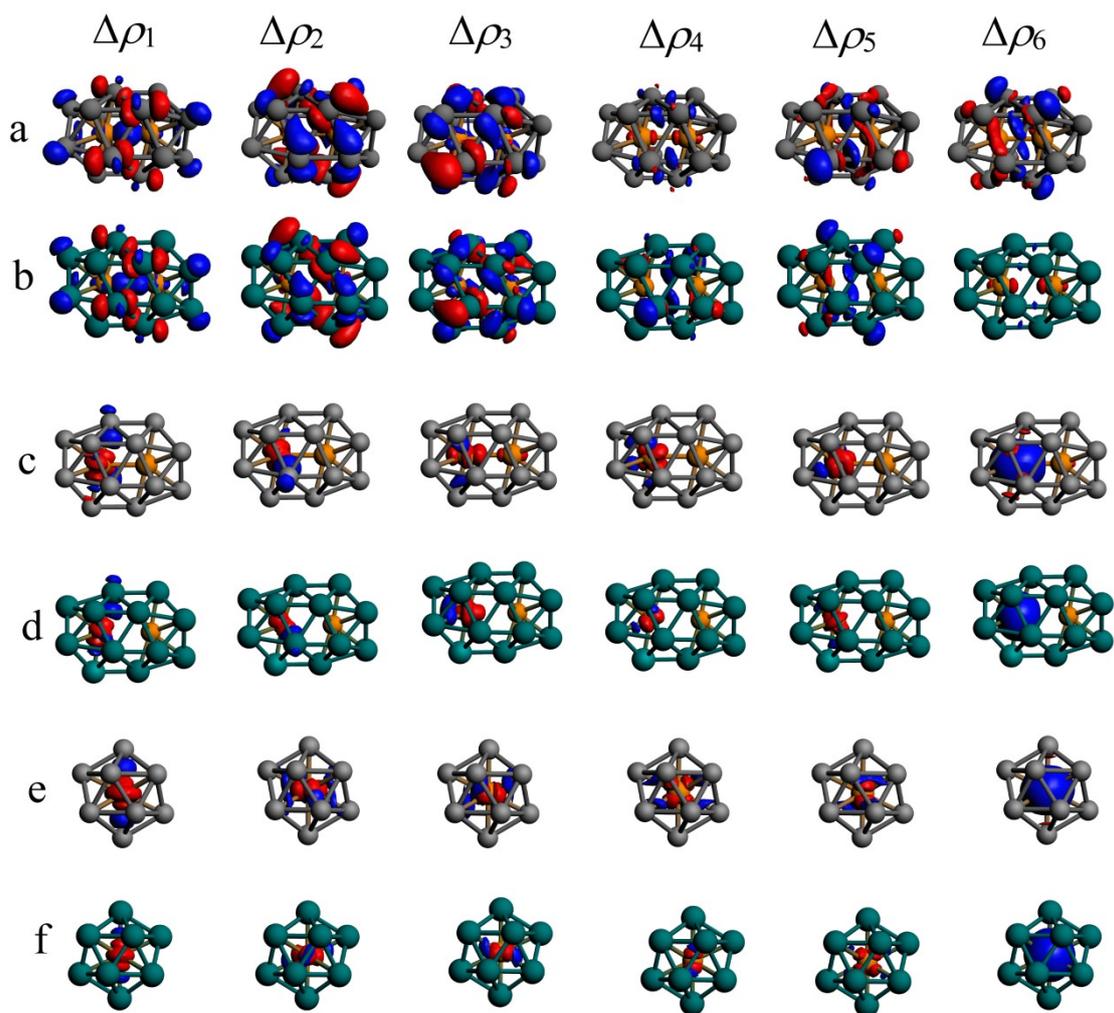
Figure S4. Isosurface for the individual deformation densities ($\Delta\rho_n$) related to the interaction between $[Pd@Ge_9]^{2-}/[Pd@Ge_9]^{2-}$ (a), $[Pd@Sn_9]^{2-}/[Pd@Sn_9]^{2-}$ (b), $Pd/[Pd@Ge_{18}]^{4-}$ (c), $Pd/[Pd@Sn_{18}]^{4-}$ (d), $Pd/[Ge_{12}]^{2-}$ (e), $Pd/[Sn_{12}]^{2-}$ (e).

Figure S5. Contour-plot representation for magnetic response properties under different orientations of the external field (B_z^{ind}, B_x^{ind}, and B_y^{ind}) and their isotropic (averaged) term (NICS), for: $[Pd@Ge_{12}]^{2-}$ (a), $[Pd_2@Ge_{18}]^{4-}$ (b), $[Pd@Sn_{12}]^{2-}$ (c), $[Pd_2@Sn_{18}]^{4-}$ (d). Color bar between -5.0 to 5.0 ppm, positive values means shielding; negative values means deshielding.

Table S2. Energy decomposition analysis (EDA) at the hybrid TZ2P/PBE0 level of theory for $[Pd@E_9]^{2-}/[Pd@E_9]^{2-}$ interaction from homolytic fragmentation ($^5[Pd@E_9]^{2-}/^5[Pd@E_9]^{2-}$), denoting the individual contribution from relevant deformation density channels. Values in kcal/mol.
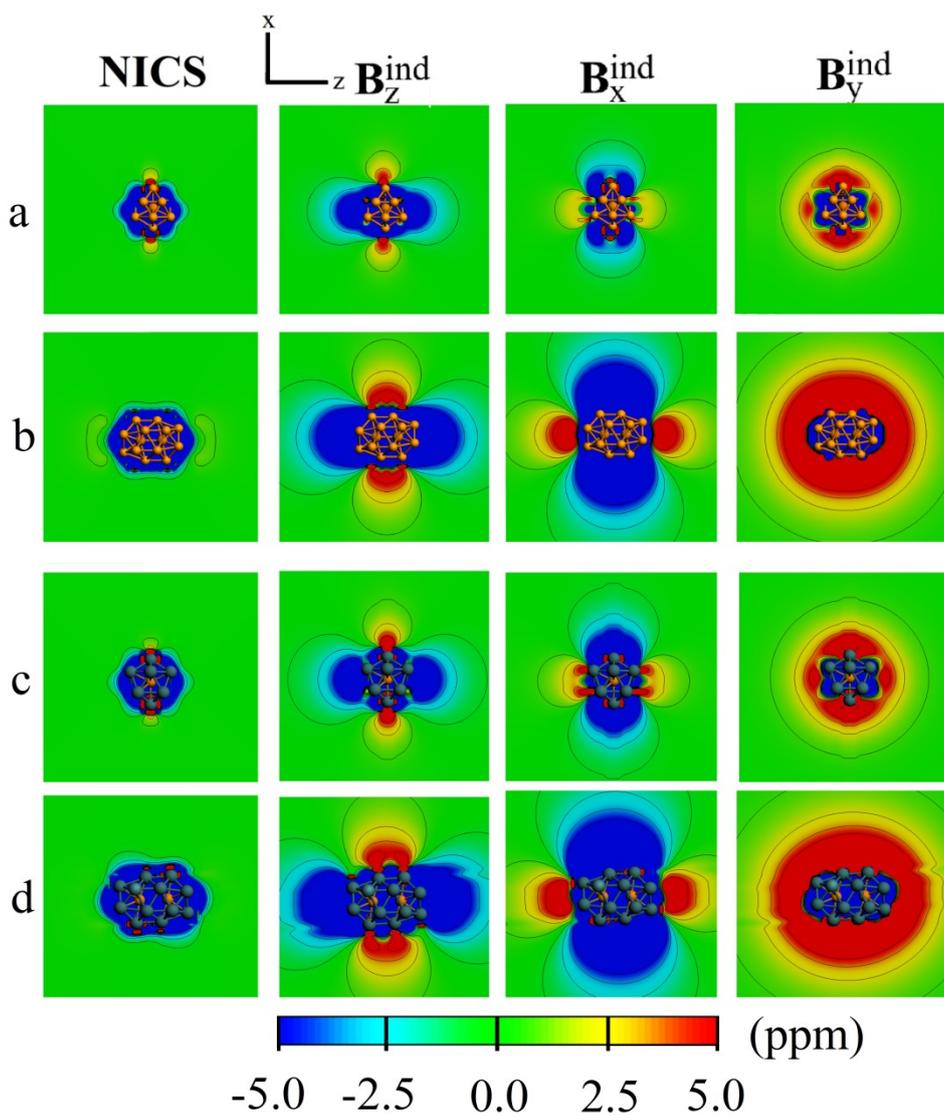
	$[Pd_2@Ge_{18}]^{4-}$		$[Pd_2@Sn_{18}]^{4-}$	
ΔE_{Pauli}	512.1		481.1	
$\Delta E_{elestat}$	-176.3	21.3%	-176.1	24.6%
ΔE_{orb}	-629.8	76.2%	-521.0	72.9%
ΔE_{disp}	-20.4	2.5%	-17.7	2.5%
ΔE_{int}	-314.4		-233.7	
$\Delta \rho_1$	-92.0	14.6%	-100.1	19.2%
$\Delta \rho_2$	-92.0	14.6%	-76.8	14.7%
$\Delta \rho_3$	-102.1	16.2%	-76.8	14.7%
$\Delta \rho_4$	-40.7	6.5%	-27.7	5.3%
$\Delta \rho_5$	-34.2	5.4%	-27.7	5.3%
$\Delta \rho_6$	-34.3	5.4%	-26.3	5.1%

Table S3. Energy decomposition analysis (EDA) at the at the hybrid TZ2P/PBE0 level of theory for Pd/[Pd@E_{18}]$^{4-}$ and Pd/[@E_{12}]$^{2-}$ interaction, denoting the individual contribution from relevant deformation density channels. Values in kcal/mol.

	E=Ge		E=Sn	
Pd/[Pd@E_{18}]$^{4-}$				
ΔE_{Pauli}	328.3		257.4	
$\Delta E_{elestat}$	-307.9	66.6%	-262.7	68.3%
ΔE_{orb}	-147.7	31.9%	-113.9	29.6%
ΔE_{disp}	-6.8	1.5%	-8.2	2.1%
ΔE_{int}	-134.2		-127.4	
$\Delta\rho_1$	-31.7	21.5%	-23.9	21.0%
$\Delta\rho_2$	-31.7	21.5%	-23.9	21.0%
$\Delta\rho_3$	-23.4	15.9%	-12.0	10.5%
$\Delta\rho_4$	-18.0	12.2%	-14.0	12.3%
$\Delta\rho_5$	-18.0	12.2%	-12.7	11.1%
$\Delta\rho_6$	-7.2	4.9%	-12.7	11.1%
Endo				
Pd/[E_{12}]$^{2-}$				
ΔE_{Pauli}	415.7		280.9	
$\Delta E_{elestat}$	-369.8	68.1%	-277.1	67.5%
ΔE_{orb}	-169.0	31.1%	-127.2	31.0%
ΔE_{disp}	-4.3	0.8%	-6.1	1.5%
ΔE_{int}	-122.8		-128.0	
$\Delta\rho_1$	-32.6	19.3%	-21.4	16.8%
$\Delta\rho_2$	-29.8	17.7%	-19.6	15.4%
$\Delta\rho_3$	-29.8	17.7%	-19.6	15.4%
$\Delta\rho_4$	-27.5	16.3%	-18.3	14.4%
$\Delta\rho_5$	-27.5	16.3%	-18.3	14.4%
$\Delta\rho_6$	-5.0	3.0%	-15.0	11.8%