Supplementary Information for:

Exploring the stability and aromaticity of rare earth doped tin cluster MSn_{16}^- (M = Sc, Y, La)

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Table S1. Calculated relative energy and HOMO-LUMO gaps of MSn_{16}^- (M = Sc, Y, La) clusters obtained by using Scalar (SR) and Spin Orbit (SO) approach as obtained at PBE0/Sc/def2-TZVP//Y/dhf-TZVP-2c//La/ECP28WMB//Sn/dhf-TZVP-2c level. (All energies are in eV)

Clusters	SO		SR	
	ΔE	Gap	ΔE	Gap
$ScSn_{16}^-$ -I	0.00	2.39	0.00	2.52
$ScSn_{16}^-$ -II	0.79	1.73	0.82	1.65
$ScSn_{16}^-$ -III	1.28	2.16	1.27	2.21
YSn_{16}^- -I	0.00	2.48	0.00	2.61
YSn_{16}^- -II	0.66	1.79	0.69	1.71
YSn_{16}^- -III	1.41	2.14	1.40	2.23
$LaSn_{16}^-$ -I	0.00	2.49	0.00	2.63
$LaSn_{16}^-$ -II	0.76	1.83	0.79	1.75
$LaSn_{16}^-$ -III	1.80	2.06	1.79	2.16

Table S2. The relative energy of a few low-lying energy isomers of MSn_{16}^- (M = Sc, Y, La) obtained at five different methods.

Clusters	PBE0	PBE	B3PW91	B3LYP	DLPNO-CCSD(T)
$ScSn_{16}^-$ - I	0.00	0.00	0.00	0.00	0.00
$ScSn_{16}^-$ - II	0.82	0.70	0.73	0.51	0.70
$ScSn_{16}^-$ - III	1.27	1.17	1.18	0.95	1.15
YSn_{16}^- - I	0.00	0.00	0.00	0.00	0.00
YSn_{16}^- - II	0.70	0.57	0.61	0.38	0.64
YSn_{16}^- - III	1.41	1.28	1.31	1.08	1.37
$LaSn_{16}^-$ - I	0.00	0.00	0.00	0.00	0.00
$LaSn_{16}^-$ - II	0.77	0.48	0.60	0.14	0.85
$LaSn_{16}^-$ - III	1.79	1.46	1.61	1.13	1.84

Table S3. Calculated Cartesian coordinates for the low-lying energy isomers of MSn_{16}^- (M = Sc, Y, La) clusters at PBE0/def2-TZVP level.

$ScSn_{16}^-$-I

Element	X	Y	Z
Sn	1.028905	3.143169	1.028905
Sn	1.822917	-1.822917	1.822917
Sn	-1.028905	-3.143169	1.028905
Sn	1.028905	1.028905	3.143169
Sn	3.143169	1.028905	1.028905
Sn	1.028905	-1.028905	-3.143169
Sn	-3.143169	1.028905	-1.028905
Sn	-1.028905	3.143169	-1.028905
Sn	1.028905	-3.143169	-1.028905
Sn	-1.028905	1.028905	-3.143169
Sn	-1.028905	-1.028905	3.143169
Sn	3.143169	-1.028905	-1.028905
Sn	-3.143169	-1.028905	1.028905
Sn	-1.822917	1.822917	1.822917
Sn	1.822917	1.822917	-1.822917
Sn	-1.822917	-1.822917	-1.822917
Sc	0.000000	0.000000	0.000000

$ScSn_{16}^-$-II

Element	X	Y	Z
Sn	-1.460383	1.852343	2.321779
Sn	0.000000	2.136837	-2.403457
Sn	-1.460383	-1.852343	2.321779
Sn	0.000000	-2.136837	-2.403457

Sn	-2.267435	0.000000	-2.355253
Sn	-3.341521	0.000000	0.912027
Sn	1.460383	1.852343	2.321779
Sn	2.469987	-2.440464	-0.593742
Sc	0.000000	0.000000	0.109931
Sn	-2.469987	2.440464	-0.593742
Sn	-2.469987	-2.440464	-0.593742
Sn	1.460383	-1.852343	2.321779
Sn	2.469987	2.440464	-0.593742
Sn	0.000000	-3.864515	0.367523
Sn	0.000000	3.864515	0.367523
Sn	2.267435	0.000000	-2.355253
Sn	3.341521	0.000000	0.912027

$ScSn_{16}^{-}$-III

Element	X	Y	Z
Sn	-2.243036	-1.711650	1.872985
Sn	2.533327	-0.344711	2.243410
Sn	-2.554669	1.236375	1.515221
Sn	0.560488	-2.523813	-2.680884
Sn	-0.579463	-3.510914	0.000000
Sn	-1.303488	3.527773	0.000000
Sn	1.587217	4.512647	0.000000
Sn	1.070698	2.066382	-1.487442
Sn	-0.390851	0.267113	3.454671
Sn	-2.554669	1.236375	-1.515221
Sn	0.560488	-2.523813	2.680884
Sn	-2.243036	-1.711650	-1.872985
Sn	-0.390851	0.267113	-3.454671

Sn	1.070698	2.066382	1.487442
Sn	2.533327	-0.344711	-2.243410
Sn	2.357233	-2.377692	0.000000
Sc	-0.031935	-0.312397	0.000000

YSn_{16}^{-}-I

Element	X	Y	Z
Sn	1.035402	3.160370	1.035402
Sn	1.861908	-1.861908	1.861908
Sn	-1.035402	-3.160370	1.035402
Sn	1.035402	1.035402	3.160370
Sn	3.160370	1.035402	1.035402
Sn	1.035402	-1.035402	-3.160370
Sn	-3.160370	1.035402	-1.035402
Sn	-1.035402	3.160370	-1.035402
Sn	1.035402	-3.160370	-1.035402
Sn	-1.035402	1.035402	-3.160370
Sn	-1.035402	-1.035402	3.160370
Sn	3.160370	-1.035402	-1.035402
Sn	-3.160370	-1.035402	1.035402
Sn	-1.861908	1.861908	1.861908
Sn	1.861908	1.861908	-1.861908
Sn	-1.861908	-1.861908	-1.861908
Y	0.000000	0.000000	0.000000

YSn_{16}^{-}-II

Element	X	Y	Z

Sn	-1.479706	1.951512	2.344812
Sn	0.000000	2.152954	-2.442461
Sn	-1.479706	-1.951512	2.344812
Sn	0.000000	-2.152954	-2.442461
Sn	-2.309605	0.000000	-2.373459
Sn	-3.328427	0.000000	0.975503
Sn	1.479706	1.951512	2.344812
Sn	2.496116	-2.446092	-0.603888
Y	0.000000	0.000000	0.118930
Sn	-2.496116	2.446092	-0.603888
Sn	-2.496116	-2.446092	-0.603888
Sn	1.479706	-1.951512	2.344812
Sn	2.496116	2.446092	-0.603888
Sn	0.000000	-3.869623	0.312185
Sn	0.000000	3.869623	0.312185
Sn	2.309605	0.000000	-2.373459
Sn	3.328427	0.000000	0.975503

YSn_{16}^{-}-III

Element	X	Y	Z
Sn	-2.176739	-1.802533	2.046572
Sn	2.592632	-0.265420	2.193413
Sn	-2.733573	1.086678	1.526305
Sn	0.678317	-2.474880	-2.697718
Sn	-0.58632	-3.50626	0.000000
Sn	-1.378072	3.299787	0.000000
Sn	1.357279	4.666933	0.000000
Sn	1.145578	2.189516	-1.511245
Sn	-0.374372	0.344102	3.446731

Sn	-2.733573	1.086678	-1.526305
Sn	0.6783170	-2.474880	2.697718
Sn	-2.176739	-1.802533	-2.046572
Sn	-0.374372	0.344102	-3.446731
Sn	1.145578	2.189516	1.511245
Sn	2.592632	-0.265420	-2.193413
Sn	2.402066	-2.410245	0.000000
Y	-0.075179	-0.262999	0.000000

$LaSn_{16}^{-}$-I

Element	X	Y	Z
Sn	1.043687	3.185318	1.043687
Sn	1.900874	-1.900874	1.900874
Sn	-1.043687	-3.185318	1.043687
Sn	1.043687	1.043687	3.185318
Sn	3.185318	1.043687	1.043687
Sn	1.043687	-1.043687	-3.185318
Sn	-3.185318	1.043687	-1.043687
Sn	-1.043687	3.185318	-1.043687
Sn	1.043687	-3.185318	-1.043687
Sn	-1.043687	1.043687	-3.185318
Sn	-1.043687	-1.043687	3.185318
Sn	3.185318	-1.043687	-1.043687
Sn	-3.185318	-1.043687	1.043687
Sn	-1.900874	1.900874	1.900874
Sn	1.900874	1.900874	-1.900874
Sn	-1.900874	-1.900874	-1.900874
La	0.000000	0.000000	0.000000

$LaSn_{16}^{-}$-II

Element	X	Y	Z
Sn	-1.516189	2.082220	2.403022
Sn	0.000000	2.171873	-2.529973
Sn	-1.516189	-2.082220	2.403022
Sn	0.000000	-2.171873	-2.529973
Sn	-2.428751	0.000000	-2.431578
Sn	-3.365960	0.000000	1.096702
Sn	1.516189	2.082220	2.403022
Sn	2.570006	-2.498669	-0.634425
La	0.000000	0.000000	0.132142
Sn	-2.570006	2.498669	-0.634425
Sn	-2.570006	-2.498669	-0.634425
Sn	1.516189	-2.082220	2.403022
Sn	2.570006	2.498669	-0.634425
Sn	0.000000	-3.943014	0.252333
Sn	0.000000	3.943014	0.252333
Sn	2.428751	0.000000	-2.431578
Sn	3.365960	0.000000	1.096702

$LaSn_{16}^{-}$-III

Element	X	Y	Z
Sn	-2.169058	-1.864525	2.224307
Sn	2.709324	-0.232420	2.200419
Sn	-2.897817	1.016959	1.559078
Sn	0.763222	-2.465840	-2.792684

Sn	-0.655518	-3.598442	0.000000
Sn	-1.442671	3.248685	0.000000
Sn	1.259111	4.816045	0.000000
Sn	1.219769	2.270090	-1.539631
Sn	-0.379280	0.443550	3.529683
Sn	-2.897817	1.016959	-1.559078
Sn	0.763222	-2.465840	2.792684
Sn	-2.169058	-1.864525	-2.224307
Sn	-0.379280	0.443550	-3.529683
Sn	1.219769	2.270090	1.539631
Sn	2.709324	-0.232420	-2.200419
Sn	2.462459	-2.493461	0.000000
La	-0.101492	-0.270575	0.000000

Table S4. The root-mean-square deviation (RMSD) between experimental and simulated PES (X, A, B, C in eV) for Sn_{16}^-.

	X	A	B	C	RMSD
Exp.[S1]	2.98	3.64	3.84	4.32	/
Isomer A	3.00	3.72	3.82	4.24	0.058
Isomer B	2.88	3.48	3.76	4.28	0.104

As shown in Table S2 and Figure S1, the isomer A match the PES better than isomer B. DFT calculations indicate that isomer A has lower energy than B, which is consistent with the ref. [S2]. Isomer A is the most likely lowest energy isomer, both in terms of DFT calculations and PES and TIED [S2] experiment. In addition, the result is also consistent with ref. [S3]. Therefore, we consider isomer A as the lowest energy structure for pure Sn_{16}^- cluster in this article.

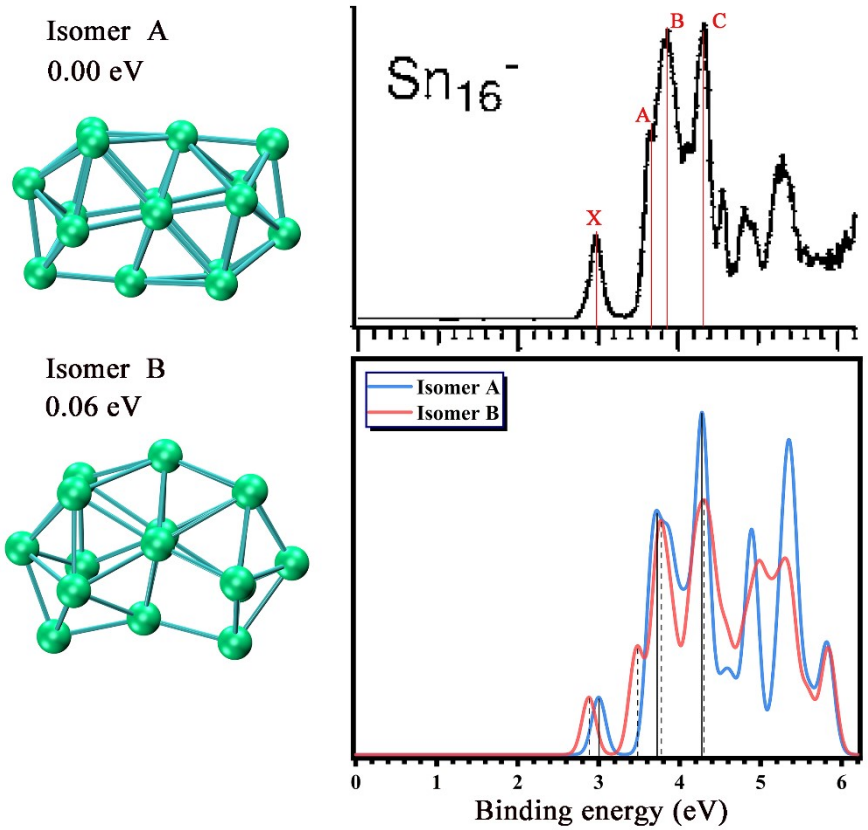

Figure S1 Comparing the Experimental and simulated PES of Sn_{16}^{-}. Comparison of two possible low-lying isomers with experimental PES. The structure and experimental PES are extracted from refs. [S1, S2]. The relative energy is carried out at the PBE0/Lanl08(d) level. The positions of the first four peaks in the experiment are marked with the letters X, A, B, and C.

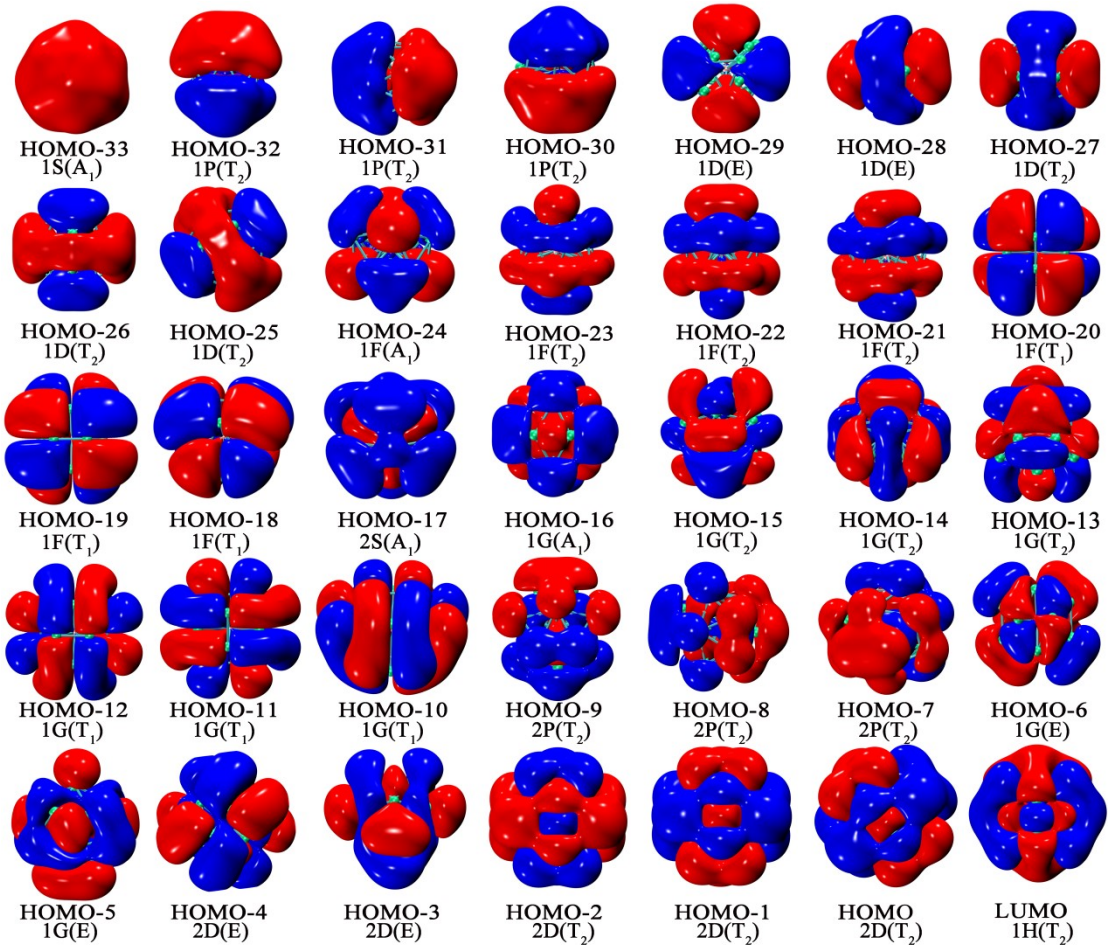

Figure S2. Valence molecular orbitals diagram of $ScSn_{16}^{-}$.

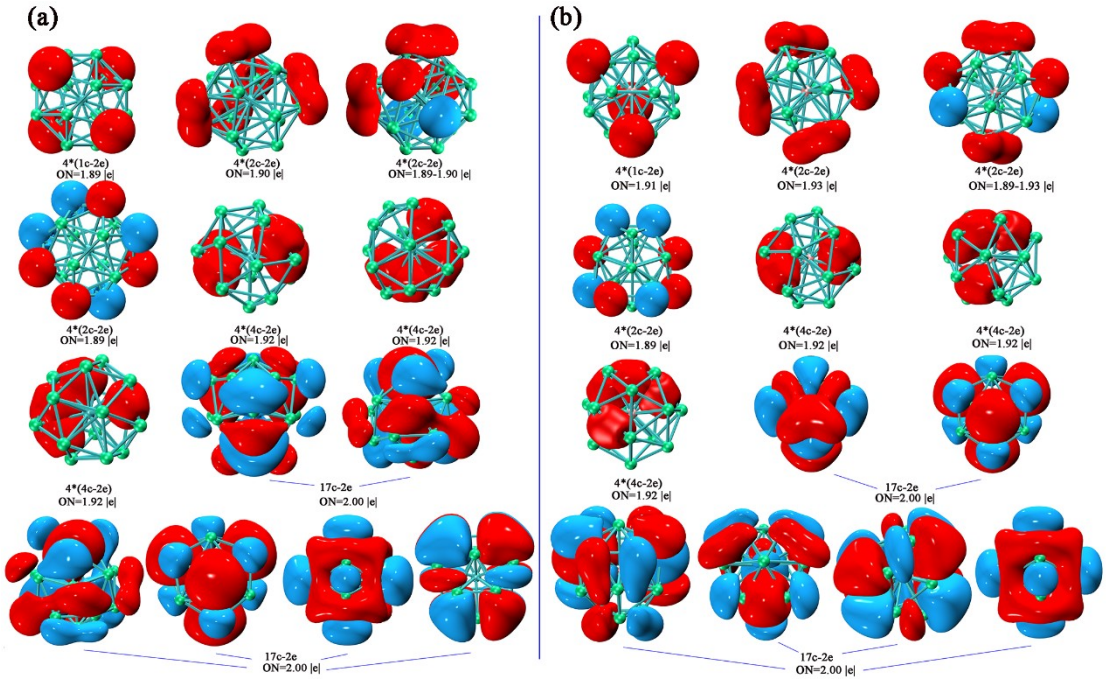

Figure S3. AdNDP orbits of (a) YSn_{16}^{-} ; (b) $LaSn_{16}^{-}$.

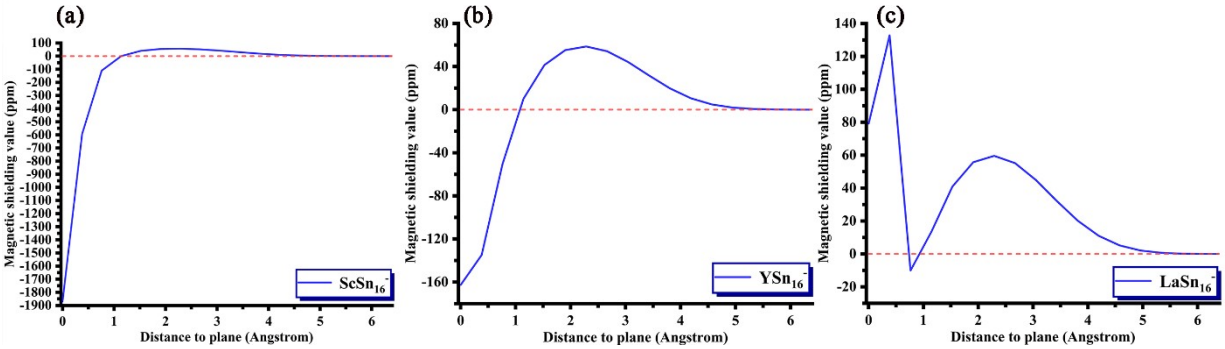

Figure S4. ICSS curve plot along the Z-axis from the center of the (a) Sc; (b) Y; (c) La atom.

Supplemental References

[1] L.F. Cui, L.M. Wang and L.S. Wang, *J. Chem. Phys.*, 2007, **126**, 64505.

[2] A. Wiesel, N. Drebov, T. Rapps, R. Ahlrichs, U. Schwarz, R. Kelting, P. Weis, M. M. Kappes and D. Schooss, *Phys. Chem. Chem. Phys.*, 2012, **14**, 234-245.

[3] D. Wu, D.Y. Q, X. Wu, R.L. Shi, L.W. Sai, X.Q. Liang, X.M. Huang and J.J. Zhao, *J. Chem. Phys.*, 2019, **150**, 174304.