Electronic Supplementary Material (ESI)

Actinide endohedral inter-metalloid clusters of the group 15 elements

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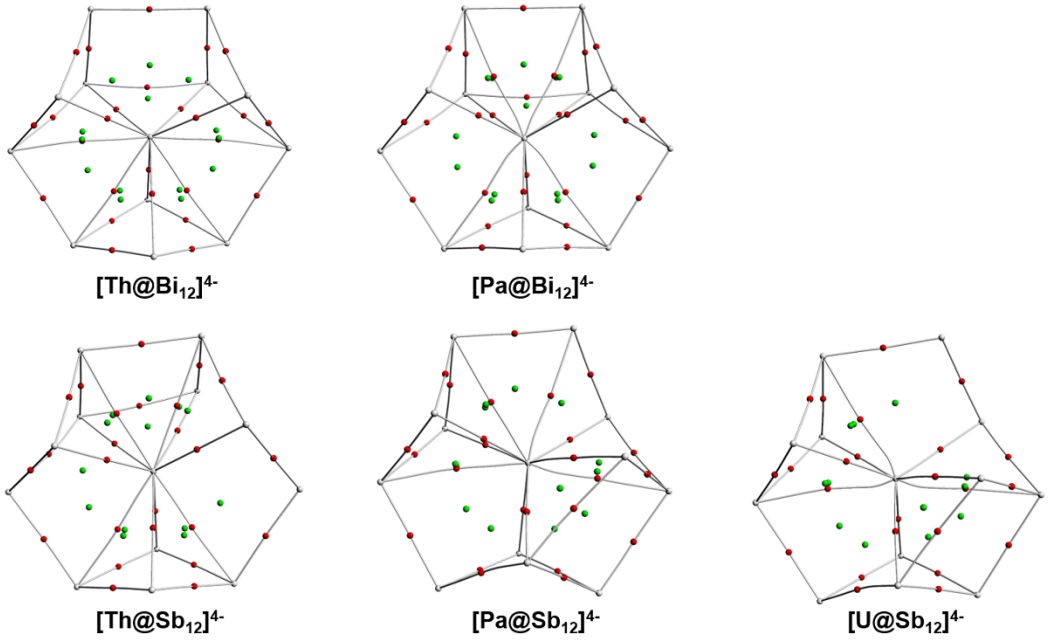

Figure S1. QTAIM analysis of $[An@Bi_{12}]^{4-}$ (An = Th, Pa) and $[An@Sb_{12}]^{4-}$ (An = Th, Pa, U). Red points represent bond critical points, gray lines represent bond paths, and green points represent ring critical points at the PBE-D3/RECP theoretical level.

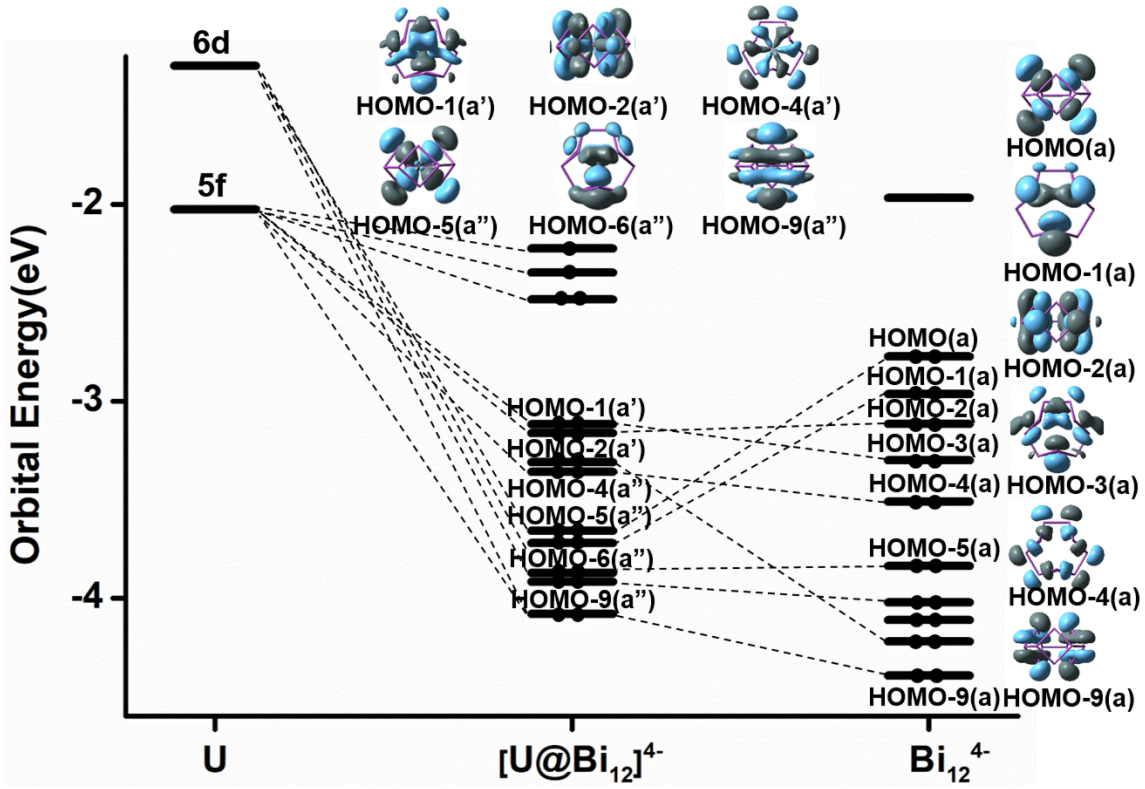

Figure S2. Orbital interaction diagram of $[U@Bi_{12}]^{4-}$.

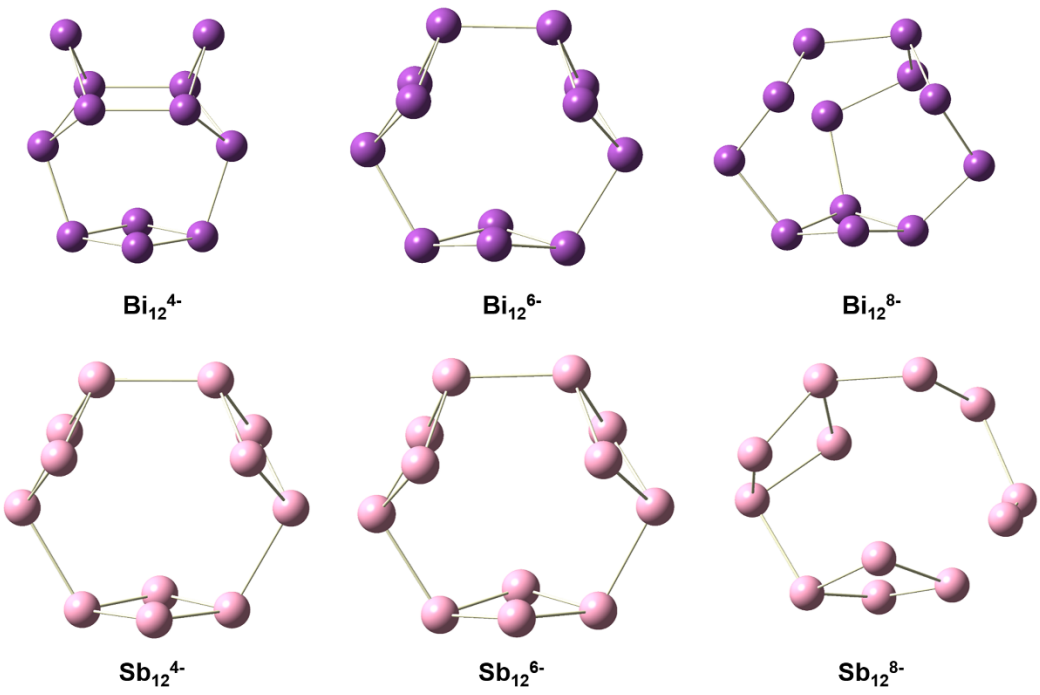

Figure S3. The optimized structures of the empty cages.

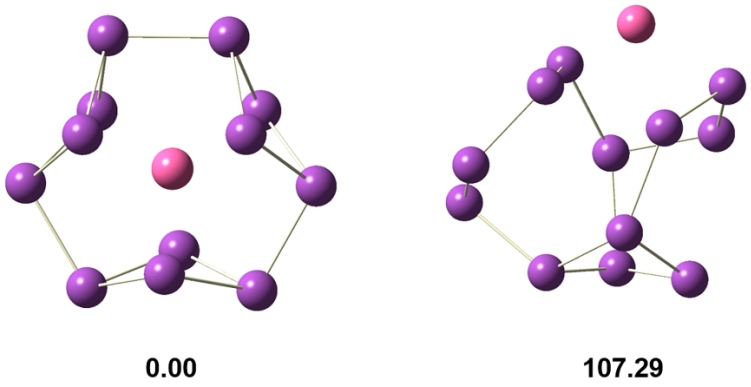

Figure S4. The optimized structures of the endohedral isomer and side-attached isomers of $[U@Bi_{12}]^{4-}$ with the relative energy (kcal/mol) at the theoretical level of PBE-D3/RECP.

Table S1. Relative energies (kcal/mol) for the $[An@Bi_{12}]^{4-}$/$[An@Sb_{12}]^{4-}$ structures.

Species	Singlet	Triplet	Quintet	
$[Th@Bi_{12}]^{4-}$	0.00	6.40	29.02	
$[Th@Sb_{12}]^{4-}$	0.00	10.36	37.47	
Species	Doublet	Quartet	Sextet	
$[Pa@Bi_{12}]^{4-}$	0.00	7.54	28.07	
$[Pa@Sb_{12}]^{4-}$	0.00	10.81	35.64	
Species	Singlet	Triplet	Quintet	Septet
$[U@Bi_{12}]^{4-}$	12.63	0.00	7.14	23.95
$[U@Sb_{12}]^{4-}$	6.81	0.00	6.66	30.48

Table S2. Comparison of U-Bi bond distances of $[U@Bi_{12}]^{3-}$ and $[U@Bi_{12}]^{4-}$.

Bonds	$[U@Bi_{12}]^{3-}$	$[U@Bi_{12}]^{4-}$	Bonds	$[U@Bi_{12}]^{3-}$	$[U@Bi_{12}]^{4-}$
U-Bi1	3.531	3.689	U-Bi7	3.533	3.613
U-Bi2	3.119	3.168	U-Bi8	3.134	3.177
U-Bi3	3.495	3.692	U-Bi9	3.545	3.690
U-Bi4	3.131	3.168	U-Bi10	3.150	3.168
U-Bi5	3.537	3.614	U-Bi11	3.514	3.688
U-Bi6	3.167	3.177	U-Bi12	3.127	3.168
Average $U–Bi_A$	3.526	3.664	Average $U–Bi_B$	3.138	3.171

Table S3. The experimental (Exp.) and calculated (Calc.) Th-Bi bond distances (Å) for the $[Th@Bi_{12}]^{4-}$ complex at the PBE-D3/RECP theoretical level.

Bonds	Exp.	Calc.	Bonds	Exp.	Calc.
Th-Bi1	3.659	3.662	Th-Bi7	3.254	3.296
Th-Bi2	3.659	3.648	Th-Bi8	3.254	3.203
Th-Bi3	3.659	3.603	Th-Bi9	3.254	3.296
Th-Bi4	3.254	3.203	Th-Bi10	3.659	3.603
Th-Bi5	3.659	3.648	Th-Bi11	3.659	3.662
Th-Bi6	3.254	3.310	Th-Bi12	3.254	3.274
Average Th–Bi_A	3.659	3.638	Average Th–Bi_B	3.254	3.264

Table S4. The molecular orbital composition analysis of Th for $[Th@Bi_{12}]^{4-}$ at the theoretical level of PBE-D3/RECP.

$[Th@Bi_{12}]^{4-}$	atom	s %	p %	d %	f %
HOMO-1(a″)	Th			6.60	4.35
	Bi		89.26		
HOMO-2(a′)	Th			7.79	3.80
	Bi		88.25		
HOMO-3(a″)	Th				4.72
	Bi		93.00		
HOMO-5(a′)	Th	2.42	2.80	4.89	
	Bi		87.74		
HOMO-6(a′)	Th			15.66	0.97
	Bi		81.51		
HOMO-7(a″)	Th			5.35	0.84
	Bi		91.46		

Table S5. The molecular orbital composition analysis of Pa for $[Pa@Bi_{12}]^{4-}$ at the theoretical level of PBE-D3/RECP.

$[Pa@Bi_{12}]^{4-}$	atom	s %	p %	d %	f %
SOMO(a)	Pa	2.04	2.10		54.23
	Bi		41.04		
HOMO-1(a)	Pa			6.54	11.24
	Bi		81.06		
HOMO-2(a)	Pa			5.99	11.92
	Bi		80.32		
HOMO-3(a)	Pa				11.04
	Bi		86.23		
HOMO-5(a)	Pa			13.92	2.85
	Bi		82.57		
HOMO-6(a)	Pa			15.11	2.54
	Bi		80.69		
HOMO-7(a)	Pa			4.54	2.24
	Bi		89.44		

Table S6. The molecular orbital composition analysis of U for $[U@Bi_{12}]^{4-}$ at the theoretical level of PBE-D3/RECP.

$[U@Bi_{12}]^{4-}$	atom	s %	p %	d %	f %
SOMO(a″)	U			4.06	84.64
	Bi		8.85		
SOMO-1(a′)	U	1.12			83.93
	Bi		11.60		
HOMO-1(a′)	U			4.89	12.93
	Bi		80.60		
HOMO-2(a″)	U			5.44	12.45
	Bi		80.68		
HOMO-4(a′)	U				10.23
	Bi		87.73		
HOMO-5(a″)	U			19.10	4.67
	Bi		73.85		
HOMO-6(a″)	U			16.63	5.33
	Bi		77.06		
HOMO-9(a″)	U			1.55	2.55
	Bi	1.08	92.20		

Table S7. QTAIM analysis of $[An@Bi_{12}]^{4-}$/$[An@Sb_{12}]^{4-}$ at the PBE-D3/RECP theoretical level

Clusters	BCPs	ρ(r)	H(r)	$\nabla^2\rho(r)$	DI_{total}
C_s $[Th@Bi_{12}]^{4-}$	$An\text{-}Bi_A$	0.02041	-0.00241	0.02403	1.60899
	$An\text{-}Bi_B$	0.03821	-0.00909	0.02334	3.33904
C_1 $[Pa@Bi_{12}]^{4-}$	$An\text{-}Bi_A$	0.02178	-0.00294	0.02447	1.99986
	$An\text{-}Bi_B$	0.04397	-0.01155	0.02294	4.22372
C_s $[U@Bi_{12}]^{4-}$	$An\text{-}Bi_A$	0.02014	-0.00240	0.02449	1.74464
	$An\text{-}Bi_B$	0.04165	-0.01010	0.03004	4.09088
C_1 $[Th@Sb_{12}]^{4-}$	$An\text{-}Sb_A$	0.02378	-0.00335	0.02845	1.66499
	$An\text{-}Sb_B$	0.03866	-0.00901	0.02258	3.19679
C_1 $[Pa@Sb_{12}]^{4-}$	$An\text{-}Sb_A$	0.02552	-0.00417	0.02623	2.15315
	$An\text{-}Sb_B$	0.04398	-0.01142	0.01966	4.01572
C_1 $[U@Sb_{12}]^{4-}$	$An\text{-}Sb_A$	0.02355	-0.00348	0.03041	1.96317
	$An\text{-}Sb_B$	0.04246	-0.01063	0.02401	3.81413

Table S8. Formation energies (ΔE, kcal/mol) of $[An@Bi_{12}]^{4-}$/$[An@Sb_{12}]^{4-}$ at the PBE-D3/RECP theoretical level.

Reactions	Formation Energies
$Th^{4+} + Bi_{12}^{8-} \rightarrow [Th@Bi_{12}]^{4-}$	-461.6
$Pa^{4+} + Bi_{12}^{8-} \rightarrow [Pa@Bi_{12}]^{4-}$	-512.6
$U^{4+} + Bi_{12}^{8-} \rightarrow [U@Bi_{12}]^{4-}$	-538.0
$Th^{4+} + Sb_{12}^{8-} \rightarrow [Th@Sb_{12}]^{4-}$	-466.8
$Pa^{4+} + Sb_{12}^{8-} \rightarrow [Pa@Sb_{12}]^{4-}$	-517.4
$U^{4+} + Sb_{12}^{8-} \rightarrow [U@Sb_{12}]^{4-}$	-542.0

Table S9. Bond dissociation energies (BDEs, ΔH, kcal/mol) of $[An@Bi_{12}]^{4-}$/$[An@Sb_{12}]^{4-}$ at the PBE-D3/RECP theoretical level.

Reactions	Th	Pa	U
$[An@Bi_{12}]^{4-} \rightarrow An + Bi_{12}^{4-}$	238.9	245.8	270.1
$[An@Bi_{12}]^{4-} \rightarrow An^{2+} + Bi_{12}^{6-}$	241.9	240.1	254.6
$[An@Bi_{12}]^{4-} \rightarrow An^{4+} + Bi_{12}^{8-}$	462.1	513.0	538.4
$[An@Sb_{12}]^{4-} \rightarrow An + Sb_{12}^{4-}$	202.3	220.7	240.0
$[An@Sb_{12}]^{4-} \rightarrow An^{2+} + Sb_{12}^{6-}$	246.8	255.6	265.4
$[An@Sb_{12}]^{4-} \rightarrow An^{4+} + Sb_{12}^{8-}$	467.6	518.0	542.5

Table S10. BDEs (ΔH, kcal/mol) of $[An@Bi_{12}]^{4-}$ at the PBE-D3/RECP theoretical level.

Reactions	Th	Pa	U
$[An@Bi_{12}]^{4-} \rightarrow Bi^{3+} + AnBi_{11}^{7-}$	100.6	90.2	96.2
$[An@Bi_{12}]^{4-} \rightarrow Bi + AnBi_{11}^{4-}$	94.5	78.5	85.7