

Supplementary Information

Planar Tetracoordinate Oxygen Stabilized within Triel–Chalcogen Dicationic Frameworks

Leinner Motta,^{a,b} Jennifer Cuellar,^{a,b} Williams García-Argote,^{a,c} Dumer S.
Sacanamboy,^{a,b} Viviana Roman-Ventura,^{a,b} Angelita Espinoza-Gomez,^d Diego
Inostroza,^c Luis Leyva-Parra,^{a,*} and William Tiznado.^{a,*}

^a *Centro de Investigación para el Diseño de Materiales (CEDEM), Facultad de Ciencias Exactas, Departamento de Ciencias Químicas, Universidad Andrés Bello, Avenida República 275, Santiago 8370146, Chile*

^b *Doctorado en Físicoquímica Molecular, Facultad de Ciencias Exactas, Universidad Andrés Bello, República 275, Santiago 8370146, Chile.*

^c *Centro de Modelación Ambiental y Dinámica de Sistemas (CEMADIS), Facultad de Ingeniería y Negocios, Universidad de Las Américas, Santiago 7500975, Chile*

^d *Grupo de Química Inorgánica y Materiales Moleculares, Facultad de Ingeniería, Universidad Autónoma de Chile, Del Valle Sur 534, Huechuraba, Santiago, Chile*

E-mail: luis.leyva@unab.cl

wtiznado@unab.cl

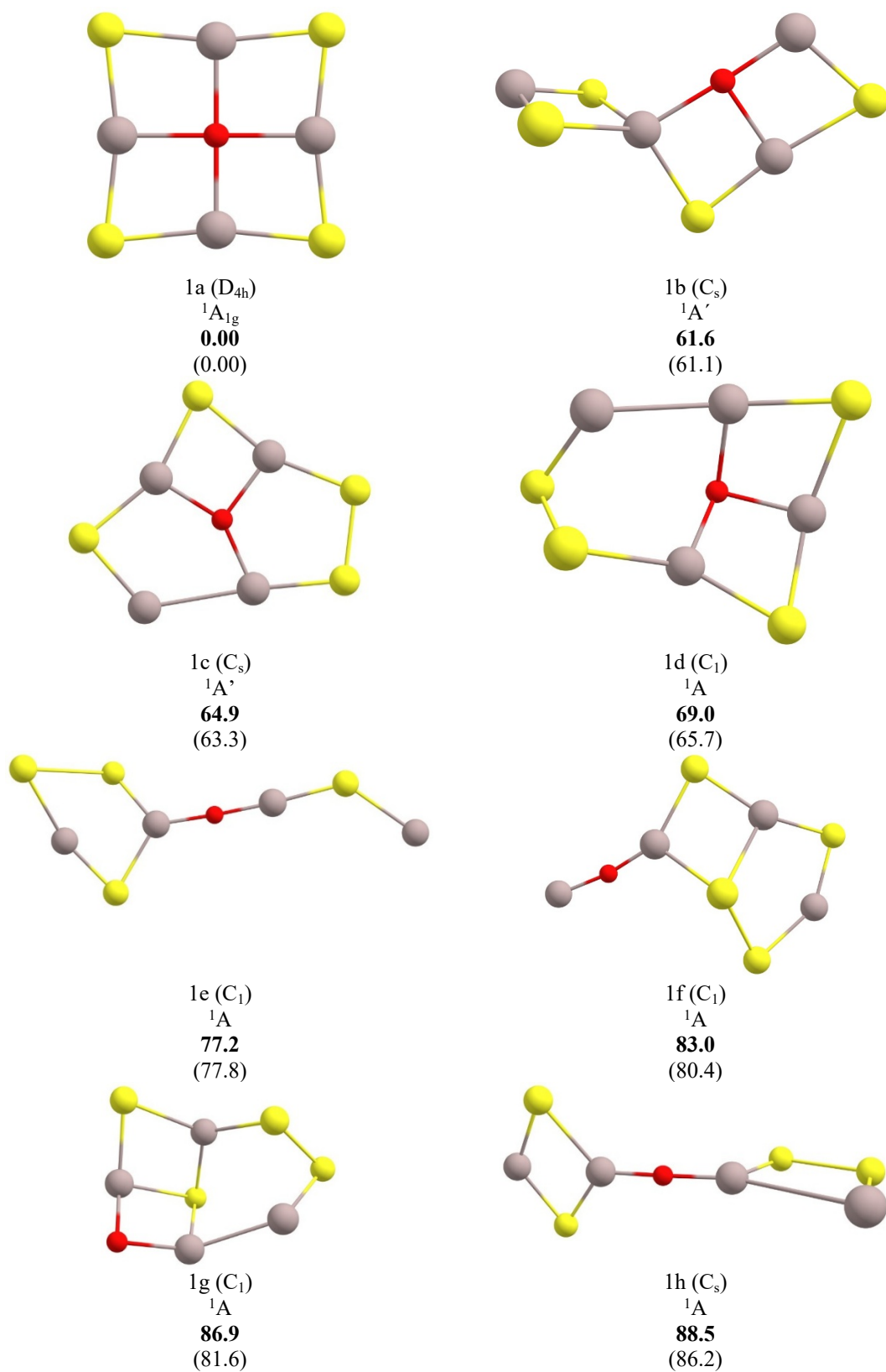
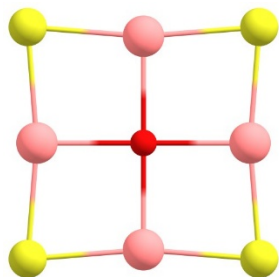
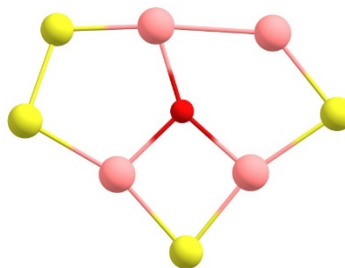


Fig. S1 Optimized structures within the range of 0-90 kcal.mol⁻¹ with respect to the global minimum structure of the O@X₄E₄²⁺ cluster (X = Al; E = S) at the PBE0-GD3/def2-TZVP level. Relative energies are listed in kcal.mol⁻¹ at the single-point CCSD(T)/def2-

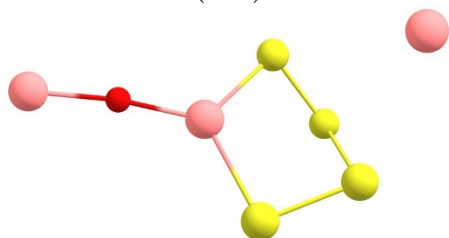
TZVP//PBE0-GD3/def2-TZVP (in bold) an PBE0-GD3/def2-TZVP (in parentheses)
levels, with zero-point energy (ZPE) correction.



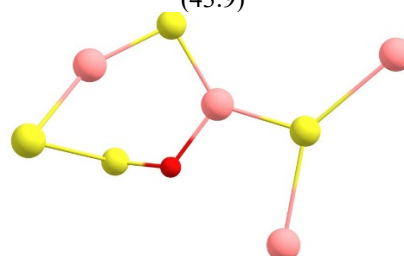
2a (D_{4h})
 $^1A_{1g}$
0.00
(0.00)



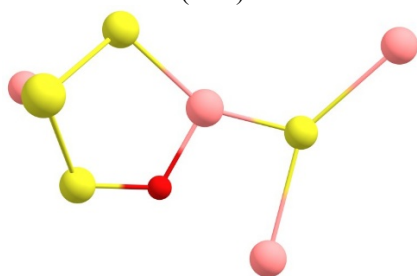
2b (C_1)
 1A
50.7
(43.9)



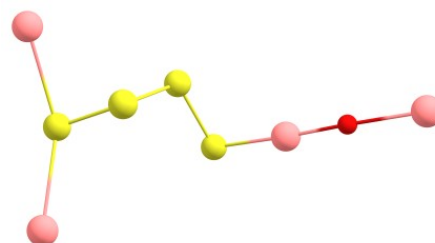
2c (C_1)
 $^1A'$
64.9
(49.2)



2d (C_1)
 1A
70.4
(51.8)



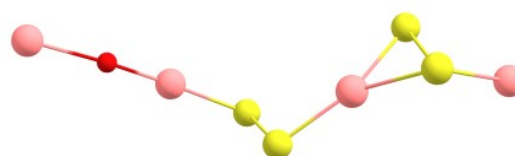
2e (C_1)
 1A
77.2
(56.3)



2f (C_1)
 1A
83.0
(65.0)

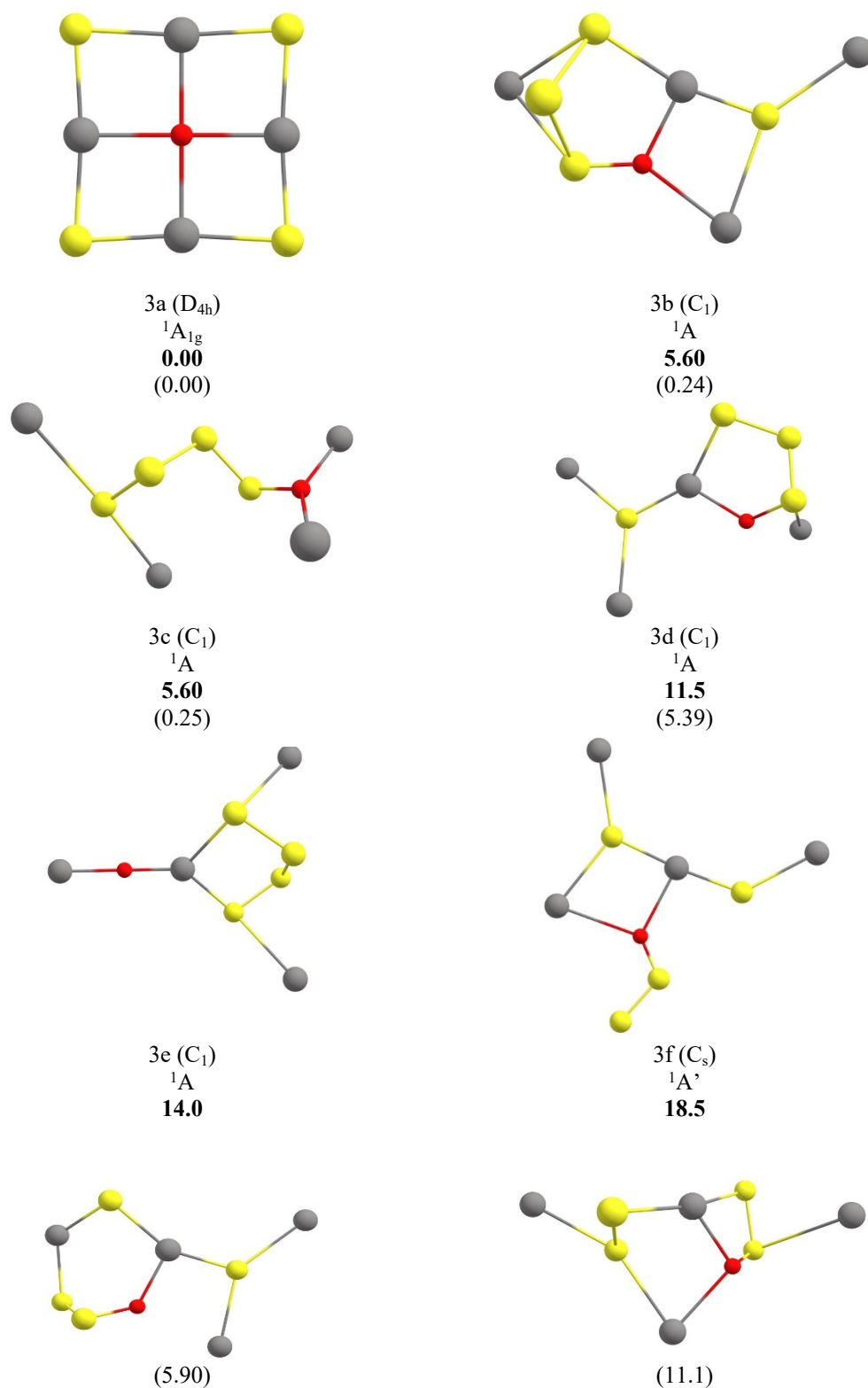


2g (C_1)
 1A
86.9
(66.9)



2h (C_s)
 1A
88.5
(67.5)

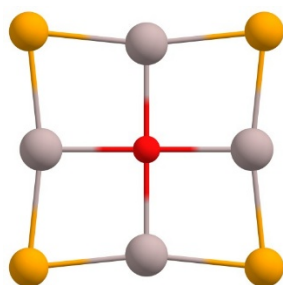
Fig. S2 Optimized structures within the range of 0-90 kcal.mol⁻¹ with respect to the global minimum structure of the O@X₄E₄²⁺ cluster (X = Ga; E = S) at the PBE0-GD3/def2-TZVP level. Relative energies are listed in kcal.mol⁻¹ at the single-point CCSD(T)/def2-TZVP//PBE0-GD3/def2-TZVP (in bold) and PBE0-GD3/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) correction.



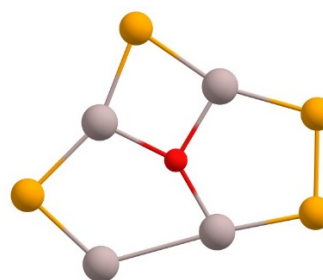
3g (C₁)
¹A
21.8
 (18.9)

3h (C_s)
¹A
22.3
 (19.9)

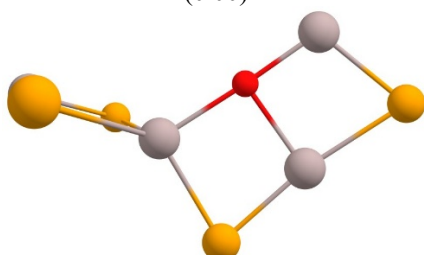
Fig. S3 Optimized structures within the range of 0-30 kcal.mol⁻¹ with respect to the global minimum structure of the O@X₄E₄²⁺ cluster (X = In; E = S) at the PBE0-GD3/def2-TZVP level. Relative energies are listed in kcal.mol⁻¹ at the single-point CCSD(T)/def2-TZVP//PBE0-GD3/def2-TZVP (in bold) an PBE0-GD3/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) correction.



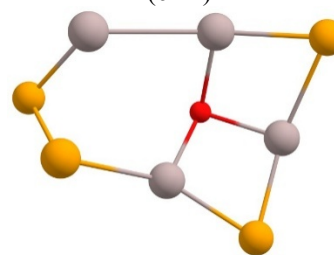
4a (D_{4h})
¹A_{1g}
0.00
 (0.00)



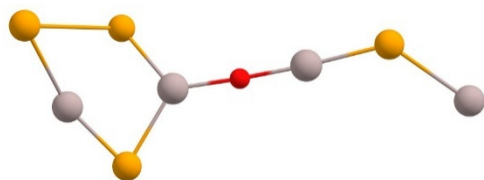
4b (C_s)
¹A
60.4
 (61.1)



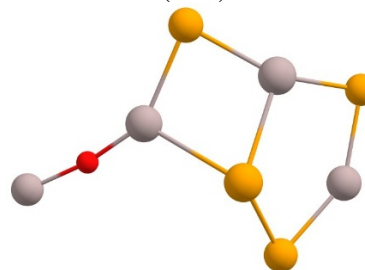
4c (C_s)
¹A'
63.5
 (63.3)



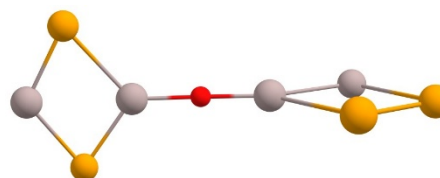
4d (C₁)
¹A
67.3
 (65.7)

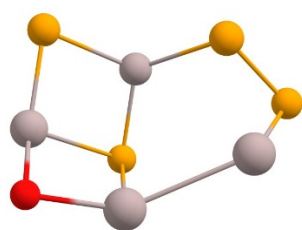


4e (C₁)
¹A
81.3
 (77.8)



4f (C₁)
¹A
83.5
 (80.4)

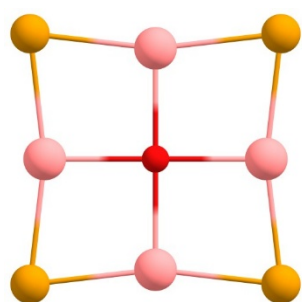




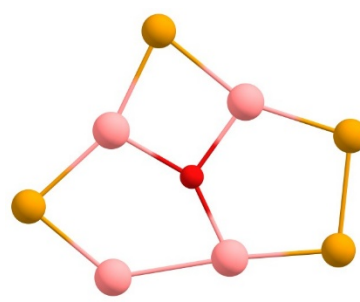
4g (C_1)
 1A
89.1
 (81.6)

4h (C_s)
 1A
95.1
 (86.2)

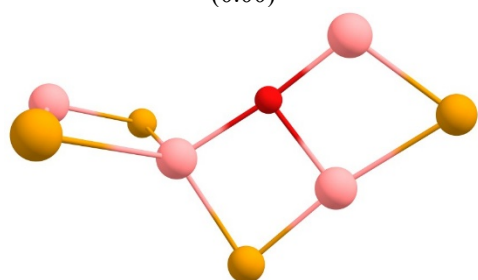
Fig. S4 Optimized structures within the range of 0-100 kcal.mol⁻¹ with respect to the global minimum structure of the O@X₄E₄²⁺ cluster (X = Al; E = Se) at the PBE0-GD3/def2-TZVP level. Relative energies are listed in kcal.mol⁻¹ at the single-point CCSD(T)/def2-TZVP//PBE0-GD3/def2-TZVP (in bold) an PBE0-GD3/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) correction.



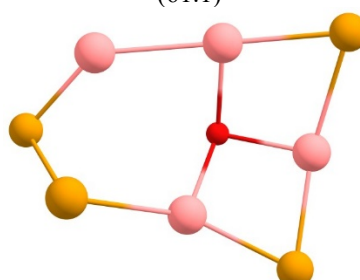
4a (D_{4h})
 $^1A_{1g}$
0.00
 (0.00)



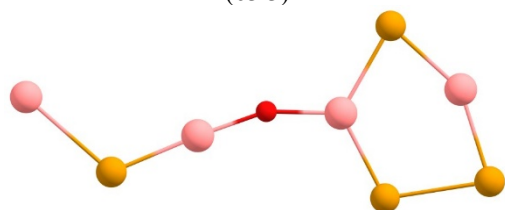
4b (C_s)
 1A
60.4
 (61.1)



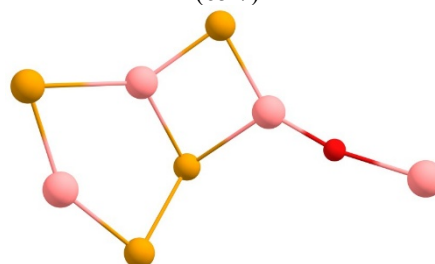
4c (C_s)
 $^1A'$
63.9
 (63.3)



4d (C_1)
 1A
63.9
 (65.7)



4e (C_1)
 1A
79.1



4f (C_1)
 1A
83.6

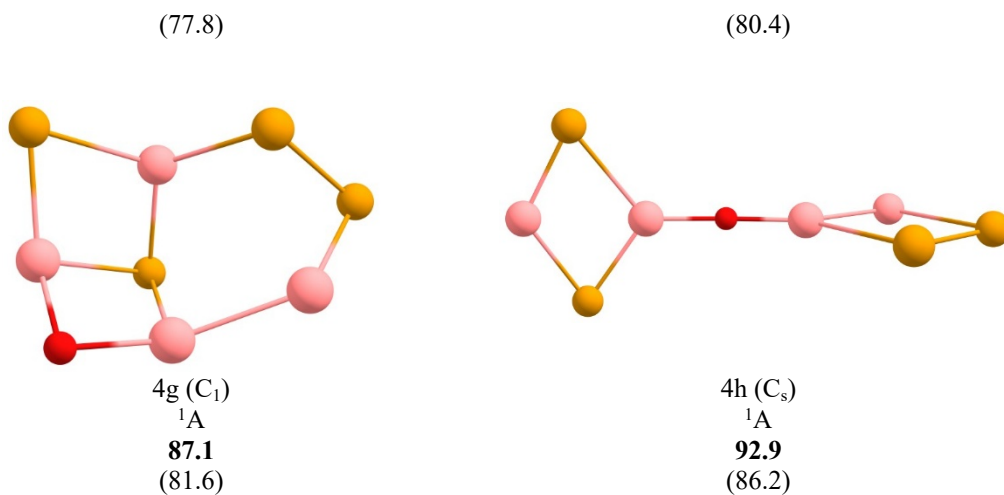
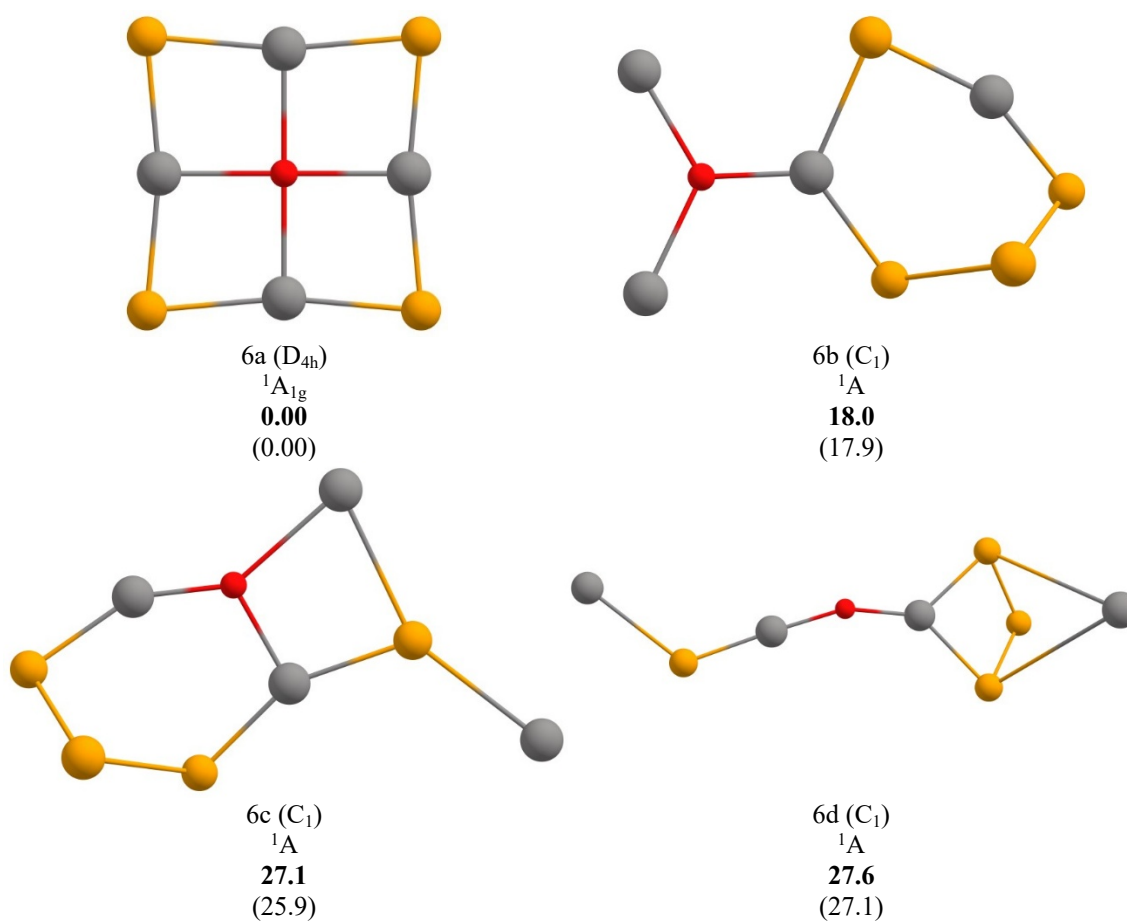


Fig. S5 Optimized structures within the range of 0-100 kcal.mol⁻¹ with respect to the global minimum structure of the O@X₄E₄²⁺ cluster (X = Ga; E = Se) at the PBE0-GD3/def2-TZVP level. Relative energies are listed in kcal.mol⁻¹ at the single-point CCSD(T)/def2-TZVP//PBE0-GD3/def2-TZVP (in bold) an PBE0-GD3/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) correction.



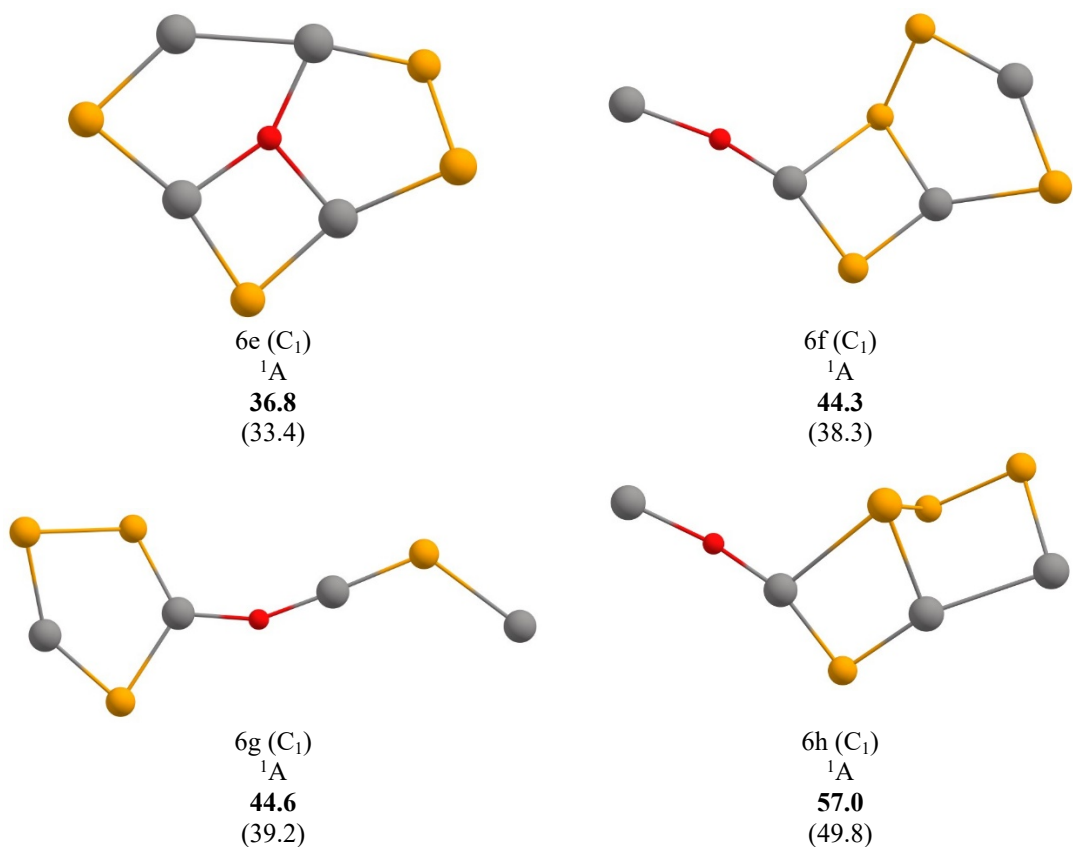
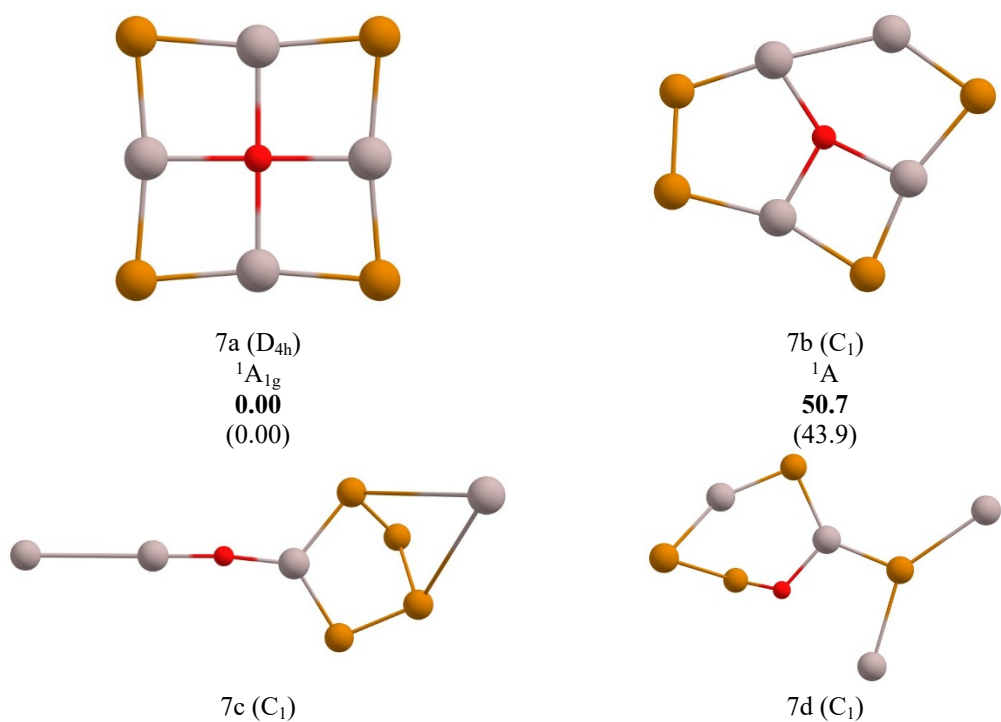


Fig. S6 Optimized structures within the range of 0-60 kcal.mol⁻¹ with respect to the global minimum structure of the $OCX_4E_4^{2+}$ cluster ($X = In$; $E = Se$) at the PBE0-GD3/def2-TZVP level. Relative energies are listed in kcal.mol⁻¹ at the single-point CCSD(T)/def2-TZVP//PBE0-GD3/def2-TZVP (in bold) an PBE0-GD3/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) correction.



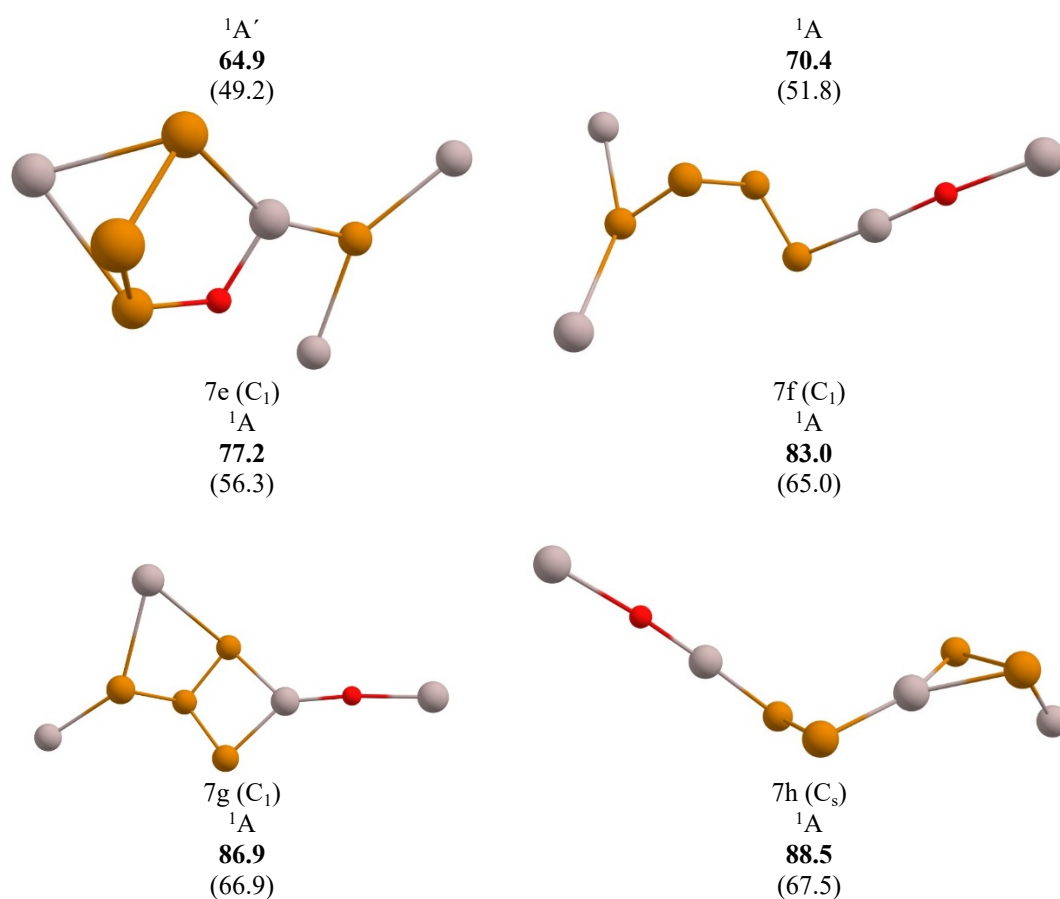
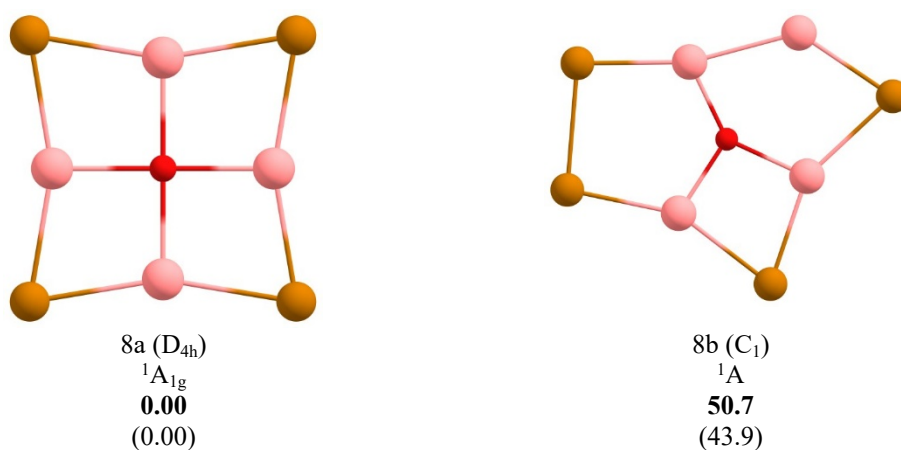


Fig. S7 Optimized structures within the range of 0-90 kcal.mol⁻¹ with respect to the global minimum structure of the O@X₄E₄²⁺ cluster (X = Al; E = Te) at the PBE0-GD3/def2-TZVP level. Relative energies are listed in kcal.mol⁻¹ at the single-point CCSD(T)/def2-TZVP//PBE0-GD3/def2-TZVP (in bold) an PBE0-GD3/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) correction.



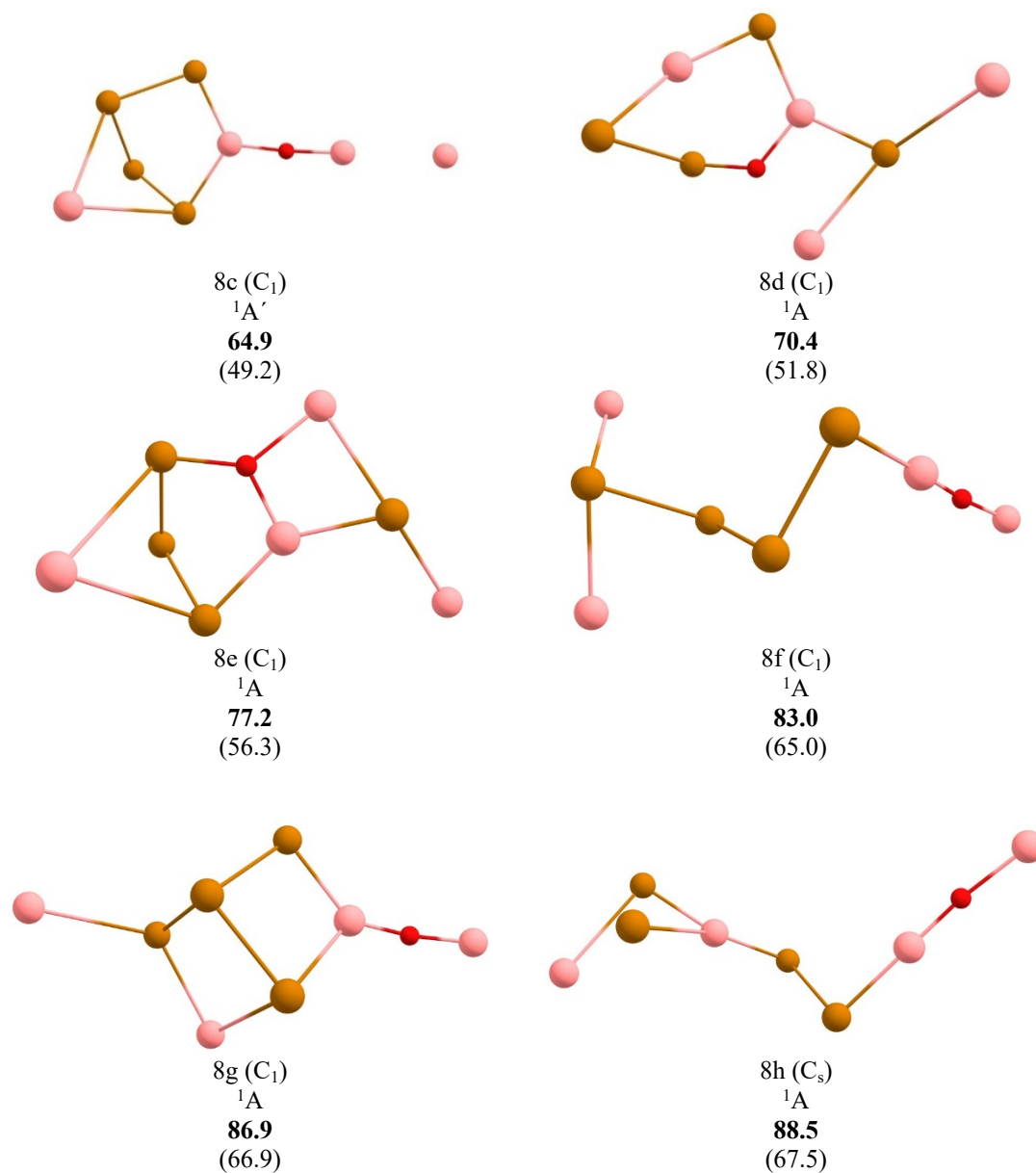
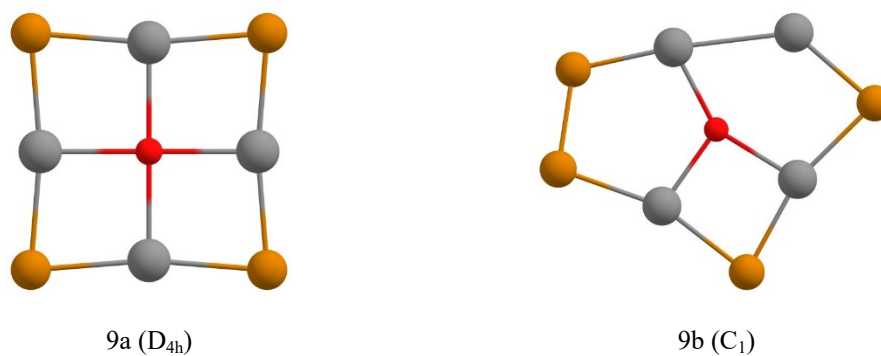


Fig. S8 Optimized structures within the range of 0-90 kcal.mol⁻¹ with respect to the global minimum structure of the O@X₄E₄²⁺ cluster (X = Ga; E = Te) at the PBE0-GD3/def2-TZVP level. Relative energies are listed in kcal.mol⁻¹ at the single-point CCSD(T)/def2-TZVP//PBE0-GD3/def2-TZVP (in bold) an PBE0-GD3/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) correction.



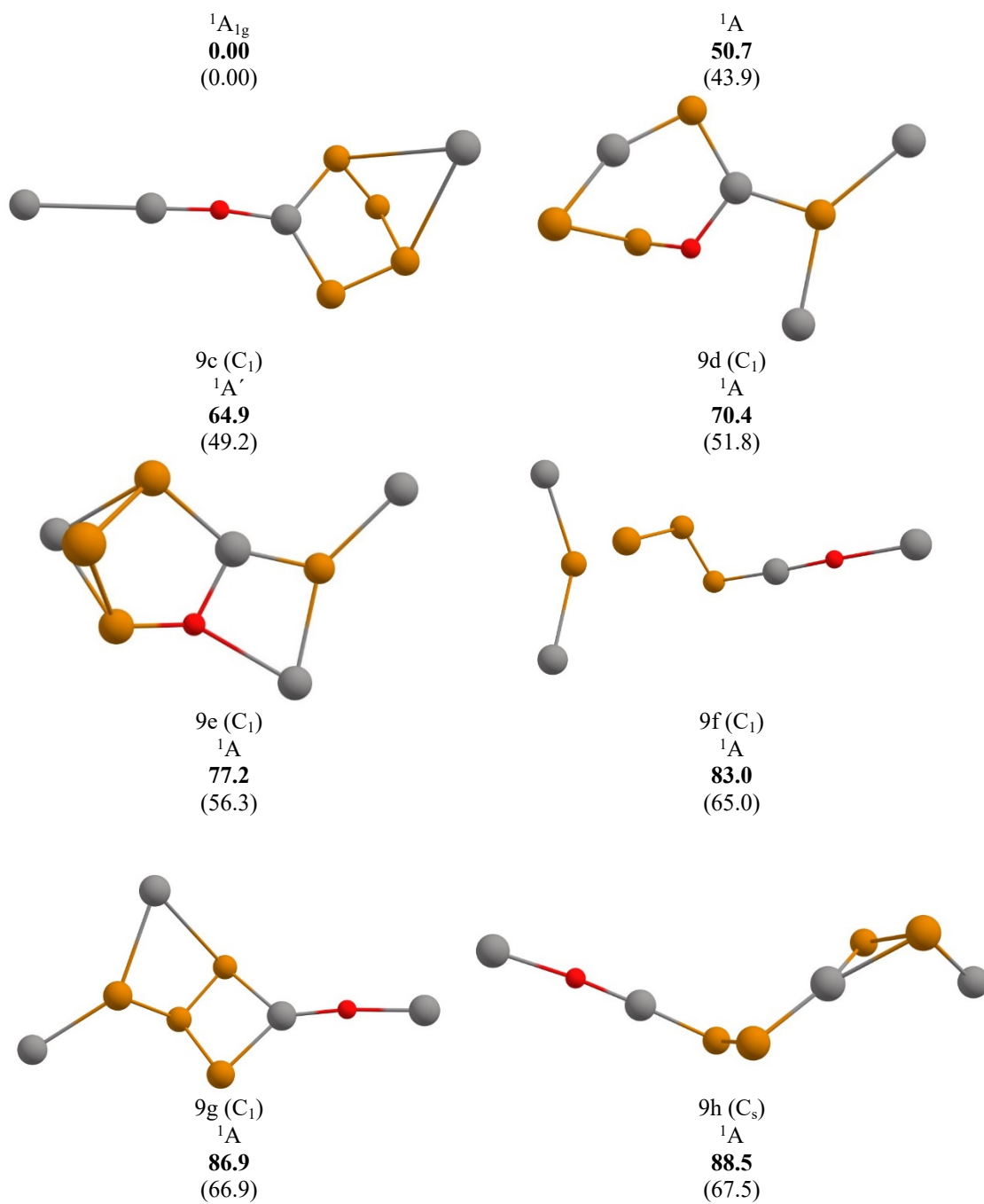


Fig. S9 Optimized structures within the range of 0-90 kcal.mol⁻¹ with respect to the global minimum structure of the O@X₄E₄²⁺ cluster (X = In; E = Te) at the PBE0-GD3/def2-TZVP level. Relative energies are listed in kcal.mol⁻¹ at the single-point CCSD(T)/def2-TZVP//PBE0-GD3/def2-TZVP (in bold) an PBE0-GD3/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) correction.

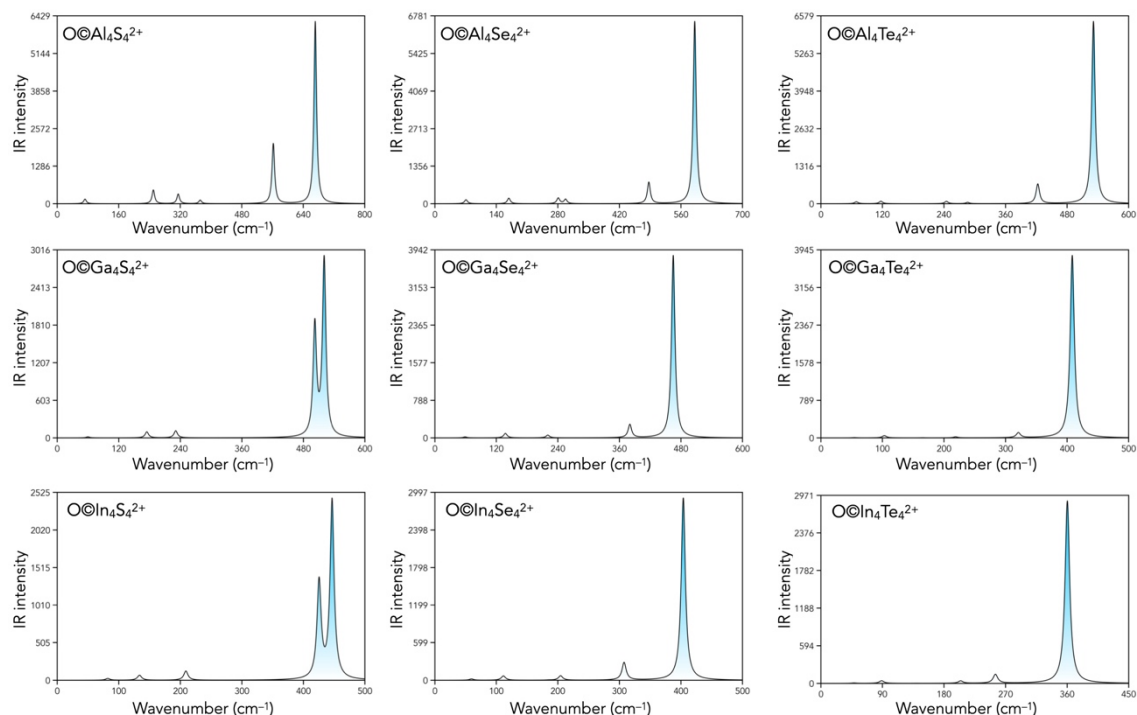


Figure S10. IR spectra for the global minimum $O@X_4E_4^{2+}$ ($X= Al/Ga/In$, $E= S/Se/Te$) PBE0-GD3/def2-TZVP.

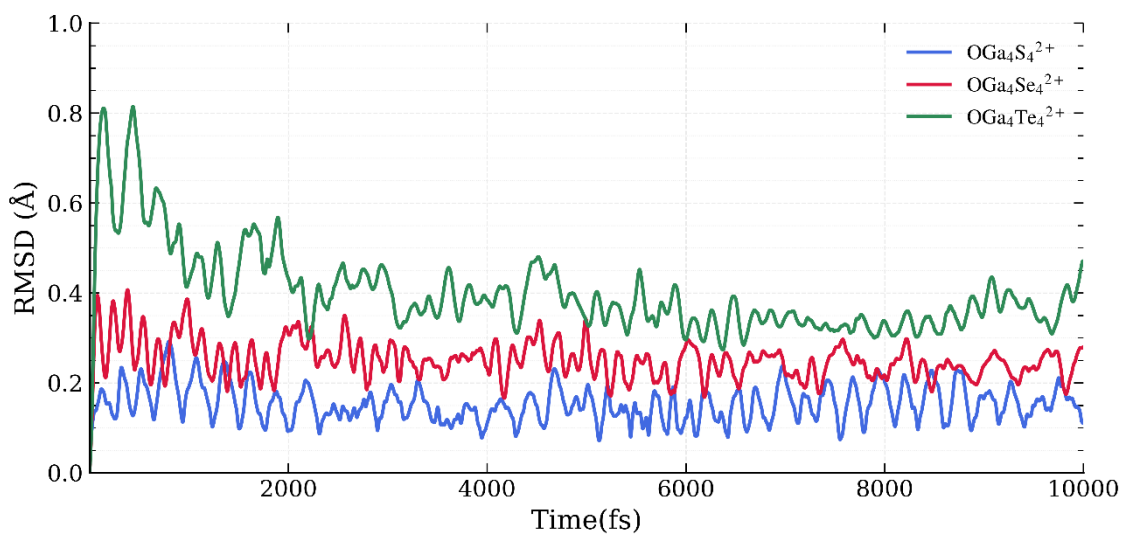


Figure S11. RMSD curves along the trajectories of Born-Oppenheimer molecular dynamics for a) $O@(GaE)_4^{2+}$ systems ($E= S, Se, Te$). The X-axis shows time in femtoseconds(fs), while the Y-axis shows RMSD in angstroms (\AA). Systems E: (Blue =S, red=Se and green=Te). Temperature (500 K).

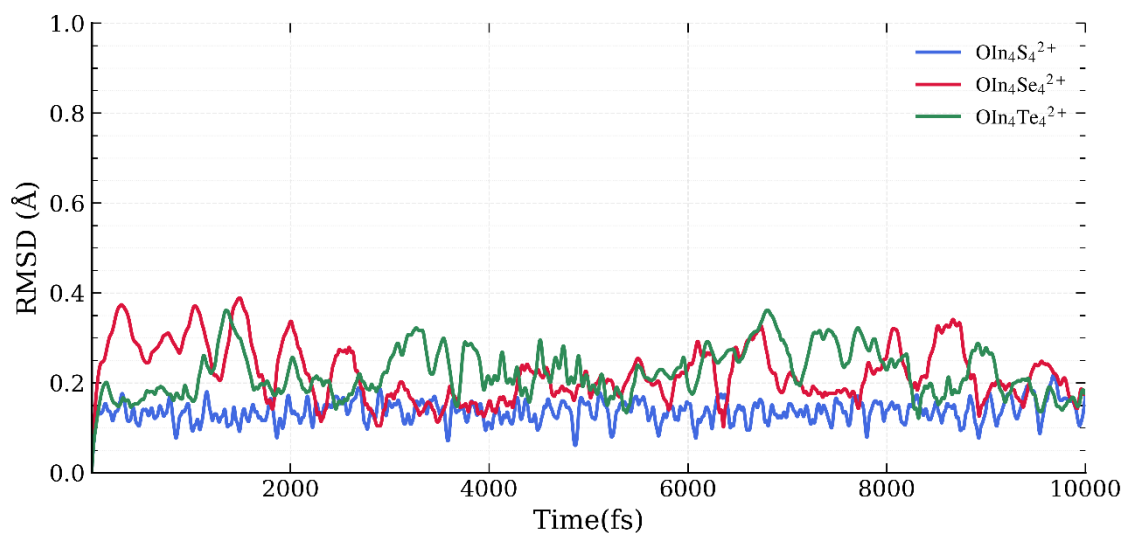


Figure S12. RMSD curves along the trajectories of Born-Oppenheimer molecular dynamics for a) $O\text{O}(\text{InE})_4^{2+}$ systems ($E= \text{S, Se, Te}$). The X-axis shows time in femtoseconds(fs), while the Y-axis shows RMSD in angstroms (\AA). Systems E: (Blue =S, red=Se and green=Te). Temperature (500 K).

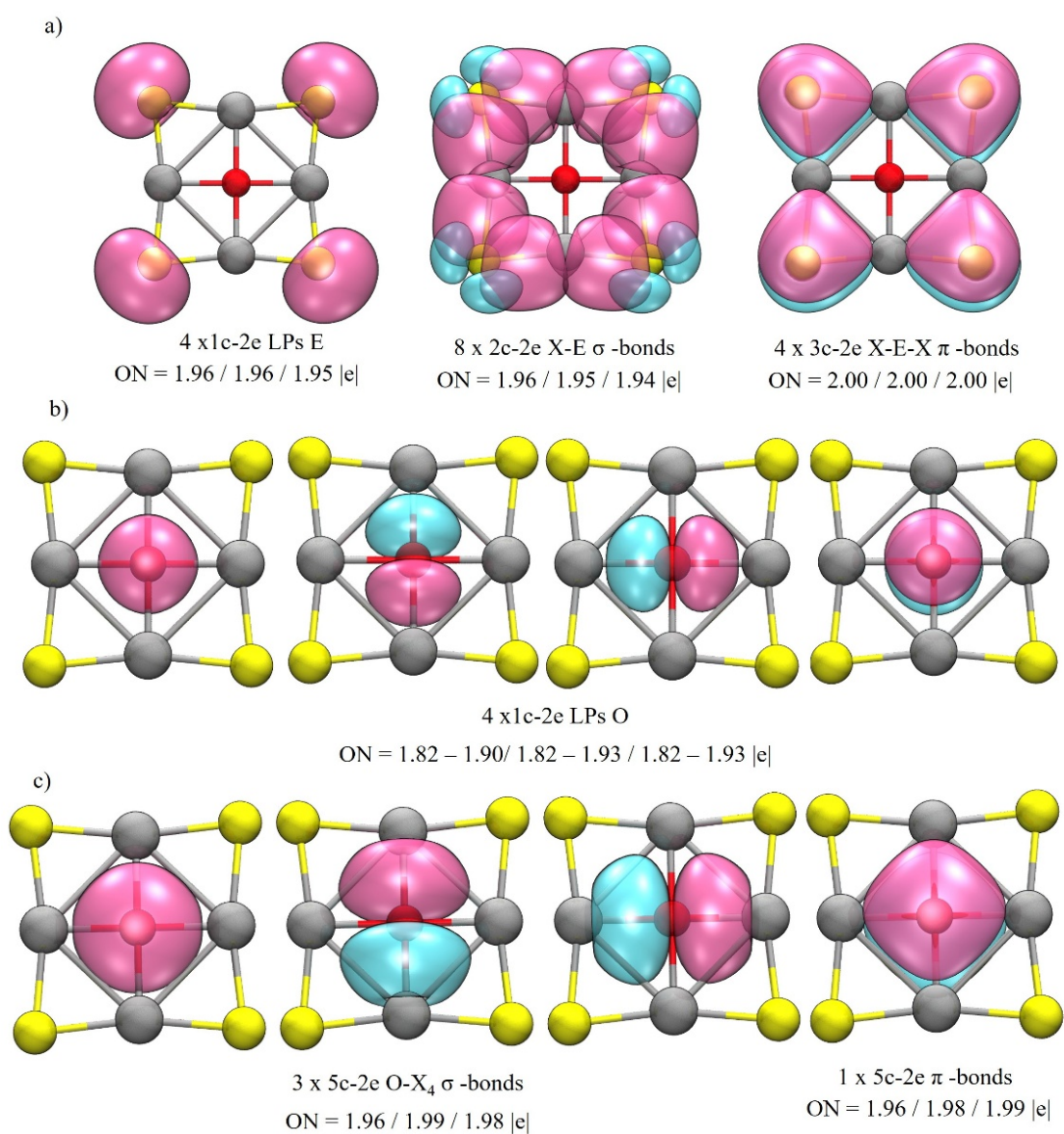


Figure S13. AdNDP bonding pattern of $O^\ominus(AlE)_4^{2+}$ ($E = S\text{--}Te$). a) AdNDP scheme with four 1c-2e E lone pairs, eight 2c-2e Al-E σ -bonds and four 3c-2e Al-E-Al π -bonds. b) Alternative pattern in line with an electrostatic model. c) Alternative pattern in line with delocalized bonding model. Occupation numbers are show.

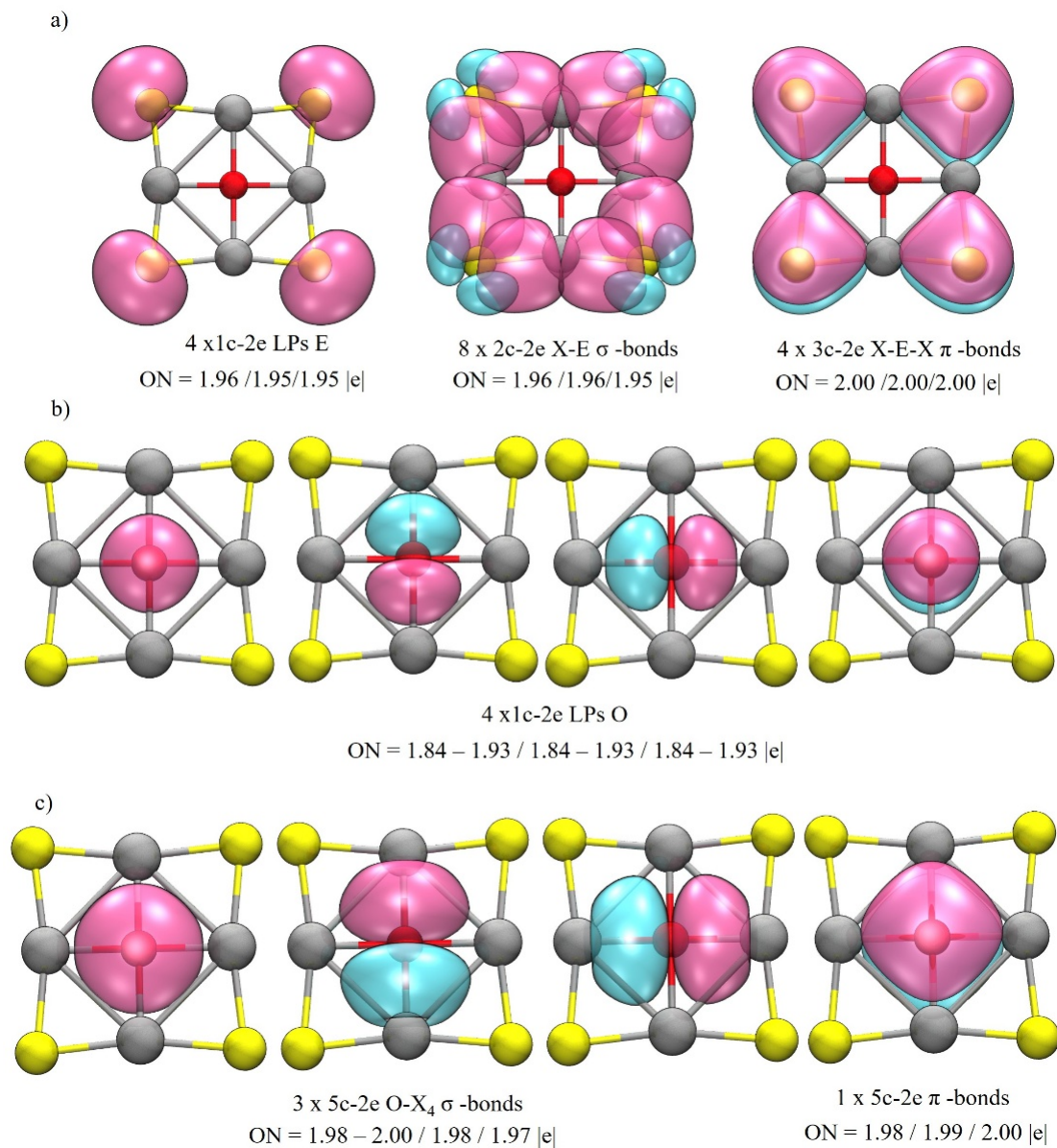


Figure S14. AdNDP bonding pattern of $\text{O}^\ominus(\text{GaE})_4^{2+}$ ($\text{E} = \text{S}-\text{Te}$). a) AdNDP scheme with four 1c-2e E lone pairs, eight 2c-2e Ga-E σ -bonds and four 3c-2e Ga-E-Ga π -bonds. b) Alternative pattern in line with an electrostatic model. c) Alternative pattern in line with delocalized bonding model. Occupation numbers are show.

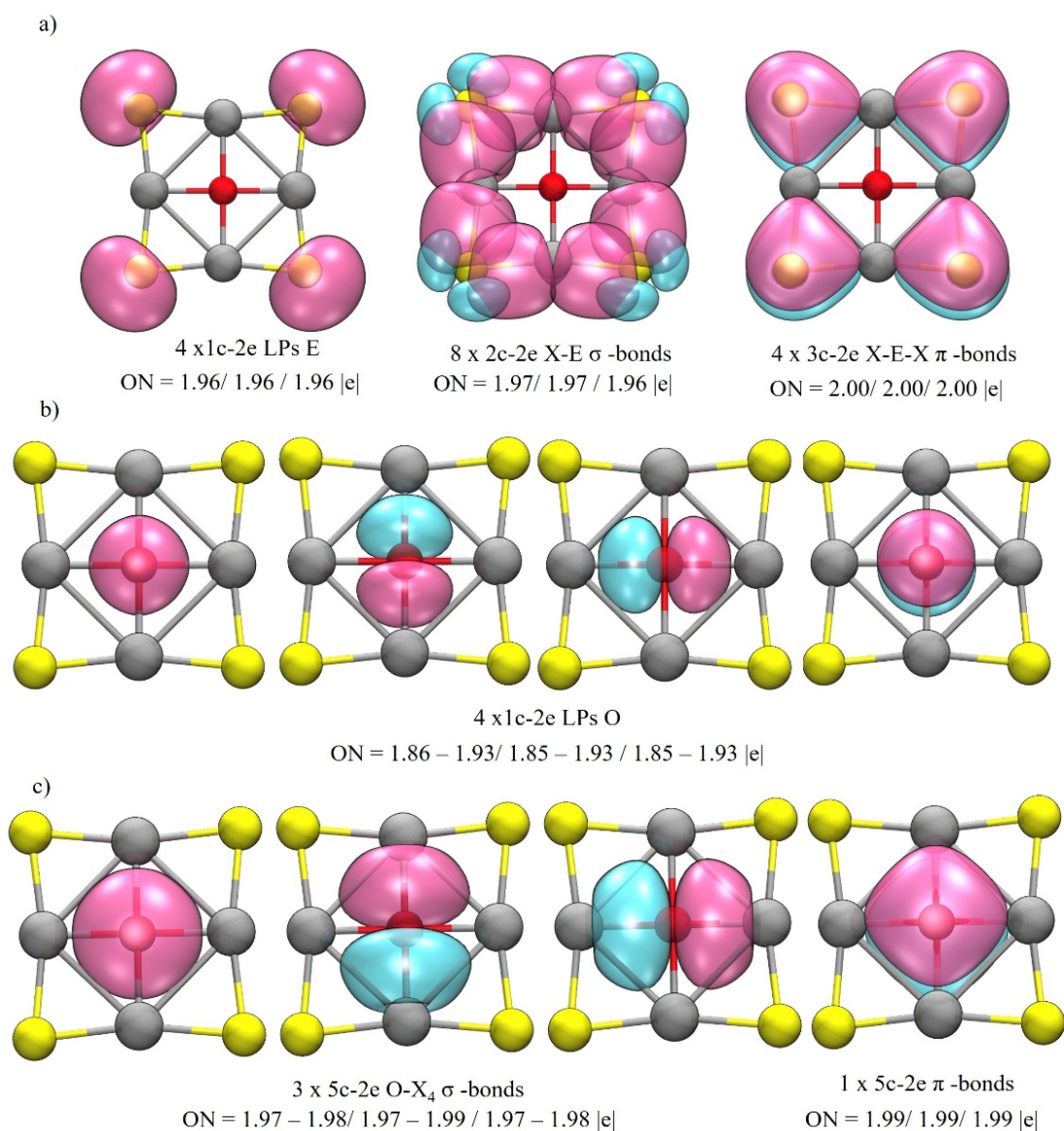


Figure S15. AdNDP bonding pattern of $\text{O}@\text{(InE)}_4^+$ ($\text{E} = \text{S}-\text{Te}$). a) AdNDP scheme with four 1c-2e E lone pairs, eight 2c-2e In-E σ -bonds and four 3c-2e In-E-In π -bonds. b) Alternative pattern in line with an electrostatic model. c) Alternative pattern in line with delocalized bonding model. Occupation numbers are shown.

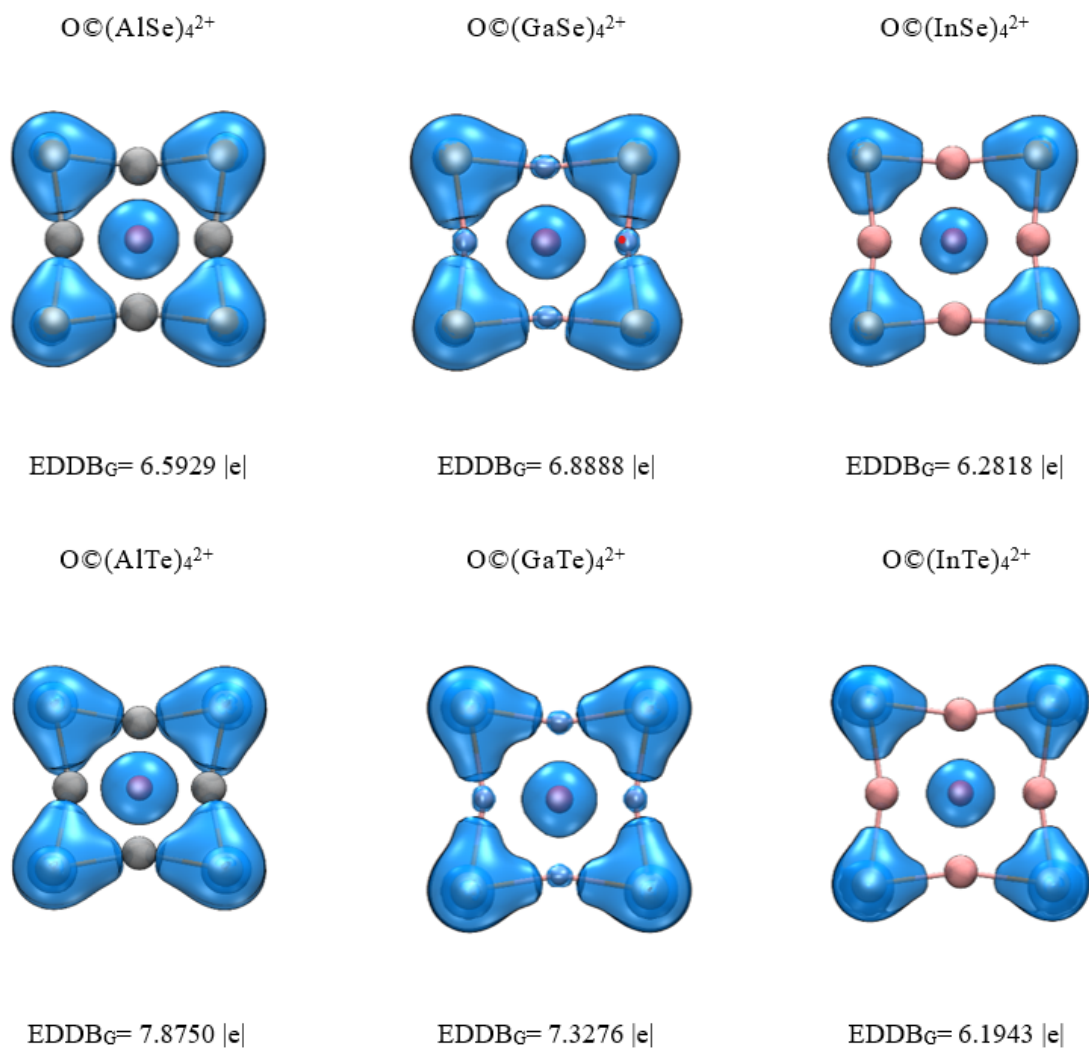


Figure S16. Isosurface contour by global EDDB_G function (isocontour of 0.006 a.u.) with the corresponding population of delocalized electrons for $\text{O}^\ominus\text{X}_4\text{E}_4^{2+}$ (X= Al/Ga/In, E= Se/Te) for each system at the $\omega\text{B97XD}/\text{def2-TZVP}$ level.

Table S1. Lowest vibrational frequencies (ν , cm^{-1}) for $D_{4h}\text{-O}\text{C}(\text{XE})_4^{2+}$, where X represents group 13 elements and E denotes chalcogens at PBE0-GD3/def2-TZVP level.

System	ν_{\min}	System	ν_{\min}	System	ν_{\min}
$\text{O}\text{C}(\text{BO})_4^{2+}$	-462.2	$\text{O}\text{C}(\text{AlO})_4^{2+}$	-190.6	$\text{O}\text{C}(\text{GaO})_4^{2+}$	-163.9
$\text{O}\text{C}(\text{BS})_4^{2+}$	-194.3	$\text{O}\text{C}(\text{AlS})_4^{2+}$	67.8	$\text{O}\text{C}(\text{GaS})_4^{2+}$	59.8
$\text{O}\text{C}(\text{BSe})_4^{2+}$	-123.9	$\text{O}\text{C}(\text{AlSe})_4^{2+}$	35.9	$\text{O}\text{C}(\text{GaSe})_4^{2+}$	32.6
$\text{O}\text{C}(\text{BTe})_4^{2+}$	-139.5	$\text{O}\text{C}(\text{AlTe})_4^{2+}$	20.4	$\text{O}\text{C}(\text{GaTe})_4^{2+}$	17.7
$\text{O}\text{C}(\text{BPO})_4^{2+}$	-156.6	$\text{O}\text{C}(\text{AlPO})_4^{2+}$	13.8	$\text{O}\text{C}(\text{GaPO})_4^{2+}$	11.5
System	ν_{\min}	System	ν_{\min}		
$\text{O}\text{C}(\text{InO})_4^{2+}$	-41.3	$\text{O}\text{C}(\text{TlO})_4^{2+}$	19.4		
$\text{O}\text{C}(\text{InS})_4^{2+}$	45.1	$\text{O}\text{C}(\text{TlS})_4^{2+}$	38.8		
$\text{O}\text{C}(\text{InSe})_4^{2+}$	27.4	$\text{O}\text{C}(\text{TlSe})_4^{2+}$	23.5		
$\text{O}\text{C}(\text{InTe})_4^{2+}$	15.3	$\text{O}\text{C}(\text{TlTe})_4^{2+}$	11.1		
$\text{O}\text{C}(\text{InPO})_4^{2+}$	10.0	$\text{O}\text{C}(\text{TlPO})_4^{2+}$	6.3		

Table S2. HOMO-LUMO energy gaps, singlet-triplet energy differences, smallest vibrational frequencies, T1-diagnostics for the global minimum $\text{O}\text{C}\text{X}_4\text{E}_4^{2+}$ (X= Al/Ga/In, E= S/Se/Te).

System	$\Delta E_{\text{H-L}}$ (eV)	$\Delta E_{\text{S-T}}$ (kcal/mol)	T ₁ Diagnostic
$\text{O}\text{C}(\text{AlS})_4^{2+}$	5.5	63.9	0.008
$\text{O}\text{C}(\text{AlSe})_4^{2+}$	5.2	85.7	0.009
$\text{O}\text{C}(\text{AlTe})_4^{2+}$	4.8	82.3	0.006
$\text{O}\text{C}(\text{GaS})_4^{2+}$	5.1	57.7	0.009
$\text{O}\text{C}(\text{GaSe})_4^{2+}$	4.8	84.0	0.006
$\text{O}\text{C}(\text{GaTe})_4^{2+}$	4.0	76.5	0.010
$\text{O}\text{C}(\text{InS})_4^{2+}$	4.5	72.0	0.011
$\text{O}\text{C}(\text{InSe})_4^{2+}$	4.3	73.1	0.008
$\text{O}\text{C}(\text{InTe})_4^{2+}$	3.8	64.9	0.010

Table S3. Energy components of IQA for the $D_{4h}\text{-O}\text{C}(\text{XE})_4^{2+}$ systems (X=Al-In and E=S-Te); $V_{\text{IQA}}^{\text{int}}$, V_c^{int} , and $V_{\text{XC}}^{\text{int}}$ are interatomic IQA interaction energy and their coulombic and exchange-correlation energy components, respectively, in kcal/mol.

	$\text{O}\text{C}(\text{AlS})_4^{2+}$	$\text{O}\text{C}(\text{GaS})_4^{2+}$	$\text{O}\text{C}(\text{InS})_4^{2+}$
ΔE_{IQA}	0.0	0.0	0.0

V_{IQA}^{int} (O-X)	-744.2	-426.2	-348.2
V_C^{int} (O-X)	-714.9	-368.4	-291.7
V_{XC}^{int} (O-X)	-29.2	-57.8	-56.6
δ (O-X)	0.196	0.390	1.061
V_{IQA}^{int} (X-X)	661.2	280.8	215.8
V_C^{int} (X-X)	662.0	285.0	221.2
V_{XC}^{int} (X-X)	-0.8	-4.2	-5.4
δ (X-X)	0.011	0.048	0.062
V_{IQA}^{int} (E-X)	-665.5	-294.1	-239.9
V_C^{int} (E-X)	-598.1	-170.3	-117.4
V_{XC}^{int} (E-X)	-67.4	-123.8	-122.5
δ (E-X)	0.538	0.961	1.003
	O\odot(AlSe)$_4^{2+}$	O\odot(GaSe)$_4^{2+}$	O\odot(InSe)$_4^{2+}$
ΔE_{IQA}	0.0	0.0	0.0
V_{IQA}^{int} (O-X)	-719.6	-388.1	-318.1
V_C^{int} (O-X)	-689.3	-329.6	-261.6
V_{XC}^{int} (O-X)	-30.3	-58.5	-56.5
δ (O-X)	0.21	0.40	0.12
V_{IQA}^{int} (X-X)	606.7	219.4	169.3
V_C^{int} (X-X)	607.7	224.6	175.8
V_{XC}^{int} (X-X)	-1	-5.2	-6.5
δ (X-X)	0.01	0.06	0.12
V_{IQA}^{int} (E-X)	-603.3	-230.1	-192
V_C^{int} (E-X)	-532.6	-106.3	-71.1
V_{XC}^{int} (E-X)	-70.7	-123.9	-120.9
δ (E-X)	0.59	1.00	1.03
	O\odot(AlTe)$_4^{2+}$	O\odot(GaTe)$_4^{2+}$	O\odot(InTe)$_4^{2+}$
ΔE_{IQA}	0.0	0.0	0.0
V_{IQA}^{int} (O-X)	-678.8	-328	-274.2
V_C^{int} (O-X)	-646.4	-268.5	-217.6

V_{XC}^{int} (O-X)	-32.4	-59.5	-56.6
δ (O-X)	0.68	0.42	0.01
V_{IQA}^{int} (X-X)	520	134.7	108.6
V_C^{int} (X-X)	521.4	142.3	117.1
V_{XC}^{int} (X-X)	-1.4	-7.5	-8.4
δ (X-X)	0.003	0.08	0.14
V_{IQA}^{int} (E-X)	-56.8	-152.1	-136.5
V_C^{int} (E-X)	-430	-29.4	-19
V_{XC}^{int} (E-X)	-76.8	-122.8	-117.6
δ (E-X)	0.26	1.06	1.07

Cartesian Coordinates

Cartesian Coordinates of the $O\odot X_4E_4^{2+}$ (X = Al; E = S) clusters calculated at the PBE0-GD3/def2-TZVP level of theory.

1a				1b			
S	2.232221000	2.232221000	0.000000000	S	0.288000000	3.134110000	0.043833000
S	-2.232221000	-2.232221000	0.000000000	S	-0.330869000	-3.126478000	0.012158000
Al	0.000000000	1.995835000	0.000000000	Al	1.583158000	1.280060000	-0.031631000
S	2.232221000	-2.232221000	0.000000000	Al	-1.551029000	-1.260676000	0.061869000
S	-2.232221000	2.232221000	0.000000000	O	0.024721000	0.013698000	0.015812000
Al	0.000000000	-1.995835000	0.000000000	Al	-1.254281000	1.519597000	-0.034081000
Al	1.995835000	0.000000000	0.000000000	Al	1.239409000	-1.517679000	-0.041236000
O	0.000000000	0.000000000	0.000000000	S	-3.133359000	0.317583000	-0.032236000
Al	-1.995835000	0.000000000	0.000000000	S	3.149845000	-0.349371000	0.004967000
1c				1d			
Al	-27.688771000	0.137568000	-0.345665000	Al	-27.101860000	-0.037132000	-0.084990000
Al	3.915173000	-0.877330000	-1.267211000	S	5.605361000	0.950349000	-0.683888000
S	2.703891000	2.538689000	1.508810000	S	5.635893000	-1.304913000	-0.127372000
Al	3.809617000	1.901030000	-0.419259000	Al	3.618035000	1.595416000	0.232493000
Al	2.196875000	0.258196000	1.337478000	Al	3.417565000	-1.675382000	0.271938000
O	3.093581000	0.256428000	-0.186446000	Al	1.171230000	0.164592000	0.252193000
S	1.930880000	-1.999922000	1.526354000	S	1.173028000	-2.095920000	-0.169862000
S	3.156542000	-2.792440000	-0.281500000	S	1.440586000	2.412390000	0.066565000
S	5.097671000	0.972144000	-2.096033000	O	2.994686000	-0.000989000	0.737707000

Table S4. Cartesian Coordinates of the $O\odot X_4E_4^{2+}$ (X = Ga; E = S) clusters calculated at the PBE0-GD3/def2-TZVP level of theory.

2a				2b			
S	1.209228000	-1.577620000	0.628960000	S	2.257123000	2.257123000	0.000000000
Ga	5.509676000	0.320994000	-0.383242000	S	-2.257123000	-2.257123000	0.000000000
O	4.008492000	0.000415000	0.809233000	Ga	0.000000000	2.076253000	0.000000000

S	5.424553000	-1.902958000	-1.024006000	S	2.257123000	-2.257123000	0.000000000
Ga	2.982575000	1.558217000	0.472167000	S	-2.257123000	2.257123000	0.000000000
Ga	3.476011000	-1.747269000	0.263165000	Ga	0.000000000	-2.076253000	0.000000000
S	4.886802000	2.533514000	-0.511983000	Ga	2.076253000	0.000000000	0.000000000
S	0.910405000	0.620179000	0.087254000	O	0.000000000	0.000000000	0.000000000
Ga	-19.418705000	0.036666000	-0.137814000	Ga	-2.076253000	0.000000000	0.000000000
2c				2d			
S	-2.875538000	-2.682025000	0.679913000	S	-0.616861000	-0.703629000	1.094258000
Ga	-2.414811000	1.786352000	-0.121178000	Ga	1.193300000	-1.583551000	-0.010673000
S	-3.607057000	1.601332000	1.906132000	Ga	1.691651000	1.711563000	-0.078596000
Ga	-3.696115000	-0.580868000	1.159936000	Ga	-10.579361000	-0.042028000	-0.229372000
Ga	12.385207000	-0.076919000	0.473559000	Ga	3.898068000	-0.272425000	-0.426000000
Ga	-1.862168000	-1.412404000	-0.982144000	S	3.431021000	-2.458400000	0.108637000
O	-3.020353000	0.033659000	-0.564131000	S	-0.480644000	1.548314000	0.599487000
S	-0.498198000	1.916489000	-1.405875000	S	4.041570000	1.980008000	0.044995000
S	-0.057499000	-0.302688000	-1.925314000	O	1.960655000	-0.010129000	-0.809271000

Table S5. Cartesian Coordinates of the $\text{O}@\text{X}_4\text{E}_4^{2+}$ ($\text{X} = \text{In}$; $\text{E} = \text{S}$) clusters calculated at the PBE0-GD3/def2-TZVP level of theory.

3a				3b			
S	2.390760000	2.390760000	0.000000000	In	2.141370000	-4.806382000	-0.029436000
S	-2.390760000	-2.390760000	0.000000000	In	-14.586017000	0.393810000	0.124231000
In	0.000000000	2.223940000	0.000000000	S	3.004531000	-2.416856000	-0.839900000
S	2.390760000	-2.390760000	0.000000000	S	2.903468000	4.420333000	-0.857349000
S	-2.390760000	2.390760000	0.000000000	In	3.552599000	-0.390054000	0.100050000
In	0.000000000	-2.223940000	0.000000000	In	4.057499000	2.835599000	0.579384000
In	2.223940000	0.000000000	0.000000000	O	2.920392000	1.461627000	-0.587157000
O	0.000000000	0.000000000	0.000000000	S	4.987558000	0.927142000	1.677297000
In	-2.223940000	0.000000000	0.000000000	S	2.450052000	2.362585000	-2.057545000
3c				3d			
In	15.496422000	-0.937801000	-0.106503000	In	11.259063000	0.673299000	0.566215000
S	0.662106000	1.388152000	0.723594000	In	-5.315034000	2.685860000	0.693627000
In	-1.327872000	2.458184000	-0.193294000	In	-2.913904000	-2.584792000	1.160433000
In	-6.708561000	-3.315988000	-0.162970000	S	-3.775449000	0.448526000	0.499011000
O	-1.995954000	0.415408000	-0.090892000	S	-0.033861000	-2.502868000	-1.238090000
S	-5.608156000	-0.984393000	-0.017292000	S	-0.235594000	0.655730000	-2.555319000
In	-4.074592000	0.698624000	0.018082000	S	1.212028000	-0.702087000	-1.400926000
S	-3.612601000	3.106529000	-0.373942000	O	-1.354069000	-1.735164000	-0.219509000
S	-0.811153000	-0.358486000	1.074937000	In	-1.884032000	0.194868000	-0.851269000

Table S6. Cartesian Coordinates of the $\text{O}@\text{X}_4\text{E}_4^{2+}$ ($\text{X} = \text{Al}$; $\text{E} = \text{Se}$) clusters calculated at the PBE0-GD3/def2-TZVP level of theory.

4a				4b			
Se	2.144664000	-2.144664000	0.000000000	Se	2.144583000	2.144583000	0.000000000
Al	0.000000000	1.922328000	0.000000000	Se	-2.144583000	-2.144583000	0.000000000
Al	0.000000000	-1.922328000	0.000000000	Al	0.000000000	1.922119000	0.000000000
Se	2.144664000	2.144664000	0.000000000	Se	2.144583000	-2.144583000	0.000000000
Se	-2.144664000	-2.144664000	0.000000000	Se	-2.144583000	2.144583000	0.000000000
Se	-2.144664000	2.144664000	0.000000000	Al	0.000000000	-1.922119000	0.000000000
Al	1.922328000	0.000000000	0.000000000	Al	1.922119000	0.000000000	0.000000000
O	0.000000000	0.000000000	0.000000000	O	0.000000000	0.000000000	0.000000000
Al	-1.922328000	0.000000000	0.000000000	Al	-1.922119000	0.000000000	0.000000000
4c				4d			
Se	0.860941000	-3.697829000	0.000000000	Se	1.392523000	-2.714640000	0.000000000
Al	-1.595248000	2.919669000	0.000000000	Se	-1.665862000	2.954831000	0.000000000
Al	1.392109000	-1.512488000	0.000000000	Al	-1.713301000	0.765419000	0.000000000
Se	-0.936256000	2.005679000	1.772961000	Al	0.480958000	2.845965000	0.000000000

Al	-0.936256000	-2.587222000	0.000000000	Se	-2.617702000	-1.189683000	0.000000000
Se	-0.936256000	2.005679000	-1.772961000	Al	1.715654000	0.581247000	0.000000000
Se	2.191781000	0.416783000	0.000000000	Se	2.887183000	-1.215208000	0.000000000
O	-0.469649000	-0.971080000	0.000000000	O	0.000000000	0.152640000	0.000000000
Al	-0.024156000	0.878785000	0.000000000	Al	-0.478562000	-1.622316000	0.000000000

Table S7. Cartesian Coordinates of the $O@X_4E_4^{2+}$ ($X = Ga$; $E = Se$) clusters calculated at the PBE0-GD3/def2-TZVP level of theory.

5a				5b			
Se	2.144664000	-2.144664000	0.000000000	Se	0.860941000	-3.697829000	0.000000000
Ga	0.000000000	1.922328000	0.000000000	Ga	-1.595248000	2.919669000	0.000000000
Ga	0.000000000	-1.922328000	0.000000000	Ga	1.392109000	-1.512488000	0.000000000
Se	2.144664000	2.144664000	0.000000000	Se	-0.936256000	2.005679000	1.772961000
Se	-2.144664000	-2.144664000	0.000000000	Ga	-0.936256000	-2.587222000	0.000000000
Se	-2.144664000	2.144664000	0.000000000	Se	-0.936256000	2.005679000	-1.772961000
Ga	1.922328000	0.000000000	0.000000000	Se	2.191781000	0.416783000	0.000000000
O	0.000000000	0.000000000	0.000000000	O	-0.469649000	-0.971080000	0.000000000
Ga	-1.922328000	0.000000000	0.000000000	Ga	-0.024156000	0.878785000	0.000000000
5c				5d			
Se	1.392523000	-2.714640000	0.000000000	Se	1.673136000	2.950913000	0.000000000
Se	-1.665862000	2.954831000	0.000000000	Se	-2.889208000	-1.208918000	0.000000000
Ga	-1.713301000	0.765419000	0.000000000	Ga	-0.473480000	2.846436000	0.000000000
Ga	0.480958000	2.845965000	0.000000000	Se	2.614275000	-1.195549000	0.000000000
Se	-2.617702000	-1.189683000	0.000000000	Se	-1.398217000	-2.711972000	0.000000000
Ga	1.715654000	0.581247000	0.000000000	Ga	0.474359000	-1.622775000	0.000000000
Se	2.887183000	-1.215208000	0.000000000	Ga	1.714253000	0.761380000	0.000000000
O	0.000000000	0.152640000	0.000000000	O	0.000000000	0.153072000	0.000000000
Ga	-0.478562000	-1.622316000	0.000000000	Ga	-1.715115000	0.586023000	0.000000000

Table S8. Cartesian Coordinates of the $O@X_4E_4^{2+}$ ($X = In$; $E = Se$) clusters calculated at the PBE0-GD3/def2-TZVP level of theory.

6a				6b			
Se	2.144664000	-2.144664000	0.000000000	Se	0.860941000	-3.697829000	0.000000000
In	0.000000000	1.922328000	0.000000000	In	-1.595248000	2.919669000	0.000000000
In	0.000000000	-1.922328000	0.000000000	In	1.392109000	-1.512488000	0.000000000
Se	2.144664000	2.144664000	0.000000000	Se	-0.936256000	2.005679000	1.772961000
Se	-2.144664000	-2.144664000	0.000000000	In	-0.936256000	-2.587222000	0.000000000
Se	-2.144664000	2.144664000	0.000000000	Se	-0.936256000	2.005679000	-1.772961000
In	1.922328000	0.000000000	0.000000000	Se	2.191781000	0.416783000	0.000000000
O	0.000000000	0.000000000	0.000000000	O	-0.469649000	-0.971080000	0.000000000
In	-1.922328000	0.000000000	0.000000000	In	-0.024156000	0.878785000	0.000000000
6c				6d			
Se	1.392523000	-2.714640000	0.000000000	Se	1.673136000	2.950913000	0.000000000
Se	-1.665862000	2.954831000	0.000000000	Se	-2.889208000	-1.208918000	0.000000000
In	-1.713301000	0.765419000	0.000000000	In	-0.473480000	2.846436000	0.000000000
In	0.480958000	2.845965000	0.000000000	Se	2.614275000	-1.195549000	0.000000000
Se	-2.617702000	-1.189683000	0.000000000	Se	-1.398217000	-2.711972000	0.000000000
In	1.715654000	0.581247000	0.000000000	In	0.474359000	-1.622775000	0.000000000
Se	2.887183000	-1.215208000	0.000000000	In	1.714253000	0.761380000	0.000000000
O	0.000000000	0.152640000	0.000000000	O	0.000000000	0.153072000	0.000000000
In	-0.478562000	-1.622316000	0.000000000	In	-1.715115000	0.586023000	0.000000000

Table S9. Cartesian Coordinates of the $O@X_4E_4^{2+}$ ($X = Al$; $E = Te$) clusters calculated at the PBE0-GD3/def2-TZVP level of theory.

7a				7b			
Te	2.179386000	2.179386000	0.000000000	Al	1.840714000	-1.709971000	-0.006282000
Te	-2.179386000	-2.179386000	0.000000000	Te	-3.246097000	0.330622000	-0.174802000
Al	0.000000000	2.006028000	0.000000000	Te	3.256568000	-0.046581000	-0.010022000
Te	2.179386000	-2.179386000	0.000000000	Te	-2.782160000	-1.686398000	0.182516000
Te	-2.179386000	2.179386000	0.000000000	Al	-0.626117000	-1.766952000	-0.038873000
Al	0.000000000	-2.006028000	0.000000000	Te	0.173784000	3.000051000	0.047381000
Al	2.006028000	0.000000000	0.000000000	Al	1.476893000	1.257992000	0.001300000
O	0.000000000	0.000000000	0.000000000	Al	-1.346809000	1.392254000	0.024457000
Al	-2.006028000	0.000000000	0.000000000	O	-0.014828000	0.007985000	-0.014978000
7c				7d			
Te	1.461230000	2.196864000	-0.454756000	Te	-3.830514000	0.660252000	-0.811870000
Al	4.259898000	-1.349028000	-0.730219000	Al	4.122244000	-1.596391000	-0.132571000
Te	3.373425000	1.426448000	-0.268098000	Al	0.072039000	-0.349413000	0.157370000
Te	1.893836000	-1.173013000	0.864147000	Te	2.131326000	0.227369000	-0.026465000
Al	-3.093542000	-0.099279000	-0.057160000	O	-0.996753000	1.188371000	0.194963000
Te	3.290799000	0.282399000	1.431714000	Te	-2.508098000	1.139180000	0.767528000
Al	0.392096000	0.325160000	0.052965000	Al	-2.901826000	-1.123023000	-0.091264000
Al	-6.387223000	-0.288003000	-0.067907000	Te	-1.102303000	-2.247302000	0.242787000
O	-1.327090000	0.002810000	-0.037021000	Al	1.705202000	2.875957000	-0.072612000

Table S10. Cartesian Coordinates of the $O@X_4E_4^{2+}$ ($X = Ga$; $E = Te$) clusters calculated at the PBE0-GD3/def2-TZVP level of theory.

8a				8b			
Te	2.179386000	2.179386000	0.000000000	Ga	1.840714000	-1.709971000	-0.006282000
Te	-2.179386000	-2.179386000	0.000000000	Te	-3.246097000	0.330622000	-0.174802000
Ga	0.000000000	2.006028000	0.000000000	Te	3.256568000	-0.046581000	-0.010022000
Te	2.179386000	-2.179386000	0.000000000	Te	-2.782160000	-1.686398000	0.182516000
Te	-2.179386000	2.179386000	0.000000000	Ga	-0.626117000	-1.766952000	-0.038873000
Ga	0.000000000	-2.006028000	0.000000000	Te	0.173784000	3.000051000	0.047381000
Ga	2.006028000	0.000000000	0.000000000	Ga	1.476893000	1.257992000	0.001300000
O	0.000000000	0.000000000	0.000000000	Ga	-1.346809000	1.392254000	0.024457000
Ga	-2.006028000	0.000000000	0.000000000	O	-0.014828000	0.007985000	-0.014978000
8c				8d			
Te	1.461230000	2.196864000	-0.454756000	Te	-3.830514000	0.660252000	-0.811870000
Ga	4.259898000	-1.349028000	-0.730219000	Ga	4.122244000	-1.596391000	-0.132571000
Te	3.373425000	1.426448000	-0.268098000	Ga	0.072039000	-0.349413000	0.157370000
Te	1.893836000	-1.173013000	0.864147000	Te	2.131326000	0.227369000	-0.026465000
Ga	-3.093542000	-0.099279000	-0.057160000	O	-0.996753000	1.188371000	0.194963000
Te	3.290799000	0.282399000	1.431714000	Te	-2.508098000	1.139180000	0.767528000
Ga	0.392096000	0.325160000	0.052965000	Ga	-2.901826000	-1.123023000	-0.091264000
Ga	-6.387223000	-0.288003000	-0.067907000	Te	-1.102303000	-2.247302000	0.242787000
O	-1.327090000	0.002810000	-0.037021000	Ga	1.705202000	2.875957000	-0.072612000

Table S11. Cartesian Coordinates of the $O@X_4E_4^{2+}$ ($X = In$; $E = Te$) clusters calculated at the PBE0-GD3/def2-TZVP level of theory.

9a				9b			
Te	2.179386000	2.179386000	0.000000000	In	1.840714000	-1.709971000	-0.006282000
Te	-2.179386000	-2.179386000	0.000000000	Te	-3.246097000	0.330622000	-0.174802000
In	0.000000000	2.006028000	0.000000000	Te	3.256568000	-0.046581000	-0.010022000
Te	2.179386000	-2.179386000	0.000000000	Te	-2.782160000	-1.686398000	0.182516000
Te	-2.179386000	2.179386000	0.000000000	In	-0.626117000	-1.766952000	-0.038873000
In	0.000000000	-2.006028000	0.000000000	Te	0.173784000	3.000051000	0.047381000
In	2.006028000	0.000000000	0.000000000	In	1.476893000	1.257992000	0.001300000

O	0.000000000	0.000000000	0.000000000	In	-1.346809000	1.392254000	0.024457000
In	-2.006028000	0.000000000	0.000000000	O	-0.014828000	0.007985000	-0.014978000
9c				9d			
Te	1.461230000	2.196864000	-0.454756000	Te	-3.830514000	0.660252000	-0.811870000
In	4.259898000	-1.349028000	-0.730219000	In	4.122244000	-1.596391000	-0.132571000
Te	3.373425000	1.426448000	-0.268098000	In	0.072039000	-0.349413000	0.157370000
Te	1.893836000	-1.173013000	0.864147000	Te	2.131326000	0.227369000	-0.026465000
In	-3.093542000	-0.099279000	-0.057160000	O	-0.996753000	1.188371000	0.194963000
Te	3.290799000	0.282399000	1.431714000	Te	-2.508098000	1.139180000	0.767528000
In	0.392096000	0.325160000	0.052965000	In	-2.901826000	-1.123023000	-0.091264000
In	-6.387223000	-0.288003000	-0.067907000	Te	-1.102303000	-2.247302000	0.242787000
O	-1.327090000	0.002810000	-0.037021000	In	1.705202000	2.875957000	-0.072612000