SUPPORTING INFORMATION

$HLi_4Cl_4^-$: A Planar Tetracoordinate Hydrogen Superhalogen Anion

Hui-Feng Yan and Jin-Chang Guo*

Key Laboratory of Materials for Energy Conversion and Storage of Shanxi Province,

Institute of Molecular Science, Shanxi University, Taiyuan, 030006, China

E-mail: guojc@sxu.edu.cn

Supporting Information

Table S1. The lowest vibrational frequency at ten classical theoretical levels for the global-minimum structure **1** (D_{4h}, $^1A_{1g}$) of $HLi_4Cl_4^-$ cluster.

Table S2. Orbital composition analysis of canonical molecular orbitals (CMOs) of **1**.

Table S3. Energy components of IQA for $HLi_4Cl_4^-$ at the PBE0/TZ2P level; V_{IQA}^{int}, V_C^{int}, and V_{XC}^{int} are the interatomic IQA interaction energy, the coulombic and exchange-correlation energy components, respectively, in kcal mol^{-1}.

Figure S1. Optimized structures for top 12 low-lying isomers of $HLi_4Cl_4^-$ at the PBE0-D3(BJ)/def2-TZVPP level. Relative energies are listed in kcal mol^{-1} at the single-point CCSD(T)/def2-TZVPP//PBE0-D3(BJ)/def2-TZVPP levels, with zero-point energy (ZPE) corrections. The T_1 diagnostic values of the converged CCSD wavefunction are shown within parentheses.

Figure S2. Optimized structures of cube-like Li_4Cl_4 (T_d, $^1A_1$) and star-like Li_4Cl_4 (D_{4h}, $^1A_{1g}$) at the PBE0-D3(BJ)/def2-TZVPP level. The bond distances (in Å) are shown. Relative energies are listed in kcal mol^{-1} at the PBE0-D3(BJ)/def2-TZVPP levels, with zero-point energy (ZPE) corrections.

Figure S3. Canonical molecular orbitals (CMOs) of the ptH **1** cluster. (a) Twelve lone pairs CMOs for one-center two-electron (1c-2e) of Cl atoms. (b) Four σ CMOs for

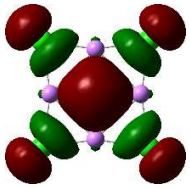
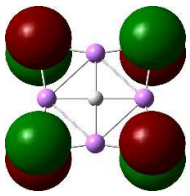
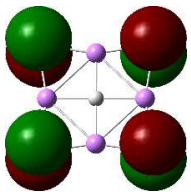
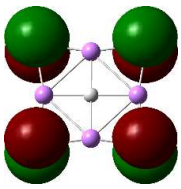
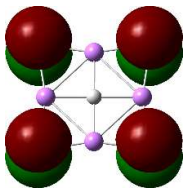
(3c-2e) Li–Cl–Li bonds. (c) One delocalized σ CMO over HLi_4 unit.

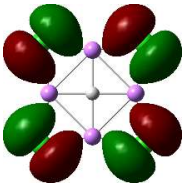
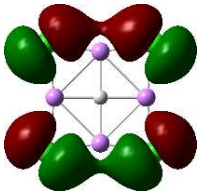
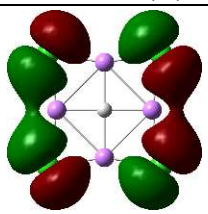
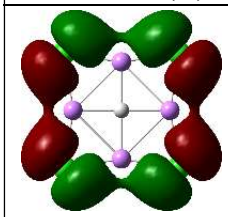
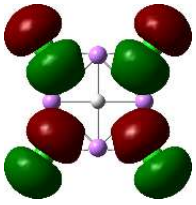
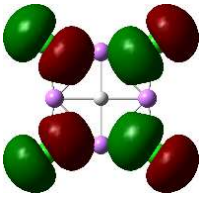
Cartesian coordinates of optimized structures of 12 low-lying isomers of $HLi_4Cl_4^-$.

Table S1. The lowest vibrational frequency at ten classical theoretical levels for the global-minimum structure **1** (D_{4h}, $^1A_{1g}$) of $HLi_4Cl_4^-$ cluster.

	Theoretical level	Lowest vibrational frequency (cm^{-1})
1	PBE0-D3(BJ)/def2-TZVPP	35.1
2	BP86-D3(BJ)/def2-TZVPP	32.1
3	B3LYP-D3(BJ)/def2-TZVPP	34.1
4	B2PLYP-D3(BJ)/def2-TZVPP	35.1
5	B3PW91-D3(BJ)/def2-TZVPP	32.5
6	CCSD/def2-TZVPP	34.6
7	TPSS-D3(BJ)/def2-TZVPP	31.8
8	WB97XD/def2-TZVPP	33.1
9	TPSSh/def2-TZVPP	36.1
10	MP2/def2-TZVPP	35.6

Table S2. Orbital composition analysis of canonical molecular orbitals (CMOs) of **1**.

CMO	H (%)		Li_4 (%)		Cl_4 (%)	
	s/p	total	s/p	total	s/p	total
 HOMO (a_{1g})	47.10/0.00	47.10	0.00/5.22	5.22	0.00/46.62	46.62
 HOMO−1 (b_{1u})	0.00/0.00	0.00	0.00/0.00	0.00	0.00/99.80	99.80
 HOMO−2 (e_g)	0.00/0.00	0.00	0.00/2.39	2.39	0.00/97.42	97.42
 HOMO−2′ (e_g)	0.00/0.00	0.00	0.00/2.39	2.39	0.00/97.42	97.42
 HOMO−3 (a_{2u})	0.00/0.00	0.00	0.00/5.45	5.45	0.00/94.36	94.36

CMO	H (%)		Li_4 (%)		Cl_4 (%)	
	s/p	total	s/p	total	s/p	total
 HOMO–4 (a_{2g})	0.00/0.00	0.00	0.00/0.00	0.00	0.00/98.84	98.84
 HOMO–5 (e_u)	0.00/0.00	0.00	0.00/3.48	3.48	0.00/96.40	96.40
 HOMO–5′ (e_u)	0.00/0.00	0.00	0.00/3.48	3.48	0.00/96.40	96.40
 HOMO–6 (b_{1g})	0.00/0.00	0.00	2.88/2.88	5.76	0.00/93.62	93.62
 HOMO–7 (a_{1g})	0.00/0.00	0.00	1.25/1.27	2.52	0.00/95.76	95.76
 HOMO–7′ (e_u)	0.00/0.00	0.00	1.25/1.27	2.52	0.00/95.76	95.76

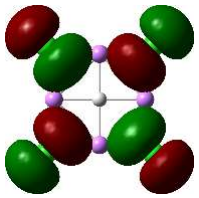
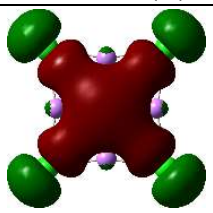
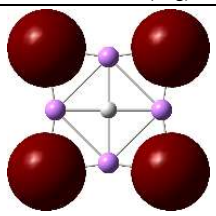
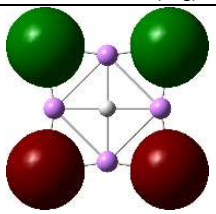
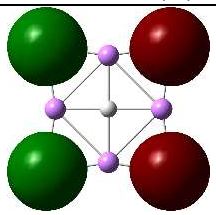
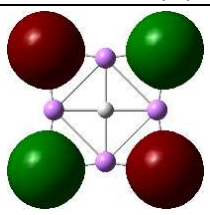
CMO	H (%)		Li_4 (%)		Cl_4 (%)	
	s/p	total	s/p	total	s/p	total
 HOMO−8 (e_u)	0.00/0.00	0.00	0.00/0.00	0.00	0.00/97.61	97.61
 HOMO−9 (a_{1g})	32.81/0.00	32.81	6.95/7.48	14.43	0.00/50.12	50.12
 HOMO−10 (a_{1g})	0.00/0.00	0.00	4.40/0.00	4.40	90.94/0.00	90.94
 HOMO−11 (e_u)	0.00/0.00	0.00	1.93/4.39	6.32	89.00/0.00	89.00
 HOMO−11′ (e_u)	0.00/0.00	0.00	1.93/4.39	6.32	89.00/0.00	89.00
 HOMO−12 (b_{2g})	0.00/0.00	0.00	0.00/7.58	7.58	87.98/0.00	87.98

Table S3. Energy components of IQA for $HLi_4Cl_4^-$ at the PBE0/TZ2P level; V_{IQA}^{int}, V_C^{int}, and V_{XC}^{int} are the interatomic IQA interaction energy, the coulombic and exchange-correlation energy components, respectively, in kcal mol^{-1}.

	$HLi_4Cl_4^-$
V_{IQA}^{int}(H–Li)	−128.72
V_C^{int} (H– Li)	−120.65 (93.73%)
V_{XC}^{int} (H– Li)	–8.07 (6.27%)
V_{IQA}^{int} (Li –Li)	96.49
V_C^{int} (Li–Li)	96.64 (99.85%)
V_{XC}^{int} (Li–Li)	–0.15 (0.15%)
V_{IQA}^{int} (Li –Cl)	−138.62
V_C^{int} (Li – Cl)	−125.11 (90.25%)
V_{XC}^{int} (Li – Cl)	−13.51 (9.75%)

Figure S1. Optimized structures for top 12 low-lying isomers of $HLi_4Cl_4^-$ at the PBE0-D3(BJ)/def2-TZVPP level. Relative energies are listed in kcal mol^{-1} at the single-point CCSD(T)/def2-TZVPP//PBE0-D3(BJ)/def2-TZVPP levels, with zero-point energy (ZPE) corrections. The T_1 diagnostic values of the converged CCSD wavefunction are shown within parentheses.

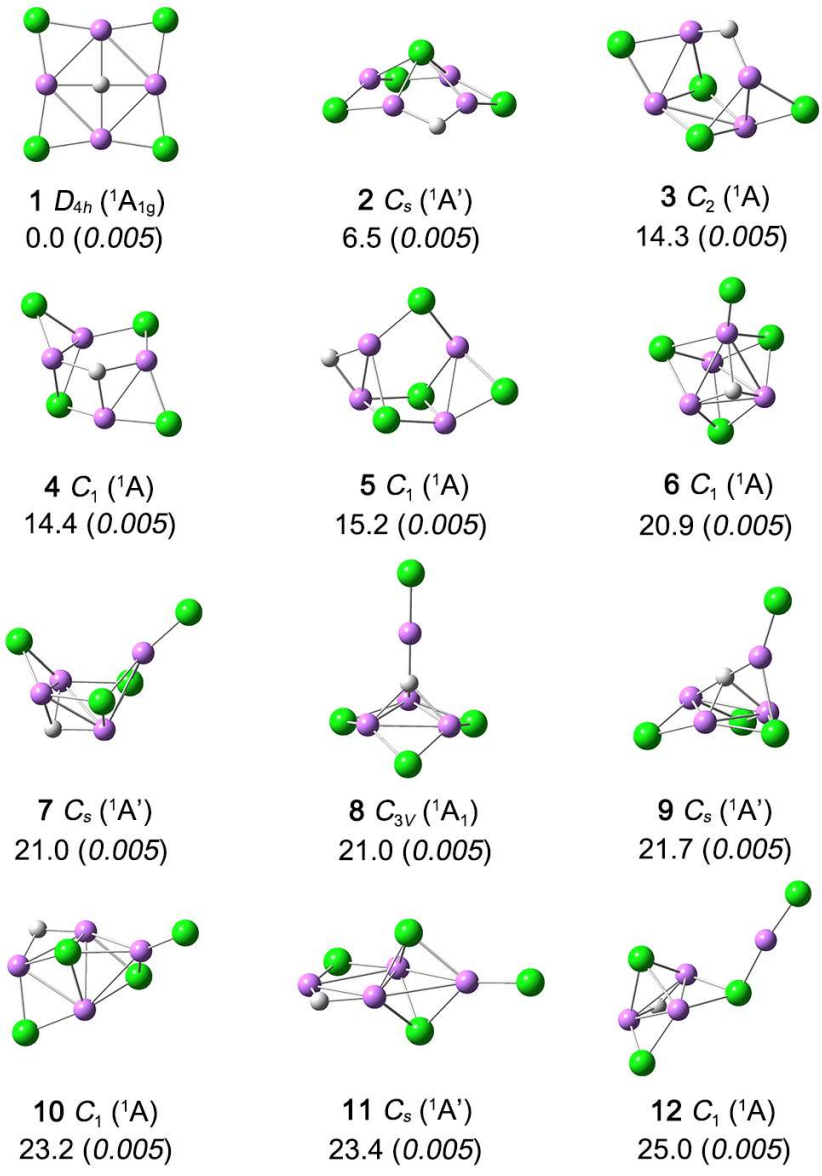
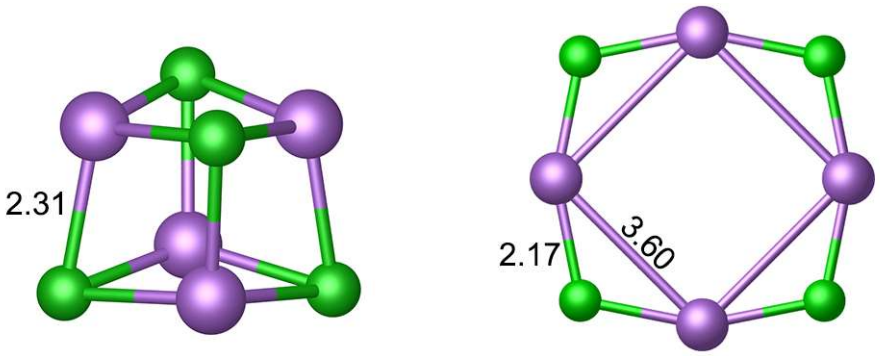


Figure S2. Optimized structures of cube-like Li_4Cl_4 (T_d, $^1A_1$) and star-like Li_4Cl_4 (D_{4h}, $^1A_{1g}$) at the PBE0-D3(BJ)/def2-TZVPP level. The bond distances (in Å) are shown. Relative energies are listed in kcal mol^{-1} at the PBE0-D3(BJ)/def2-TZVPP levels, with zero-point energy (ZPE) corrections.



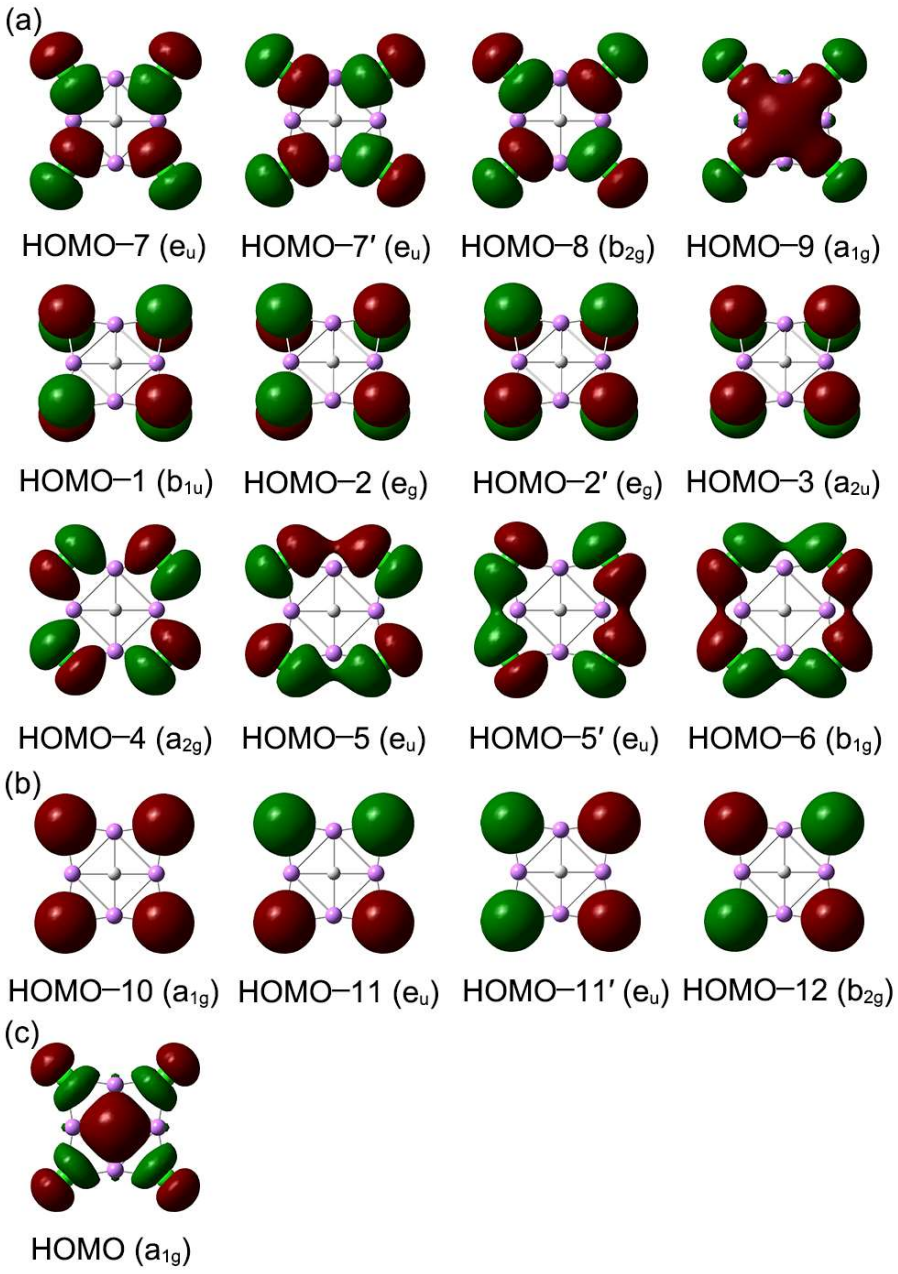
Li_4Cl_4 (T_d, $^1A_1$)

0.0

Li_4Cl_4 (D_{4h}, $^1A_{1g}$)

18.8

Figure S3. Canonical molecular orbitals (CMOs) of the ptH **1** cluster. (a) Twelve lone pairs CMOs for one-center two-electron (1c-2e) of Cl atoms. (b) Four σ CMOs for (3c-2e) Li–Cl–Li bonds. (c) One delocalized σ CMO over HLi_4 unit.



Cartesian coordinates of optimized structures of 12 low-lying isomers of $HLi_4Cl_4^-$.

1

Cl	2.21188900	-2.21188900	0.00000000
Cl	-2.21188900	-2.21188900	0.00000000
Cl	-2.21188900	2.21188900	0.00000000
Cl	2.21188900	2.21188900	0.00000000
H	0.00000000	0.00000000	0.00000000
Li	0.00000000	1.87098500	0.00000000
Li	1.87098500	0.00000000	0.00000000
Li	0.00000000	-1.87098500	0.00000000
Li	-1.87098500	0.00000000	0.00000000

2

Li	-0.82093600	-1.85729700	1.31254600
Li	-0.82093600	-1.85729700	-1.31254600
Li	0.21244200	0.80385300	1.42540700
Li	0.21244200	0.80385300	-1.42540700
Cl	0.21244200	-0.79156600	-3.00077000
Cl	-1.55098900	0.05777100	0.00000000
Cl	0.21244200	-0.79156600	3.00077000
Cl	1.38967800	2.07544100	0.00000000
H	-0.82977600	-3.03068400	0.00000000

3

Li	0.55768100	-1.37955000	-0.85027300
Li	-0.55768100	1.37955000	-0.85027300
Li	0.61342900	1.30006300	1.42539200
Li	-0.61342900	-1.30006300	1.42539200
Cl	-0.55768100	3.07121300	0.58724900
Cl	-1.64976600	-0.60801200	-0.75919500
Cl	1.64976600	0.60801200	-0.75919500
Cl	0.55768100	-3.07121300	0.58724900
H	0.00000000	0.00000000	2.39543600

4

Li	1.36778900	-1.42729500	0.43835200
Li	-1.29305500	0.46373600	-0.81953600
Li	1.31974300	0.96053300	0.89770200
Li	-1.18858900	-1.01154700	1.21309300
Cl	3.22702200	-0.22520700	0.42735600
Cl	0.15411800	2.14880900	-0.61185500

Cl	-3.00112900	0.13061600	0.65372200
Cl	-0.44112500	-1.84600500	-0.87654500
H	0.42126900	-0.49591800	1.73564600

5

Li	-0.47228100	-1.43310800	-0.49295500
Li	-1.05890700	0.80146500	0.65316500
Li	2.09042700	-0.90493600	0.94219000
Li	1.98425000	1.21869800	-0.23396500
Cl	1.58421200	-1.03861900	-1.34757200
Cl	-2.40548700	-0.37521200	-0.75014900
Cl	0.21796400	2.55030900	0.10133600
Cl	-0.02816200	-1.11036800	1.78710700
H	3.10455900	0.50977500	0.95241200

6

H	0.07836800	-0.00017600	1.81315300
Li	1.41297600	-0.00045000	0.36700500
Li	-1.36621800	-0.00020000	-1.11444100
Li	-0.95889700	-1.28744600	1.20275200
Li	-0.95902500	1.28768700	1.20414900
Cl	3.55693900	0.00047100	0.50485100
Cl	-0.18917700	1.89089800	-0.81338900
Cl	-2.85502200	-0.00083600	0.72262100
Cl	-0.18714500	-1.89045000	-0.81358500

7

H	2.28359800	1.76200200	0.00000000
Li	-0.48994000	-1.26960800	0.00000000
Li	0.89734000	1.86373000	1.24553700
Li	2.18631600	-0.00420800	0.00000000
Li	0.89734000	1.86373000	-1.24553700
Cl	0.89734000	-0.36830100	-1.81980300
Cl	-1.97287500	-2.79974300	0.00000000
Cl	-0.57220400	2.99970200	0.00000000
Cl	0.89734000	-0.36830100	1.81980300

8

H	0.00000000	0.00000000	0.43014300
Li	0.00000000	1.52590900	-0.73812500
Li	-1.32147600	-0.76295400	-0.73812500
Li	0.00000000	0.00000000	2.16598800
Li	1.32147600	-0.76295400	-0.73812500

Cl	0.00000000	-2.43453700	-1.42499900
Cl	0.00000000	0.00000000	4.25823300
Cl	-2.10837100	1.21726800	-1.42499900
Cl	2.10837100	1.21726800	-1.42499900

9

H	-0.72164900	-0.27255300	0.00000000
Li	0.62076500	-0.11993600	1.32715100
Li	-1.03113800	1.60272000	0.00000000
Li	-0.36768300	-2.11391600	0.00000000
Li	0.62076500	-0.11993600	-1.32715100
Cl	-2.62163900	2.99477900	0.00000000
Cl	1.45031600	1.57658300	0.00000000
Cl	0.62076500	-2.21139400	2.03278800
Cl	0.62076500	-2.21139400	-2.03278800

10

H	-2.01328400	0.01449500	2.60620700
Li	1.74105100	-0.01865000	-0.04930900
Li	-0.48582200	0.45890200	1.91053800
Li	-1.16007700	0.38320200	-0.78364000
Li	-2.52930200	-0.87198300	1.18034100
Cl	3.79440500	-0.35624700	-0.44511000
Cl	0.27811600	1.86984100	0.24092600
Cl	-0.19698800	-1.41928400	0.42143800
Cl	-3.32754900	-0.08659900	-0.76902000

11

Li	0.10140638	-2.17351503	0.00000000
Li	1.28645079	0.58484506	0.00000000
Li	-1.39327558	0.42266488	0.00000000
Li	-0.41444529	2.96960903	0.00000000
Cl	0.01842309	-0.41617896	-1.65430300
Cl	-1.87482281	2.11344862	0.00000000
Cl	0.15812207	-4.39279044	0.00000000
Cl	1.75394815	2.79341669	0.00000000
H	0.01842309	-0.41617896	1.65430300

12

H	2.27022400	0.55068800	2.50306600
Li	0.67842700	0.66466100	1.79089700
Li	3.03029400	0.65397500	0.90218600
Li	1.17546000	-0.36246500	-0.73515800

Li	-2.53871500	-0.39171300	0.08051600
Cl	-0.52190800	-1.08802400	0.73478400
Cl	-4.52208500	0.04607200	-0.42950700
Cl	1.17568500	1.85740400	-0.13798600
Cl	3.32086000	-0.94745500	-0.67425500