SUPPLEMENTARY INFORMATION

CB_4Se_5: planar tetracoordinate carbon CB_4 core stabilized by the peripheral Se/Se_2 bridges

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Table of Contents

Five lone pairs (LPs) of Se atoms. (b) Nine CMOs, corresponding to eight localized two-center two-electron (2c-2e) B-Se bonds and one Se-Se bond. (c) Five CMOs, corresponding to two 2c-2e B-Se and three three-center two-electron (3c-2e) B-Se-B bonds. (d) One delocalized π CMO. (e) Three delocalized σ CMOs.

Figure S6. Plot of the Laplacian of electron density, bond paths and critical points for CB_4Se_5 (**1**). The red dashed lines denote the areas of charge concentration ($\nabla^2\rho(r) < 0$) and the blue area is vice versa. The brown sticks between the atoms represent bond paths. The brown and yellow dots are bond and ring critical points, respectively.

Figure S7. Selected canonical molecular orbitals (CMOs) and energy level diagram of C_{2v} CB_4Se_5 (**1**) at PBE0/def2-TZVPP level.

Figure S8. Selected canonical molecular orbitals (CMOs) and energy level diagram of CB_4Se_5 (C_s, $^3A'$) at PBE0/def2-TZVPP level.

Figure S9. Nucleus independent chemical shifts (NICSs) for cluster **1**. NICS (0) is calculated at the center of a triangle. NICS (1), shown in red, is calculated at 1 Å above the center of a triangle and above the C center.

Figure S10. Simulated IR spectrum of CB_4Se_5 at the PBE0-D3/def2-TZVPP level.

Figure S11. Optimized structure of $CB_4Se_5[Al(CH_3)_3]_5$ at the PBE0/def2-TZVP level.

Cartesian coordinates of optimized structures of top 20 low-lying isomers of CB_4Se_5.

Table S1. The lowest vibrational frequency at eight classical theoretical levels for the global-minimum structure **1** (C_{2v}, $^1A_1$) of CB_4Se_5 cluster.

	Theoretical level	Lowest vibrational frequency (cm^{-1})
1	PBE0-D3(BJ)/aug-cc-pvtz	13.6
2	BP86-D3(BJ)/aug-cc-pvtz	12.8
3	B3LYP-D3(BJ)/aug-cc-pvtz	16.4
4	TPSS-D3(BJ)/aug-cc-pvtz	9.9
5	ωB97X-D/aug-cc-pvtz	21.9
6	M062x/aug-cc-pvtz	12.5
7	B2PLYP-D3(BJ)/aug-cc-pvtz	17.9
8	MP2/aug-cc-pvtz	15.0

Table S2. Orbital composition analysis of canonical molecular orbitals (CMOs) of the global-minimum structure **1** (C_{2v}, $^1A_1$) of CB_4Se_5 cluster.

CMO	C (%)		B_4 (%)		Se_5 (%)	
	s/p	total	s/p	total	s/p	total
 HOMO (a″)	0.00/0.00	0.00	0.00/9.69	9.69	0.00/89.69	**89.69**
 HOMO-1 (a″)	0.00/**29.17**	**29.17**	0.00/0.00	0.00	0.00/**69.76**	**69.76**
 HOMO-2 (a″)	0.00/4.87	4.87	0.00/4.52	4.52	0.00/**89.70**	**89.70**
 HOMO-3 (a′)	0.00/5.26	5.26	0.00/**16.10**	**16.10**	0.00/**75.86**	**75.86**
 HOMO-4 (a′)	0.00/**20.03**	**20.03**	0.00/9.38	9.38	0.95/**65.51**	**66.46**
 HOMO-5 (a″)	0.00/0.00	0.00	0.00/**34.84**	**34.84**	0.00/**64.55**	**64.55**

CMO	C (%)		B_4 (%)		Se_5 (%)	
	s/p	total	s/p	total	s/p	total
 HOMO-6 (a′)	0.00/12.10	12.10	0.00/**20.69**	**20.69**	4.22/**61.10**	**65.32**
 HOMO-7 (a″)	0.00/0.00	0.00	0.00/**18.42**	**18.42**	0.00/**80.55**	**80.55**
 HOMO-8 (a′)	1.96/0.00	1.96	1.48/6.77	8.25	4.13/**83.31**	**87.44**
 HOMO-9 (a′)	0.00/1.87	1.87	12.67/**19.96**	**32.63**	8.38/**54.80**	**63.18**
 HOMO-10 (a′)	3.28/1.55	4.83	10.82/13.25	**24.07**	10.94/**57.90**	**68.84**
 HOMO-11 (a′)	0.00/3.74	3.74	1.19/**20.03**	**21.22**	**17.41**/**55.22**	**72.63**
 HOMO-12 (a″)	0.00/**31.87**	**31.87**	0.00/**46.28**	**46.28**	0.00/**20.91**	**20.91**

CMO	C (%)		B_4 (%)		Se_5 (%)	
	s/p	total	s/p	total	s/p	total
 HOMO-13 (a′)	1.56/2.09	3.65	8.99/**24.29**	**33.28**	2.74/**58.49**	**61.23**
 HOMO-14 (a′)	0.00/0.00	0.00	**29.00**/**17.70**	**46.70**	4.83/**46.73**	**51.56**
 HOMO-15 (a′)	1.19/**37.95**	**39.14**	13.38/6.81	**20.19**	**20.09**/**16.04**	**36.13**
 HOMO-16 (a′)	0.00/**42.76**	**42.76**	5.18/12.94	**18.12**	**27.32**/8.05	**35.37**
 HOMO-17 (a′)	0.00/0.00	0.00	6.76/13.99	**20.75**	**68.66**/5.14	**73.80**
 HOMO-18 (a′)	**15.60**/0.00	**15.60**	0.00/**25.89**	**25.89**	**52.92**/0.00	**52.92**
 HOMO-19 (a′)	2.05/0.00	2.05	1.45/**32.06**	**33.51**	**55.45**/0.99	**56.44**

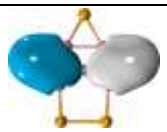
CMO	C (%)		B_4 (%)		Se_5 (%)	
	s/p	total	s/p	total	s/p	total
 HOMO-20 (a′)	0.00/10.58	10.58	**15.62**/**18.22**	**33.84**	**46.68**/3.12	**49.80**
 HOMO-21 (a′)	0.00/4.66	4.66	7.24/13.48	**20.72**	**63.60**/5.13	**68.73**
 HOMO-22 (a′)	**25.58**/1.36	**26.94**	**33.21**/11.20	**44.41**	**18.50**/3.95	**22.45**

Figure S1. Optimized structures of C_{4v} CB_4X_4 (X = O, S, Se, Te) and C_{2v} CB_4Po_4 at the PBE0-D3(BJ)/def2-TZVPP level. The lowest vibrational frequencies are shown.

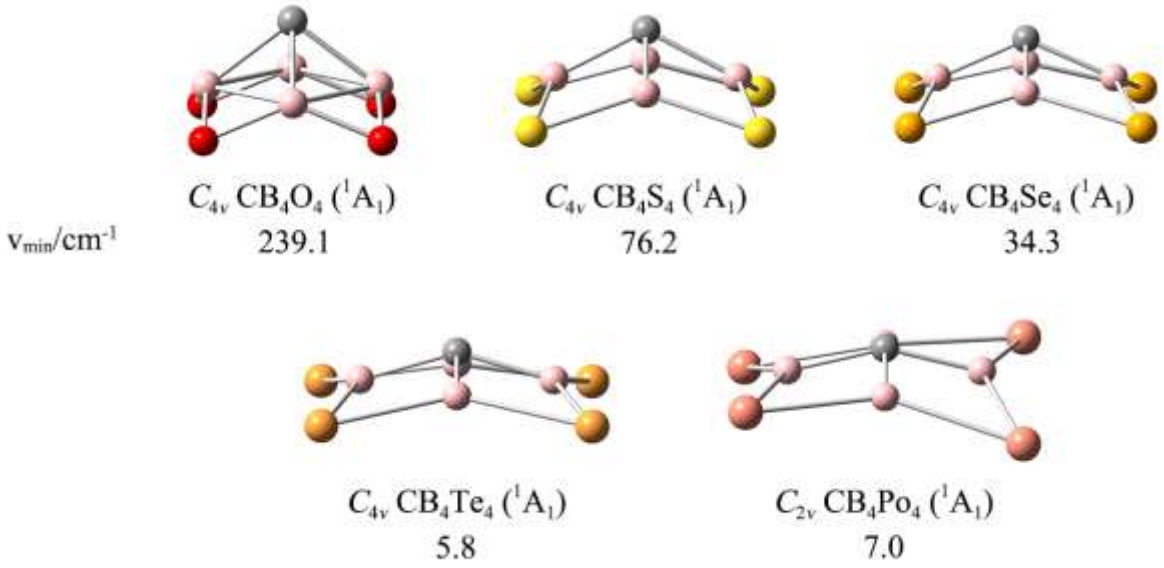


Figure S2. Optimized structures of C_s CB_4X_5 (X = O, S, Te, Po) and C_{2v} CB_4Se_5 minima at the PBE0-D3(BJ)/def2-TZVPP level. The lowest vibrational frequencies are shown.

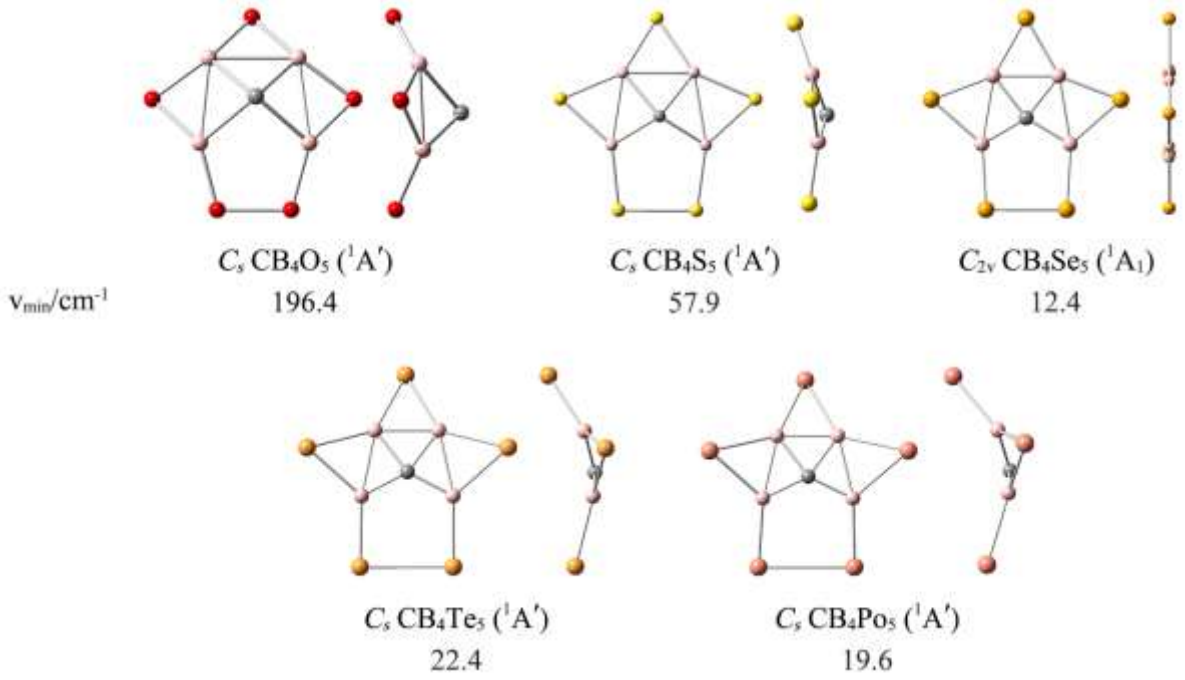


Figure S3. Alternative optimized low-lying isomeric structures of CB_4Se_5 cluster at the PBE0-D3(BJ)/def2-TZVPP level. Relative energies are listed in kcal mol^{-1} at the single-point CCSD(T)/def2-TZVPP//PBE0-D3(BJ)/def2-TZVPP level, with zero-point energy (ZPE) corrections at PBE0-D3(BJ).

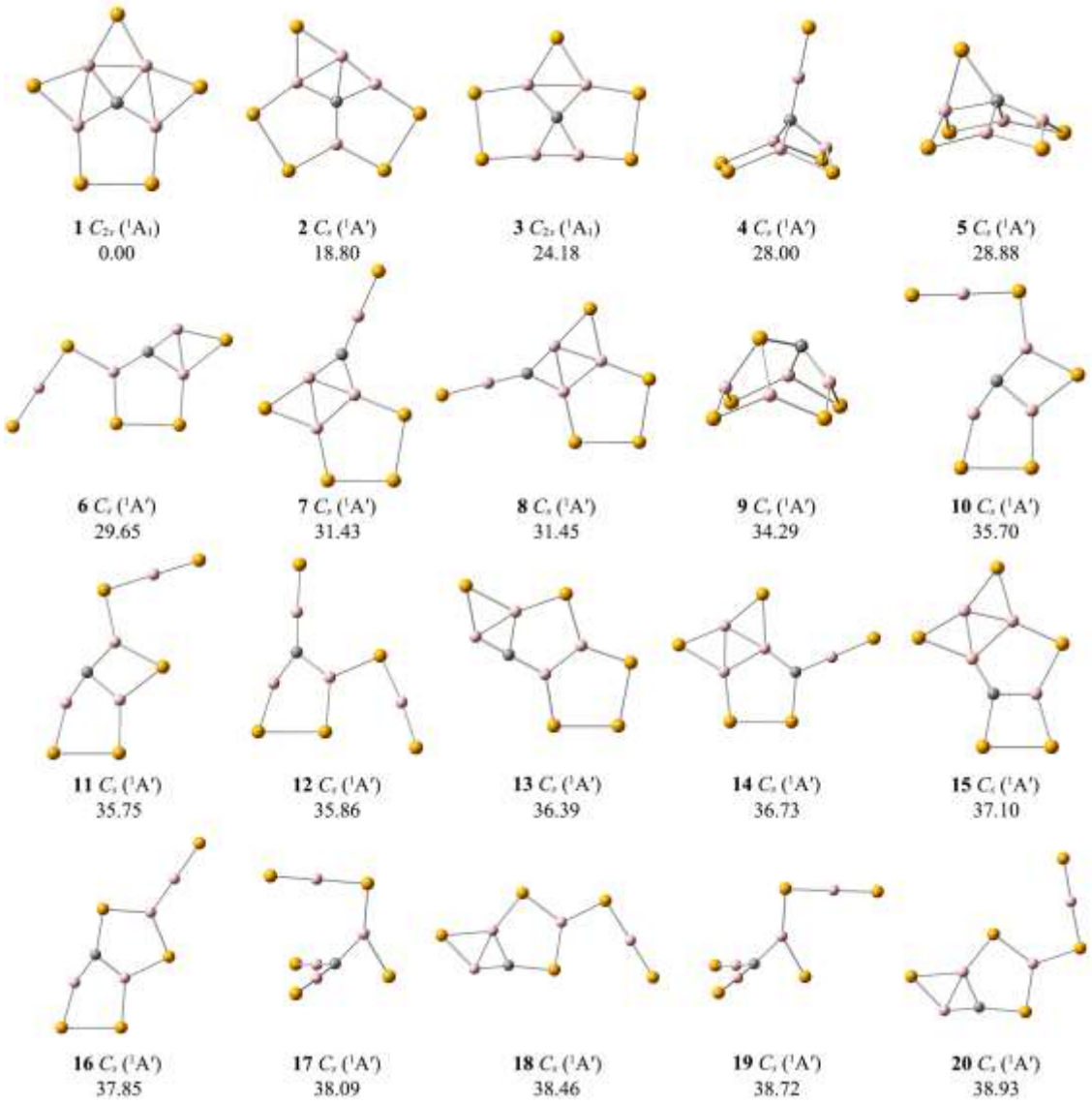


Figure S4. Calculated root-mean-square deviations (RMSDs) of GM clusters of CB_4Se_5 during the Born-Oppenheimer molecular dynamics (BOMD) simulations at 298, 600 and 1000 K.

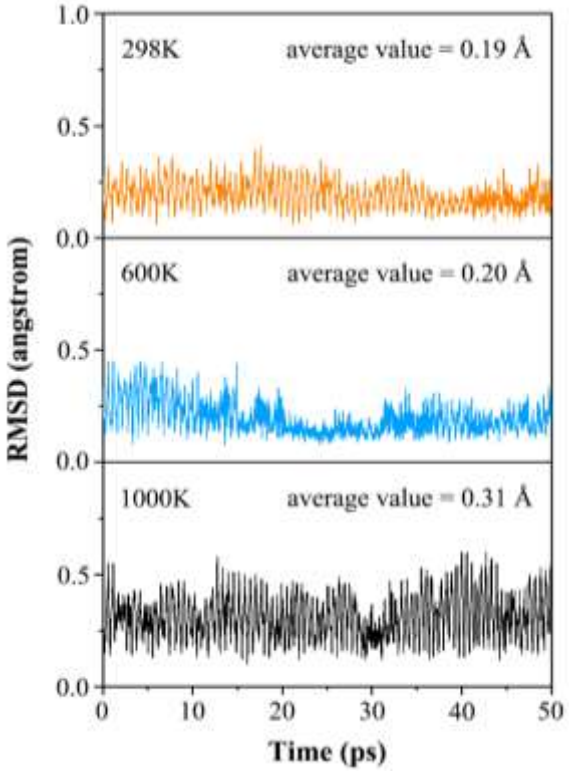


Figure S5. Analysis of canonical molecular orbitals (CMOs) of C_{2v} CB_4Se_5 (**1**) cluster. (a) Five lone pairs (LPs) of Se atoms. (b) Nine CMOs, corresponding to eight localized two-center two-electron (2c-2e) B-Se bonds and one Se-Se bond. (c) Five CMOs, corresponding to two 2c-2e B-Se and three three-center two-electron (3c-2e) B-Se-B bonds. (d) One delocalized π CMO. (e) Three delocalized σ CMOs.

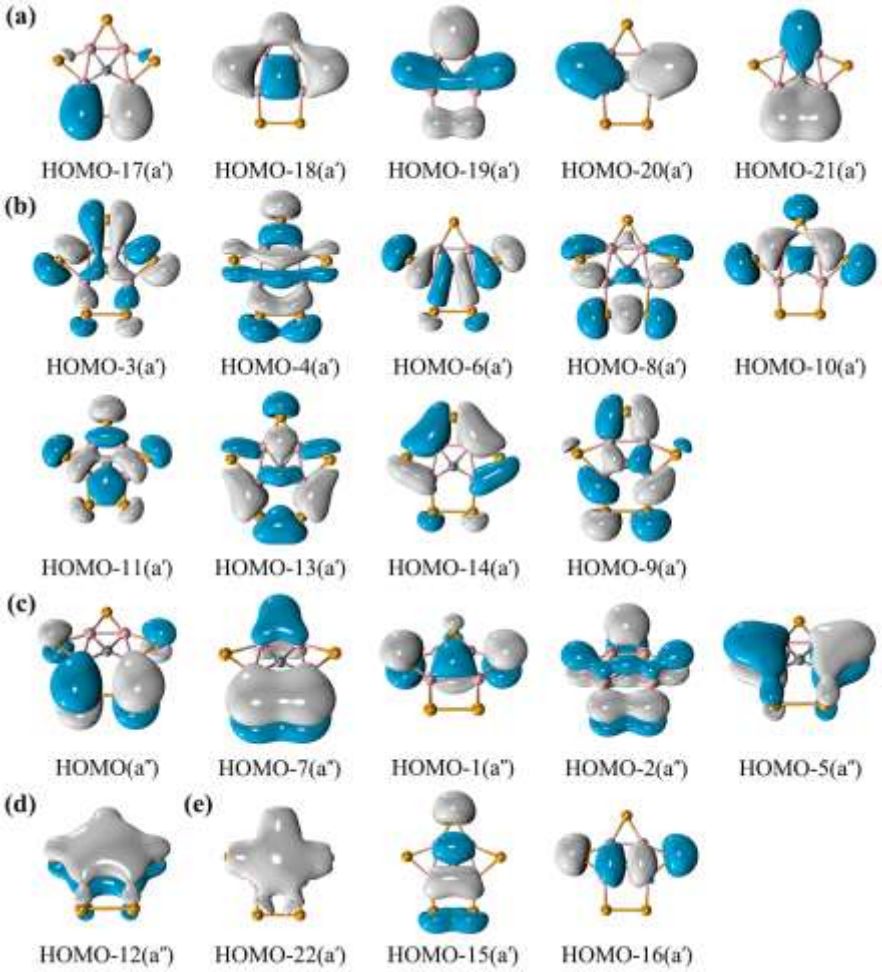
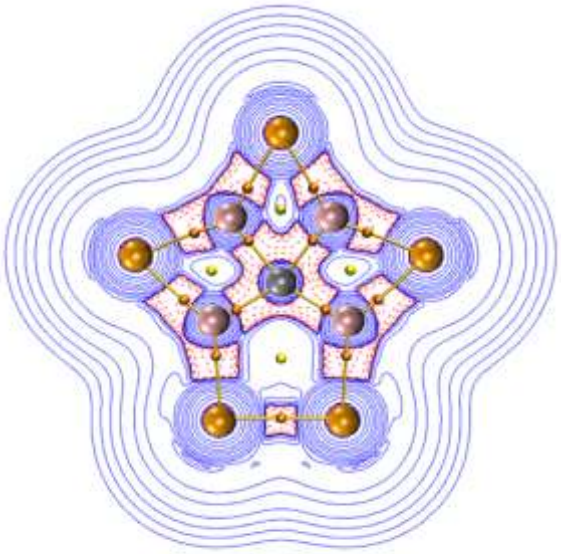
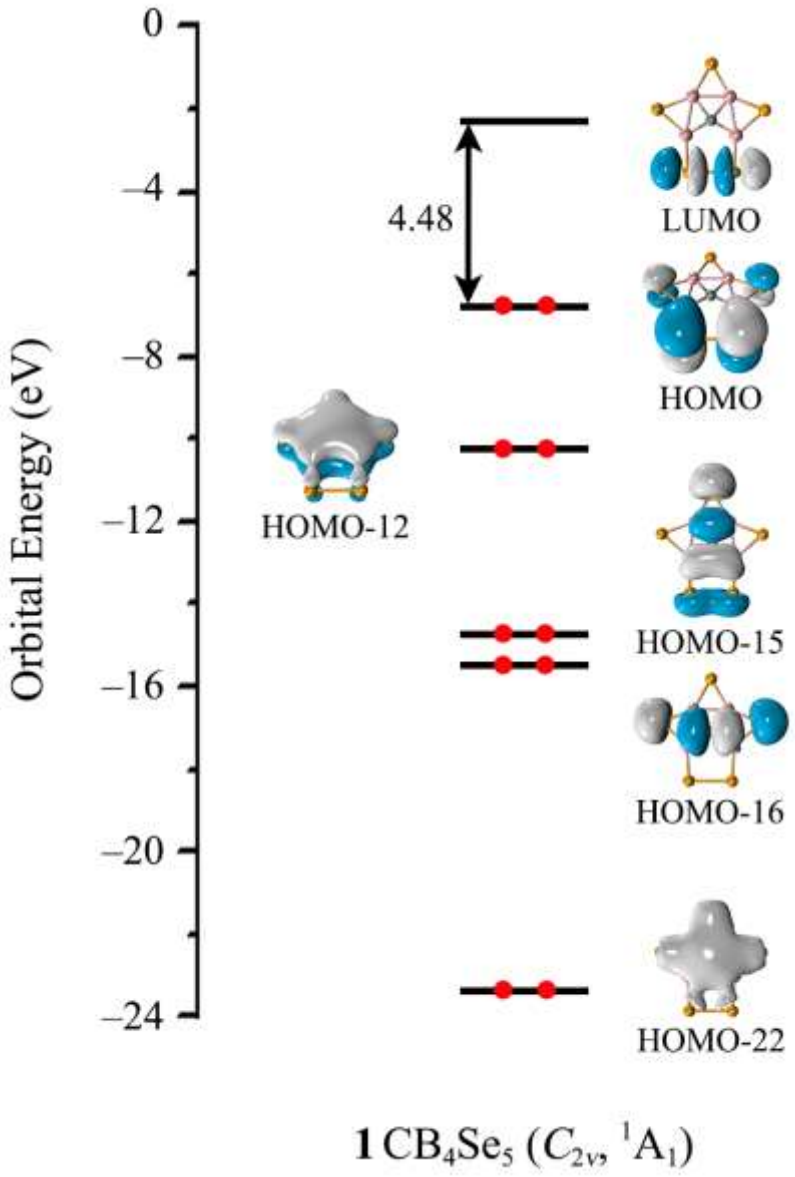


Figure S6. Plot of the Laplacian of electron density, bond paths and critical points for CB_4Se_5 (**1**). The red dashed lines denote the areas of charge concentration ($\nabla^2\rho(r) < 0$) and the blue area is vice versa. The brown sticks between the atoms represent bond paths. The brown and yellow dots are bond and ring critical points, respectively.



1 CB_4Se_5

Figure S7. Selected canonical molecular orbitals (CMOs) and energy level diagram of C_{2v} CB_4Se_5 (**1**) at PBE0/def2-TZVPP level.



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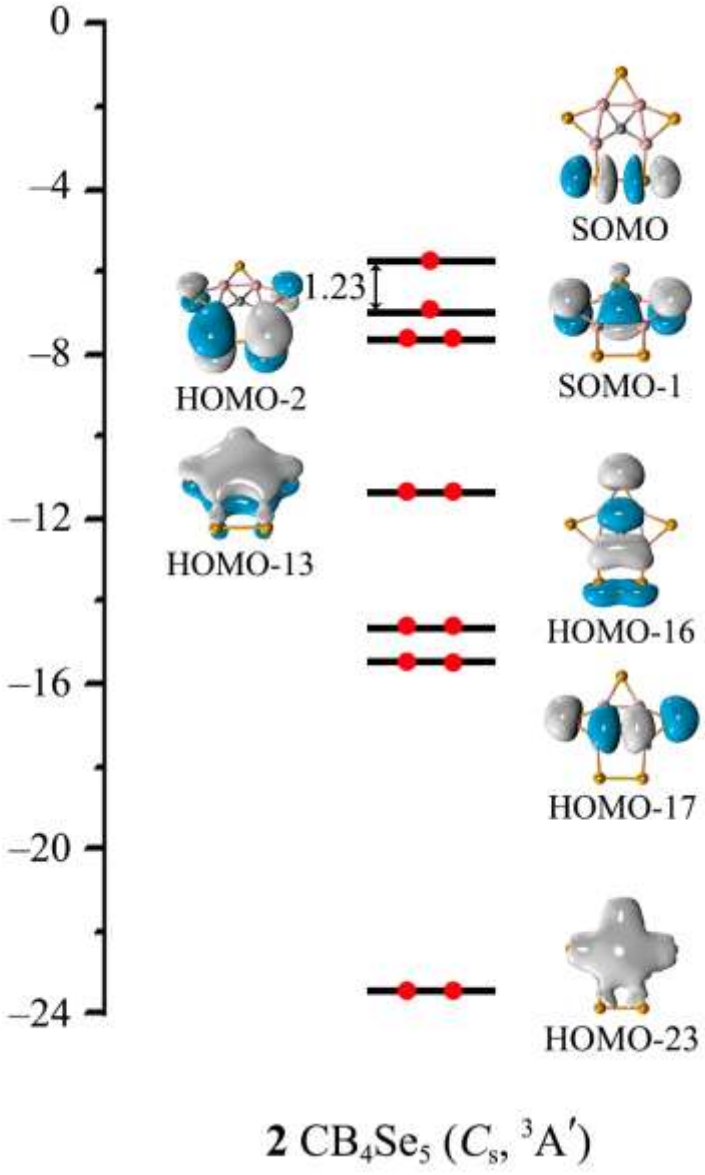

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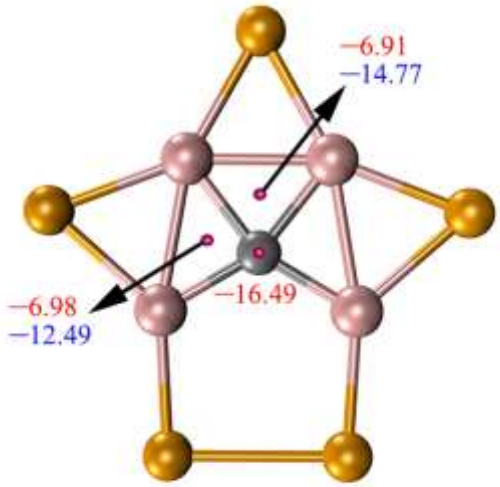
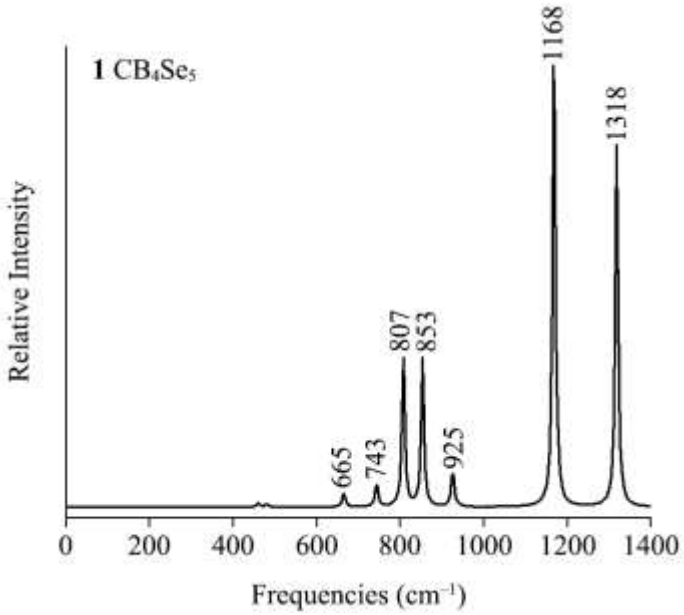


1 CB_4Se_5 (C_{2v}, $^1A_1$)

Figure S10. Simulated IR spectrum of CB_4Se_5 at the PBE0-D3/def2-TZVPP level.



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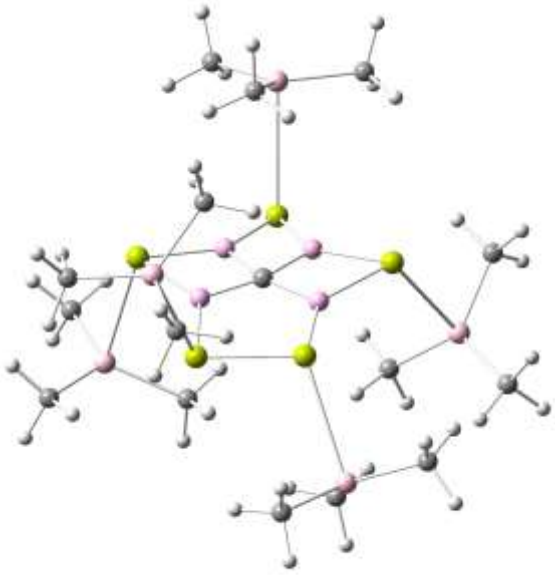

$CB_4Se_5[Al(CH_3)_3]_5$ (C_1, ^1A)

Cartesian coordinates of optimized structures of top 20 low-lying isomers of CB_4Se_5.

1

C	0.00000000	0.21323398	0.00000000
B	0.96027659	1.44960773	0.00000000
B	-0.96027659	1.44960773	0.00000000
B	1.29812700	-0.55512315	0.00000000
B	-1.29812700	-0.55512315	0.00000000
Se	1.18482413	-2.48078017	0.00000000
Se	-1.18482413	-2.48078017	0.00000000
Se	0.00000000	3.14502715	0.00000000
Se	2.78181115	0.75433982	0.00000000
Se	-2.78181115	0.75433982	0.00000000

2

C	-0.01065924	0.56416727	0.00000000
B	-0.54532680	2.09901598	0.00000000
B	0.95771313	1.73710367	0.00000000
B	-1.56899236	0.53897199	0.00000000
B	0.66179840	-0.80660423	0.00000000
Se	-2.45226255	-1.15115407	0.00000000
Se	-2.44137511	2.32399471	0.00000000
Se	2.82137586	1.48315799	0.00000000
Se	-0.44531365	-2.40234895	0.00000000
Se	2.59222231	-0.87798618	0.00000000

3

C	0.00000000	-0.25459103	0.00000000
B	0.76534400	-1.60287303	0.00000000
B	-1.03306500	0.89378597	0.00000000
B	-0.76534400	-1.60287303	0.00000000
B	1.03306500	0.89378597	0.00000000
Se	2.92786000	0.59674397	0.00000000
Se	-2.92786000	0.59674397	0.00000000
Se	0.00000000	2.57073097	0.00000000
Se	-2.65589600	-1.75536803	0.00000000
Se	2.65589600	-1.75536803	0.00000000

4

C	-0.11411088	0.61302325	0.00000000
B	-0.59731682	2.01688570	0.00000000

B	1.43585487	0.39337214	0.00000000
B	-0.07082189	-0.34164025	1.22768900
B	-0.07082189	-0.34164025	-1.22768900
Se	1.79264970	-0.12184789	-1.86102200
Se	-1.15216906	3.66781082	0.00000000
Se	-1.25773879	-1.89313143	-1.20722900
Se	1.79264970	-0.12184789	1.86102200
Se	-1.25773879	-1.89313143	1.20722900

5

C	0.69593361	0.07404951	0.00000000
B	-0.10960321	0.19246698	1.40100700
B	0.48057335	1.61261587	0.00000000
B	-0.04810270	-1.47223194	0.00000000
B	-0.10960321	0.19246698	-1.40100700
Se	-1.00228378	-1.43512184	1.80679500
Se	-0.05196778	2.10261908	-1.82374300
Se	-1.00228378	-1.43512184	-1.80679500
Se	-0.05196778	2.10261908	1.82374300
Se	1.95432890	-1.42531468	0.00000000

6

C	-1.26301923	1.10378829	0.00000000
B	3.03022758	0.75692421	0.00000000
B	0.16225408	0.67351041	0.00000000
B	-2.34956762	-0.03088154	0.00000000
B	-2.52677286	1.66872531	0.00000000
Se	0.52461557	-1.23036185	0.00000000
Se	1.61733926	2.00727038	0.00000000
Se	4.31042001	-0.42350180	0.00000000
Se	-1.77245295	-1.83851394	0.00000000
Se	-4.20940985	0.83910363	0.00000000

7

C	0.54641658	1.77363656	0.00000000
B	-0.05999515	0.40635496	0.00000000
B	0.11942247	3.17527764	0.00000000
B	1.60939378	0.82899126	0.00000000
B	1.13677516	-0.90806822	0.00000000
Se	0.55576292	-2.69615374	0.00000000
Se	3.04542287	-0.41108477	0.00000000

Se	-1.77674555	-2.44924319	0.00000000
Se	-1.90586814	-0.10340774	0.00000000
Se	-0.42758624	4.83181305	0.00000000

8

C	1.77515795	0.53560624	0.00000000
B	0.83473590	1.60261520	0.00000000
B	-0.90399608	1.13677612	0.00000000
B	3.17706996	0.10937130	0.00000000
B	0.40561397	-0.06495482	0.00000000
Se	4.83531699	-0.43233562	0.00000000
Se	-2.45798395	-1.76976095	0.00000000
Se	-0.11264994	-1.90880085	0.00000000
Se	-0.39971417	3.04345314	0.00000000
Se	-2.69491206	0.56354204	0.00000000

9

C	-1.57021164	0.94464663	0.00000000
B	-0.04530590	-1.25251610	1.02617900
B	-0.04530590	-1.25251610	-1.02617900
B	-0.52444345	1.44417979	-0.93945900
B	-0.52444345	1.44417979	0.93945900
Se	0.86660997	-2.66165209	0.00000000
Se	0.29768933	2.98021487	0.00000000
Se	0.52110913	0.20433676	-2.13963300
Se	-1.76184806	-0.95031032	0.00000000
Se	0.52110913	0.20433676	2.13963300

10

C	-0.05740737	0.13293629	0.00000000
B	3.11686302	0.34992799	0.00000000
B	0.71570114	-1.14976184	0.00000000
B	-0.89624973	1.20812329	0.00000000
B	-1.37792678	-0.71066959	0.00000000
Se	2.64058203	-1.48351559	0.00000000
Se	-0.67052730	-2.56240774	0.00000000
Se	-2.53069936	2.16514715	0.00000000
Se	3.58262029	2.02522823	0.00000000
Se	-3.24101960	-0.12344373	0.00000000

11

C	0.88378690	1.10570220	0.00000000
B	-3.40433612	0.52997736	0.00000000
B	1.27364484	-0.41633882	0.00000000
B	2.23422791	1.29389914	0.00000000
B	-0.55903912	0.68423025	0.00000000
Se	4.08442889	0.88442607	0.00000000
Se	3.03217181	-1.26832589	0.00000000
Se	-0.50750119	-1.28600975	0.00000000
Se	-2.09454007	1.89552331	0.00000000
Se	-4.60353617	-0.72835059	0.00000000

12

C	0.69386613	1.62167804	0.00000000
B	1.94139228	0.98057848	0.00000000
B	-1.90117565	-1.72267721	0.00000000
B	0.03489965	2.93802736	0.00000000
B	0.02581803	0.26320574	0.00000000
Se	-0.82308877	4.45474772	0.00000000
Se	-1.63889876	-3.45070313	0.00000000
Se	1.05318428	-1.45119690	0.00000000
Se	3.22976822	-0.35264082	0.00000000
Se	-1.95825521	0.15197725	0.00000000

13

C	1.40108848	-1.28978123	0.00000000
B	-0.21933368	0.80567759	0.00000000
B	-0.03195248	-0.85661972	0.00000000
B	2.72655447	-1.66845567	0.00000000
B	2.34681461	-0.00556123	0.00000000
Se	-3.24653014	-0.31141929	0.00000000
Se	1.51478133	1.74019159	0.00000000
Se	-1.58903180	-1.96538685	0.00000000
Se	4.28822352	-0.61172833	0.00000000
Se	-1.92382366	1.62962179	0.00000000

14

C	-0.99957142	-0.47463138	0.00000000
B	1.67564441	-0.10551888	0.00000000
B	0.03187820	0.55694744	0.00000000
B	1.41258081	1.59819146	0.00000000
B	-2.43132044	-0.09958515	0.00000000

Se	-4.10946436	0.38948430	0.00000000
Se	-0.15969912	2.58476139	0.00000000
Se	1.70616808	-1.99232822	0.00000000
Se	-0.59666220	-2.30139809	0.00000000
Se	3.23476094	1.11646926	0.00000000

15

C	0.57962247	0.79273854	0.00000000
B	0.88308873	-0.60721516	0.00000000
B	-0.83920023	1.27033454	0.00000000
B	0.59594476	-2.29241556	0.00000000
B	-0.88277301	-1.40165254	0.00000000
Se	-2.28034625	-0.09720970	0.00000000
Se	-0.75726539	3.20583316	0.00000000
Se	1.52187614	2.44288131	0.00000000
Se	2.42388132	-1.89822033	0.00000000
Se	-0.97470570	-3.34745173	0.00000000

16

C	1.11280726	0.81820067	0.00000000
B	1.25033213	2.19691408	0.00000000
B	0.09451875	-1.76667862	0.00000000
B	-0.02799371	-3.40468160	0.00000000
B	-0.38235034	1.01921487	0.00000000
Se	0.75974851	4.01255312	0.00000000
Se	-1.45906134	-0.61714204	0.00000000
Se	1.80795322	-0.90394604	0.00000000
Se	-1.28962467	2.78881827	0.00000000
Se	-0.15282094	-5.13713766	0.00000000

17

C	-0.99368426	-0.01385174	0.000000000
B	-0.97747080	-0.76344626	1.30934200
B	-0.97747080	-0.76344626	-1.30934200
B	2.21300094	0.67521592	0.00000000
B	-0.40149968	1.42306122	0.00000000
Se	-0.91865461	-1.59166847	-2.83231000
Se	1.27564926	2.33536051	0.00000000
Se	-2.26700884	1.62119162	0.00000000
Se	-0.91865461	-1.59166847	2.83231000
Se	3.02511901	-0.85479790	0.00000000

18

C	-1.58575930	-1.38081128	0.00000000
B	-2.92462946	-1.70680814	0.00000000
B	-2.41044307	-0.08744901	0.00000000
B	3.13150495	0.28110995	0.00000000
B	0.28346367	0.62744517	0.00000000
Se	4.23860469	-1.05916169	0.00000000
Se	0.26280725	-1.30292135	0.00000000
Se	-4.42202128	-0.55811145	0.00000000
Se	-1.43057159	1.56886572	0.00000000
Se	1.91338904	1.72525165	0.00000000

19

C	-0.14590355	-1.25125968	0.00000000
B	-0.02992976	-1.99422798	1.30748900
B	-0.02992976	-1.99422798	-1.30748900
B	0.18076097	0.26969354	0.00000000
B	0.61368278	2.98216856	0.00000000
Se	1.70533380	1.42153606	0.00000000
Se	-1.68715278	0.14495029	0.00000000
Se	0.14300421	-2.81781374	-2.82493800
Se	0.14300421	-2.81781374	2.82493800
Se	-0.38646885	4.39827430	0.00000000

20

C	-2.43059798	-1.07245220	0.00000000
B	2.99199094	0.15833133	0.00000000
B	-2.10516736	0.42726622	0.00000000
B	0.31761716	-0.94056755	0.00000000
B	-3.61162500	-0.36286378	0.00000000
Se	-0.24365498	0.92724969	0.00000000
Se	3.76301418	1.71600429	0.00000000
Se	2.18518766	-1.55060131	0.00000000
Se	-3.86578641	1.50594434	0.00000000
Se	-1.05583370	-2.30377694	0.00000000