Supporting Information

Breakdown of periodicity in oxidation states of actinide metal doped AnB_{12} (An= Th to Cm) clusters

Shu-Xian Hu,*[a] Mingyang Chen,[a] Bingyun Ao*[b]

[a] *Beijing Computational Science Research Center, Beijing 100193, China.*

[c] *Science and Technology on Surface Physics and Chemistry Laboratory, Mianyang 621908, China.*

Table S1. Relative energies (ΔE, kcal/mol) of different spin state of AnB_{12} (An = Th to Cm) computed at theory levels of PBE and B3LYP.

An	Spin state	PBE		B3LYP	
		Total E(kcal/mol)	ΔE(kcal/mol)	Total E (a.u.)	ΔE(kcal/mol)
Th	Triplet	-1733.92	0.0	-705.767681	0.0
	Singlet	-1727.88	6.0	-705.760519	4.5
Pa	Doublet	-1754.24	0.0		
	Quartet	-1743.34	10.9		
U	Triplet	-1750.9	0.0	-774.998651	0.0
	Singlet	-1748.59	2.3	-774.962505	22.7
Np	Quartet	-1764.26	0.0	-812.514317	0.0
	Doublet	-1760.56	3.7	-812.4881493	16.4
	Quartet ($^4A_1$)	-1723.24	41.0		
	Quartet ($^4A_2$)	-1733.65	30.6		
Pu	Septet	-1754.56	0.0	-852.004715	0.0
	Triplet	-1731.67	16.0		
	Quintet	-1747.66	6.9	-852.009303	2.9
	Singlet	-1672.1	75.6		
Am	Octet	-1765.03	0.0	-893.571014	0.0
	Sextet	-1764.75	0.3	-893.566156	3.0
	Quartet	-1742.88	22.1		
	Doublet	-1709.32	55.7		
Cm	Quintet	-1840.09	0.0	-937.168256	0.0
	Septet	-1825.25	14.8		
	Nonet	-1823.97	16.1	-937.169887	-1.0
	Triple	-1767.98	72.1		

Table S2. Optimized geometrical structures (bond length, Å) and formation energies (SR-E_f, kcal/mol) for the reaction of An + B_{12} = AnB_{12} (An = Th to Cm) at SR-B3LYP/M/ECP60MWB_SEG//B/aug-cc-pVTZ levels of theory. (All calculations are fully optimization without constrain.)

Species	Spin/GS	Elec. Conf.	OS	An-B, Å	SR-E_f
Th	^{3}A	f^0	IV	2.586,2.681,2.667,2.671,2.918,2.777, 2.949,2.697,2.742,2.759,2.790,2.772	-129.4
Pa	^{2}A	f^0	V	2.530,2.530,2.541,2.579,2.631,2.631, 2.700,2.700,2.729,2.729,2.736,2.736	-137.4
U	^{3}A	f^2	IV	2.648,2.660,2.670,2.711,2.717,2.718, 2.797,2.827,2.859,2.833,2.834,2.875	-118.9
Np	^{4}A	f^4	III	2.664,2.665,2.666,2.721,2.729,2.730, 2.823,2.824,2.853,2.852,2.855,2.855	-76.3
Pu	^{7}A”	f^5	III	2.686,2.686,2.881,2.749,2.887,2.753, 2.726,2.858,2.858,2.749,2.881,2.887	-56.2
Am	^{8}A	f^7	II	2.760,2.811,2.871,2.870,2.975,2.912, 2.913,2.903,2.905,2.975,3.046,3.046	-39.4
Cm	^{9}A	f^7	III	2.618,2.740,2.740,2.741,2.743,2.743, 2.801,2.802,2.814,2.814,2.956,2.956	-73.3

Table S3. Average Mayer, Gopinathan-Jug (G-J) and Nalewajski-Mrozek (N-M) bond orders for 12 An−B bonds on the B3LYP optimized geometry of GS AnB_{12} at the PBE/TZ2P level.

Species	Mayer	G-J	N-M (1)	N-M (2)	N-M (3)
Th	0.41	0.35	0.41	0.47	0.36
Pa	0.51	0.50	0.58	0.61	0.56
U	0.43	0.41	0.56	0.59	0.53
Np	0.42	0.40	0.58	0.61	0.55
Pu	0.37	0.24	0.33	0.46	0.26
Am	0.29	0.16	0.20	0.31	0.13
Cm	0.32	0.30	0.36	0.39	0.32

Table S4. Average charges and spin populations on the metal and boron atoms on the B3LYP optimized geometry of GS AnB_{12} at the PBE/TZ2P level.

Species	Atom	Charge				Spin	
		Mulliken	Hirshfeld	VDD	MDC_q	Mulliken	MDC_q
Th	Th	0.35	0.79	0.74	1.21	0.54	0.09
	Aver. B	-0.04	-0.07	-0.06	-0.08	0.12	0.16
Pa	Pa	0.27	0.90	0.88	1.25	0.41	0.19
	Aver. B	-0.03	-0.07	-0.07	-0.10	0.05	0.07
U	U	0.42	0.84	0.80	1.16	2.42	2.50

	Aver. B	-0.03	-0.07	-0.07	-0.10	-0.03	-0.04
Np	Np	0.35	0.78	0.73	1.07	3.74	3.91
	Aver. B	-0.04	-0.06	-0.06	-0.10	-0.06	-0.07
Pu	Pu	0.46	0.86	0.82	1.01	5.06	5.32
	Aver. B	-0.04	-0.07	-0.07	-0.08	-0.09	-0.11
Am	Am	0.53	0.78	0.74	0.91	6.91	6.93
	Aver. B	-0.05	-0.06	-0.06	-0.09	0.01	0.01
Cm	Cm	0.50	0.74	0.69	1.02	6.11	6.71
	Aver. B	-0.05	-0.06	-0.06	-0.09	-0.17	-0.22
B_{12}	Aver. B	0.00	0.00	0.00	0.00		

Table S5. The calculated natural localized molecular orbitals (NLMOs) of AnB_{12} (An = Th to Cm).

An	Type	Occ.	NLMO
Th	LP	1.00	$24.9\%Th(s^{1.00}d^{22.14}f^{4.68})+75.1\%B(p)$
	LP	1.00	$15.9\%Th(s^{1.00}d^{10.14}f^{1.47})+84.1\%B(p)$
	4C	2.00	$17.0\%Th(d^{6.31}f^{1.00})+83.0\%B(p)$
	6C	2.00	$27.5\%Th(s^{1.00}d^{18.1}f^{3.8})+72.5\%B(sp^{7.03})$
	6C	2.00	$18.5\%Th(d^{13.10}f^{1.00})+81.5\%B(sp^{17.26})$
	6C	2.00	$2.4\%Th(d^{0.70}f)+97.6\%B(sp^{3.90})$
	6C	2.00	$2.3\%Th(d^{2.17}f)+97.7\%B(p)$
	6C	2.00	$16.6\%Th(s^{1.00}d^{2.16}f^{0.46})+83.4\%B(sp^{6.24})$
Pa	LP	1.00	$28.2\%Pa(s^{1.00}d^{6.55}f^{5.05})+71.8\%B(s^{1.00}p^{13.30})$
	LP	2.00	$28.4\%Pa(s^{1.00}d^{6.13}f^{4.87})+71.6\%B(s^{1.00}p^{14.75})$
	LP	2.00	$32.3\%Pa(s^{1.00}d^{8.05}f^{8.88})+67.7\%B(s^{1.00}p^{10.78})$
	LP	2.00	$25.1\%Pa(d^{1.59}f^{1.00})+74.9\%B(s^{1.00}p^{17.85})$
	LP	2.00	$21.1\%Pa(d^{2.14}f^{1.00})+78.9\%B(s^{1.00}p^{8.15})$
	4C	2.00	$20.6\%Pa(s^{1.00}d^{26.10}f^{13.60})+79.42\%B(s^{1.00}p^{13.36})$
	6C	2.00	$5.0\%Pa(s^{1.00}d^{23.33}f^{43.09})+95.0\%B(s^{1.00}p^{5.04})$
	6C	2.00	$4.1\%Pa(d^{1.14}f)+95.9\%B(p)$
	3C	2.00	$1.8\%Pa(sd^{0.69}f^{3.60})+98.2\%B(p)$
U	LP	1.00	$99.1\%U(f)+0.9\%B(s^{1.00}p^{4.43})$
	LP	1.00	$91.3\%U(f)+8.7\%B(s^{1.00}p^{14.84})$
	LP	2.00	$17.348\%U(d^{2.31}f^{1.00})+82.7\%B(p)$
	2C	2.00	$86.473\%U(f)+13.5\%B(s^{1.00}p^{19.52})$
	4C	2.00	$24.1\%U(s^{1.00}d^{4.54}f^{2.17})+75.9\%B(s^{1.00}p^{32.35})$
	5C	2.00	$12.8\%U(s^{1.00}d^{3.09}f^{0.93})+87.2\%B(s^{1.00}p^{10.52})$
	5C	2.00	$7.8\%U(d^{3.15}f^{1.00})+92.2\%B(s^{1.00}p^{21.09})$
	5C	2.00	$9.3\%U(d^{5.60}f^{1.00})+92.7\%B(s^{1.00}p^{16.62})$
	5C	2.00	$4.0\%U(d^{9.62}f)+96.0\%B(p)$

	5C	2.00	2.1%U($d^{1.28}f$)+97.9%B($sp^{4.01}$)
	5C	2.00	1.9%U($sd^{5.99}f^{3.86}$)+98.9%B($sp^{6.12}$)
Np	LP	1.00	99.1%Np(f)+0.9%B($s^{1.00}p^{4.26}$)
	LP	1.00	99.0%Np(f)+1.0%B($s^{1.00}p^{5.47}$)
	LP	1.00	96.0%Np(f)+4.0%B($s^{1.00}p^{24.75}$)
	LP	1.00	95.5%Np(f)+4.5%B($s^{1.00}p^{17.19}$)
	LP	1.00	12.0%Np($d^{3.33}f^{1.00}$)+75.9%B(p)
	5C	2.00	13.8%Np($s^{1.00}d^{2.91}f^{1.50}$)+87.2%B(p)
	5C	2.00	15.1%Np($s^{1.00}d^{3.57}f^{1.63}$)+85.9%B(p)
	5C	2.00	13.5%Np($d^{1.18}f^{1.00}$)+86.5%B(p)
	5C	2.00	8.3%Np($d^{3.57}f^{1.00}$)+91.7%B(p)
	5C	2.00	5.0%Np($d^{4.04}f^{1.00}$)+95.0%B(p)
Pu	LP	1.00	99.4%Pu(f)+0.6%B($s^{1.00}p^{6.74}$)
	LP	1.00	99.3%Pu(f)+0.7%B($s^{1.00}p^{10.21}$)
	LP	1.00	99.3%Pu(f)+0.7%B($s^{1.00}p^{8.11}$)
	LP	1.00	94.9%Pu(f)+5.1%B(p)
	LP	1.00	92.7%Pu(f)+7.3%B(p)
	LP	1.00	99.4%B(p)
	4C	2.00	43.0%Pu($d^{0.14}f^{1.00}$)+57.0%B(p)
	4C	2.00	16.4%Pu($s^{1.00}d^{1.95}f^{3.56}$)+83.6%B(p)
	5C	2.00	7.1%Pu($d^{6.46}f^{1.00}$)+92.9%B(p)
	5C	2.00	4.3%Pu($d^{7.12}f$)+95.7%B(p)
	5C	2.00	1.1%Pu($d^{9.15}$)+98.9%B(p)
	5C	2.00	1.4%Pu($d^{6.90}$)+98.6%B(p)
Am	LP	1.00	99.8%Am(f)+0.2%B($s^{1.00}p^{3.32}$)
	LP	1.00	99.8%Am(f)+0.2%B(p)
	LP	1.00	99.6%Am(f)+0.4%B(p)
	LP	1.00	99.3%Am(f)+0.7%B(p)
	LP	1.00	99.0%Am(f)+1.0%B(p)
	LP	1.00	94.5%Am(f)+5.5%B(p)
	LP	1.00	91.2%Am(f)+8.8%B(p)
	3C	2.00	7.2%Am($s^{1.00}d^{16.80}f^{0.22}$)+92.8%B(p)
	4C	2.00	6.0%Am($d^{93.0}f^{1.00}$)+94.0%B(p)
	4C	2.00	14.4%Am($s^{1.00}d^{0.65}f^{0.03}$)+85.6%B(p)
	4C	2.00	7.4%Am($s^{1.00}d^{1.51}f^{0.04}$)+92.6%B(p)
Cm	LP	1.00	99.9%Cm(f)+0.1%B($s^{1.00}p^{0.03}$)
	LP	1.00	99.9%Cm(f)+0.1%B($s^{1.00}p^{1.40}$)
	LP	1.00	99.9%Cm(f)+0.1%B($s^{1.00}p^{7.51}$)

	LP	1.00	99.8%Cm(f)+0.2%B($s^{1.00}p^{6.04}$)
	LP	1.00	99.7%Cm(f)+0.3%B($s^{1.00}p^{8.59}$)
	LP	1.00	99.7%Cm(f)+0.3%B($s^{1.00}p^{12.53}$)
	LP	1.00	99.4%Cm(f)+0.6%B(p)
	LP	1.00	10.7%Cm($s^{1.00}d^{8.00}f^{0.04}$)+89.3%B(p)
	4C	2.00	1.4%Cm($sd^{8.54}$)+98.6%B(p)
	5C	2.00	1.5%Cm($sd^{7.64}$)+98.9%B(p)
	5C	2.00	1.1%Cm($sd^{27.64}$)+98.9%B(p)
	5C	2.00	1.1%Cm($sd^{27.13}$)+98.9%B(p)

Table S6. Selected optimized geometrical structures (bond length, Å) and formation energies (kcal/mol) for the reaction of An + B_{12} = AnB_{12} (An = Th to Cm) at SR/SO-PBE/TZP levels of theory. (All calculations are fully optimization without constrain.)

Species	Spin/GS	Elec. Conf. of An	OS	An-B, Å	SR-E_f	SO-E_f
Th	^{3}A	f^0	IV	2.602-2.825 (2.732)	-187.6	-181.1
Pa	^{2}A	f^0	V	2.512-2.748 (2.636)	-194.4	-186.1
U	^{3}A	f^2	IV	2.568-2.764 (2.699)	-167.5	-168.4
Np	^{4}A	f^4	III	2.594-2.781 (2.705)	-144.5	-151.1
Pu	^{7}A”	f^5	III	2.629-2.843 (2.738)	-118.0	-124.7
Am	^{8}A	f^7	II	2.665-2.958 (2.822)	-90.9	-96.4
Cm	^{9}A	f^7	III	2.661-2.875 (2.770)	-128.4	-131.1

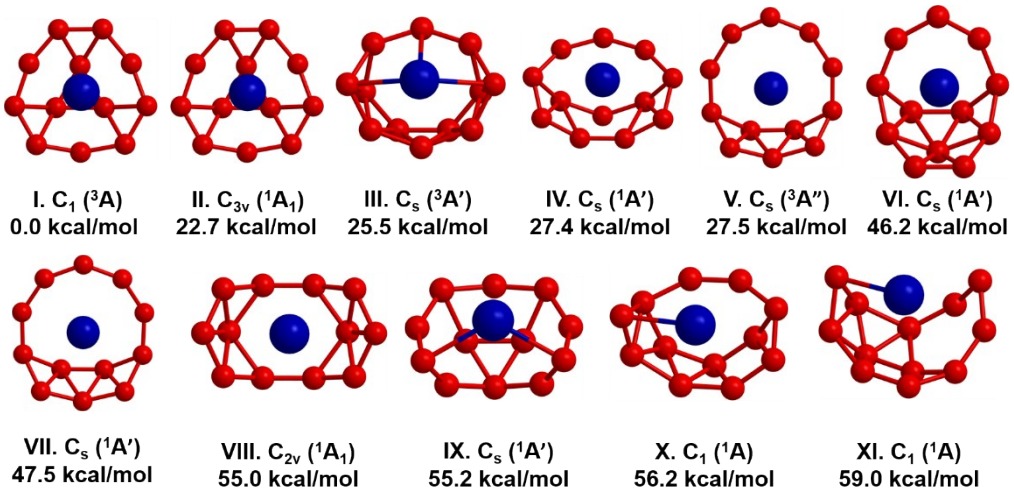

Figure S1. Optimized structures for UB_{12} at the B3LYP level. The relative energy is labeled under each structure.

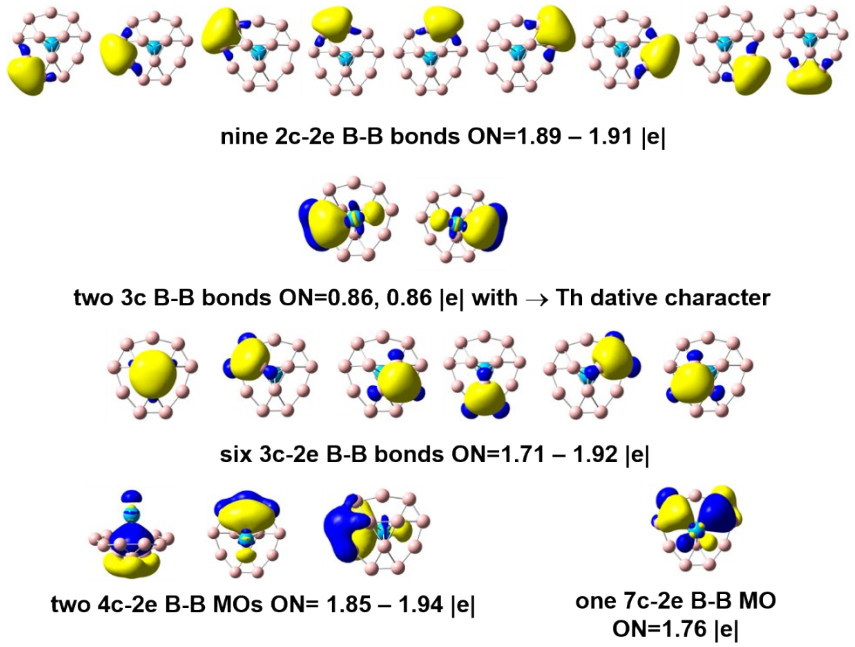

Figure S2. AdNDP analysis for ThB_{12}. ON denotes the occupation number and is equal to 2.00 |e| in the ideal case.

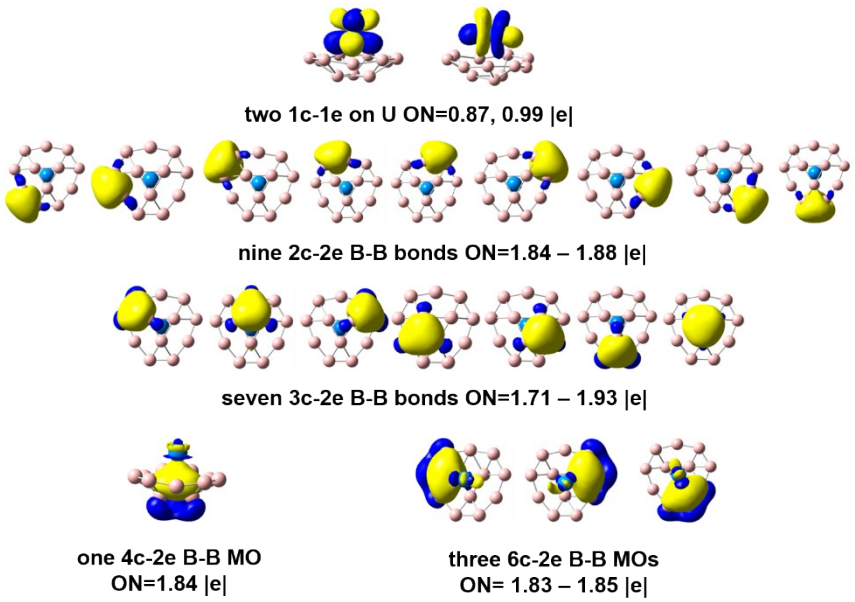

Figure S3. AdNDP analysis for UB_{12}. ON denotes the occupation number and is equal to 2.00 |e| in the ideal case.

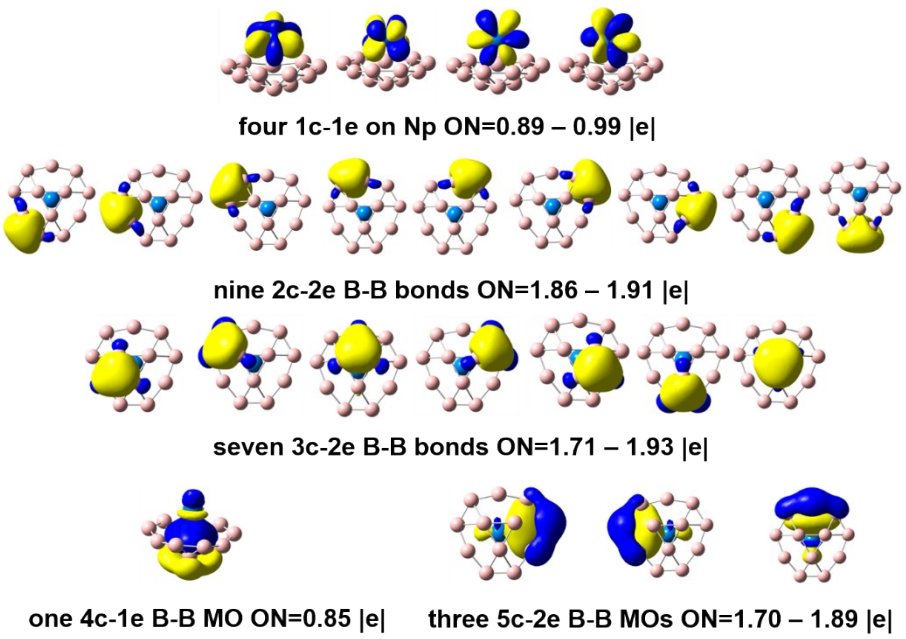

Figure S4. AdNDP analysis for NpB_{12}. ON denotes the occupation number and is equal to 2.00 |e| in the ideal case.

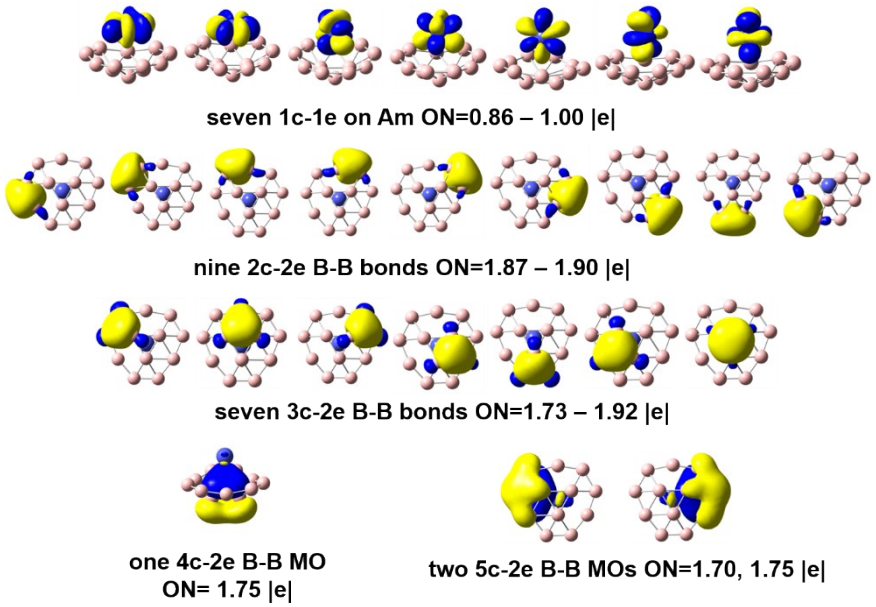

Figure S5. AdNDP analysis for AmB_{12}. ON denotes the occupation number and is equal to 2.00 |e| in the ideal case.

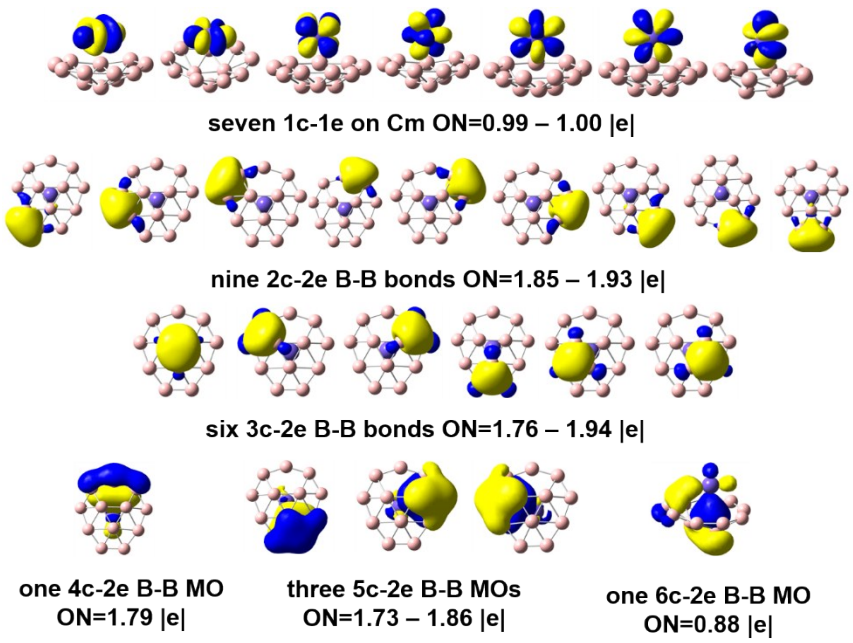

Figure S6. AdNDP analysis for CmB_{12}. ON denotes the occupation number and is equal to 2.00 |e| in the ideal case.