Supplementary Information

Investigation of Pb–B Bonding in $PbB_2(BO)_n^-$ (n = 0–2): Transformation from an Aromatic PbB_2^- to $Pb[B_2(BO)_2]^{-/0}$ Complexes with a B≡B Triple Bond

Qiang Chen,[a,c,†] Wei-Jia Chen,[b,†] Xin-Yao Wu,[a,†] Teng-Teng Chen,[b,e] Rui-Nan Yuan,[a] Hai-Gang Lu,[a,c] Dao-Fu Yuan,*[b,d] Si-Dian Li,*[a,c] and Lai-Sheng Wang*[b]

[a] *Institute of Molecular Science, Key Laboratory of Materials for Energy Conversion and Storage of Shanxi Province, Shanxi University, Taiyuan 030006, People's Republic of China. Email: chenqiang@sxu.edu.cn, lisidian@sxu.edu.cn*

[b] *Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA. Email: ydfu@ustc.edu.cn, lai-sheng_wang@brown.edu*

[c] *Key Laboratory of Chemical Biology and Molecular Engineering of Ministry of Education, Shanxi University, Taiyuan 030006, People's Republic of China*

[d] *Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China*

[e] *Department of Chemistry, The Hong Kong University of Science and Technology (HKUST), Clear Water Bay, Hong Kong SAR, China*

† These authors contributed equally to this work.

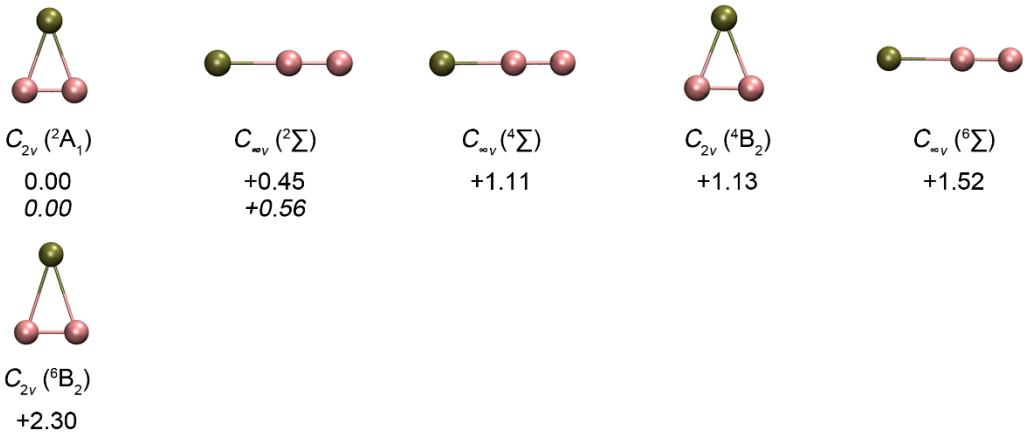


Fig. S1. Low-lying isomers of PbB_2^-, along with their relative energies indicated in eV at PBE0/AVTZ and CCSD(T)/AVTZ (in italic) levels, respectively.

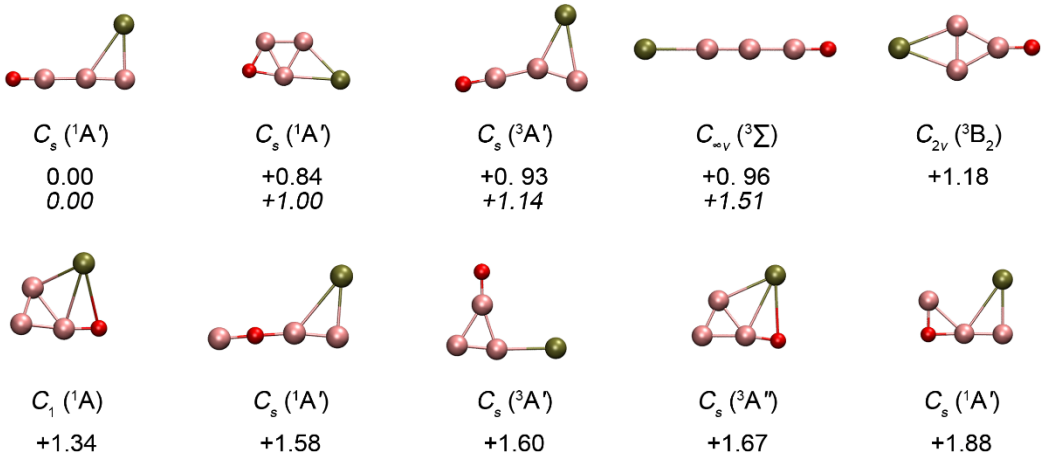


Fig. S2. Low-lying isomers of PbB_3O^-, along with their relative energies indicated in eV at PBE0/AVTZ and CCSD(T)/AVTZ (in italic) levels, respectively.

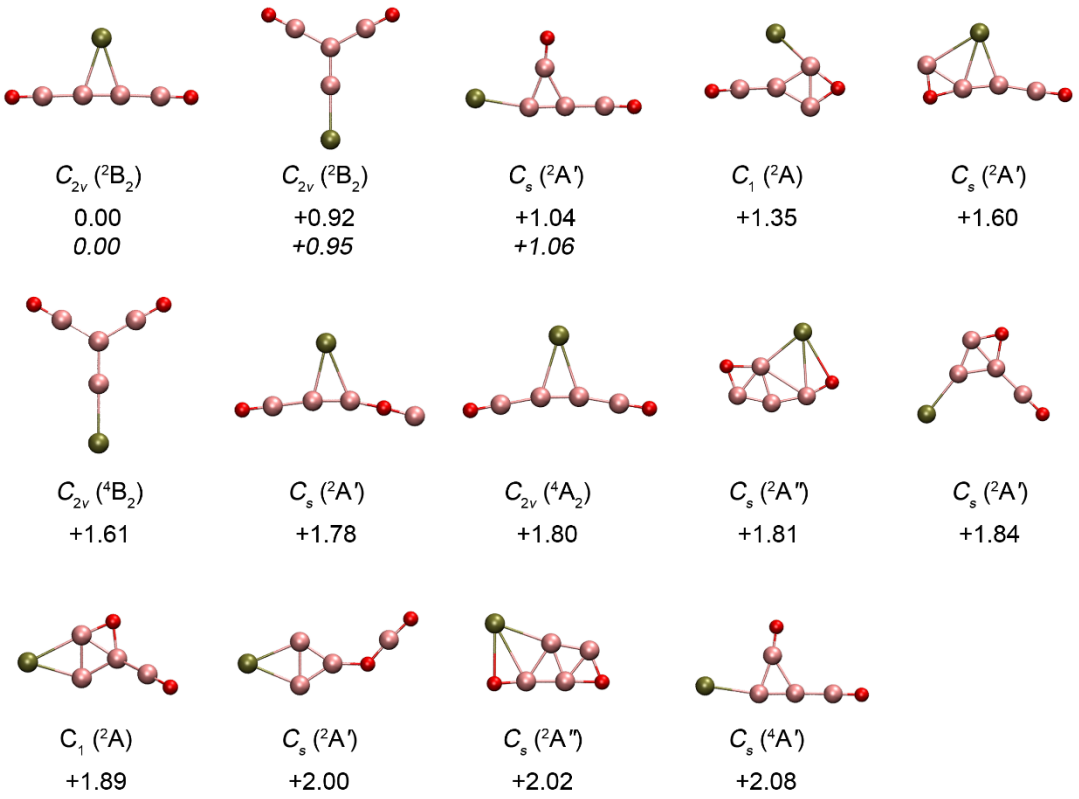


Fig. S3. Low-lying isomers of $PbB_4O_2^-$, along with their relative energies indicated in eV at PBE0/AVTZ and CCSD(T)/AVTZ (in italic) levels, respectively.

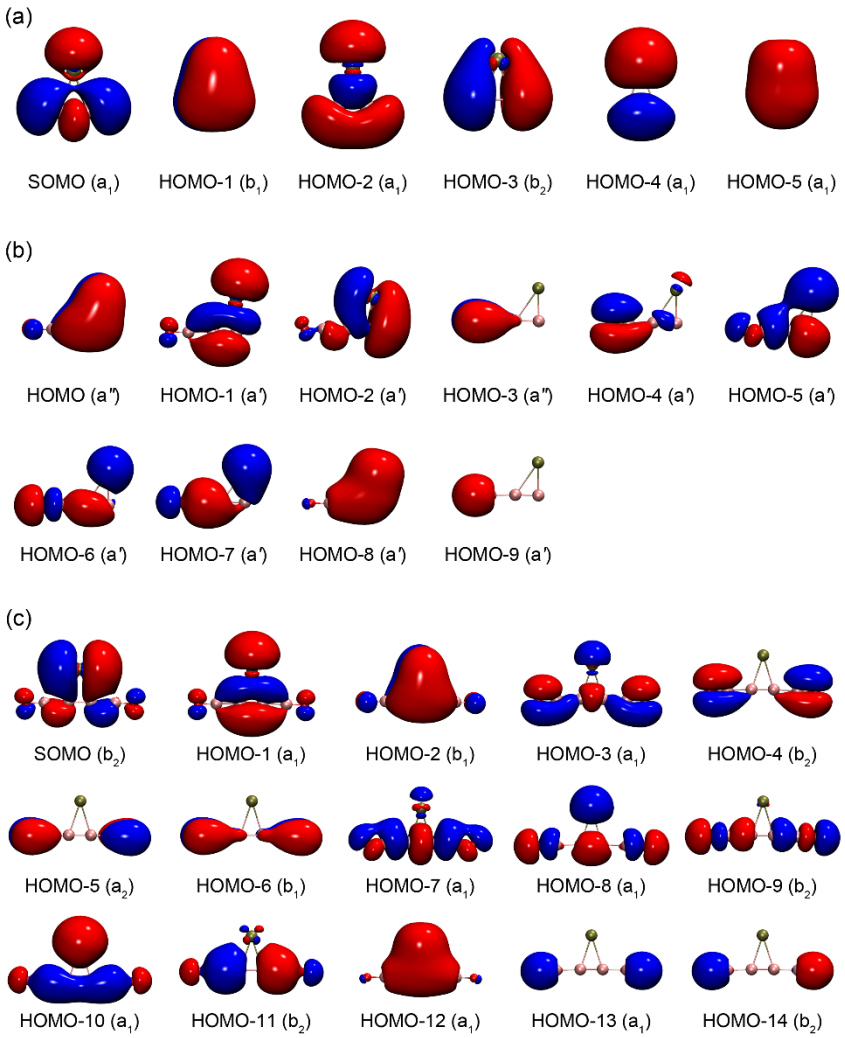


Fig. S4. Occupied valence molecular orbitals for the global minima of (a) C_{2v} PbB_2^- (**1**), (b) C_s PbB_3O^- (**2**), and (c) C_{2v} $PbB_4O_2^-$ (**3**).

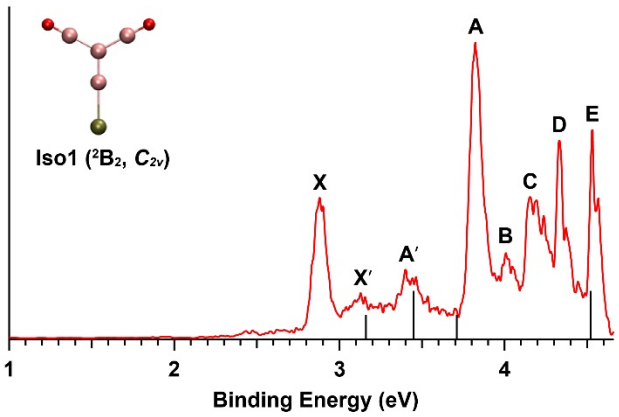
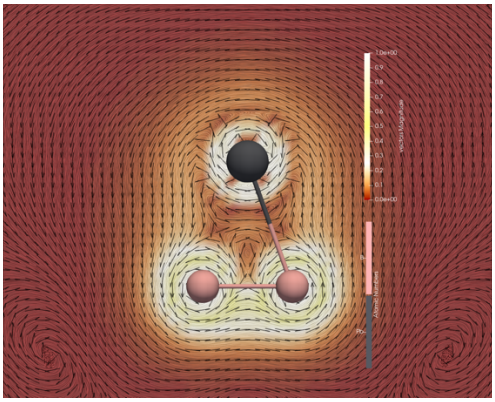
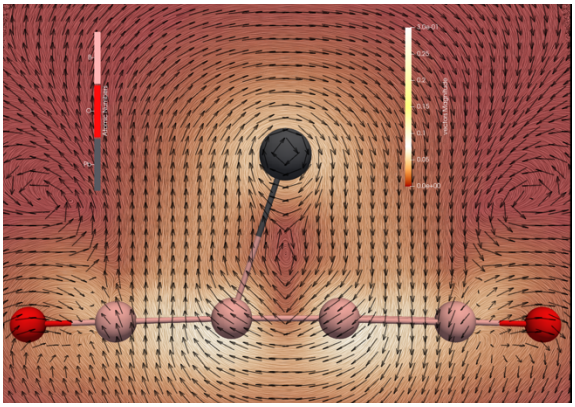


Fig. S5. Comparison between the photoelectron spectrum with the computed VDEs of $PbB_4O_2^-$ at 266 nm. The vertical bars correspond to computed VDEs using the CCSD(T) method. The longer and shorter bars correspond to transitions to triplet and singlet final states, respectively.

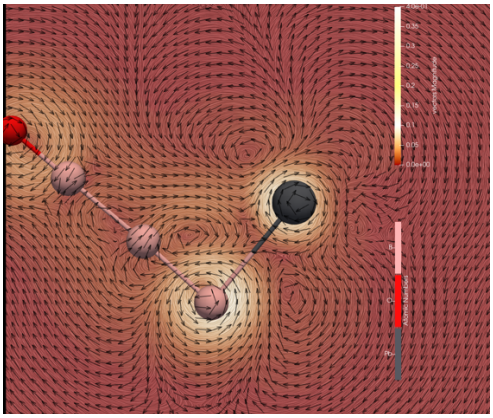
(a) C_{2v} PbB_2^- (**1**)



(c) C_{2v} $PbB_4O_2^-$ (**3**)



(b) C_s PbB_3O^- (**2**)



(d) C_{2v} PbB_4O_2 (**3′**)

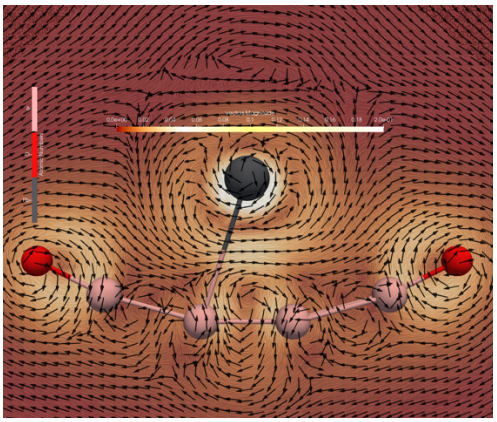


Fig. S6. The strength and direction of the induced current for (a) C_{2v} PbB_2^- (**1**) at the molecular plane, and for (b) C_s PbB_3O^- (**2**) at 1.5 a_0 above the molecular plane, and for (c) C_{2v} $PbB_4O_2^-$ (**3**) at 1.5 a_0 above the molecular plane, and for (d) C_{2v} PbB_4O_2 (**3′**) at 1.5 a_0 above the molecular plane calculated by the GIMIC program. The magnetic field is pointing out of the molecule plane.

Table S1. The experimental vertical detachment energies (VDEs) for $PbB_4O_2^-$ in comparison with theoretical VDEs for Y-shaped $PbB_4O_2^-$ at PBE0/AVTZ and CCSD(T)/AVTZ levels. All energies are given in eV.

Feature	VDE[a] (exp)	Configurations	Terms	VDE (theo.)	
				PBE0[b]	CCSD(T)[c]
X	2.88				
X′	3.13	…$1b_1^2 1a_2^2 4b_2^2 6a_1^2 7a_1^2 2b_1^2 \mathbf{5b_2^0}$	$^1A_1$	3.29	3.16
A′	3.40	…$1b_1^2 1a_2^2 4b_2^2 6a_1^2 7a_1^2 \mathbf{2b_1^1} 5b_2^1$	$^3A_2$	3.40	3.45
A	3.82	…$1b_1^2 1a_2^2 4b_2^2 6a_1^2 7a_1^2 \mathbf{2b_1^1} 5b_2^1$	$^1A_2$	3.84	3.71
B	4.01				
C	4.15				
D	4.33				
E	4.53	…$1b_1^2 1a_2^2 4b_2^2 6a_1^2 \mathbf{7a_1^1} 2b_1^2 5b_2^1$	$^3B_1$	4.47	4.52

[a] The experimental uncertainty was estimated to be ±0.02 eV.

[b] The VDEs calculated using the TD-PBE0/AVTZ method.

[c] The first two VDEs were calculated using the CCSD(T)/AVTZ method, while the higher VDEs were calculated using the TD-PBE0/AVTZ method.

Table S2. Coordinates for optimized C_{2v} PbB_2^- (**1**), C_s PbB_3O^- (**2**), and C_{2v} $PbB_4O_2^{-/0}$ (**3** and **3′**), and C_{2v} $PbB_4O_2^{-/2-}$ (**4** and **4′**) at PBE0/AVTZ level.

C_{2v} PbB_2^- (**1**)

Pb	0.23453000	0.00000000	0.00000000
B	-1.92314600	0.77147600	0.00000000
B	-1.92314600	-0.77147600	0.00000000
	-1.34797311	0.00000000	0.00000000

(Centre of current at the molecular plane, Fig. S6a)

C_s PbB_3O^- (**2**)

Pb	0.00000000	0.71644400	0.00000000
B	0.64172300	-1.77066000	0.00000000
B	-0.39546500	-3.01579200	0.00000000
B	1.65481400	-0.65065700	0.00000000
O	-1.18817000	-3.94535300	0.00000000
	0.57158000	-1.04077600	0.00000000

(Centre of current at 1.5 a_0 above the molecular plane, Fig. S6b)

C_{2v} $PbB_4O_2^-$ (**3**)

Pb	0.71202200	0.00000000	0.00000000
B	-1.61705200	2.36064400	0.00000000
B	-1.57021300	-0.74970700	0.00000000
B	-1.61705200	-2.36064400	0.00000000
B	-1.57021300	0.74970700	0.00000000
O	-1.65707100	-3.58175500	0.00000000
O	-1.65707100	3.58175500	0.00000000
	-0.89314529	0.00000000	0.00000000

(Centre of current at 1.5 a_0 above the molecular plane, Fig. S6c)

C_{2v} PbB_4O_2 (**3′**)

Pb	0.53610400	0.00000000	0.00000000
B	-1.34307400	2.29677300	0.00000000
B	-1.77506000	-0.73903100	0.00000000
B	-1.34307400	-2.29677300	0.00000000
B	-1.77506000	0.73903100	0.00000000
O	-0.79870000	-3.37985600	0.00000000
O	-0.79870000	3.37985600	0.00000000
	-1.44100246	0.00000000	0.00000000

(Centre of current at 1.5 a_0 above the molecular plane, Fig. S6d)

C_{2v} $PbB_4O_2^-$ (**4**)

Pb	0.00000000	0.00000000	1.33048900
B	0.00000000	0.00000000	-0.88573600
B	0.00000000	1.44352800	-3.21600000
B	0.00000000	0.00000000	-2.44570400
B	0.00000000	-1.44352800	-3.21600000
O	0.00000000	2.53020100	-3.76767900
O	0.00000000	-2.53020100	-3.76767900

C_{2v} $PbB_4O_2^{2-}$ (**4′**)

Pb	0.00000000	0.00000000	1.35287200
B	0.00000000	0.00000000	-0.85549600
B	0.00000000	1.41641300	-3.24880500
B	0.00000000	0.00000000	-2.43344700
B	0.00000000	-1.41641300	-3.24880500
O	0.00000000	2.47448000	-3.87517100
O	0.00000000	-2.47448000	-3.87517100

Table S3. Natural resonance theory (NRT) bond orders for the Pb–B and B–B bonds in C_{2v} PbB_2^- (**1**), C_s PbB_3O^- (**2**), C_{2v} $PbB_4O_2^{-/0}$ (**3** and **3′**), and C_{2v} $PbB_4O_2^{-/2-}$ (**4** and **4′**) at PBE0/AVTZ level.

	C_{2v} PbB_2^- (**1**)	C_s PbB_3O^- (**2**)	C_{2v} $PbB_4O_2^-$ (**3**)	C_{2v} PbB_4O_2 (**3′**)	C_{2v} $PbB_4O_2^-$ (**4**)	C_{2v} $PbB_4O_2^{2-}$ (**4′**)
Pb–B	1.04	1.55/0.63	0.78	0.63	1.72	2.08
B–B	1.68	1.78	1.76	1.84	1.59	1.69