

SUPPLEMENTARY MATERIALS

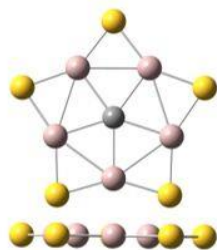
Sulphur-bridged BAI_5S_5^+ with 17 counting electrons: a regular planar pentacoordinate boron system

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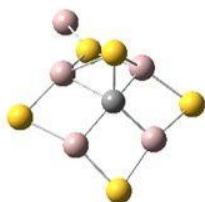
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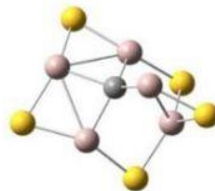
Figure S1. The optimized structures of four lowest isomers of PPC/B and quasi-PPC systems at B3LYP/def2-TZVP and the corresponding single point energies at CCSD/6-31g(d) and the lowest frequency. (Relative energies are listed in kcal mol⁻¹ and the minimum frequencies are listed in cm⁻¹)



1A $\text{CaI}_5\text{S}_5^{2+}$ D_{5h}
 $\Delta E = 0.00$
 $V_{\min} = 24.69$



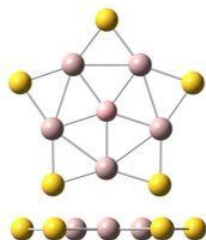
1B C_s
 $\Delta E = +14.68$
 $V_{\min} = 20.41$



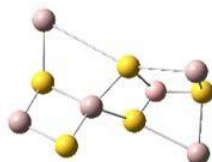
1C C_s
 $\Delta E = +30.23$
 $V_{\min} = 54.49$



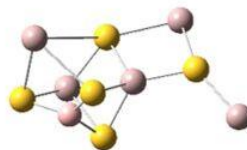
1D C_1
 $\Delta E = +51.09$
 $V_{\min} = 8.99$



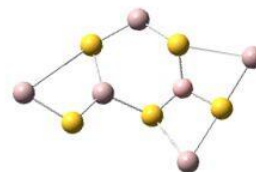
2A BaI_5S_5^+ D_{5h}
 $\Delta E = 0.00$
 $V_{\min} = 35.61$



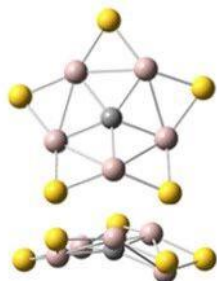
2B C_1
 $\Delta E = +28.90$
 $V_{\min} = 19.70$



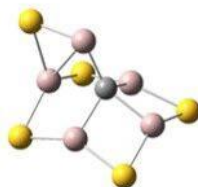
2C C_1
 $\Delta E = +29.80$
 $V_{\min} = 17.39$



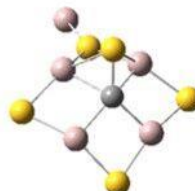
2D C_1
 $\Delta E = +45.00$
 $V_{\min} = 8.90$



3A CaI_5S_5^+ C_1
 $\Delta E = 0.00$
 $V_{\min} = 2.41$



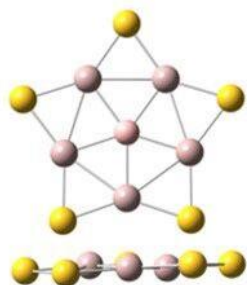
3B C_s
 $\Delta E = +16.10$
 $V_{\min} = 60.02$



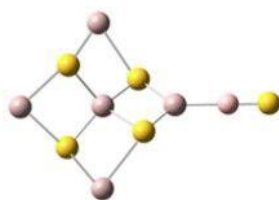
3C C_s
 $\Delta E = +39.60$
 $V_{\min} = 27.06$



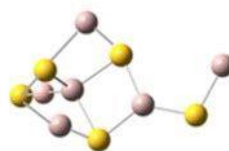
3D C_1
 $\Delta E = +41.45$
 $V_{\min} = 46.72$



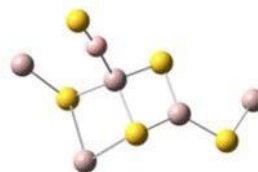
4 BAl₅S₅ C₁
 $\Delta E = 0.00$
 $V_{\min} = 7.94$



4B C₁
 $\Delta E = +37.59$
 $V_{\min} = 22.63$

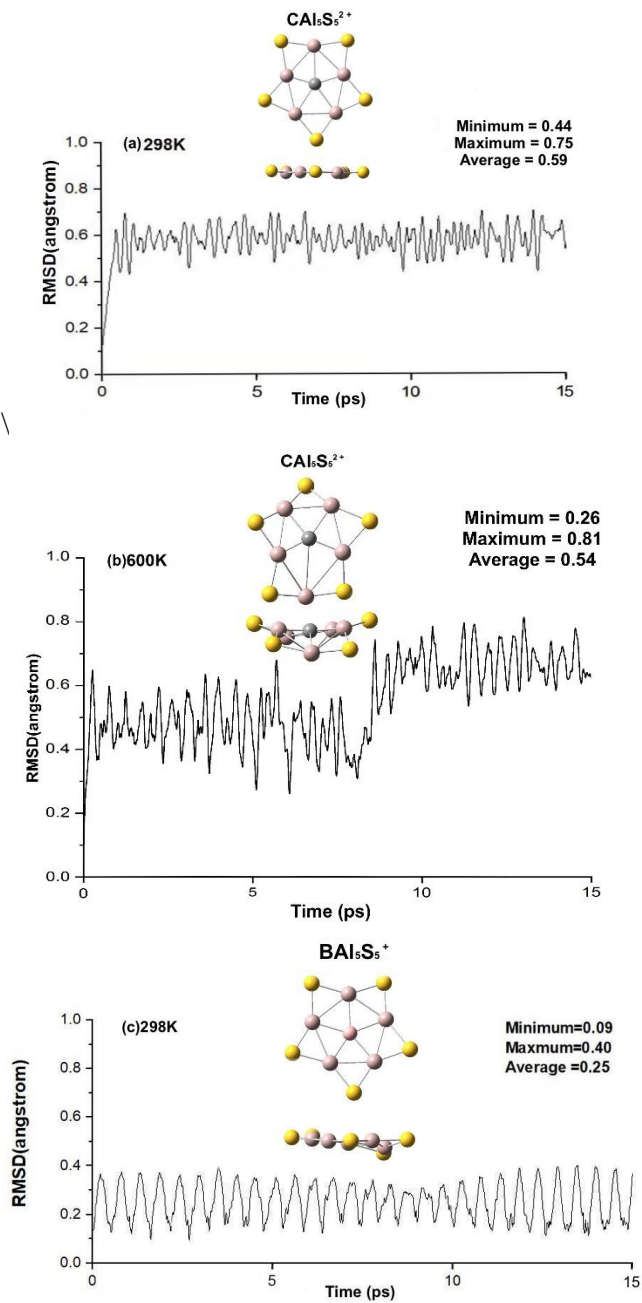


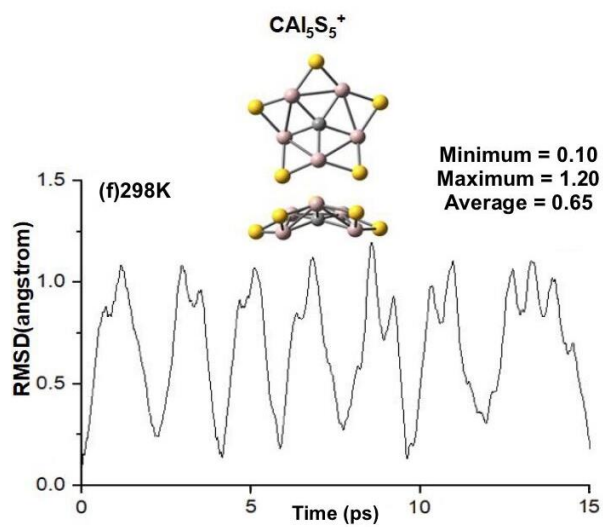
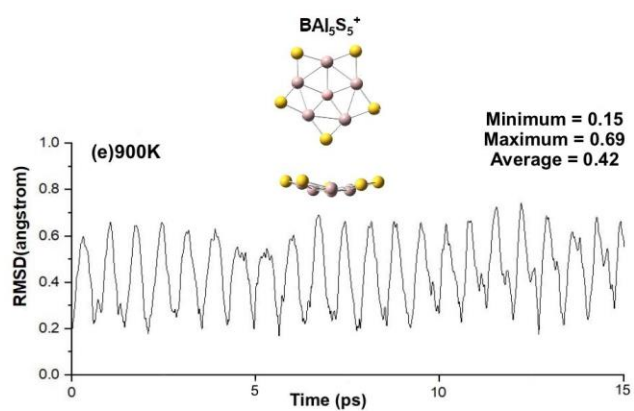
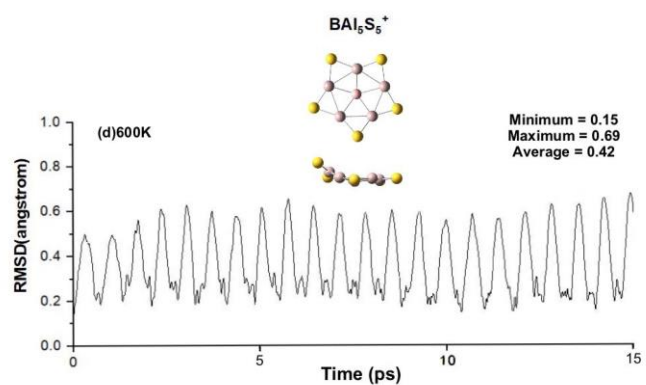
4C C₁
 $\Delta E = +40.89$
 $V_{\min} = 18.85$



4D C₁
 $\Delta E = +41.99$
 $V_{\min} = 13.26$

Figure S2. Born-Oppenheimer molecular dynamics (BOMD) simulations at different temperatures and their Root-mean-square deviations (RMSD) for four systems.





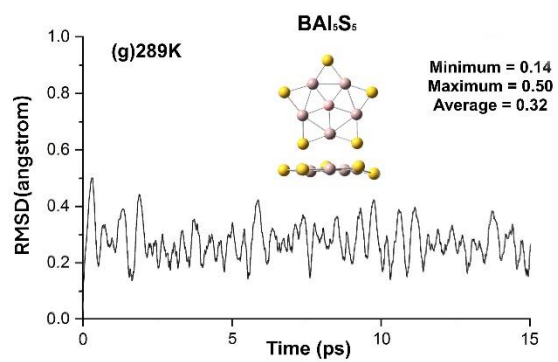
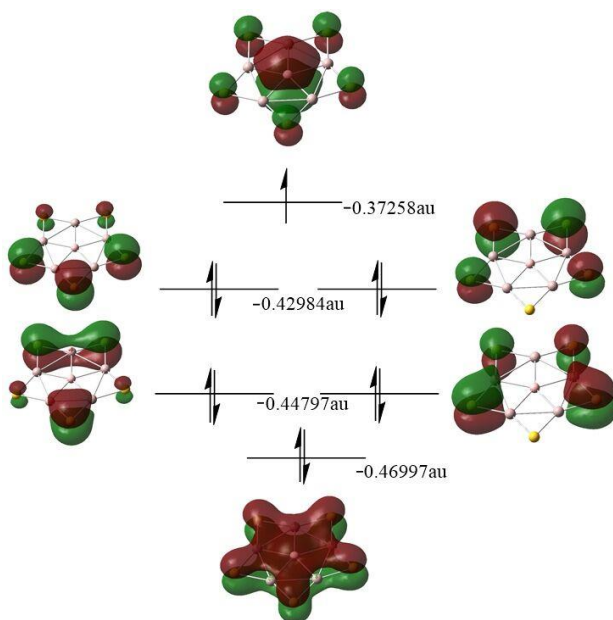


Figure S3. The α electron profile and the corresponding energy of 6 highest occupied π MOs of BAI_5S_5^+ .



FigureS4. The electron profile and the corresponding energy of 6 highest occupied π MOs of BAI_5S_5 .

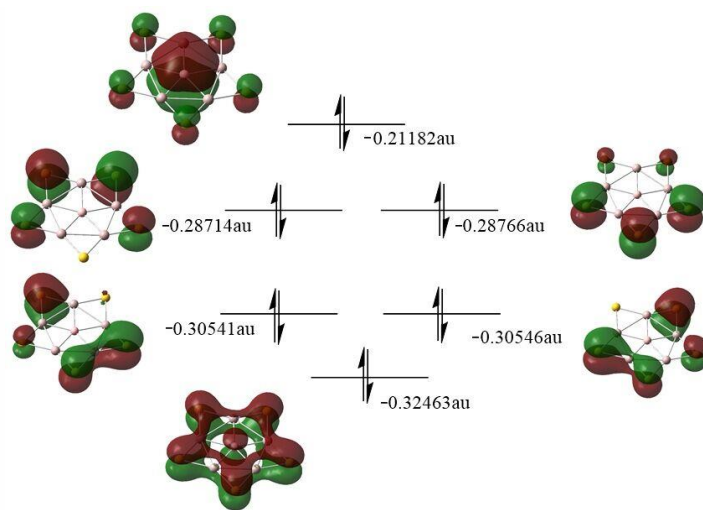


Table S1. The important information on the GEM structures of PPC/B and quasi-PPC systems at B3LYP/def2-TZVP level.

1. $\text{CAI}_5\text{S}_5^{2+}$

(D_{5h} , $^2A_2''$)

$E_{\text{total with ZPE}} = -3241.261471$ Hartree $\text{Freq}_{\text{min}} = 24.6879 \text{ cm}^{-1}$

C	0.00000000	0.00000000	0.00000000
Al	0.00000000	2.23120000	0.00000000
Al	2.121997300	0.68947871	0.00000000
Al	-2.121997300	0.68947871	0.00000000
Al	-1.311466455	-1.80507872	0.00000000
Al	1.311466456	-1.80507871	0.00000000
S	2.058719183	2.83358386	0.00000000
S	-2.058719185	2.83358386	0.00000000
S	-3.331077613	-1.08233272	0.00000000
S	0.00000000	-3.50250227	0.00000000
S	3.331077613	-1.08233272	0.00000000

2. BAI_5S_5^+

(D_{5h} , $^2A_2''$)

$E_{\text{total with ZPE}} = -3228.429483$ Hartree $\text{Freq}_{\text{min}} = 47.6385 \text{ cm}^{-1}$

B	0.00000000	0.00000019	0.00000000
Al	-0.00000004	2.21284859	0.00000000
Al	2.10454387	0.68380800	0.00000000
Al	-2.10454390	0.68380790	0.00000000
Al	-1.30067961	-1.79023179	0.00000000
Al	1.30067969	-1.79023173	0.00000000
S	2.07676105	2.85841668	0.00000000
S	-2.07676117	2.85841659	0.00000000
S	-3.36027004	-1.09181781	0.00000000
S	0.00000007	-3.53319684	0.00000000
S	3.36027009	-1.09181766	0.00000000

3. CAI_5S_5^+

(C_1 , 1A)

$E_{\text{total with ZPE}} = -3241.699475$ Hartree $\text{Freq}_{\text{min}} = 8.2409 \text{ cm}^{-1}$

C	0.00183052	0.00607964	-0.00022898
Al	0.62539807	2.01974485	-0.00745236
Al	-1.72684059	1.14419377	-0.33295140
Al	2.06717006	-0.02933438	0.34989116
Al	0.61258798	-1.90045662	-0.56768049
Al	-1.57701658	-1.23129851	0.55742595

S	-1.09320251	3.20141134	-0.56184501
S	2.70658908	2.02847855	0.56153558
S	2.77231980	-1.94851426	-0.34555980
S	-0.99914694	-3.24135668	-0.01350604
S	-3.38770491	-0.04919371	0.35950640

4. BAl₅S₅

(C₁, ¹A)

E_{total with ZPE} = -3228.685859 Hartree Freq_{min} = 12.3348 cm⁻¹

B	0.00033891	-0.00026289	-0.00021126
Al	1.21666051	1.75701594	0.10837474
Al	-1.29226048	1.70066384	-0.13412062
Al	2.05382821	-0.61724278	-0.04214532
Al	0.04414126	-2.13846365	-0.04128160
Al	-2.02197418	-0.70228322	0.10781162
S	-0.07588540	3.52494250	-0.02281492
S	3.33015928	1.16351663	0.06089086
S	2.13304280	-2.80975896	-0.07471912
S	-2.01144390	-2.89706526	0.06119449
S	-3.37629990	1.01869901	-0.02337932