Supporting Information

What Governs the Electrocatalytic N_2 Reduction Activity of sp-Hybridized Boron

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1. Method for Calculating the generalized binding free energies

For give intermediates, such as *$HNNH_2$, its generalized binding free energies can be calculated by taking N_2 and H_2 as the reference for the energy of N and H:

$$\Delta G(*HNNH_2) = G(^*HNNH_2) - G(*) - 2\mu(N) - 3\mu(H)$$

In which $\mu(N) = \frac{1}{2}G(N_2(g))$, and $\mu(H) = \frac{1}{2}G(H_2(g))$, G(*) is the free energy of the substrate. Therefore, $\Delta G(*HNNH_2)$ represents the free energy of *$HNNH_2$ on the free energy diagram at 0.0 V (Figure 6). On the other hand, the binding energy of $HNNH_2$ species can be defines as

$$E_b(*HNNH_2) = E(^*HNNH_2) - E(*) - E(HNNH_2)$$

The difference between $\Delta G(*HNNH_2)$ and $E_b(*HNNH_2)$ is a constant on different surfaces. Therefore, $\Delta G(*HNNH_2)$ also reflects the binding strength of the intermediates, which why it is called generalized binding energy. For *NH_x species, their energies are lowered by 0.44 eV so that the energies are equal to $\Delta G(*NH_x) + \Delta G(NH_3(g))$

2. Pearson correlation coefficient

The Pearson correlation coefficient between two varialbes is defined as :

$R(x,y) = \frac{\sum(x_i-\bar{x})(y_i-\bar{y})}{\sqrt{\sum(x_i-\bar{x})^2\sqrt{(y_i-\bar{y})^2}}}$, in which $\bar{x} = \sum x_i/n$, $\bar{y} = \sum y_i/n$

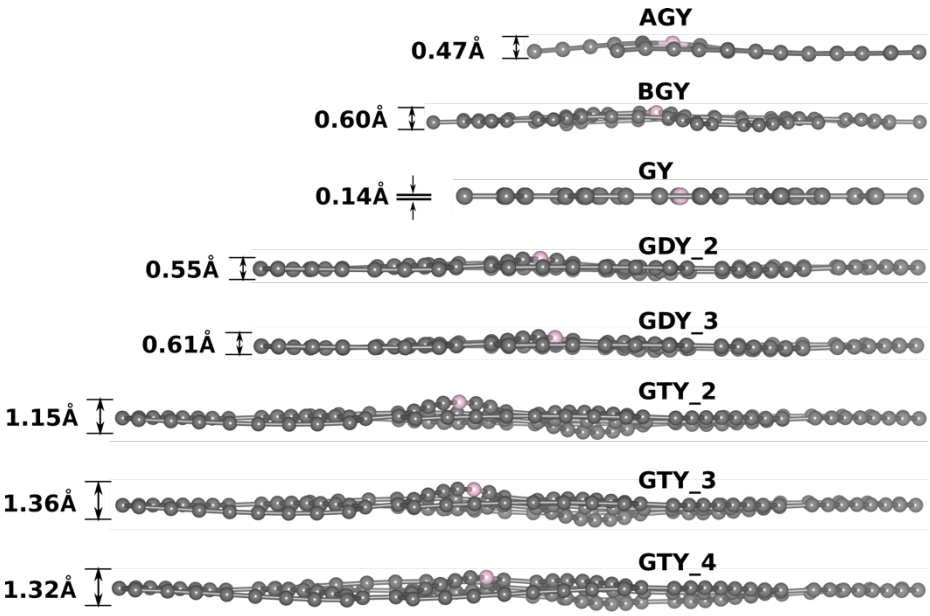

Figure S1, structure fluctuation of the B-doped GYs

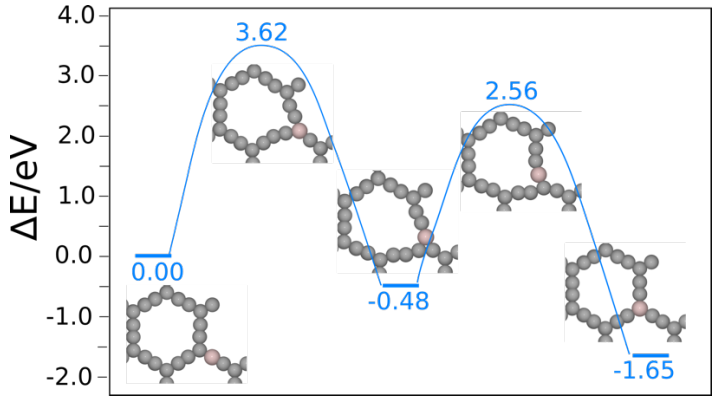

Figure S2, the potential energy surface for switching sp-B with sp^2-C on AGY. Inserted are the structures of the initial, intermediate, final and the transition states.

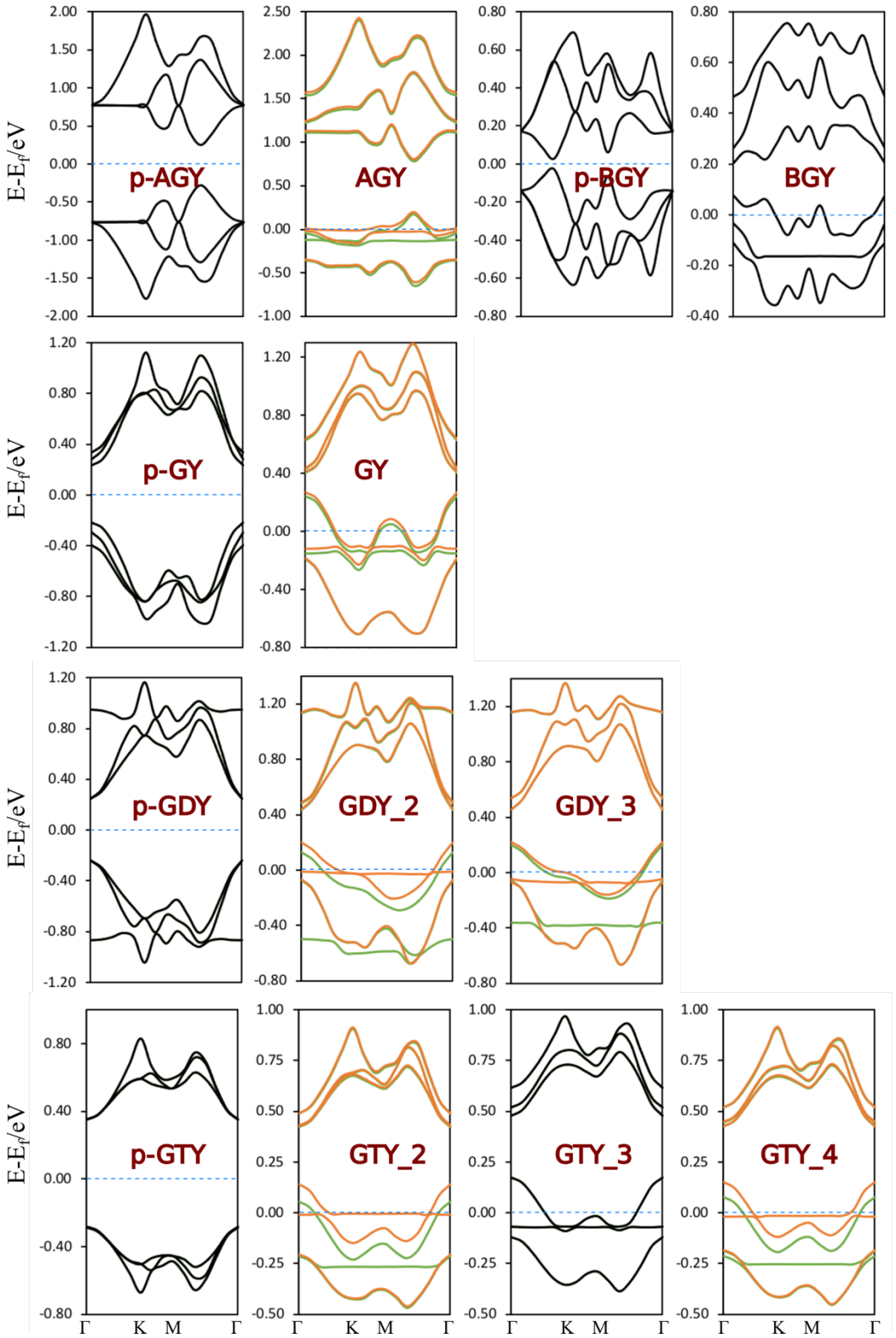

Figure S3, the band structures of the pristine and doped GYs: p-GYs means the pristine GYs, the orange and green lines represent the spin-up and the spin-down components, and the black line means the result is non-magnetic.

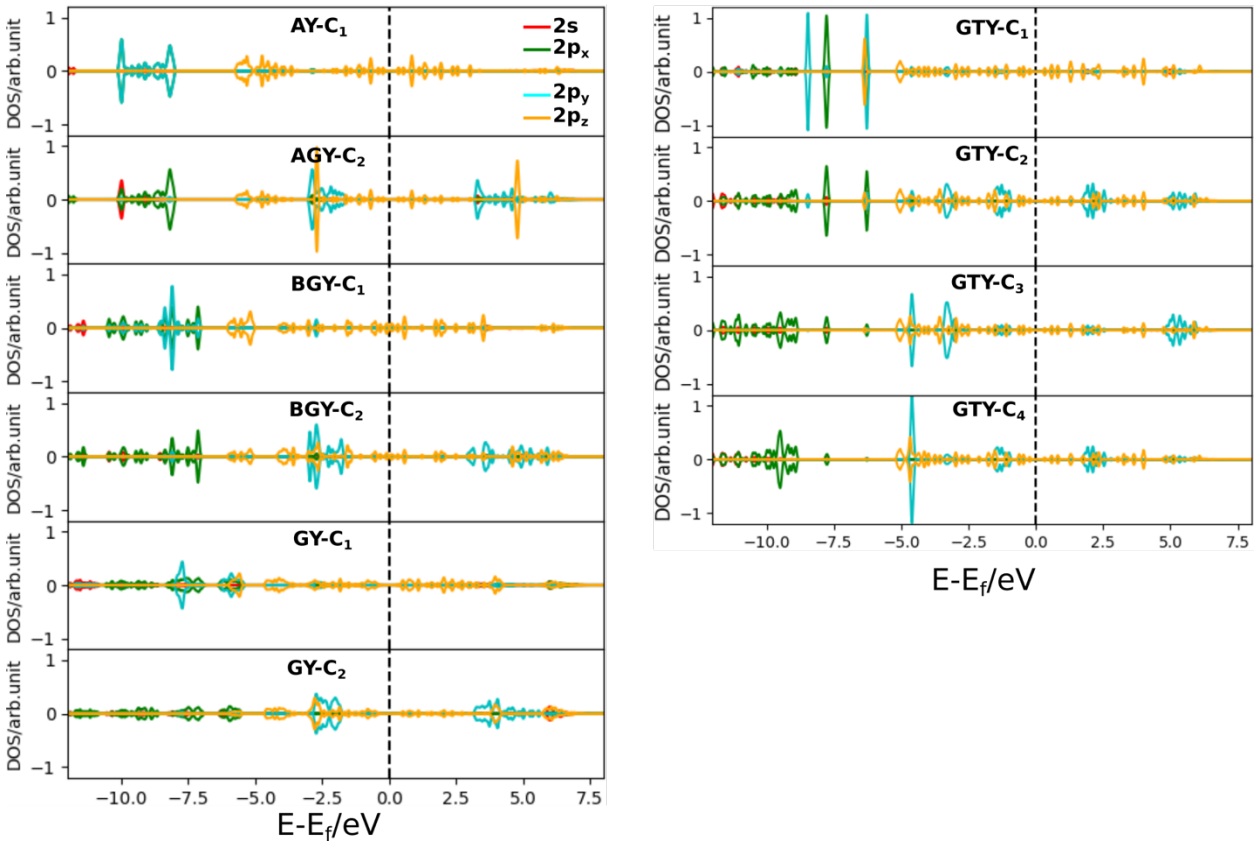

Figure S4, the projected density of states (PDOS) of the pristine GYs

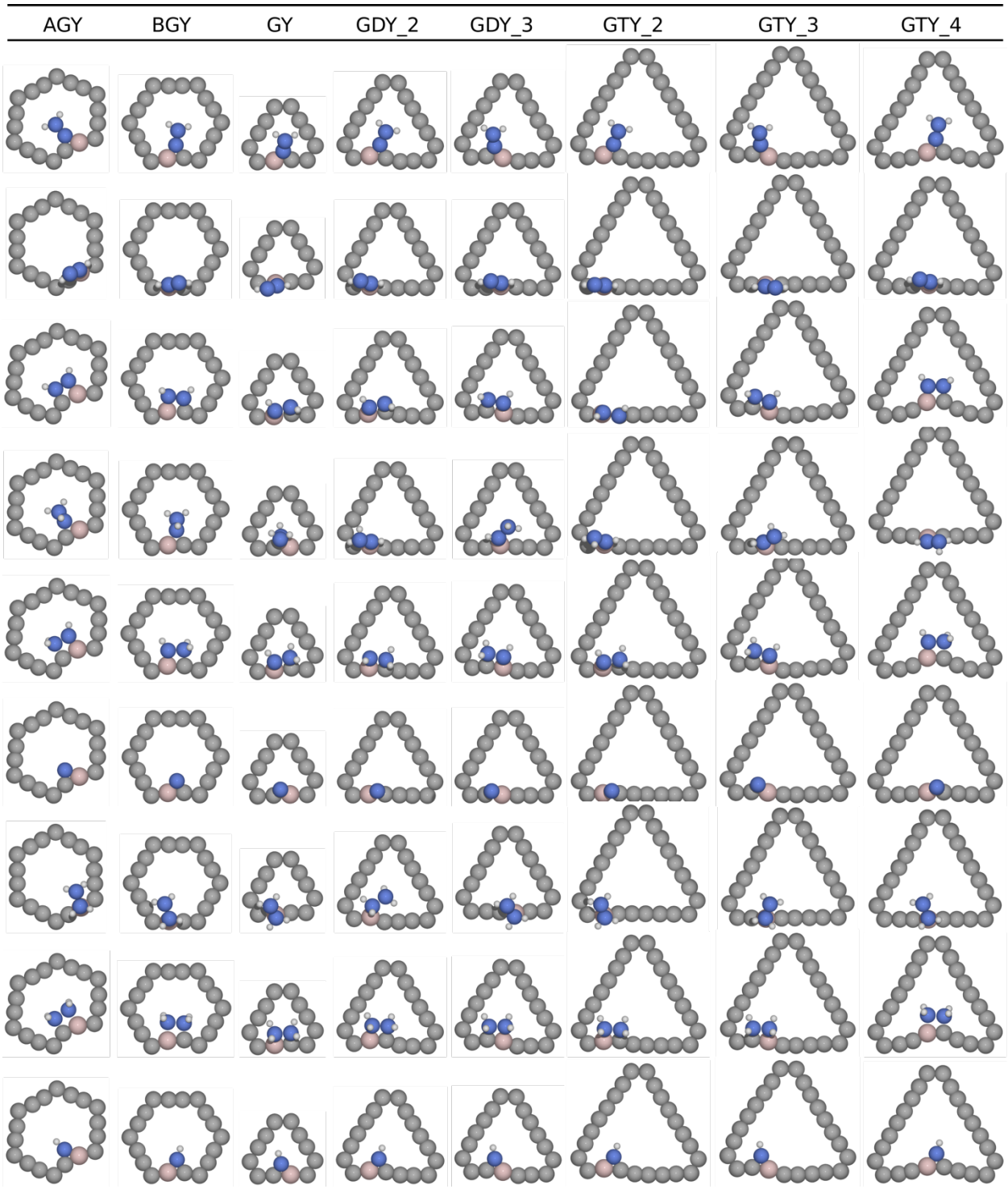

Figure S5, the adsorption structure of other intermediates on the Boron-doped GYs.

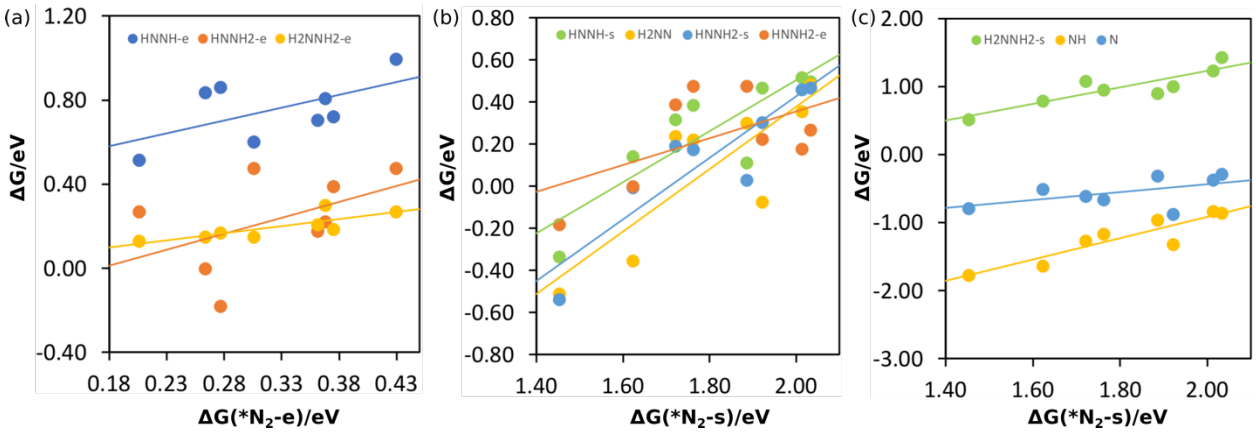

Figure S6, the scaling relations between the energies of the descriptors and other intermediates.

Table S1, the distortion-interaction analysis on the adsorption enery of N_2

Species	Surface	E_interacting/eV	E_dist(sub)/eV	E_dist(Mole)/eV	Eads
*N_2_e	AGY	-2.09	0.68	1.17	-0.25
	BGY	-2.15	0.72	1.17	-0.26
	GY	-1.96	0.63	1.17	-0.16
	GDY_2	-1.99	0.66	1.18	-0.15
	GDY_3	-1.89	0.63	1.17	-0.09
	GTY_2	-2.18	0.68	1.18	-0.32
	GTY_3	-2.01	0.70	1.17	-0.15
	GTY_4	-2.10	0.71	1.17	-0.22
*N_2_s	AGY	-2.95	1.16	2.72	0.93
	BGY	-2.50	1.10	2.50	1.10
	GY	-2.56	1.20	2.76	1.40
	GDY_2	-2.40	1.08	2.81	1.49
	GDY_3	-2.60	1.10	2.74	1.24
	GTY_2	-2.04	0.99	2.56	1.51
	GTY_3	-2.61	1.16	2.64	1.20
	GTY_4	-2.73	1.25	2.84	1.36

E_interacting, E_dist(sub), E_dist(Mole), and Eads are the interacting energy, the distortion energy of the substrate, the distortion energy of the molecule and the adsorption energy of the molecule.

Table S2, the generalized binding free energies of the intermedites.

	N_2-e	N_2-s	HNN-e	HNN-s	HNNH-e	HNNH-s	H_2NN	N
AGY	0.28	1.45	0.12	0.28	0.86	-0.33	-0.51	-0.79
BGY	0.26	1.62	0.39	0.70	0.84	0.14	-0.35	-0.51
GY	0.37	1.92	0.25	0.46	0.81	0.47	-0.08	-0.87
GDY_2	0.36	2.01	0.70	0.75	0.71	0.52	0.36	-0.37
GDY_3	0.43	1.76	0.48	0.47	1.00	0.39	0.22	-0.66
GTY_2	0.21	2.03	0.81	0.78	0.52	0.50	0.49	-0.29
GTY_3	0.37	1.72	0.52	0.44	0.72	0.32	0.24	-0.61
GTY_4	0.31	1.89	0.74	0.40	0.60	0.11	0.30	-0.31
	$HNNH_2$-e	$HNNH_2$-s	NH	NH2	H_2NNH_2-e	H_2NNH_2-s	NH3	
AGY	-0.18	-0.54	-1.77	-1.86	0.17	0.52	-1.50	
BGY	0.00	0.00	-1.64	-1.67	0.15	0.79	-1.52	
GY	0.22	0.30	-1.32	-1.49	0.30	1.01	-1.40	
GDY_2	0.18	0.46	-0.84	-1.71	0.21	1.24	-1.49	
GDY_3	0.48	0.17	-1.17	-1.46	0.27	0.95	-1.42	
GTY_2	0.27	0.47	-0.86	-2.01	0.13	1.43	-1.61	
GTY_3	0.39	0.19	-1.26	-1.43	0.19	1.08	-1.51	
GTY_4	0.48	0.03	-0.96	-1.76	0.15	0.90	-1.54	

Table S3, test calculations for the energies of key intermediates on B-doped GY(eV)

Models	$\Delta G(* H_2NN)$	$\Delta G(* HNN\_e)$	$\Delta G(* N)$	$\Delta G(* NH)$
PBE	-0.08	0.25	-0.87	-1.32
B3PW91	-0.12	0.08	-1.35	-1.60
PBE-cluster	0.39	0.17	-0.98	-1.08
B3PW91-ref	0.86	0.45	-1.30	-0.86

B3PW91-ref is from Inorg. Chem. 2019, 58, 11843–11849