Supporting Information

Exploring the Synergistic Effect of B-N Doped Defective Graphdiyne for N_2 Fixation

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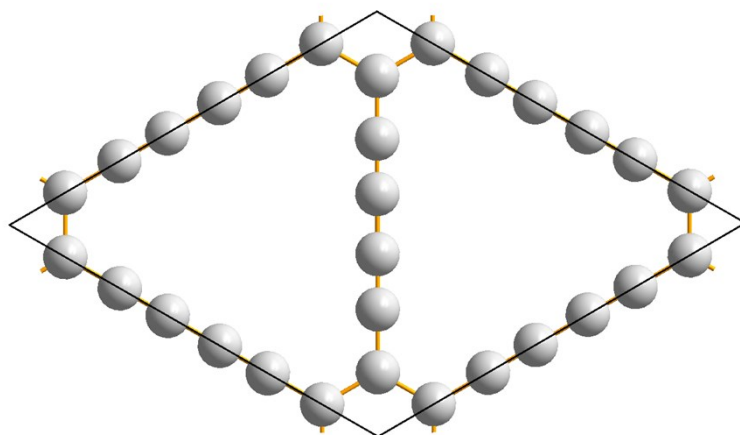
Phone: +86-010-68914863

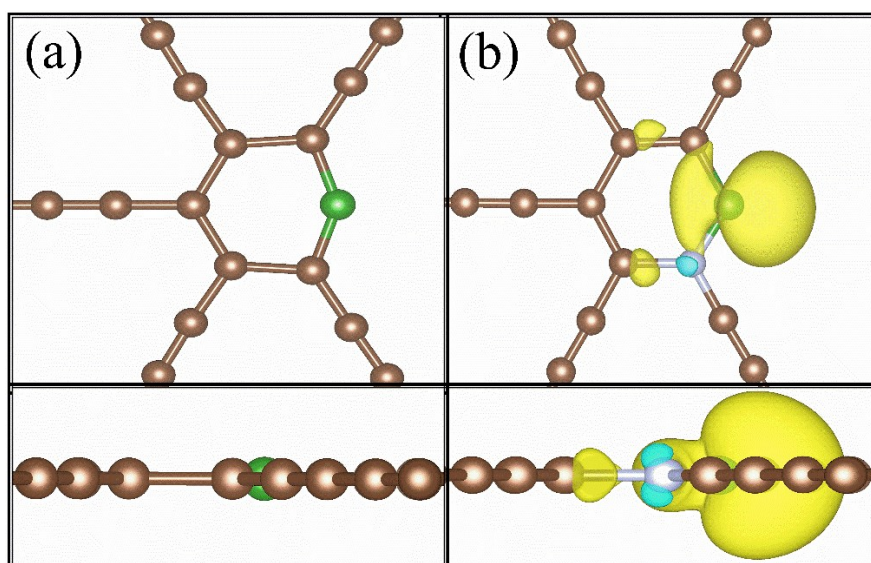**Fig. S1** The optimized primitive unit cell of pristine GDY.

Fig. S2 Spin-polarized charge density for (a) B@GDY and (b) BN@GDY with isosurface value of 0.005 e/Bohr^3.

The N$_2$ adsorption ability of different B/N doping sites

We calculated the ability of different B/N doping sites for N$_2$ adsorption. Fig. S3 show the different doping sites. In order to facilitate the calculation, we choose the most stable end-on configuration for the following discussion. The obtained results are shown as following (Fig. S4-S6).
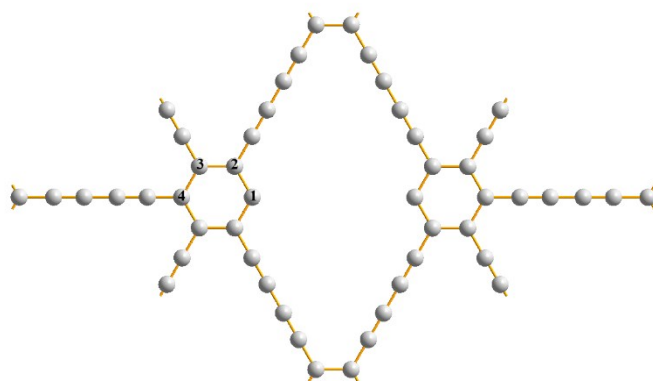

Fig. S3 Schematic diagram of different doping sites.

For the N2-doped, N3-doped and N4-doped GDY (Fig. S4), N$_2$ can only be adsorbed on N2-doped structure due to the strong electron affinity of N element. The adsorption energy of N2-doped GDY is positive, indicating that N doped GDY cannot fix N$_2$ effectively.
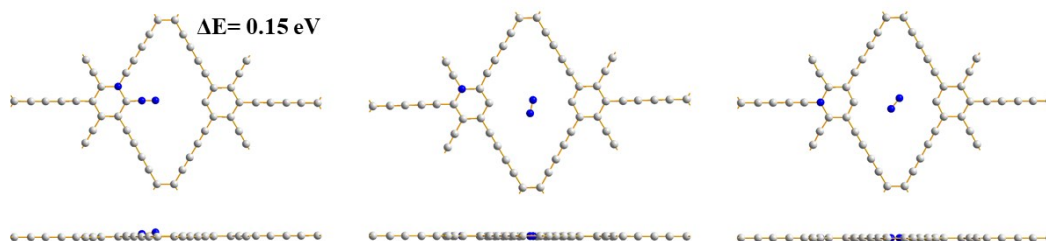

Fig. S4 N$_2$ adsorbed on different N doping sites of GDY

For the B2-doped, B3-doped and B4-doped GDY (Fig. S5), the structure of B3-doped GDY undergoes significant deformation after optimization, therefore we will not consider it. For the remaining two structures, N$_2$ can be adsorbed with negative adsorption energy, but these are greater than B1-doped GDY (-1.56 eV).
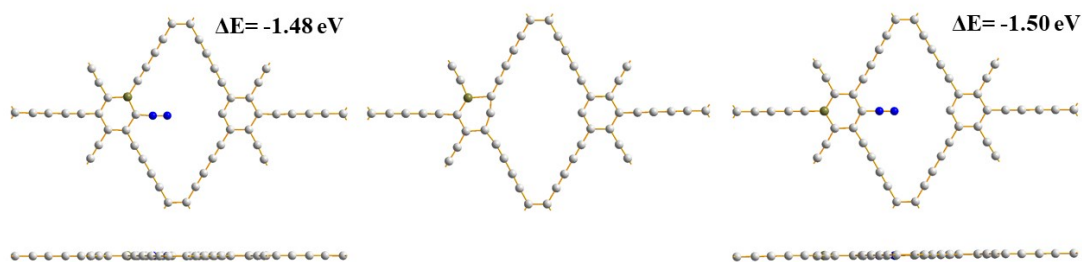
Fig. S5 N$_2$ adsorbed on different B doping sites of GDY

For the N1B2-doped, B2N3-doped, N2B3-doped, B3N4-doped and N3B4 doped GDY (Fig. S6), N$_2$ can be adsorbed on B2N3-doped and B3N4-doped GDY. Adsorption energy is larger than B1N2-doped GDY (-1.70 eV). Considering all the doping configurations, B as the catalytic active center is most conducive for N$_2$ adsorption. Thus, we mainly focus on the B1-doped and B1N2-doped structure with B active center.
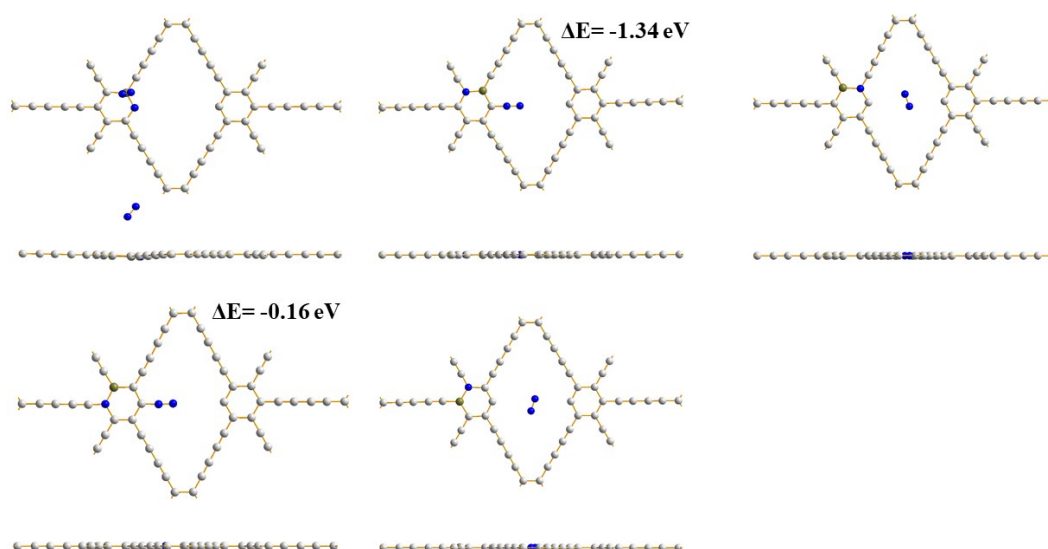

Fig. S6 N$_2$ adsorbed on different BN co-doping sites of GDY

Intermediate geometries of all three mechanistic pathways

*N-NH   *N-NH$_2$ *N-NH$_3$

*NH   *NH$_2$ *NH$_3$

Fig. S7 Geometries of all possible intermediate structures of distal pathway for B@GDY.

*N-NH   *NH-NH   *NH-NH$_2$

*NH$_2$-NH$_2$ *NH$_2$ *NH$_3$

Fig. S8 Geometries of all possible intermediate structures of alternating pathway for B@GDY.

*N-NH   ***NH-NH**   ***NH-NH$_2$**

*NH$_2$-NH$_2$ ***NH$_2$~NH$_3$**   ***NH$_3$**

Fig. S9 Geometries of all possible intermediate structures of enzymatic pathway for B@GDY.

*N-NH   ***N-NH$_2$**   ***N-NH$_3$**

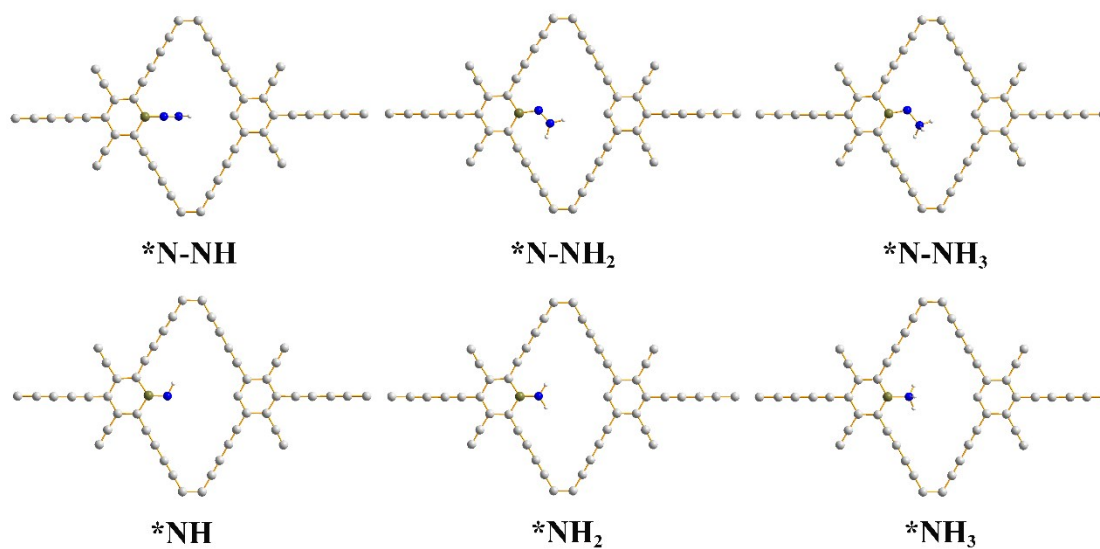***NH**   ***NH$_2$**   ***NH$_3$**

Fig. S10 Geometries of all possible intermediate structures of distal pathway for BN@GDY.
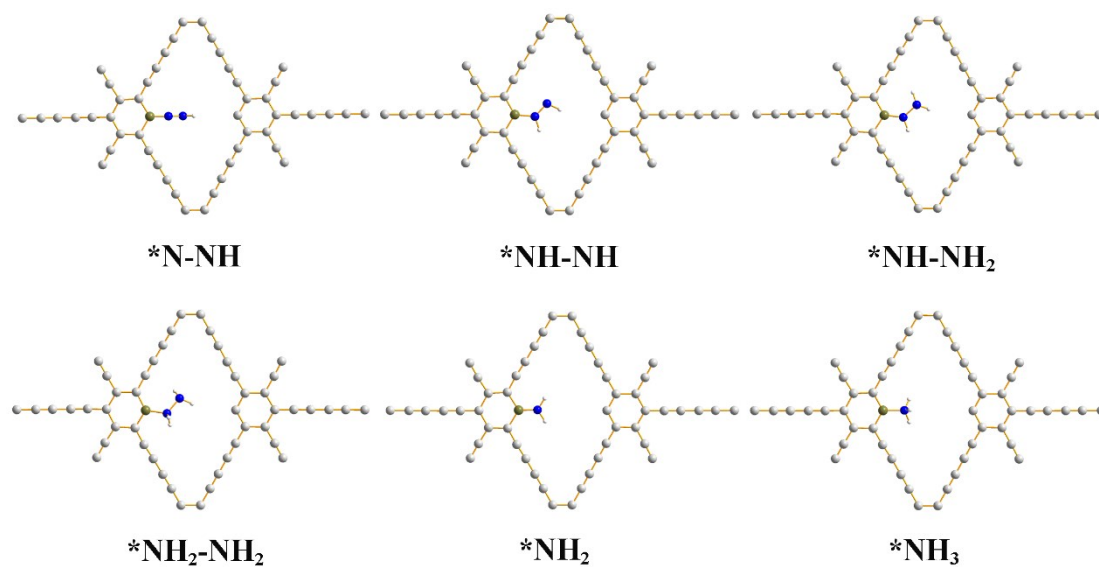
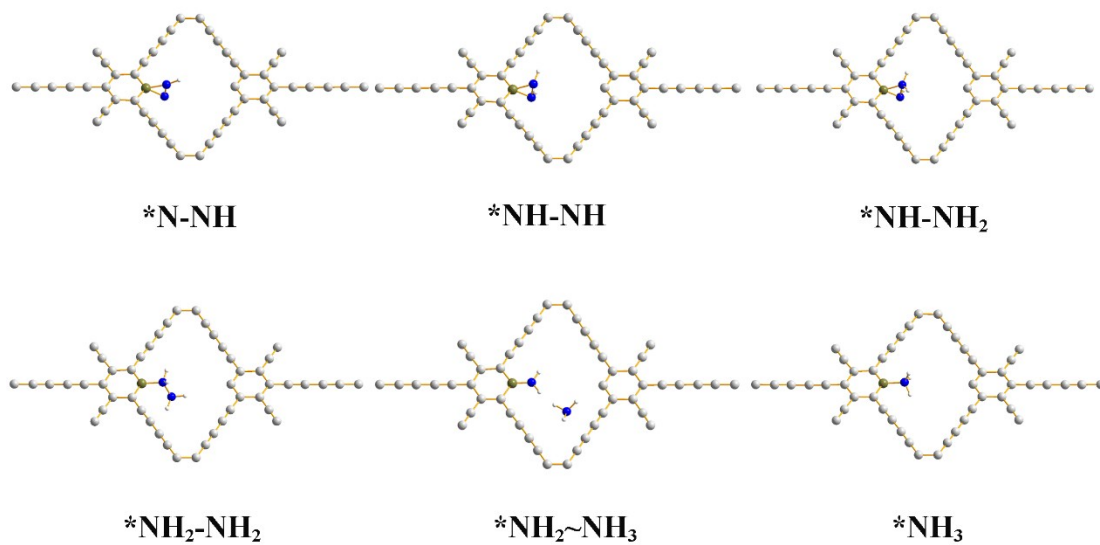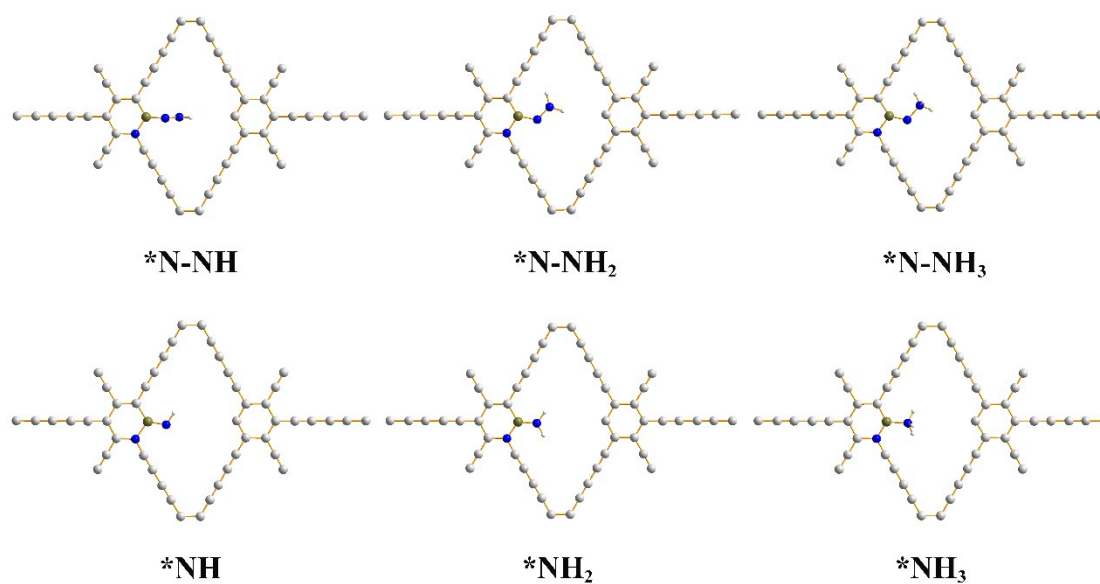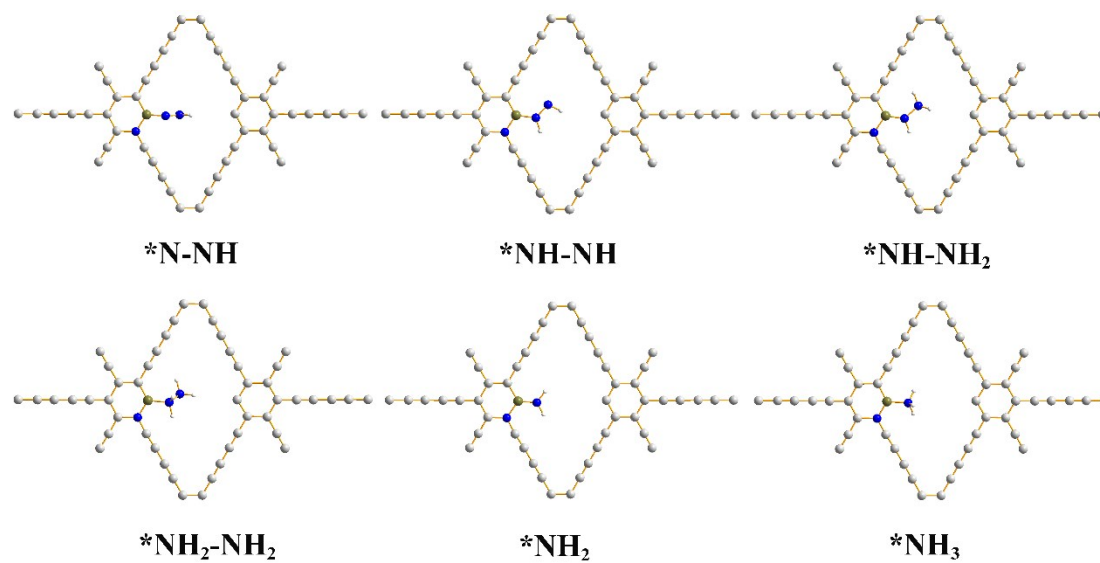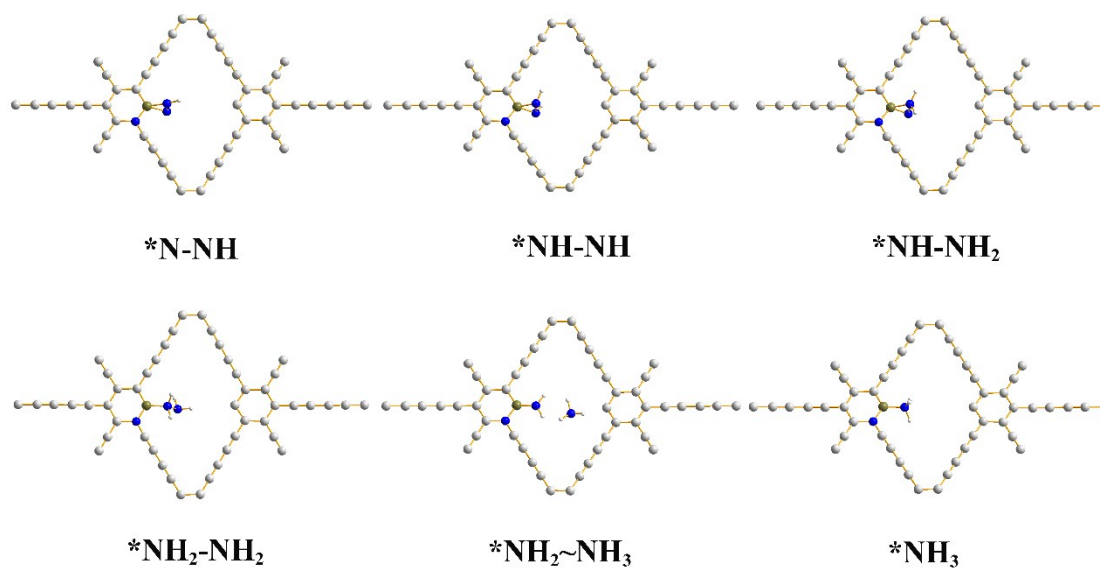**Fig. S11** Geometries of all possible intermediate structures of alternating pathway for BN@GDY.

Fig. S12 Geometries of all possible intermediate structures of enzymatic pathway for BN@GDY.

Table S1 Calculated thermal energies for gas molecules at 298.15 K.

Species	E_{ZPE} (eV)	TS (eV)
H_2	0.27	0.40
N_2	0.15	0.59
NH_3	0.91	0.60

Table S2 The calculated zero-point energies (E_{ZPE}) and entropy (TS) of different adsorption species along distal pathway on B@GDY, where * denotes the adsorption site and T is 298.15 K.

Adsorption species	E_{ZPE} (eV)	TS (eV)
*N_2	0.23	0.13
*NNH	0.50	0.14
*NNH_2	0.86	0.15
*NNH_3	1.19	0.18
*NH	0.38	0.07
*NH_2	0.74	0.09
*NH_3	1.08	0.13

Table S3 The calculated zero-point energies (E_{ZPE}) and entropy (TS) of different adsorption species along alternating pathway on B@GDY, where * denotes the adsorption site and T is 298.15 K.

Adsorption species	E_{ZPE} (eV)	TS (eV)
*N_2	0.23	0.13
*NNH	0.50	0.14
*NHNH	0.87	0.14
*$NHNH_2$	1.20	0.15
*NH_2NH_2	1.53	0.15
*NH_2	0.74	0.07
*NH_3	1.08	0.13

Table S4 The calculated zero-point energies (E_{ZPE}) and entropy (TS) of different adsorption species along enzymatic pathway on B@GDY, where * denotes the adsorption site and T is 298.15 K.

Adsorption species	E_{ZPE} (eV)	TS (eV)
*N$_2$	0.20	0.14
*NNH	0.50	0.14
*NHNH	0.83	0.15
*NHNH$_2$	1.20	0.13
*NH$_2$NH$_2$	1.54	0.18
*NH$_2$NH$_3$	1.70	0.31
*NH$_3$	1.08	0.13

Table S5 The calculated zero-point energies (E_{ZPE}) and entropy (TS) of different adsorption species along distal pathway on BN@GDY, where * denotes the adsorption site and T is 298.15 K.

Adsorption species	E_{ZPE} (eV)	TS (eV)
*N$_2$	0.22	0.13
*NNH	0.50	0.14
*NNH$_2$	0.85	0.13
*NNH$_3$	1.20	0.16
*NH	0.38	0.07
*NH$_2$	0.74	0.08
*NH$_3$	1.08	0.11

Table S6 The calculated zero-point energies (E_{ZPE}) and entropy (TS) of different adsorption species along alternating pathway on BN@GDY, where * denotes the adsorption site and T is 298.15 K.

Adsorption species	E_{ZPE} (eV)	TS (eV)
*N_2	0.22	0.13
*NNH	0.50	0.14
*NHNH	0.86	0.14
*$NHNH_2$	1.19	0.15
*NH_2NH_2	1.55	0.16
*NH_2	0.74	0.08
*NH_3	1.08	0.11

Table S7 The calculated zero-point energies (E_{ZPE}) and entropy (TS) of different adsorption species along enzymatic pathway on B@GDY, where * denotes the adsorption site and T is 298.15 K.

Adsorption species	E_{ZPE} (eV)	TS (eV)
*N_2	0.20	0.12
*NNH	0.50	0.13
*NHNH	0.83	0.12
*$NHNH_2$	1.19	0.13
*NH_2NH_2	1.54	0.18
*NH_2NH_3	1.71	0.26
*NH_3	1.08	0.12