Supplementary Information for

Anchoring Boron on Covalent Organic Framework as Efficient Single Atom Metal-Free Photo-electrocatalyst for Nitrogen Fixation: A First-Principles Analysis

Supriti Dutta, Swapan K Pati*

Theoretical Sciences Unit, School of Advanced Materials, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore 560064, India.

Corresponding author. E-mail: pati@jncasr.ac.in* Phone: 080-22082839

ORCID ID: orcid.org/0000-0002-5124-7455

The zero-point energy (ZPE) and entropy contribution (TS) of the reaction intermediates are determined by the following equations.

$$E_{ZPE} = \frac{1}{2}\sum_i h\nu_i \quad \text{(S1)}$$

And,

$$-TS = K_B T \sum_i ln\left(1 - e^{-\frac{h\nu_i}{K_B T}}\right) - \sum_i h\nu_i \left(\frac{1}{e^{\frac{h\nu_i}{K_B T}} - 1}\right) \quad \text{(S2)}$$

Where K_B is Boltzmann's constant, ν_i is the vibrational frequency of the ith vibrational mode a, and h is Planck's constant.

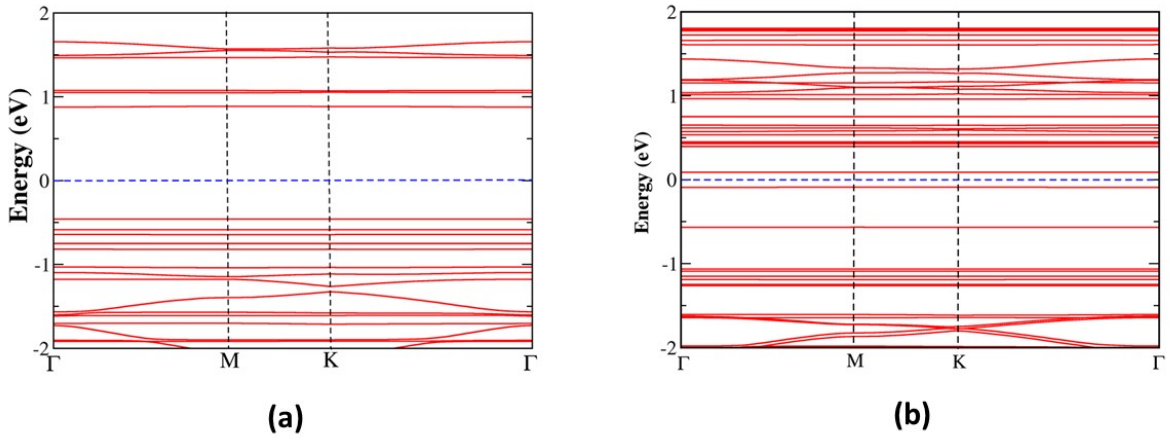

Fig. S1 Computed band structure of (a) before and (b) after the B addition on the Tp-bpy-COF surface at PBE level.

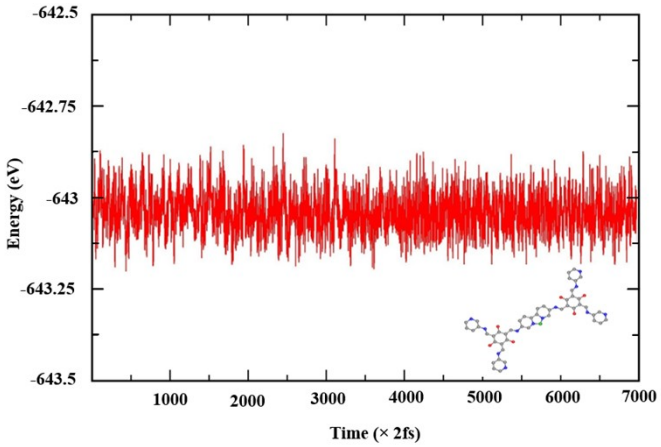

Fig. S2 Variation of energy with time for AIMD simulation of B@ Tp-bpy-COF at 500 K for a period of 14 ps with an interval of 2 fs.

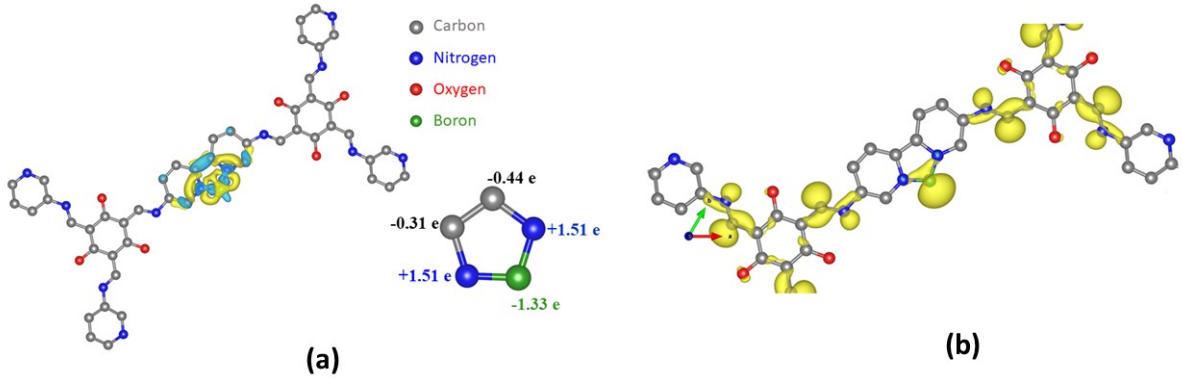

Fig. S3 (a) The charge density difference of a single B atom anchored on the Tp-bpy-COF. The charge accumulation and depletion are displayed by cyan and yellow region respectively. Isosurface value is taken as 0.005 e $Å^{-3}$. (b) Spin density for which isosurface is set to be 0.005 e $Å^{-3}$.

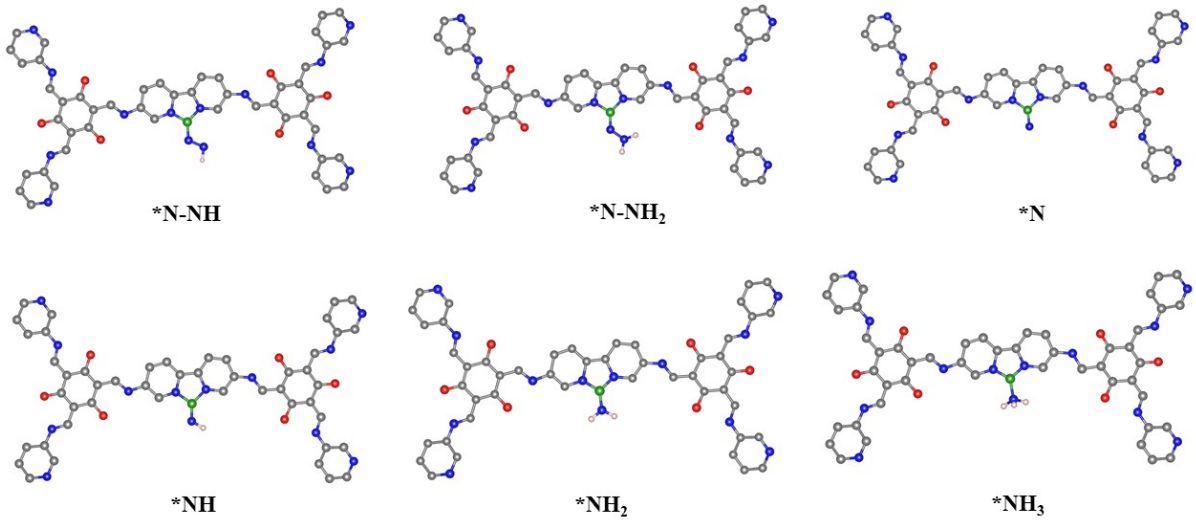

Fig. S4 Optimized geometries of all possible intermediates along distal pathway. Grey, Blue, Red and Green color represent carbon, nitrogen, oxygen and boron atom respectively.

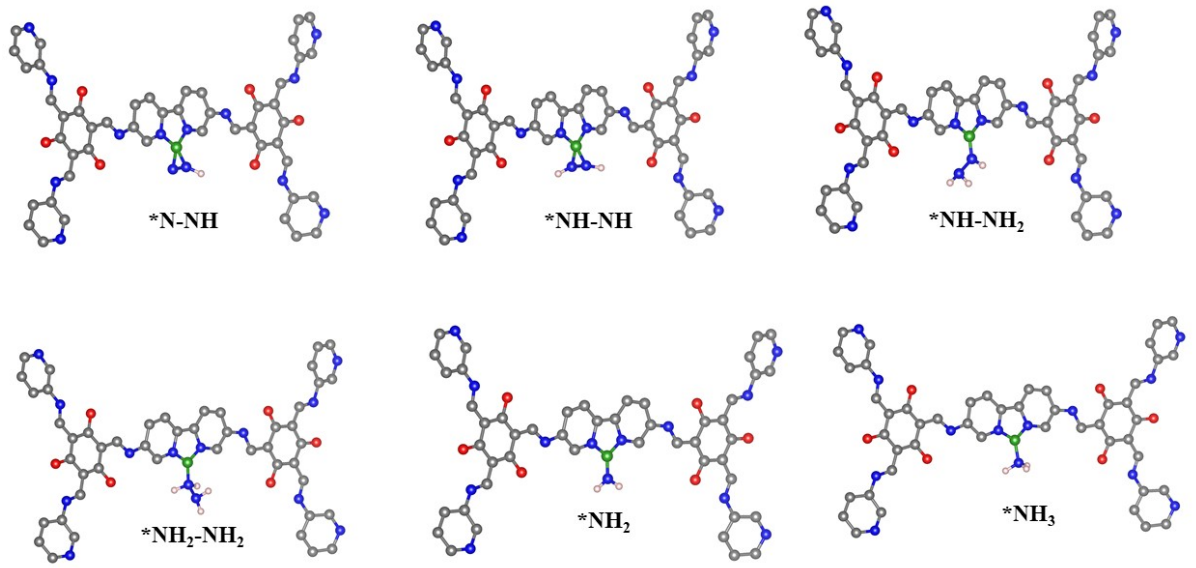

Fig. S5 Optimized geometries of all possible intermediates along enzymatic pathway. Grey, Blue, Red and Green color represent carbon, nitrogen, oxygen and boron atom respectively.

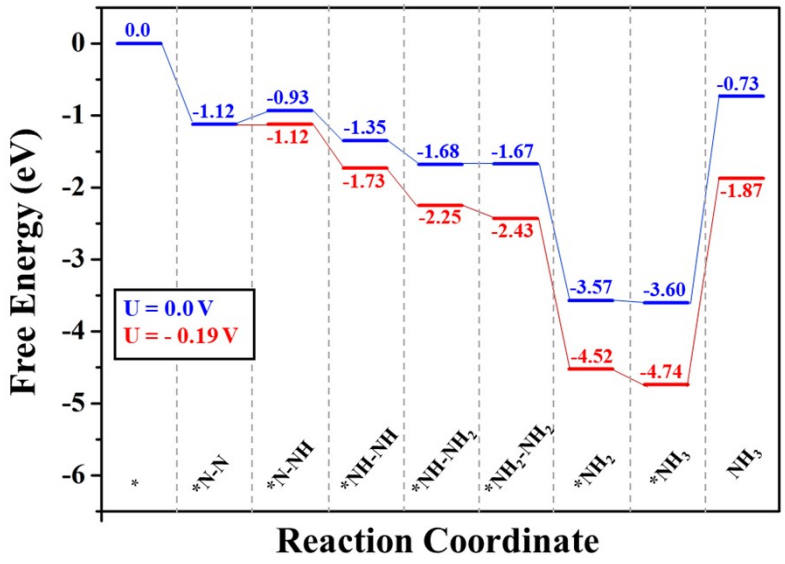

Fig. S6 Free-energy diagram for alternative pathway over the B@Tp-bpy-COF surface in presence of water solvent.

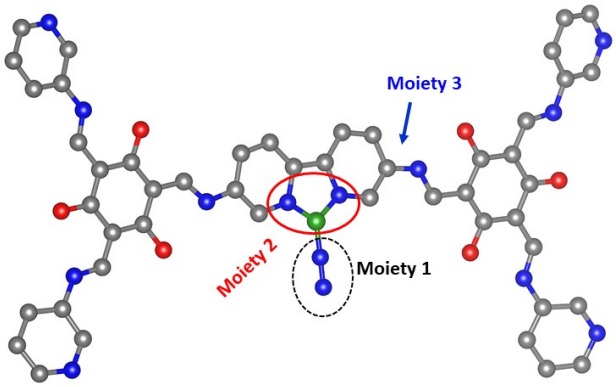

Fig. S7 Defined three moieties in N_xH_y species adsorbed on B@Tp-bpy-COF. Grey, Blue, Red and Green color represent carbon, nitrogen, oxygen and boron atom respectively.

Species	E_{ZPE} (eV)	TS (eV)
N_2	0.17	0.56
*N-N	0.22	0.12
*N-NH	0.50	0.14
*NH-NH	0.84	0.14
*NH-NH_2	1.17	0.19

$*NH_2$-NH_2	1.50	0.25
$*NH_2$	0.71	0.10
$*NH_3$	1.05	0.12
NH_3	0.89	0.60

Table S1 The calculated zero-point energy (E_{ZPE}) and the product of temperature (T=298.15 K) and entropy (S) of the different species along the alternating pathway on B@Tp-bpy-COF catalytic system. * represents the adsorption site.