

**Supplementary Information for**  
**High-throughput screening of single metal atom anchored on N-**  
**doped boron phosphide for N<sub>2</sub> reduction**

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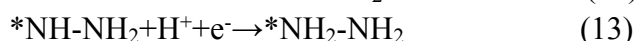
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The reactions of each possible reduction mechanisms for NRR as bellows:

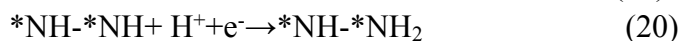
Distal:



Alternating:



Enzymatic:



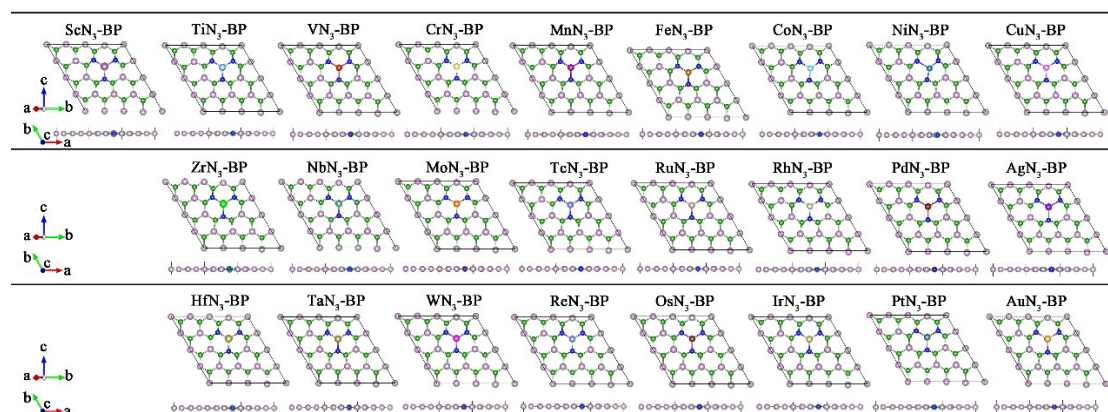
**Table S1.** The Calculated binding energies ( $E_b$ ) of all the MN<sub>3</sub>-BP systems.

| System               | $E_b$ (eV) | System               | $E_b$ (eV) |
|----------------------|------------|----------------------|------------|
| ScN <sub>3</sub> -BP | -10.42     | RuN <sub>3</sub> -BP | -7.59      |
| TiN <sub>3</sub> -BP | -10.10     | RhN <sub>3</sub> -BP | -6.02      |
| VN <sub>3</sub> -BP  | -9.44      | PdN <sub>3</sub> -BP | -4.25      |
| CrN <sub>3</sub> -BP | -9.81      | AgN <sub>3</sub> -BP | -3.69      |
| MnN <sub>3</sub> -BP | -3.90      | HfN <sub>3</sub> -BP | -11.35     |
| FeN <sub>3</sub> -BP | -4.92      | TaN <sub>3</sub> -BP | -11.49     |
| CoN <sub>3</sub> -BP | -5.03      | WN <sub>3</sub> -BP  | -10.64     |
| NiN <sub>3</sub> -BP | -5.74      | ReN <sub>3</sub> -BP | -9.62      |
| CuN <sub>3</sub> -BP | -5.08      | OsN <sub>3</sub> -BP | -8.57      |
| ZrN <sub>3</sub> -BP | -11.29     | IrN <sub>3</sub> -BP | -7.37      |
| NbN <sub>3</sub> -BP | -11.46     | PtN <sub>3</sub> -BP | -4.81      |
| MoN <sub>3</sub> -BP | -10.19     | AuN <sub>3</sub> -BP | -3.70      |

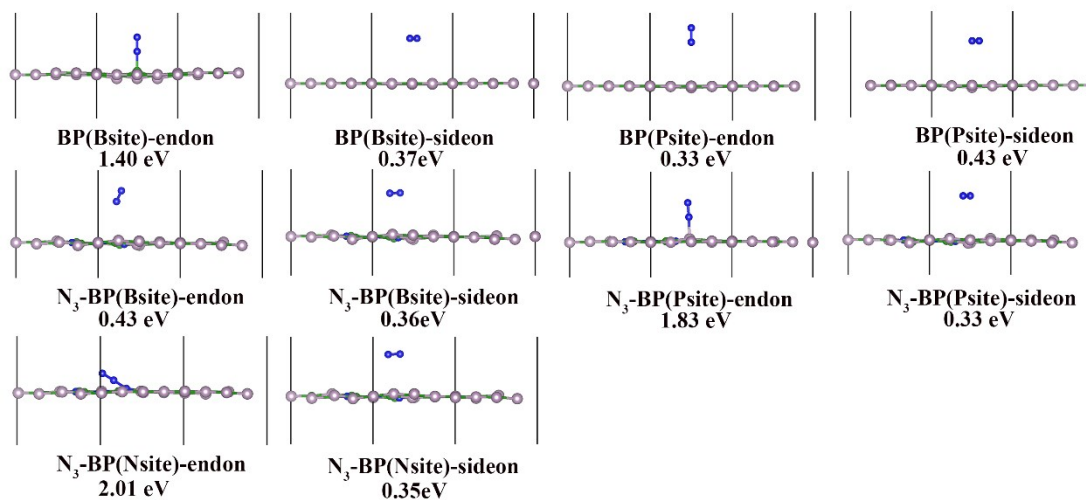
**Table S2.** The Calculated vibrational frequencies, zero point energies and entropy of different adsorption species on MoN<sub>3</sub>-BP catalyst, where \* denotes adsorption site.

| Adsorption Intermediates          | Vibrational Frequencies (cm <sup>-1</sup> ) |         |         |         |         |         | ZPE (eV) | TS (eV) |
|-----------------------------------|---------------------------------------------|---------|---------|---------|---------|---------|----------|---------|
| *N≡N                              | 2075.99                                     | 440.51  | 409.03  | 407.98  | 67.99   | 65.06   | 0.21     | 0.14    |
| *N=NH                             | 3282.54                                     | 1713.84 | 1066.51 | 563.65  | 457.63  | 411.84  | 0.48     | 0.17    |
|                                   | 152.64                                      | 74.94   | 56.99   |         |         |         |          |         |
| *N-NH <sub>2</sub>                | 3516.88                                     | 3401.24 | 1602.61 | 1471.84 | 1190.35 | 550.77  | 0.81     | 0.21    |
|                                   | 406.50                                      | 363.51  | 295.68  | 101.06  | 73.52   | 47.72   |          |         |
| *N                                | 1036.85                                     | 235.15  | 233.74  |         |         |         | 0.09     | 0.05    |
| *NH                               | 3457.41                                     | 884.80  | 477.16  | 251.20  | 197.87  | 128.45  | 0.33     | 0.10    |
| *NH-NH                            | 3305.08                                     | 3234.78 | 1471.69 | 1357.56 | 1271.16 | 969.22  | 0.83     | 0.17    |
|                                   | 589.15                                      | 553.27  | 283.89  | 228.05  | 79.53   | 62.36   |          |         |
| *NH-NH <sub>2</sub>               | 3491.96                                     | 3368.15 | 3285.54 | 1596.18 | 1429.60 | 1190.09 | 1.15     | 0.18    |
|                                   | 1138.71                                     | 721.86  | 656.11  | 607.90  | 342.25  | 314.85  |          |         |
|                                   | 246.05                                      | 77.05   | 63.08   |         |         |         |          |         |
| *NH <sub>2</sub> -NH <sub>2</sub> | 3454.90                                     | 3372.25 | 3365.26 | 3309.83 | 1633.54 | 1576.24 | 1.50     | 0.24    |
|                                   | 1430.89                                     | 1242.65 | 1115.05 | 1088.37 | 869.14  | 625.29  |          |         |
|                                   | 455.95                                      | 248.51  | 218.10  | 77.36   | 59.01   | 39.02   |          |         |

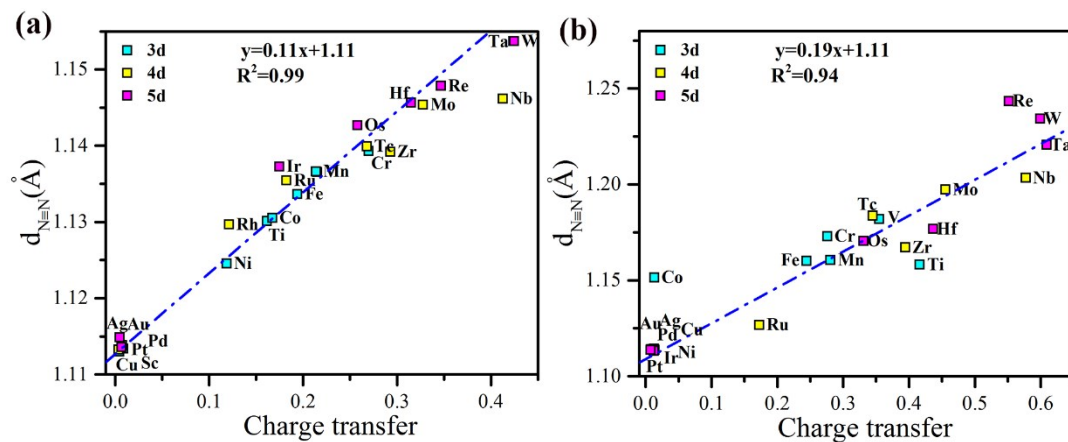
|                                    |         |         |         |         |         |         |      |      |
|------------------------------------|---------|---------|---------|---------|---------|---------|------|------|
| *N≡*N                              | 1739.44 | 609.71  | 373.54  | 219.90  | 141.43  | 87.38   | 0.20 | 0.13 |
| *N=*NH                             | 3290.63 | 1212.61 | 1068.67 | 690.94  | 572.11  | 477.26  | 0.49 | 0.11 |
|                                    | 304.87  | 163.00  | 125.26  |         |         |         |      |      |
| *NH-*NH                            | 3288.51 | 3259.74 | 1318.44 | 1149.98 | 1045.67 | 792.86  | 0.81 | 0.13 |
|                                    | 749.87  | 486.07  | 483.88  | 210.78  | 140.71  | 135.11  |      |      |
| *NH-*NH <sub>2</sub>               | 3436.41 | 3334.85 | 3305.58 | 1595.23 | 1328.24 | 1087.71 | 1.17 | 0.14 |
|                                    | 1042.41 | 918.53  | 744.28  | 714.18  | 512.61  | 430.92  |      |      |
|                                    | 182.23  | 132.40  | 100.66  |         |         |         |      |      |
| *NH <sub>2</sub> -*NH <sub>2</sub> | 3431.72 | 3427.44 | 3217.95 | 3206.57 | 1576.63 | 1562.88 | 1.50 | 0.15 |
|                                    | 1300.19 | 1059.37 | 1048.15 | 992.74  | 943.51  | 657.26  |      |      |
|                                    | 549.78  | 371.39  | 363.79  | 190.70  | 151.03  | 101.84  |      |      |
| *NH <sub>2</sub>                   | 3474.74 | 3354.67 | 1512.54 | 760.96  | 654.44  | 557.93  | 0.68 | 0.09 |
|                                    | 408.59  | 162.97  | 154.81  |         |         |         |      |      |
| *NH <sub>3</sub>                   | 3446.94 | 3431.15 | 3339.94 | 1606.30 | 1602.81 | 1242.98 | 1.03 | 0.17 |
|                                    | 677.06  | 672.64  | 427.65  | 99.36   | 91.37   | 52.71   |      |      |



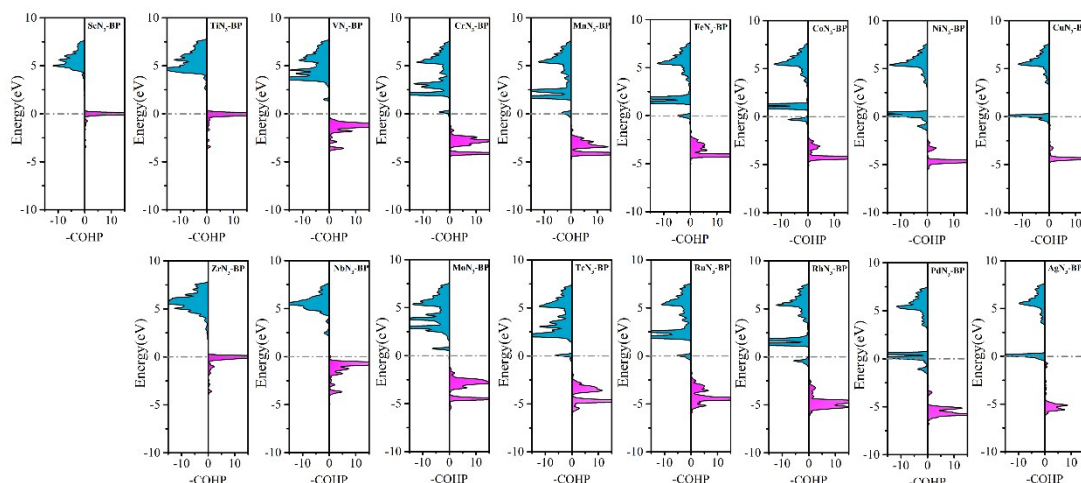
**Fig.S1** The optimized configurations of 25 MN<sub>3</sub>-BP candidates.



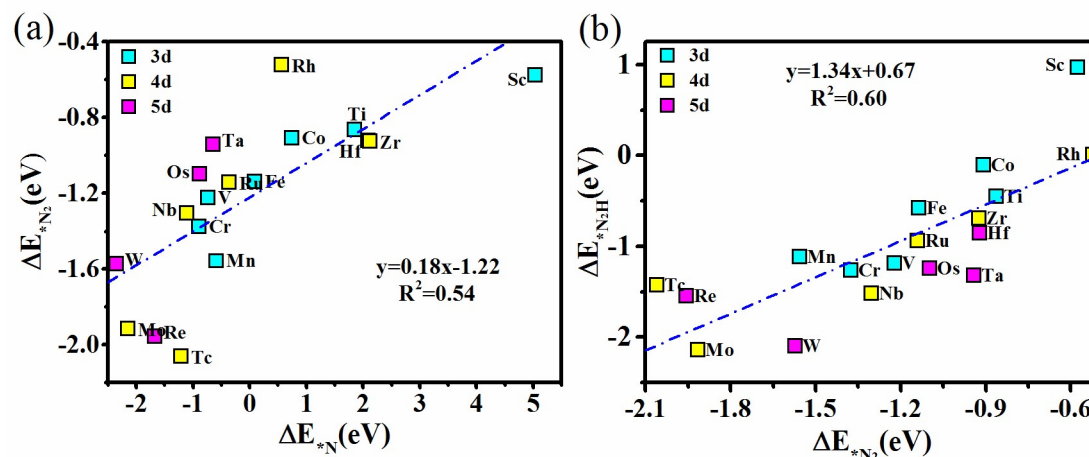
**Fig.S2** Optimized configurations and Gibbs free energy changes of N<sub>2</sub> adsorption on BP and N<sub>3</sub>-BP via end-on and side-on patterns.



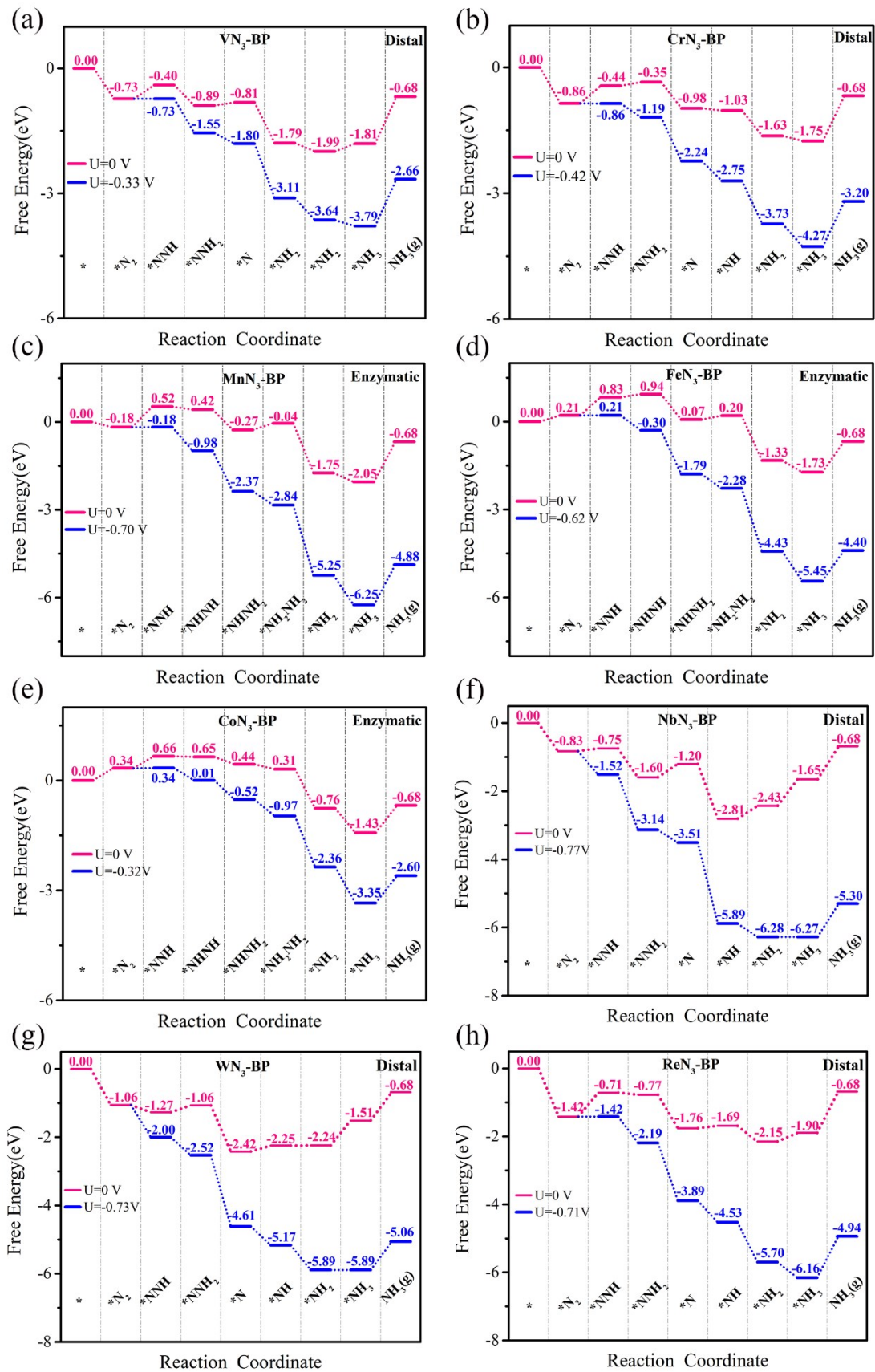
**Fig.S3** The relationship between the N≡N bond length and the charge transfer from MN<sub>3</sub>-BP substrate to \*N<sub>2</sub> via (a) end-on pattern and (b) side-on pattern.



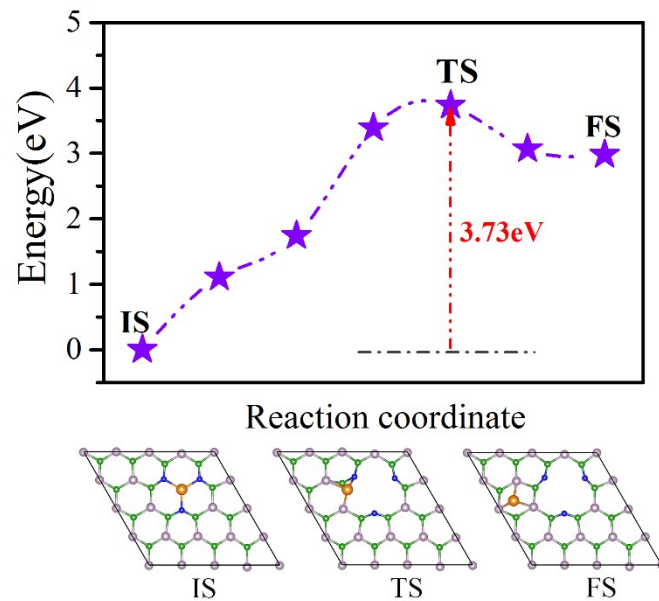
**Fig.S4** pCOHP between the 3d and 4d TM centers and \*N intermediate. The displayed on the right and left, respectively.



**Fig.S5** Scaling relationships between (a) ( $\Delta E^*_{\text{N}}$ ) versus ( $\Delta E^*_{\text{N}_2}$ ), and (b) ( $\Delta E^*_{\text{N}_2}$ ) versus ( $\Delta E^*_{\text{N}_2\text{H}}$ ).



**Fig.S6** Free energy profiles of NRR processes through the preferred pathway for (a)V-, (b) Cr-, (c) Mn-, (d) Fe-, (e) Co-, (f) Nb-, (g) W-, (h) ReN<sub>3</sub>-BP.



**Fig.S7** Minimum energy path for Mo atom on the  $V_B$ -BP substrate from B-vacancy to site to its neighboring hollow site.