

Supporting information

Transition Metal-Tetracyanoquinodimethane Monolayers as Single-Atom Catalysts for Electrocatalytic Nitrogen Reduction Reaction

Yiran Ying^a, Ke Fan^a, Xin Luo^{b}, Jinli Qiao^c, and Haitao Huang^{a*}*

^a Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom,
Kowloon, Hong Kong, P.R. China

^b School of Physics, Sun Yat-sen University, Guangzhou, Guangdong Province, P.R. China,
510275

^c College of Environmental Science and Engineering, State Key Laboratory for Modification of
Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620 (China)

Corresponding Author

*E-mail: luox77@mail.sysu.edu.cn; aphhuang@polyu.edu.hk

Table S1. Optimized lattice constants a and b for TM-TCNQ (TM=Sc-Zn, Mo, Ru-Pd, Ag, Pt, Au).

System	a (Å)	b (Å)	System	a (Å)	b (Å)
Sc-TCNQ	7.266	11.702	Zn-TCNQ	7.158	11.423
Ti-TCNQ	7.162	11.559	Mo-TCNQ	7.041	11.522
V-TCNQ	7.095	11.455	Ru-TCNQ	7.014	11.354
Cr-TCNQ	7.043	11.332	Rh-TCNQ	7.028	11.326
Mn-TCNQ	7.015	11.295	Pd-TCNQ	7.030	11.363
Fe-TCNQ	6.938	11.193	Ag-TCNQ	7.381	11.758
Co-TCNQ	6.886	11.161	Pt-TCNQ	7.022	11.368
Ni-TCNQ	6.974	11.208	Au-TCNQ	7.297	11.549
Cu-TCNQ	7.183	11.371			

Table S2. Adsorption energies E_{ad} (eV) of N_2 onto the TM-TCNQ (TM=Sc-Zn, Mo, Ru-Pd, Ag, Pt, Au) with both end-on and side-on configurations. Catalysts with favorable E_{ad} value for NRR are marked in red.

System	End-on	Side-on	System	End-on	Side-on
Sc-TCNQ	-0.63	-0.33	Zn-TCNQ	-0.11	-0.05
Ti-TCNQ	-0.97	-0.56	Mo-TCNQ	-0.06	-0.06
V-TCNQ	-1.16	-0.50	Ru-TCNQ	-0.03	-0.07
Cr-TCNQ	-1.20	-0.09	Rh-TCNQ	-0.03	-0.07
Mn-TCNQ	-0.96	-0.04	Pd-TCNQ	-0.05	-0.07
Fe-TCNQ	-0.45	-0.08	Ag-TCNQ	-0.01	-0.01
Co-TCNQ	0.08	0.04	Pt-TCNQ	-0.05	-0.07
Ni-TCNQ	0.05	0.02	Au-TCNQ	-0.27	-0.28
Cu-TCNQ	-0.05	-0.06			

Table S3. DFT-calculated total energy E_{DFT} , zero point energy E_{ZPE} , and entropic contribution term TS for NRR and HER intermediates on Sc-TCNQ.

Adsorbates	E_{DFT} (eV)	E_{ZPE} (eV)	TS (eV)
*	-162.539	0	0
*N-N	-179.776	0.177	0.141
*N-NH	-181.070	0.399	0.125
N-N	-179.468	0.161	0.145
N-NH	-182.793	0.484	0.163
N-NH₂	-186.253	0.474	0.281
NH-NH	-186.306	0.719	0.146
*N	-167.512	0.042	0.116
NH-NH₂	-191.059	1.119	0.152
NH₂-NH₂	-193.786	1.441	0.211
*NH	-173.978	0.325	0.114
*NH₂	-179.883	0.641	0.139
*NH₃	-183.323	1.014	0.174
*H	-166.185	0.145	0.027

Table S4. DFT-calculated total energy E_{DFT} , zero point energy E_{ZPE} , and entropic contribution term TS for NRR and HER intermediates on Ti-TCNQ.

Adsorbates	E_{DFT} (eV)	E_{ZPE} (eV)	TS (eV)
*	-162.820	0	0
*N-N	-180.394	0.217	0.089
*N-NH	-182.135	0.404	0.060
N-N	-179.972	0.204	0.096
N-NH	-183.212	0.481	0.114
N-NH₂	-187.236	0.826	0.104
NH-NH	-186.476	0.711	0.147
*N	-170.319	0.070	0.078
NH-NH₂	-191.484	1.123	0.213
NH₂-NH₂	-194.089	1.459	0.221
*NH	-176.090	0.348	0.090
*NH₂	-180.398	0.659	0.115
*NH₃	-183.731	1.021	0.167
*H	-166.752	0.162	0.021

Table S5. DFT-calculated total energy E_{DFT} , zero point energy E_{ZPE} , and entropic contribution term TS for NRR and HER intermediates on V-TCNQ.

Adsorbates	E_{DFT} (eV)	E_{ZPE} (eV)	TS (eV)
*	-162.840	0	0
*N-N	-180.601	0.216	0.133
*N-NH	-182.660	0.424	0.104
N-N	-179.932	0.177	0.117
N-NH	-182.884	0.477	0.107
N-NH₂	-187.238	0.825	0.097
NH-NH	-186.794	0.770	0.110
*N	-171.575	0.075	0.028
NH-NH₂	-191.076	1.115	0.157
NH₂-NH₂	-193.974	1.531	0.103
*NH	-176.181	0.341	0.051
*NH₂	-180.154	0.677	0.095
*NH₃	-183.779	1.030	0.150
*H	-166.756	0.173	0.021

Table S6. Zero point energy E_{ZPE} and entropic contribution term TS for H_2 , N_2 , and NH_3 in their gas phases. Values of TS for gases under $T=298.15$ K are extracted from NIST database (<https://doi.org/10.18434/T4D303>).

Gas	E_{ZPE} (eV)	TS (eV)
H_2	0.269	0.404
N_2	0.151	0.592
NH_3	0.939	0.596

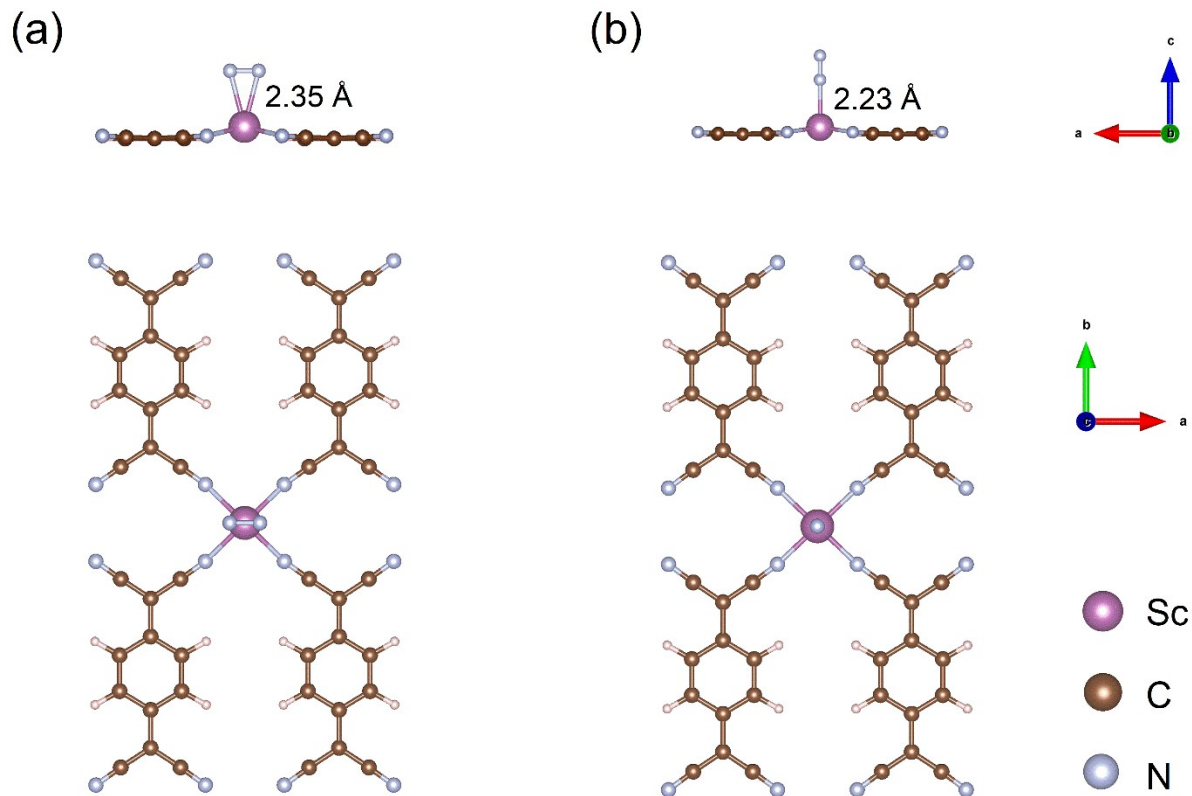


Fig. S1 Side and top view of the schematic geometric structures of N_2 adsorbed on Sc-TCNQ with (a) side-on configuration and (b) end-on configuration. Sc, C, N, H are represented in purple, brown, cyan, and pale pink, respectively. Sc-N bond length values are also marked in the figure.

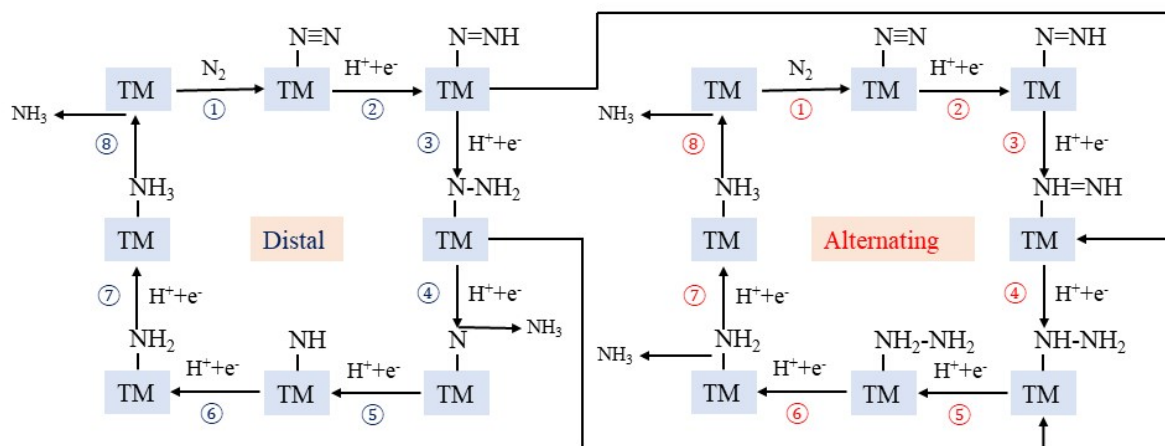


Fig. S2 Schematic illustration of distal, alternating, and their mixed mechanisms for NRR on TM-TCNQ. TM denotes transition metal atom (active site) in the figures.

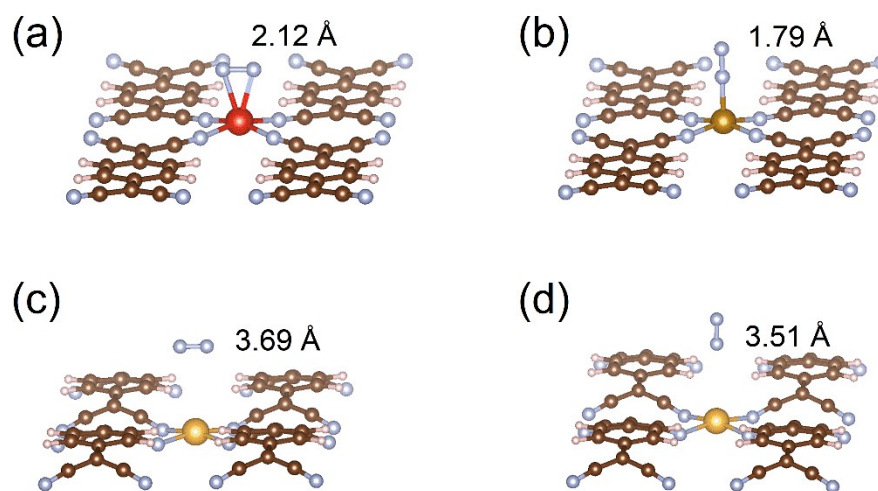


Fig. S3 DFT-optimized structures of N_2 adsorbed on (a) V-TCNQ with side-on configuration, (b) Fe-TCNQ with end-on configuration, and on Au-TCNQ with (c) side-on and (d) end-on configuration. The V-N and Fe-N bond length values in (a)(b) as well as the smallest distance between Au and N atoms in (c)(d) are marked.

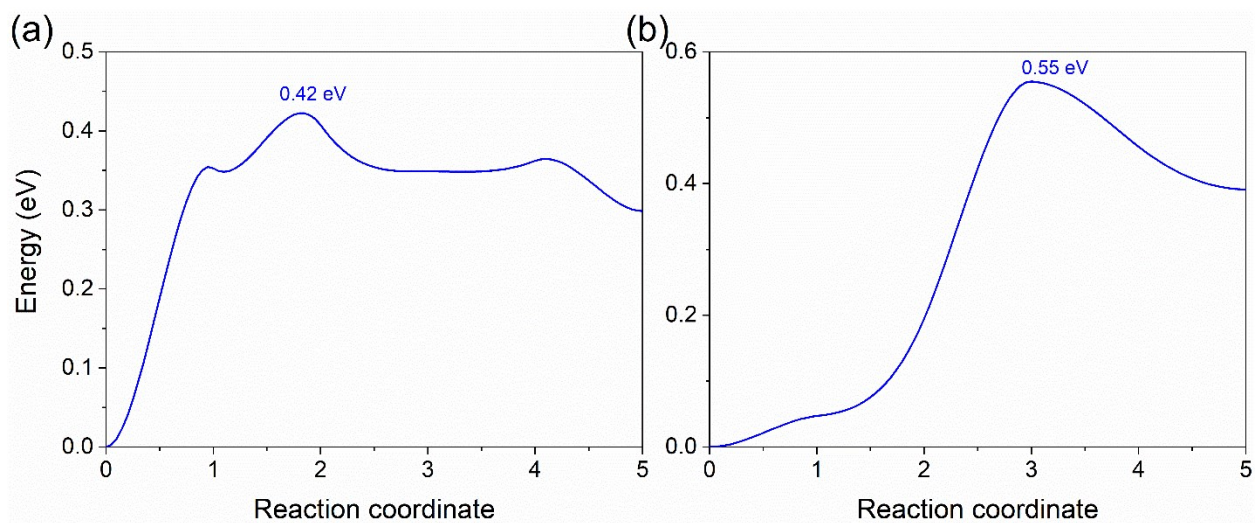


Fig. S4 Minimum energy path for the transformation from end-on to side-on N₂ adsorption on (a) Sc- and (b) Ti-TCNQ calculated by CI-NEB method.

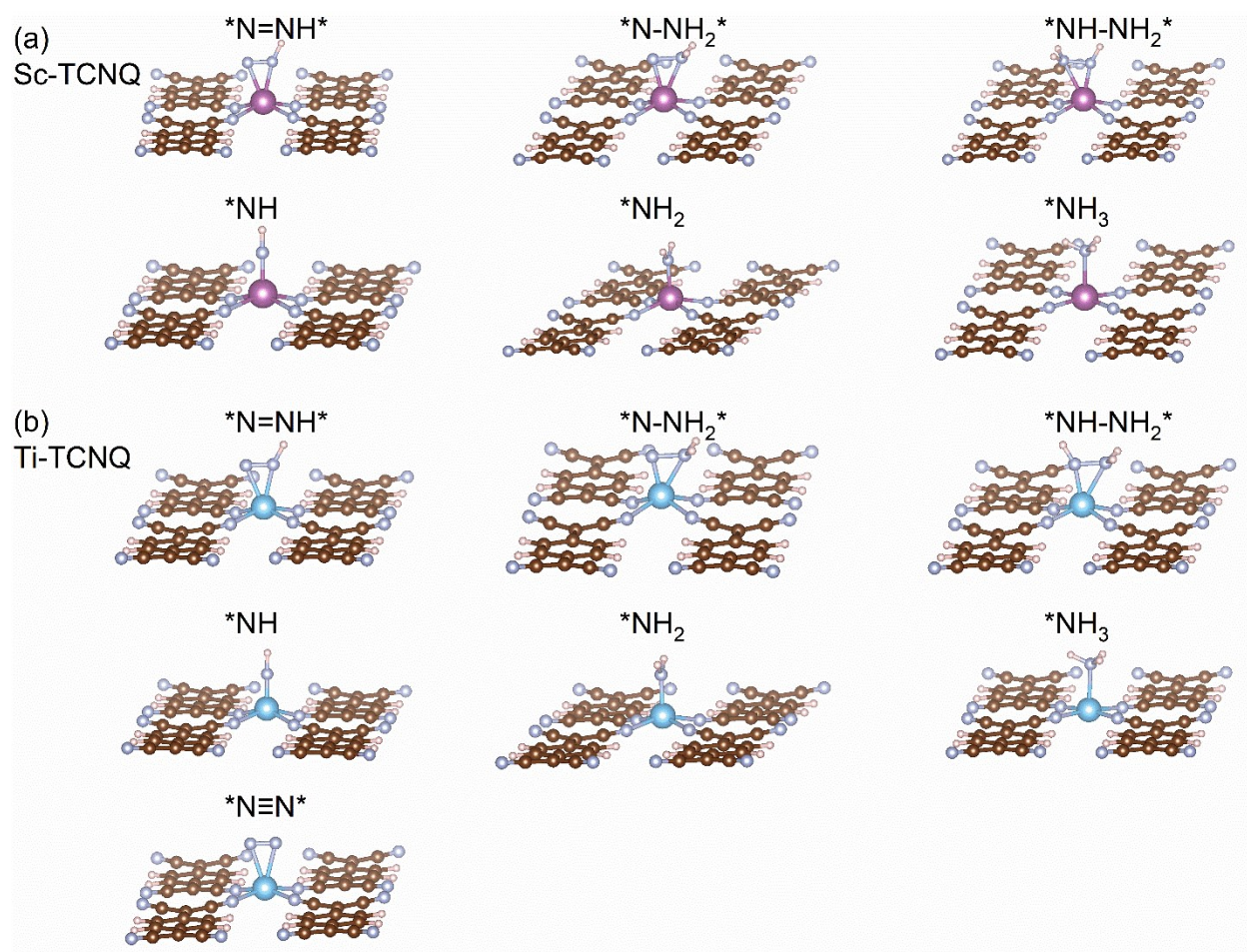


Fig. S5 DFT-optimized structures for all intermediates in the NRR along the most favorable pathway for (a) Sc-TCNQ and (b) Ti-TCNQ except for $*N\equiv N*$ on Sc-TCNQ (already shown in Fig. S1a). C, N, H, Sc, and Ti are represented in brown, cyan, pale pink, purple, and blue, respectively.

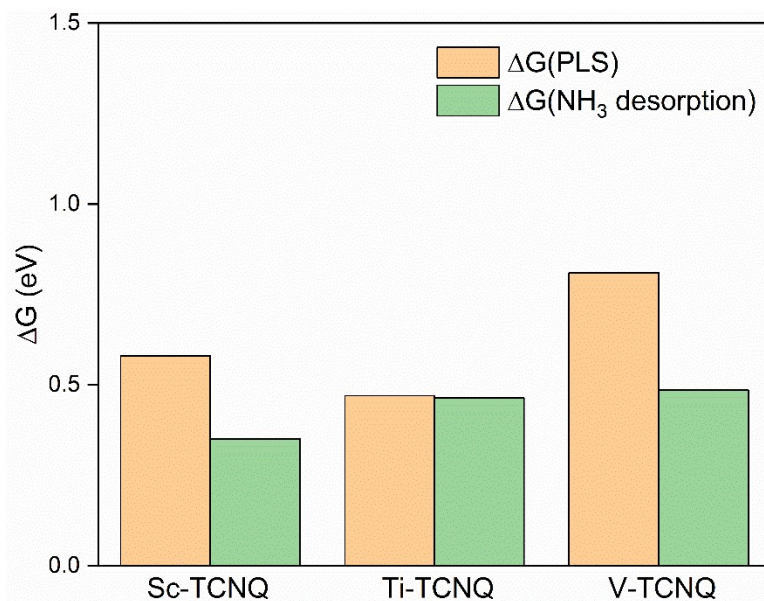


Fig. S6 Comparison between Gibbs free energy change of potential-limiting step (PLS) for NRR (marked in orange in Fig. 5) and NH_3 desorption free energy for Sc-, Ti-, and V-TCNQ.

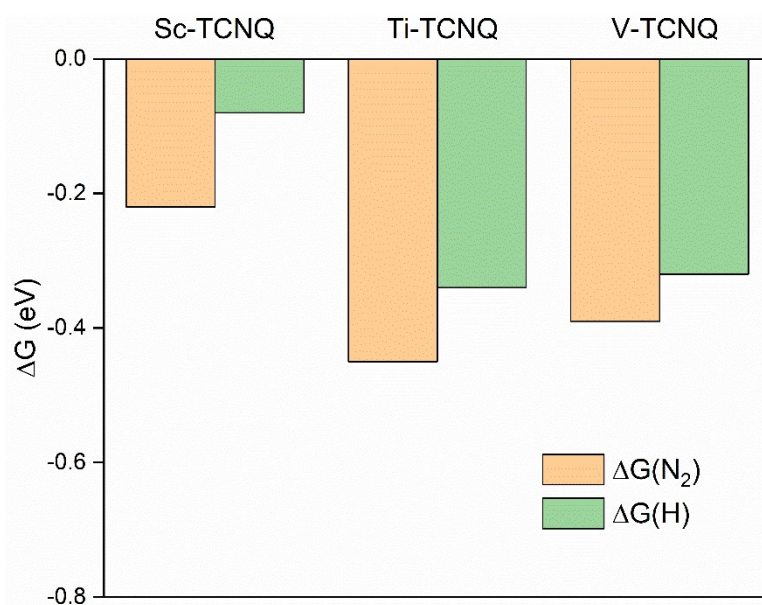


Fig. S7 Comparison between adsorption Gibbs free energy for N_2 and H for Sc-, Ti-, and V-TCNQ. The adsorption Gibbs free energy for species M was defined as $\Delta G(\text{M}) = G(*\text{M}) - G(*) - G(\text{M})$, where * denotes the active site.

Supplementary Notes 1. Justification of 4-coordinated TM-TCNQ structures in the calculations

The geometric structure of 4-coordinated transition metal atom to nitrogen in TM-TCNQ network was confirmed by pioneer experimental observations (e.g. scanning tunneling microscopy, STM) in *Phys. Rev. Lett.*, 2013, **110**, 027202; *J. Phys. Chem. C*, 2011, **115**, 10211; *J. Phys. Chem. C*, 2010, **114**, 17197, indicating that the structure is indeed stable under lab conditions. The 4-coordinated TM-TCNQ structure was used in our calculations and other theoretical work (*Phys. Chem. Chem. Phys.*, 2018, **20**, 5173; *J. Catal.*, 2019, **370**, 378; *J. Mater. Chem. A*, 2019, **7**, 3805-3814). Other configurations might be possible, but the 4-coordinated TM-TCNQ has already been experimentally fabricated, which provides our results with validity and importance.

Supplementary Notes 2. N₂ adsorption energy and adsorption free energy

There is still controversy in whether N₂ adsorption energy E_{ad} or adsorption Gibbs free energy $\Delta G(N_2)$ should be used for screening NRR catalysts. Several studies on computational NRR in recent years used the N₂ adsorption energy instead of $\Delta G(N_2)$ as an indicator (*J. Am. Chem. Soc.*, 2018, **140**, 14161; *Small Methods*, 2019, **3**, 1800376; *J. Phys. Chem. Lett.*, 2019, **10**, 6984; *J. Am. Chem. Soc.*, 2020, **142**, 308; *J. Am. Chem. Soc.*, 2020, **142**, 5709). Specifically, Ling *et al.* used $E_{ad} < -0.5$ eV as a criterion for screening NRR single-atom catalysts in a benchmark study (*Small Methods*, 2019, **3**, 1800376), and the criterion was also applied in our work. Nevertheless, to ensure the completeness of our discussion, it is necessary to check whether $\Delta G(N_2)$ can also favor the spontaneous N₂ adsorption. Fig. S7 shows the $\Delta G(N_2)$ values for side-on configuration on Sc-, Ti-, and V-TCNQ, and the negative $\Delta G(N_2)$ indicates that adsorption Gibbs free energy can also fulfill the spontaneous N₂ adsorption.

Supplementary Notes 3. Explanation of the ‘mixed’ pathway

In the main text, we mention that the energetically favorable pathway for Sc- and Ti-TCNQ is the enzymatic-consecutive mixed pathway. The conclusion is made by comparing the Gibbs free energy changes for different intermediates in NRR. Since both catalyst favors $*N-NH_2*$ to $*NH-NH*$ in the second hydrogenation step (Fig. 5), they follow step C1-C3 in the consecutive pathway (Fig. 2); however, for the third step, for Sc- and Ti-TCNQ, $*NH-NH_2*$ is more favorable than $*N+NH_3$, so C4' step instead of C4 is chosen which lead to $*NH-NH_2*$ intermediate in the enzymatic pathway, followed by E5' step (getting back to $*NH$ in the consecutive pathway) due to smaller ΔG for $*NH+NH_3$ than $*NH_2-NH_2*$. To sum up, because two reaction steps (C4' and E5') for Sc- and Ti-TCNQ include a transformation between conventional consecutive and enzymatic pathways, we define that Sc and Ti-TCNQ go through the enzymatic-consecutive mixed pathway.