Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for

A two-dimensional conductive Mo-based covalent organic framework as an efficient electrocatalyst for nitrogen fixation

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Computational details

The adsorption energy (E_{ads}) of these single TM (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Ru, Rh, Pd, Ag, W, Ir, Pt, and Au, respectively) atoms on the 2D COF substrate was defined as $E_{ads} = E_{TM\text{-}COF} - E_{TM} - E_{COF}$, where $E_{TM\text{-}COF}$, E_{TM} and E_{COF} are the total energies of the catalyst, the TM atoms, and COF substrate, respectively. A negative E_{ads} value suggests favorable adsorption. The calculation of the Gibbs free energy diagrams was performed by using the concept of computational hydrogen electrode (CHE) model.[1,2] Accordingly, the Gibbs free energy change (ΔG) can be calculated according to $\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH} + \Delta G_U$. In this equation, ΔE is the reaction energy directly obtained from DFT calculations. ΔE_{ZPE} is the zero-point energy correction, T is the temperature, and ΔS is the entropy change. $\Delta E_{ZPE} = \sum_i \frac{1}{2} h v_i$, where h is the Planck constant, i is the frequency number, v_i is the vibrational frequency with unit cm^{-1}. The entropies of gas-phase molecules are looked up in the NIST database,[3] and the vibrational entropy for adsorbed species can be obtained from $S = k_B[\sum_i ln(\frac{1}{1 - e^{-\frac{hv_i}{k_B T}}}) + \sum_i \frac{hv_i}{k_B T} \frac{1}{(e^{hv_i/k_B T} - 1)} + 1]$. ΔG_{pH} is the free energy correction of pH, which can be calculated by $\Delta G_{pH} = 2.303 k_B T pH$, and the pH value is equal to zero in this work. ΔG_U is the free energy contribution related to electrode potential U.

The limiting potential (U_L) is the required applied potential to make every elementary step exergonic, which is widely accepted as a descriptor of NRR activity.[4] This value can be deduced by the following equation as $U_L = - \Delta G_{PDS}/e$, in which ΔG_{PDS} represents the maximum of the free energy change of each elementary step in the NRR, leading to the potential determining step (PDS). The overpotential (η) is a vital indicator for electrocatalytic performance,[5] and it is investigated according to $\eta = U_{equ} - U_L$. Here, U_{equ} is the equilibrium potential (- 0.12 V for NRR).

Table S1. The optimized lattice parameters, the TM-N bond lengths (d_{TM-N}), and the total magnetic moment (Mag) of the 2D TM-COFs using the PBE functional (c = 20 Å, $\alpha = \beta = \gamma = 90°$).

TM-COF	a = b/Å	d_{TM-N}/Å	Mag/μ_B
Sc	22.75746	2.05	0.61
Ti	22.70090	2.01	1.40
V	22.65820	1.98	2.50
Cr	22.63433	1.96	3.43
Mn	22.59861	1.94	2.83
Fe	22.55941	1.92	1.53
Co	22.53749	1.90	0.54
Ni	22.55798	1.90	0.00
Cu	22.61629	1.96	0.94
Zn	22.67382	2.00	0.00
Nb	22.74463	2.04	1.92
Mo	22.71849	2.03	3.10
Ru	22.65293	1.98	0.60
Rh	22.62360	1.96	-0.51
Pd	22.62329	1.98	0.00
Ag	22.73750	2.05	0.92
W	22.70625	2.02	3.00
Ir	22.62956	1.97	0.51
Pt	22.62878	1.98	0.00
Au	22.63724	2.00	0.59

Table S2. The calculated adsorption energies (E_{ads}, eV) and the charge transfer (Q_{TM}, |*e*|) of embedding TM atom on the 2D COF substrate.

TM-COF	E_{ads}	Q_{TM}
Sc	-11.06	1.64
Ti	-11.42	1.41
V	-11.05	1.38
Cr	-9.06	1.28
Mn	-9.74	1.26
Fe	-9.58	1.06
Co	-10.41	0.77
Ni	-11.16	0.78
Cu	-8.15	0.94
Zn	-6.54	1.16
Nb	-10.47	1.72
Mo	-9.57	1.40
Ru	-10.61	0.98
Rh	-10.70	0.66
Pd	-8.68	0.76
Ag	-5.60	0.95
W	-11.59	1.57
Ir	-11.75	0.82
Pt	-10.87	0.88
Au	-5.77	1.12

Table S3. The calculated Gibbs free energy changes (ΔG, eV) of N_2 adsorption on the 2D TM-COFs with end-on and side-on patterns.

TM-COF	End-on	Side-on
Sc	-0.66	-0.53
Ti	-0.58	-0.20
V	-0.30	0.35
Cr	-0.37	0.18
Mn	0.59	0.24
Fe	-0.22	-0.31
Co	0.34	0.23
Ni	0.98	1.01
Cu	-0.26	0.36
Zn	0.28	0.29
Nb	-1.19	-1.08
Mo	-0.77	-0.26
Ru	-0.98	0.32
Rh	-0.18	-0.19
Pd	-0.25	-0.28
Ag	0.30	0.28
W	-0.95	-0.52
Ir	-0.18	-0.14
Pt	-0.26	-0.26
Au	-0.30	-0.33

Table S4. The calculated Gibbs free energy changes (ΔG, eV) of NNH formation and NH_3 formation on the 2D TM-COFs which capture N_2 thermodynamically favorable ($\Delta G_{N2} < 0$). The decisive largest ΔG values are marked in red typeface.

TM-COF	$\Delta G_{\text{e-NNH-formation}}$	$\Delta G_{\text{s-NNH-formation}}$	$\Delta G_{\text{NH3-formation}}$
Sc	1.13	0.67	0.16
Ti	0.81	0.53	0.11
V	0.90	-	-0.33
Cr	0.64	-	-0.24
Fe	1.20	1.29	-0.87
Cu	2.74	-	-2.09
Nb	0.35	0.18	0.70
Mo	0.28	0.37	0.25
Ru	1.33	-	-0.72
Rh	1.28	1.37	-0.78
Pd	2.58	2.61	-2.52
W	0.08	-0.03	0.75
Ir	1.36	1.33	-0.64
Pt	2.16	2.18	-2.18
Au	2.13	2.19	-2.01

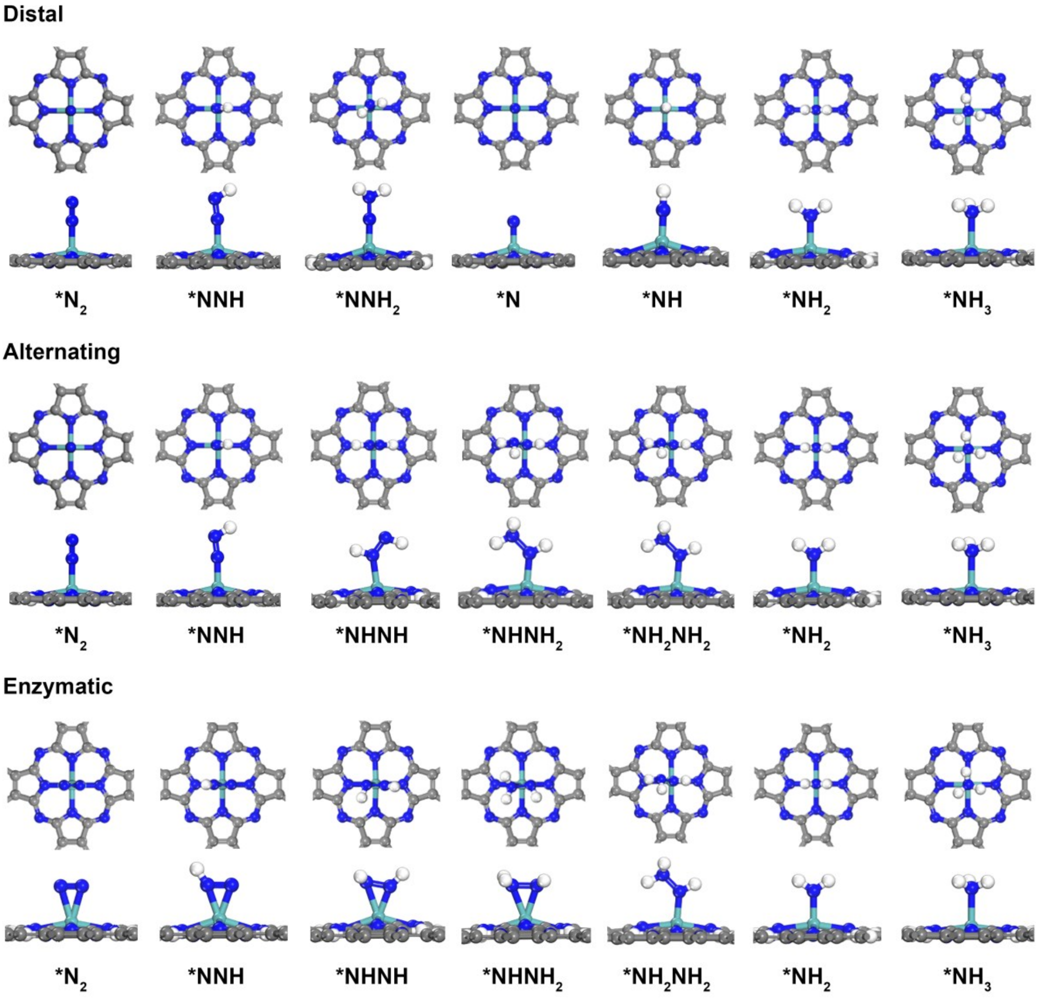

Fig. S1 The top and side views of the involved NRR species on the 2D Mo-COF along the distal, alternating, enzymatic pathways.

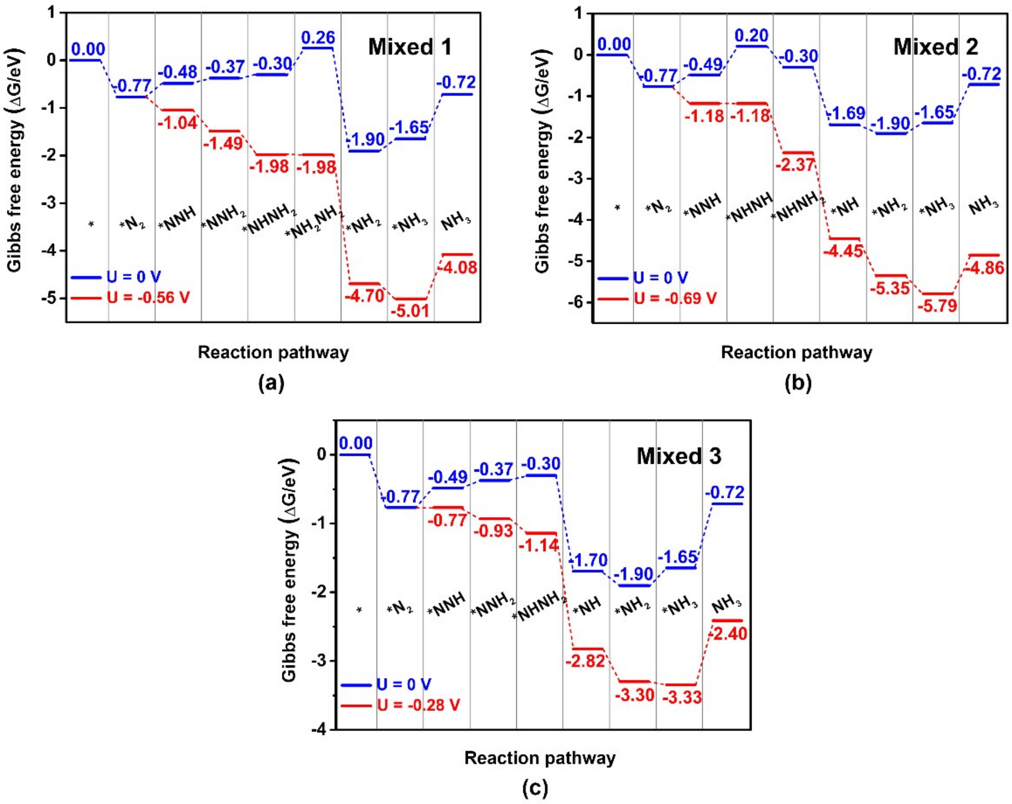

Fig. S2 Gibbs free energy diagrams for N_2 reduction on the 2D Mo-COF through (a) mixed 1, (b) mixed 2, and (c) mixed 3 mechanisms at different applied potentials.

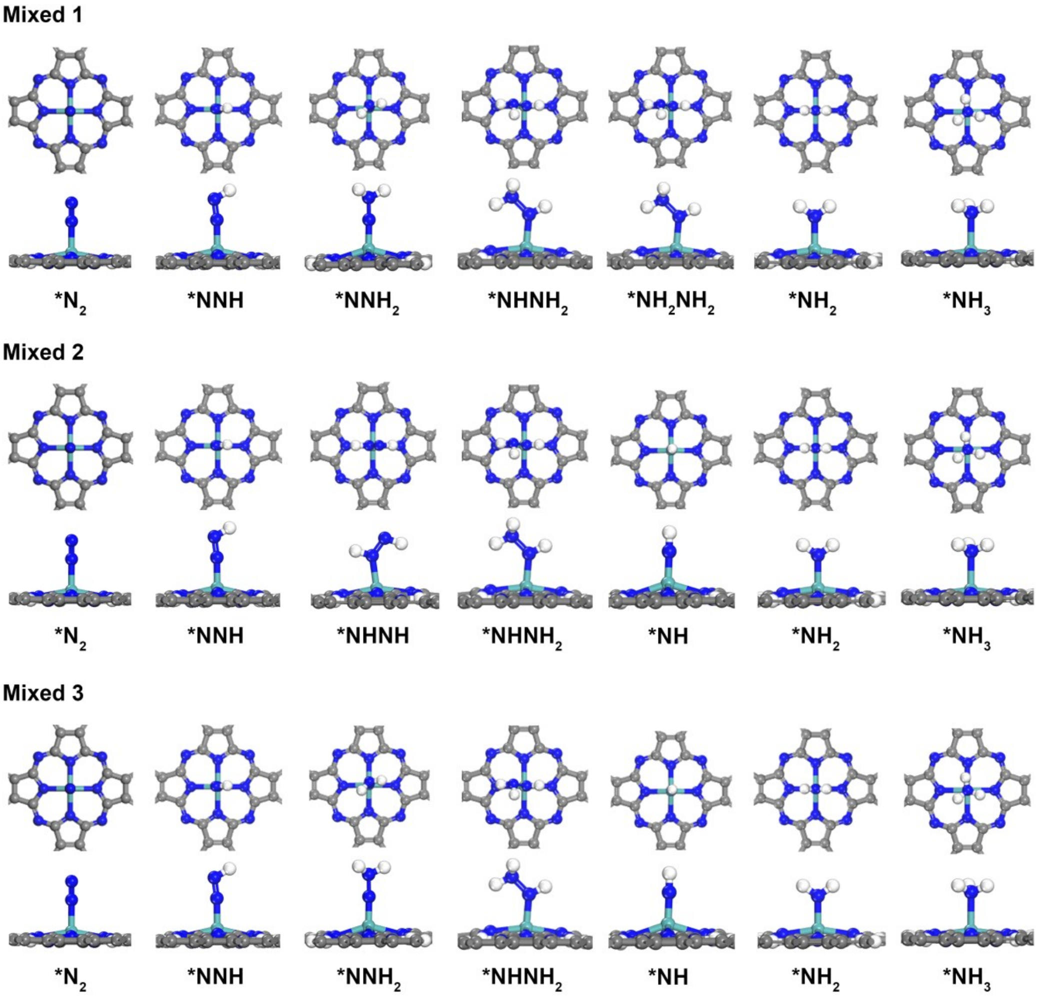

Fig. S3 The top and side views of the involved NRR species on the 2D Mo-COF along three mixed pathways.

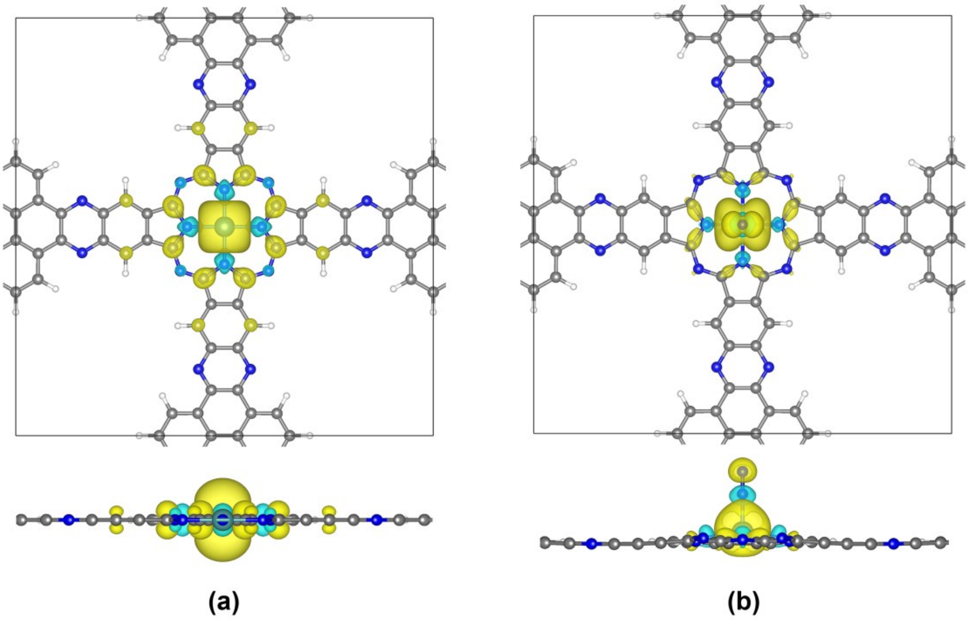

Fig. S4 The top and side views of the obtained spin density of 2D Mo-COF (a) before and (b) after N_2 adsorption, in which the level of the isosurface is set to be 0.002 e·Å^{-3}, and positive and negative charges are shown in yellow and cyan, respectively.

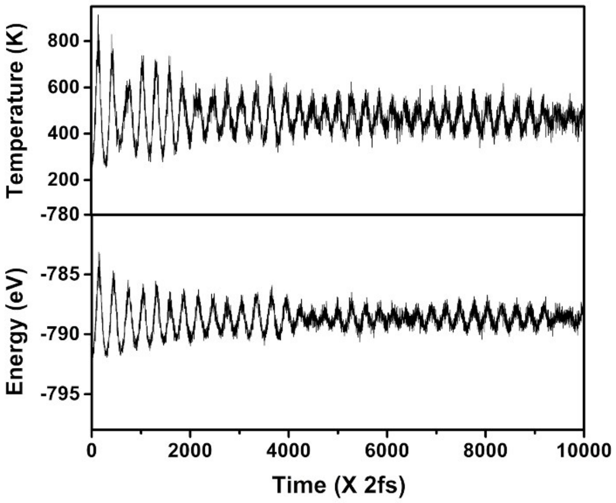

Fig. S5 Variations of temperature and energy against time of 2D Mo-COF during AIMD simulation. The simulation was run for 10 ps with time step of 2 fs at 500 K.

Supplementary references

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