Supporting Information: Electrochemical N_2 Reduction to Ammonia using Single Au/Fe Atoms Supported on Nitrogen Doped Porous Carbon

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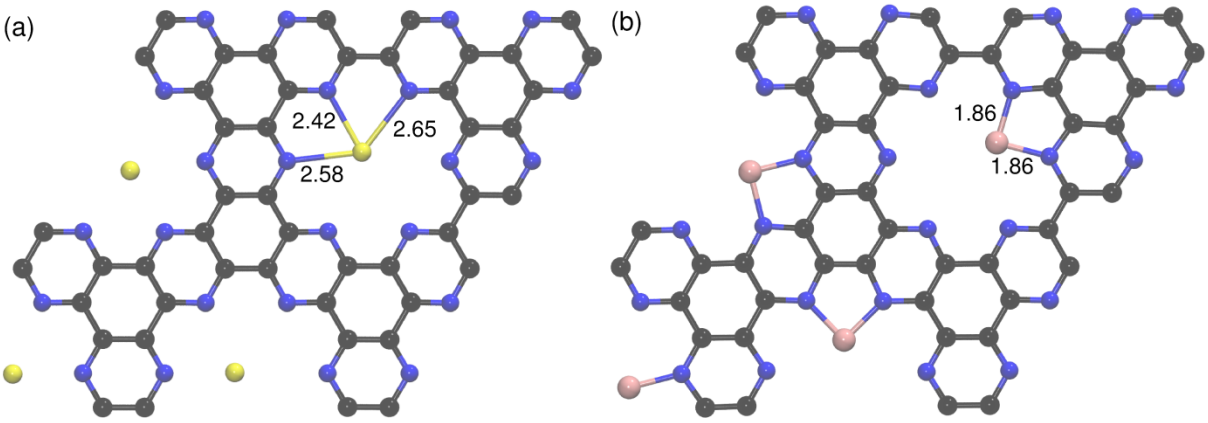

Figure S1: The structure of metal atoms supported in the C_2N framework Au-C_2N (a) and Fe-C_2N (b). The distance (in units of Å) between the metal atom and the nearest nitrogen atoms of the C_2N framework are highlighted. Atoms color: C-black, N-blue, Au-yellow and Fe-pink.

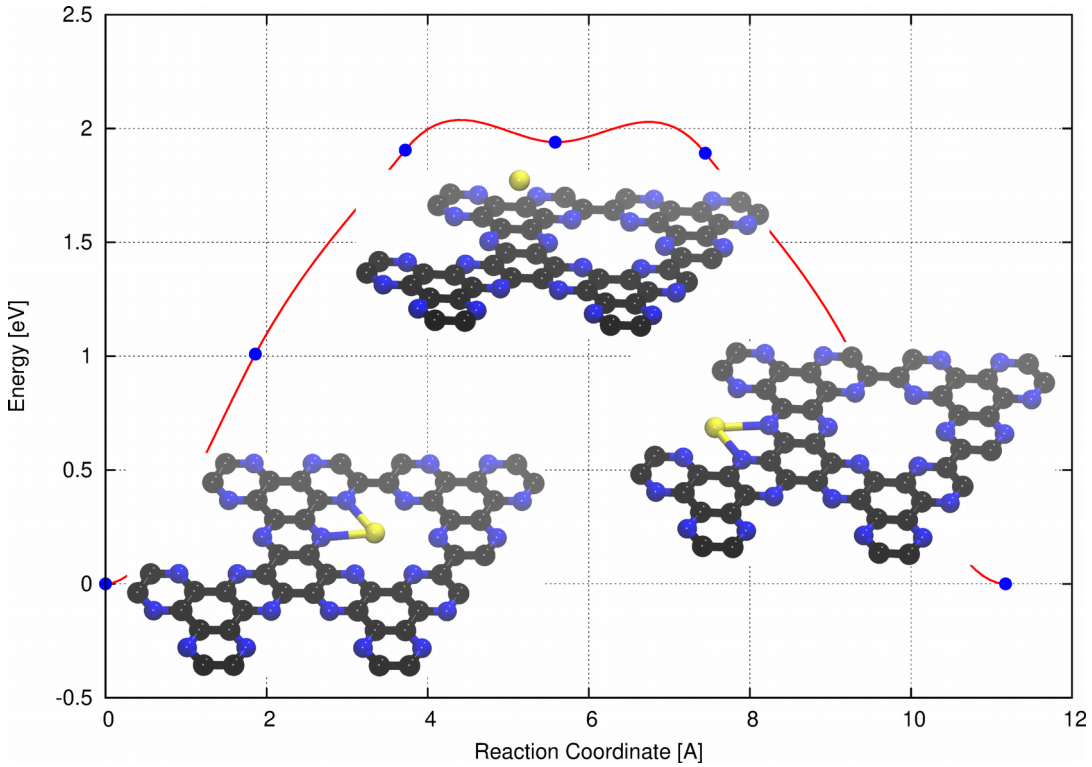

Figure S2: The potential energy surface obtained from the nudged elastic band calculation for the diffusion of a single Au atom from one site to the other on the C_2N surface.

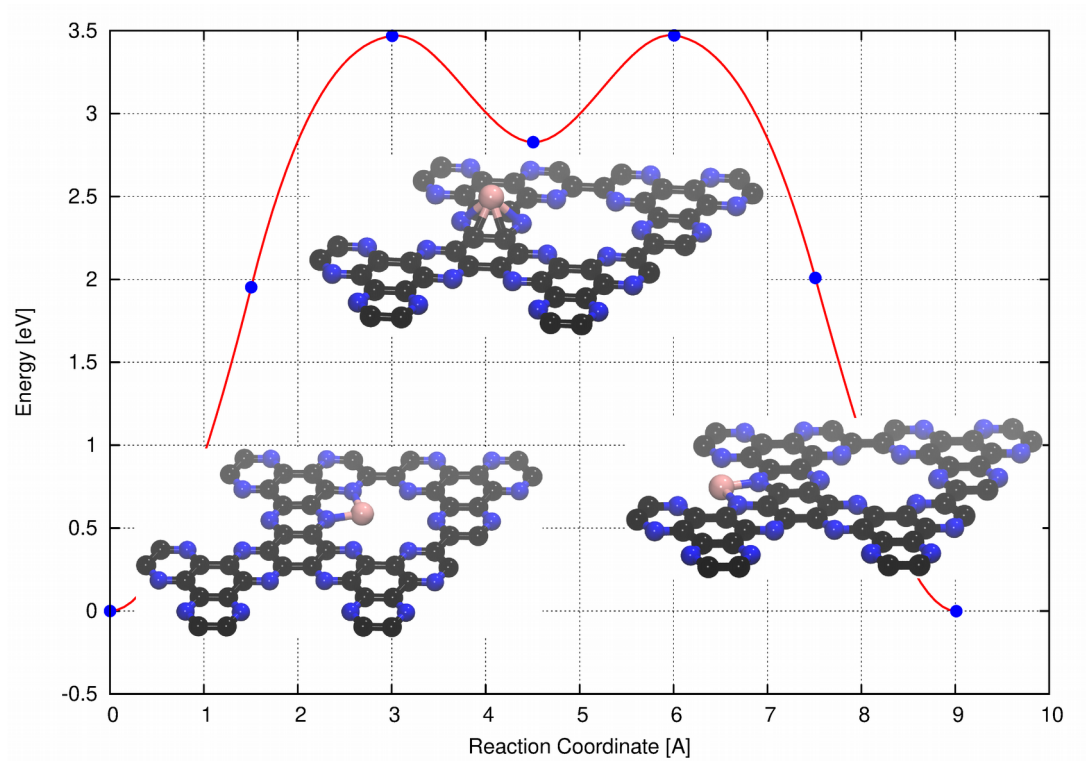

Figure S3: The potential energy surface obtained from the nudged elastic band calculation for the diffusion of a single Fe atom from one site to the other on the C_2N surface.

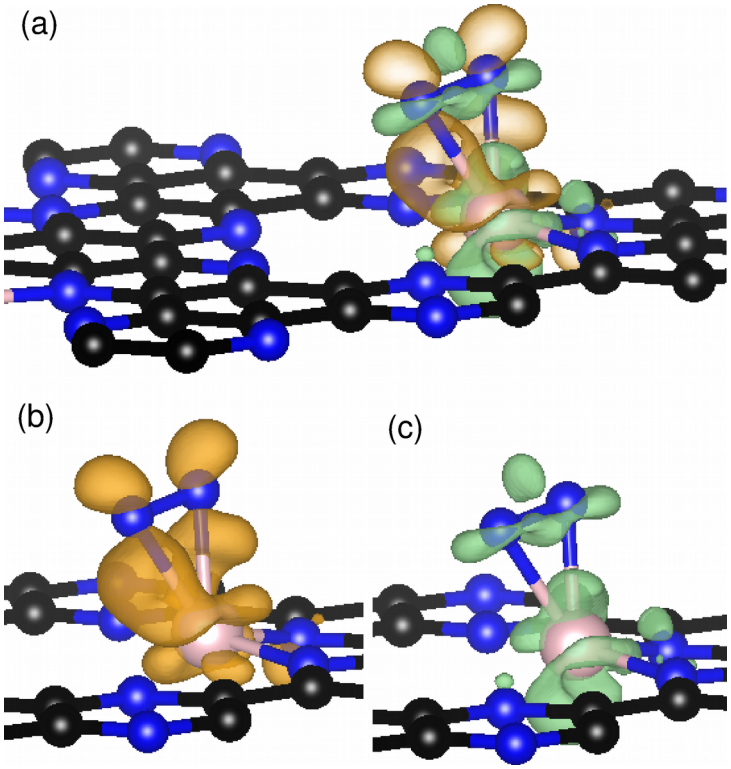

Figure S4: (a) The electron density difference (isovalue = ± 0.004 e/Å^3) plot for the N_2 adsorption over Fe-C_2N in side-wise fashion. The orange and the turquoise colors represent electron density accumulation and depletion, respectively. The accumulation and depletion of electron density are shown separately in (b) and (c), respectively.

Electrochemical N_2 reduction to NH_3

Table S1: The zero point energy (ZPE) and vibrational entropy contribution (at 300 K) of various intermediates that could be formed during the reaction using Au-C_2N as a catalyst.

Structure	ZPE (eV)	TS (eV)
NH_3	0.585	0.60006
H_2	0.265	0.40686
N_2	0.149	0.59631
Au-C_2N	10.904	4.027
N_2@ Au-C_2N	11.074	4.641
HN-N@ Au-C_2N	11.391	4.708
H_2N-N@ Au-C_2N	11.756	4.490
N@ Au-C_2N	11.091	4.251
HN@ Au-C_2N	11.313	4.485
H_2N@ Au-C_2N	11.572	4.505
H_3N@ Au-C_2N	11.986	4.395
HN-NH@ Au-C_2N	11.771	4.230
H_2N-NH@ Au-C_2N	12.069	4.673
H_2N-NH_2@ Au-C_2N	12.444	4.575

Table S2: The zero point energy (ZPE) and vibrational entropy contribution (at 300 K) of various intermediates that could be formed during the reaction using Fe-C_2N as a catalyst.

Structure	ZPE (eV)	TS (eV)
Fe-C_2N	11.111	3.2
N_2@ Fe-C_2N	11.316	3.393
HN-N@ Fe-C_2N	11.559	3.624
H_2N-N@ Fe-C_2N	11.905	3.527
N@ Fe-C_2N	11.192	3.349
HN@ Fe-C_2N	11.464	3.355
H_2N@ Fe-C_2N	11.765	3.414
H_3N@ Fe-C_2N	12.133	3.301
HN-NH@ Fe-C_2N	11.910	3.489
H_2N-NH@ Fe-C_2N	12.225	3.482
H_2N-NH_2@ Fe-C_2N	12.590	3.570
	Enzymatic pathway	
N_2@ Fe-C_2N	11.303	3.502
HN-N@ Fe-C_2N	11.580	3.485
HN-NH@ Fe-C_2N	11.914	3.445
H_2N-NH@ Fe-C_2N	12.231	3.424
$(H_2N)_2$@ Fe-C_2N	12.485	3.511
$(H_2N)(H_3N)$@ Fe-C_2N	12.839	3.537

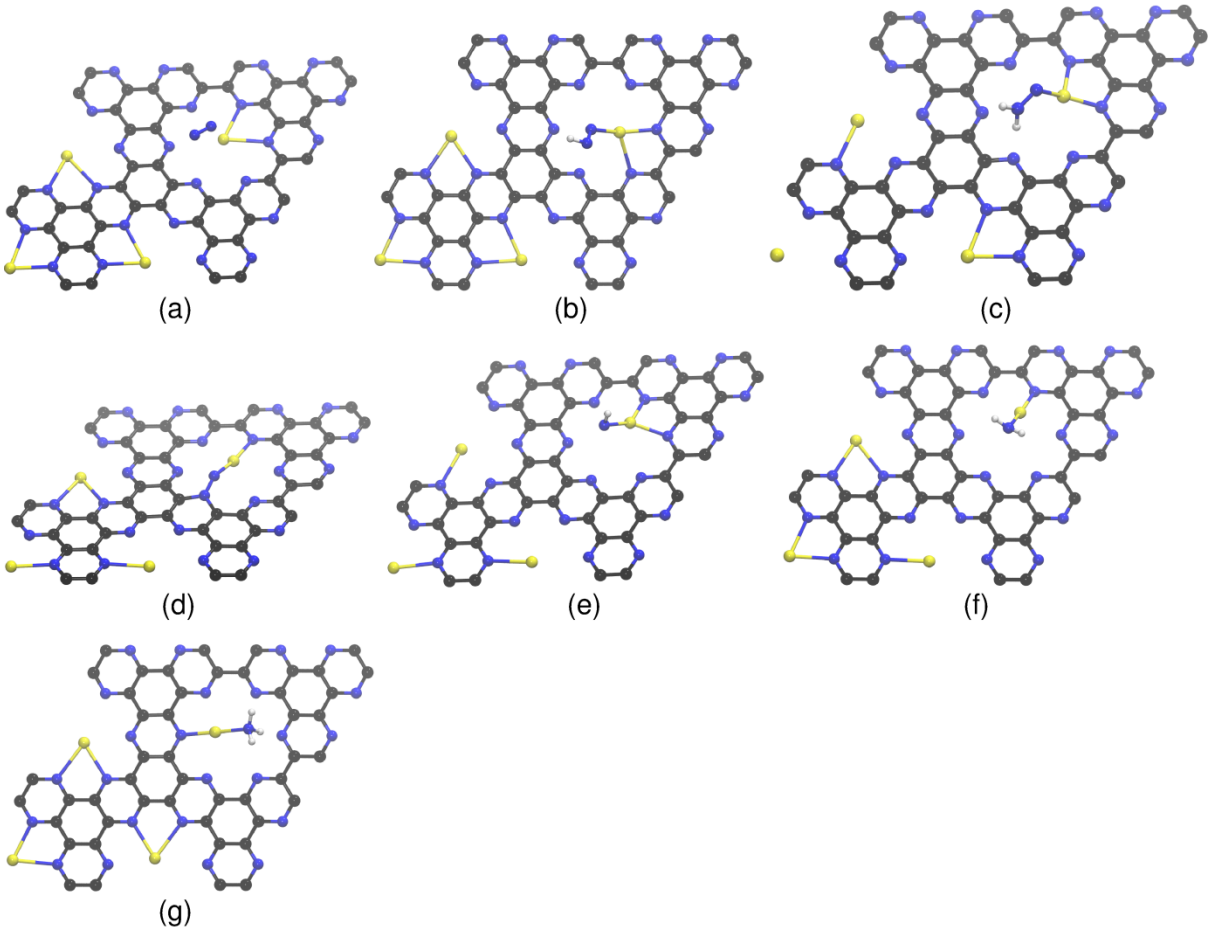

Figure S5: The atomic structure of various intermediates: (a) N_2@Au-C_2N, (b) HN-N@Au-C_2N, (c) H_2N-N@Au-C_2N, (d) N@Au-C_2N, (e) HN@Au-C_2N, (f) H_2N@Au-C_2N and (g) H_3N@Au-C_2N of the NRR through the distal pathway. Atoms color: C-black, N-blue, H-white and Au-yellow.

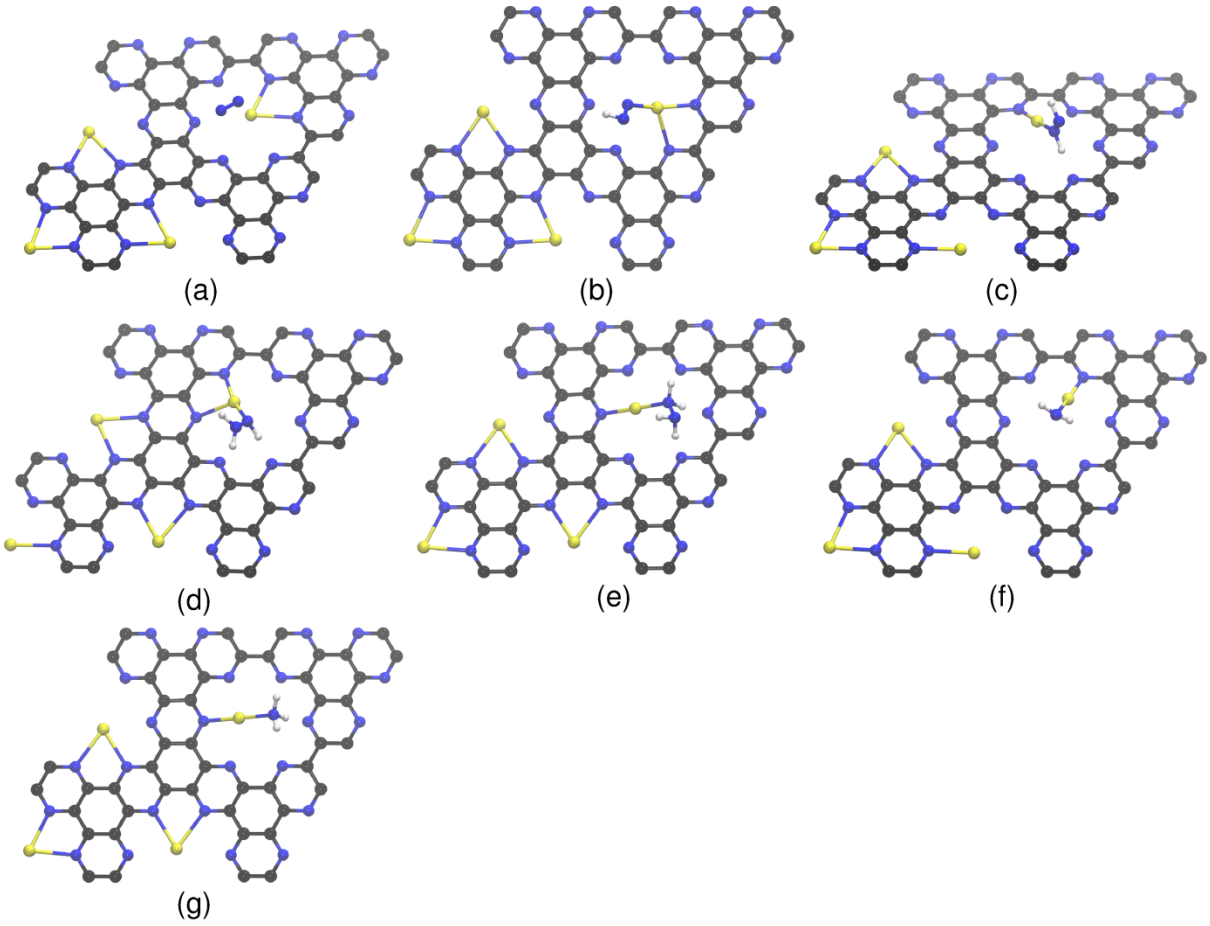

Figure S6: The atomic structure of the various intermediates: (a) N_2@Au-C_2N, (b) HN-N@Au-C_2N, (c) HN-NH@Au-C_2N, (d) H_2N-NH@Au-C_2N, (e) H_2N-NH_2@Au-C_2N, (f) H_2N@Au-C_2N and (g) H_3N@Au-C_2N of the NRR through the alternating pathway. Atoms color: C-black, N-blue, H-white and Au-yellow.

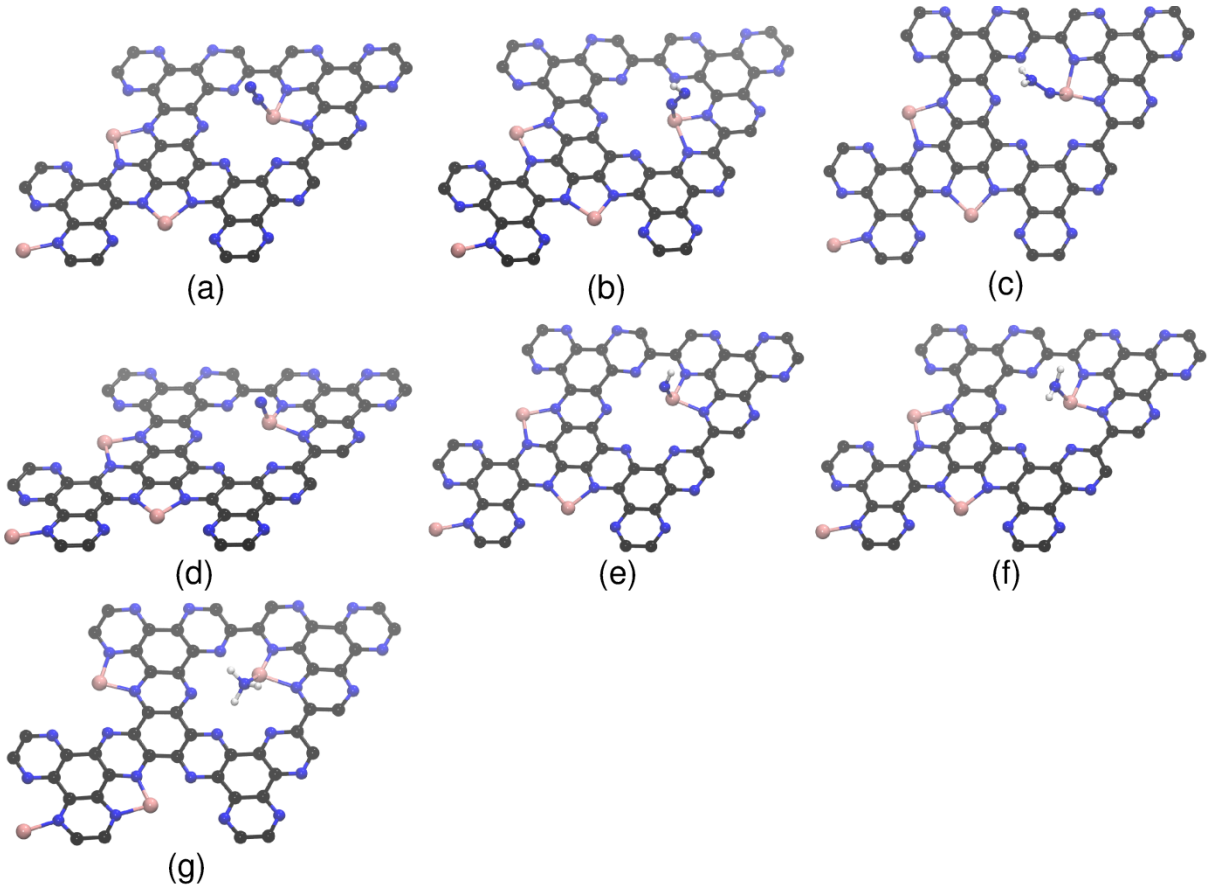

Figure S7: The atomic structure of various intermediates: (a) N_2@Fe-C_2N, (b) HN-N@Fe-C_2N, (c) H_2N-N@Fe-C_2N, (d) N@Fe-C_2N, (e) HN@Fe-C_2N, (f) H_2N@Fe-C_2N and (g) H_3N@Fe-C_2N of the electrochemical NRR through the distal pathway. Atoms color: C-black, N-blue, H-white and Fe-pink.

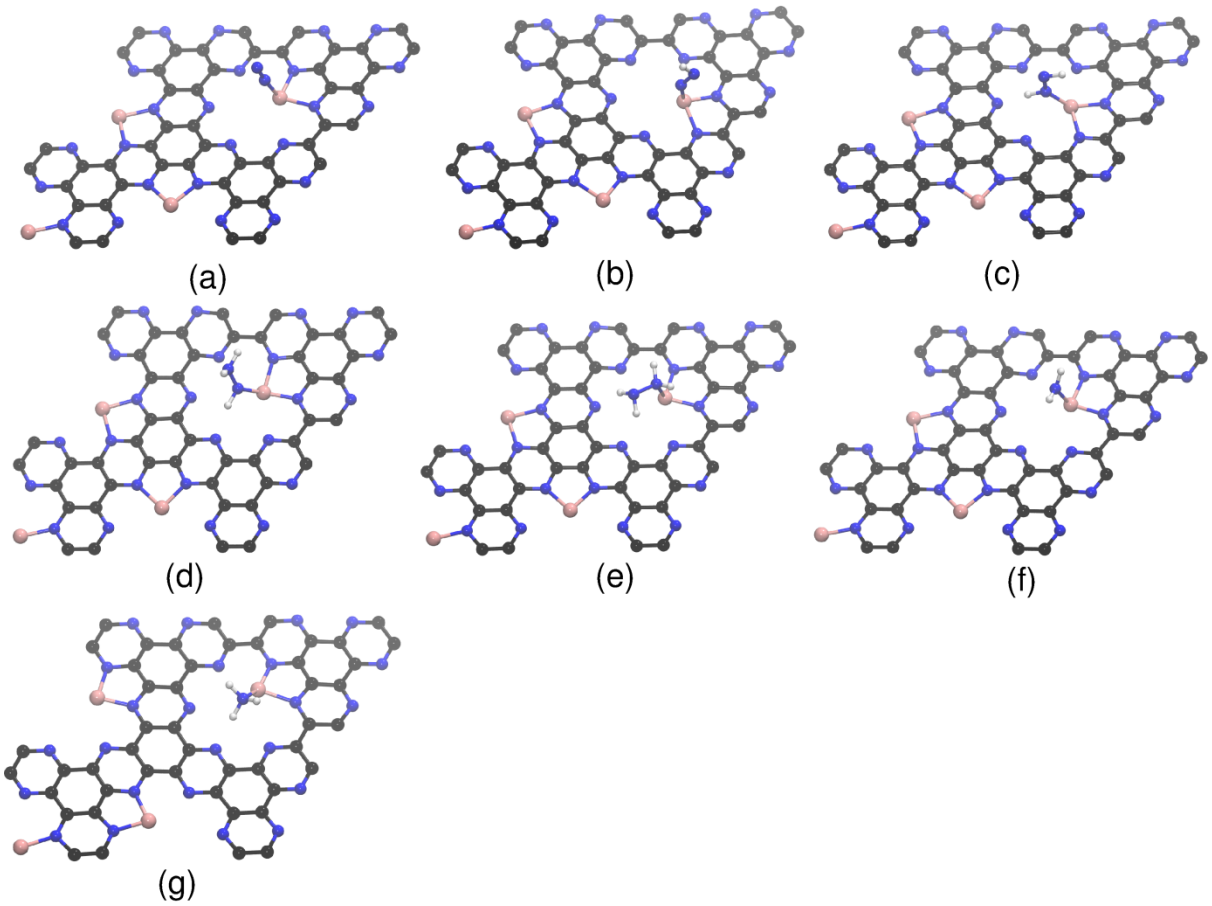

Figure S8: The atomic structure of the various intermediates: (a) N_2@Fe-C_2N, (b) HN-N@Fe-C_2N, (c) HN-NH@Fe-C_2N, (d) H_2N-NH@Fe-C_2N, (e) H_2N-NH_2@Fe-C_2N, (f) H_2N@Fe-C_2N and (g) H_3N@Fe-C_2N of the NRR through the alternating pathway. Atoms color: C-black, N-blue, H-white and Fe-pink.

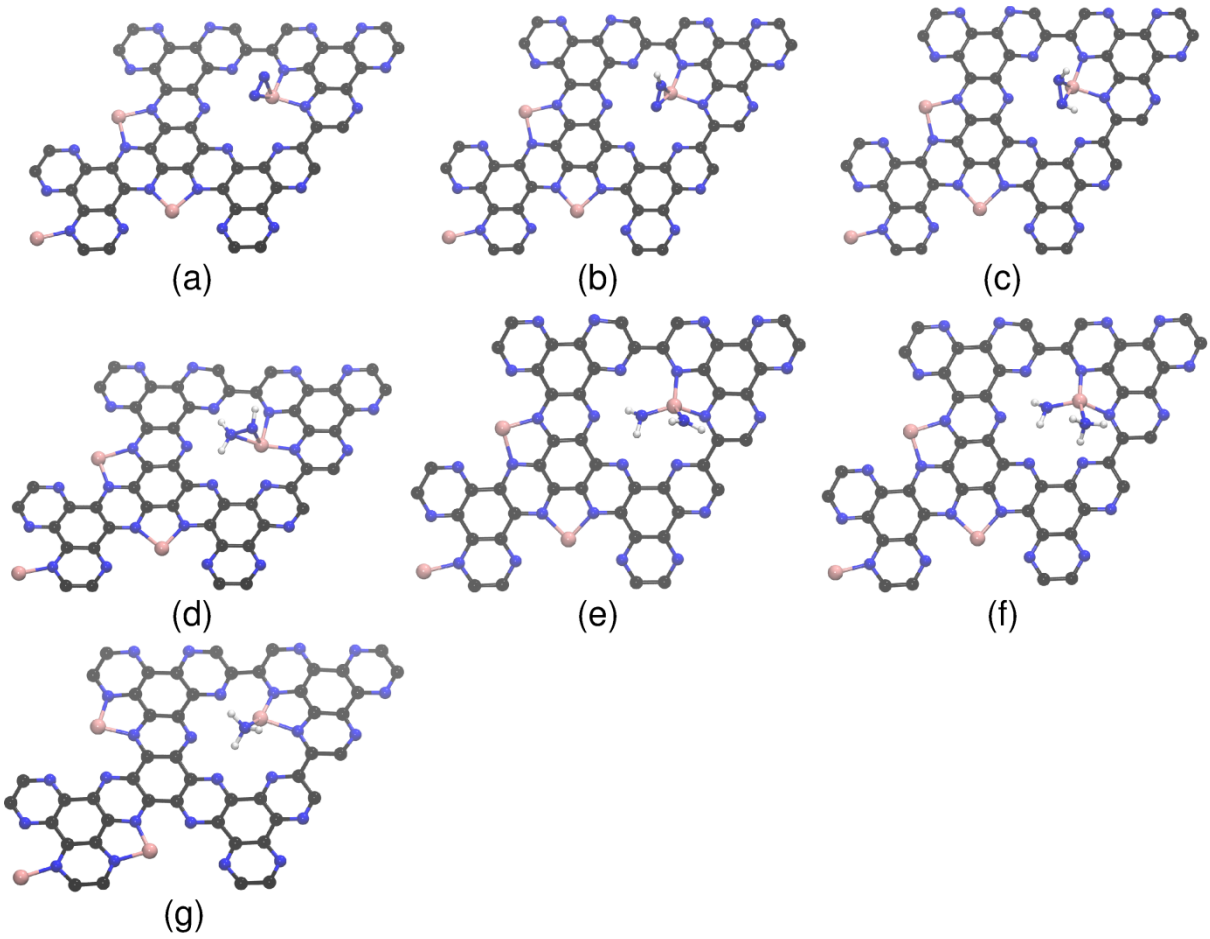

Figure S9: Structure of the various intermediates: (a) N_2@Fe-C_2N, (b) HN-N@Fe-C_2N, (c) HN-NH@Fe-C_2N, (d) H_2N-NH@Fe-C_2N, (e) $(H_2N)_2$@Fe-C_2N, (f) $(H_2N)(H_3N)$@Fe-C_2N and (g) H_3N@Fe-C_2N of the NRR through the enzymatic pathway. Atoms colour: C-black, N-blue, H-white and Fe-pink.

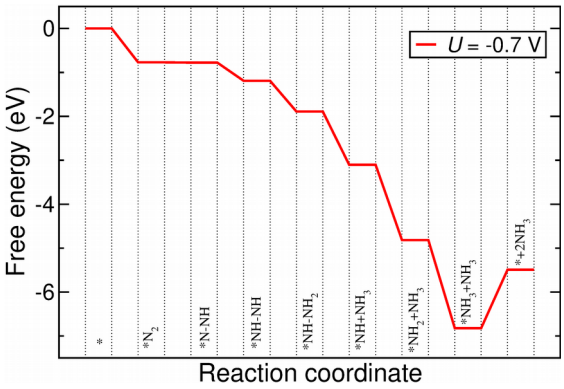

Figure S10: The minimum free energy pathway for the electrochemical NRR using Fe-C_2N as catalyst.

Hydrogen evolution reaction

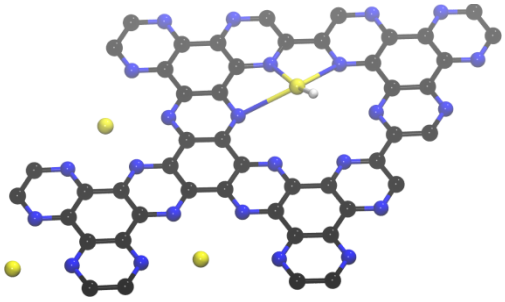

Figure S11: The structure of H@Au-C_2N, where the H atom is bonded to the Au atom.

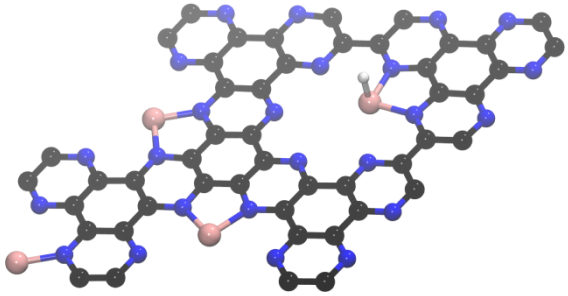

Figure S12: The structure of H@Fe-C_2N, where the H atom is bonded to the Fe atom.

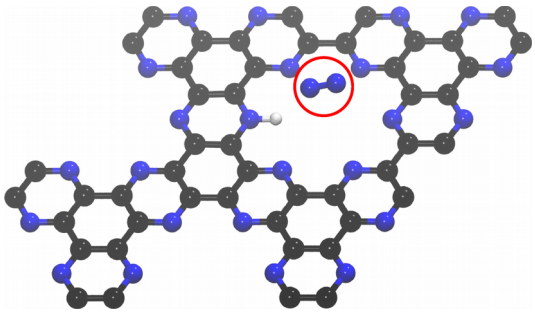

Figure S13: The final structure obtained from the geometry optimization of *NNH intermediate in bare C_2N. The N_2 molecule, which is separated from *NNH intermediate during the optimization, is highlighted in the red color circle.

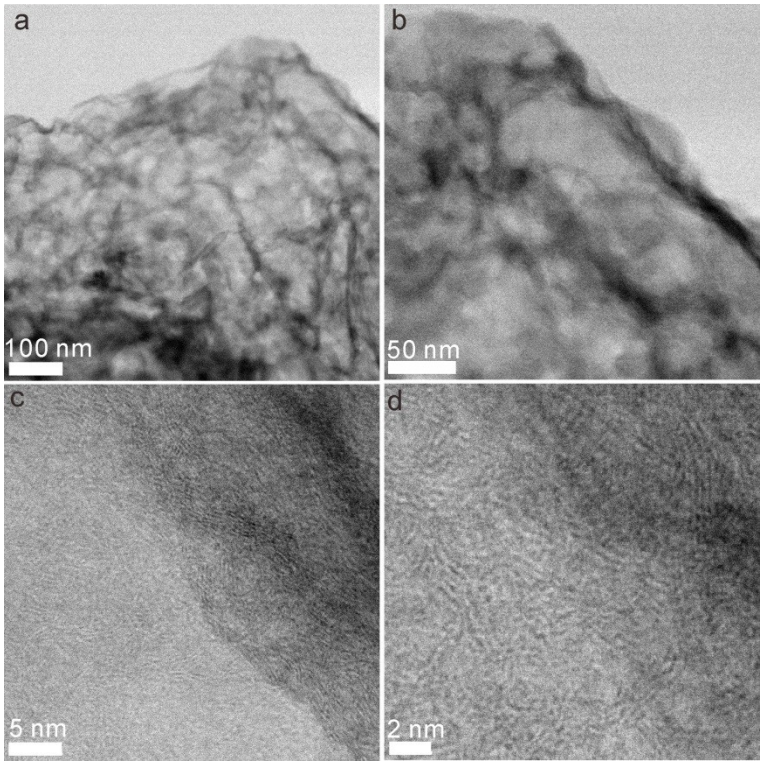

Figure S14: Representative TEM and HRTEM images of NDPC.

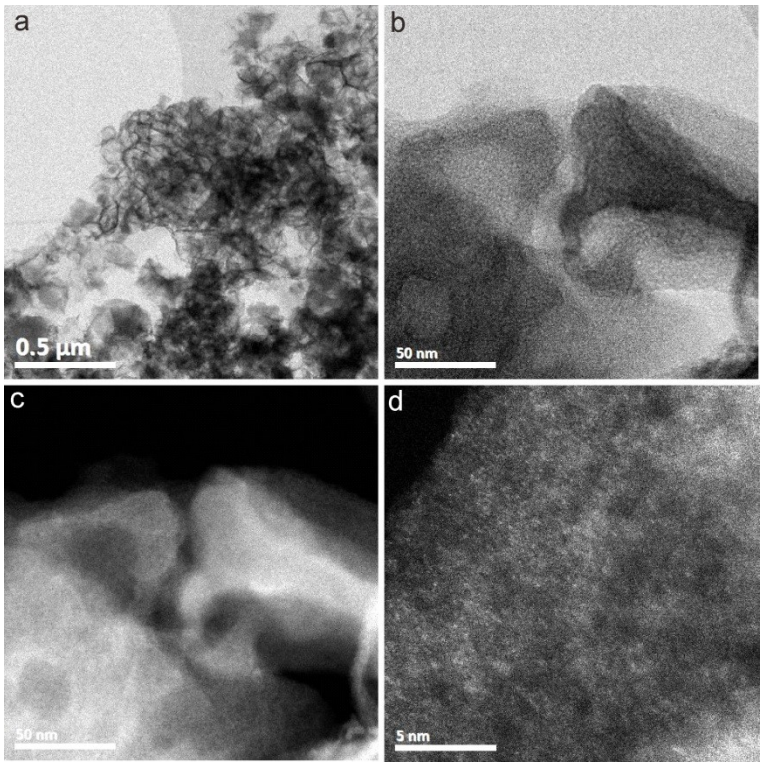

Figure S15: (a) Representative TEM image of FeSAs-NDPC. (b) Aberration-corrected STEM image in bright field mode. (c) Aberration-corrected STEM image in dark field mode. (d) High magnification HAADF-STEM image.

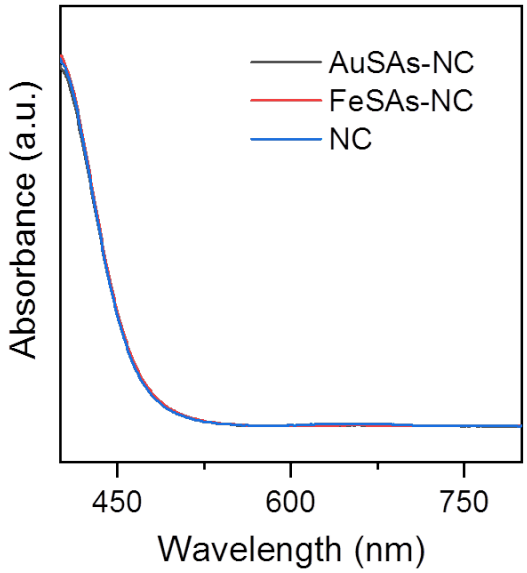

Figure S16: UV-Vis absorption spectra of the Ar-saturated electrolyte after the electrolysis at -0.2 V vs. RHE using AuSAs-NDPC, FeSAs-NDPC and NDPC as catalyst.

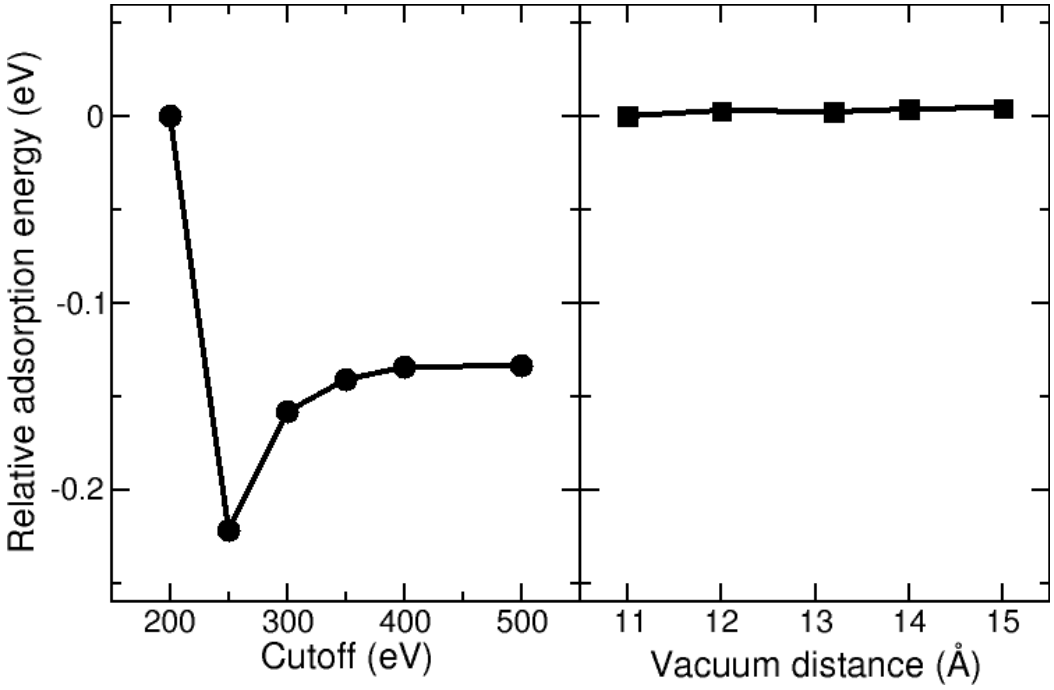

Figure S17: The relative adsorption energy of NH_3 molecule over Fe-C_2N catalyst with respect to the plane-wave cut-off energy and the vacuum distance.