Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Theoretical insights into the graphenylene-based triple-atom catalysts for efficient nitrogen fixation

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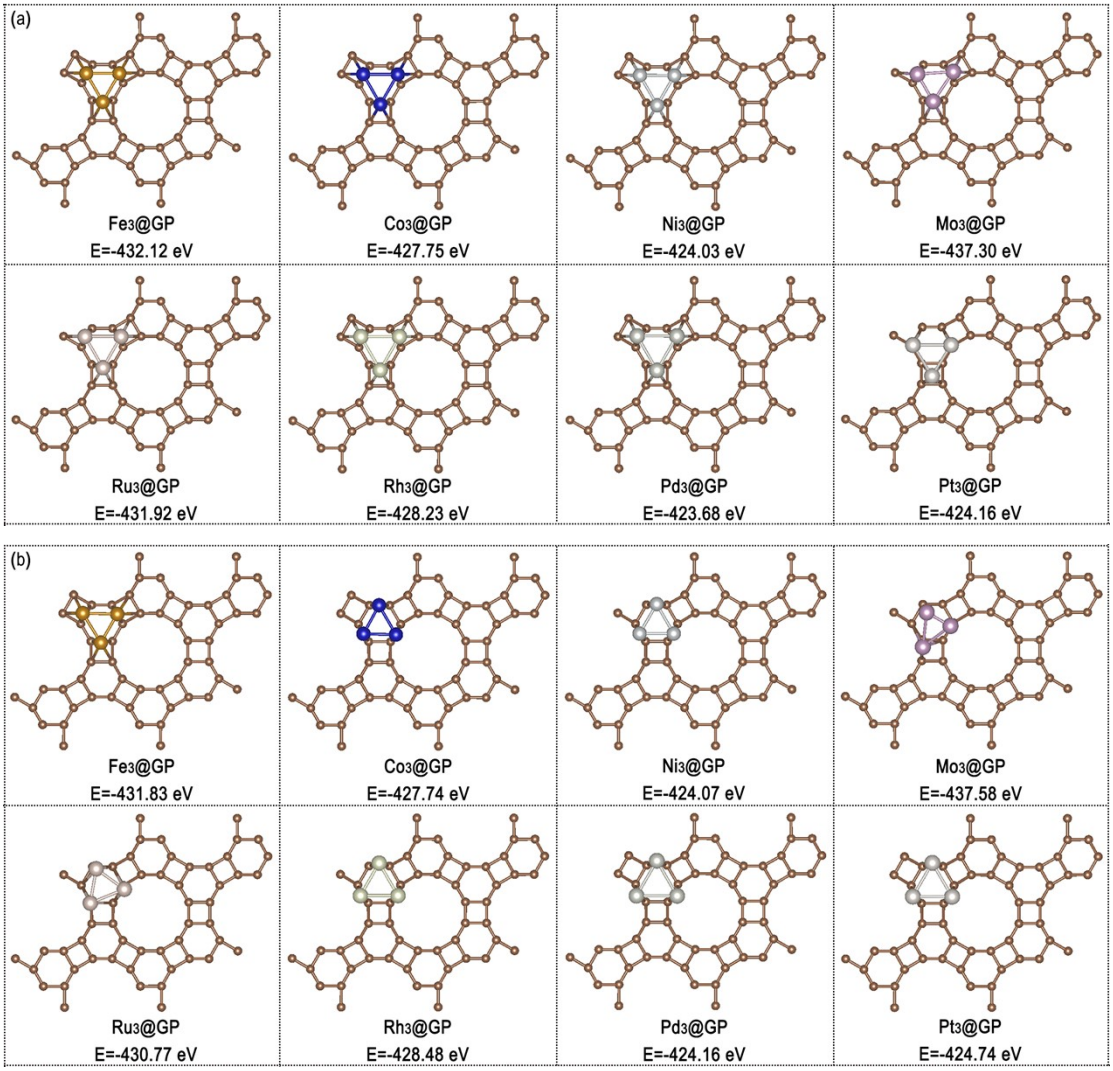

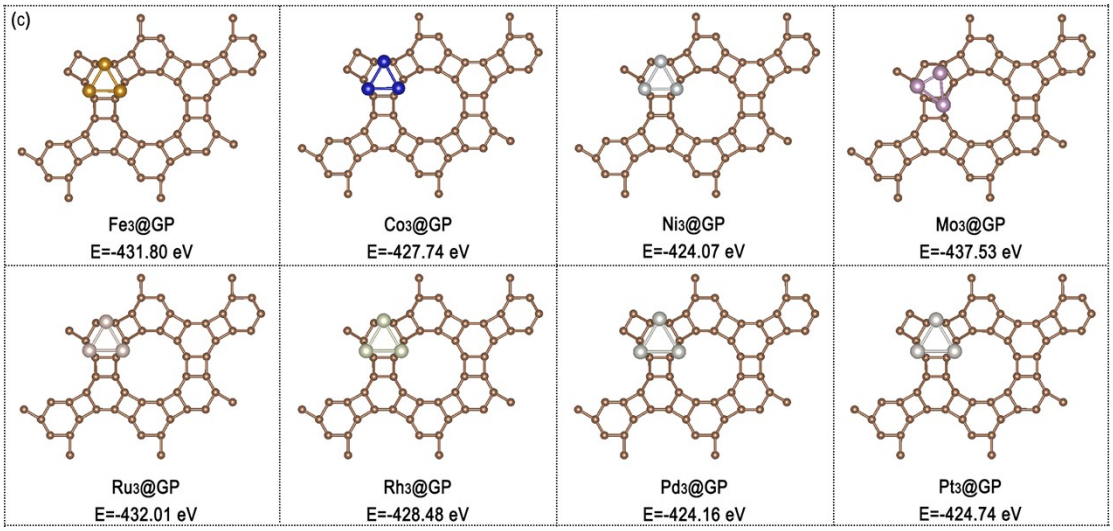

Fig. S1. Optimization geometry structures and the corresponding energies of TM_3@GP in different (a) A, (b) B, and (c) C configurations.

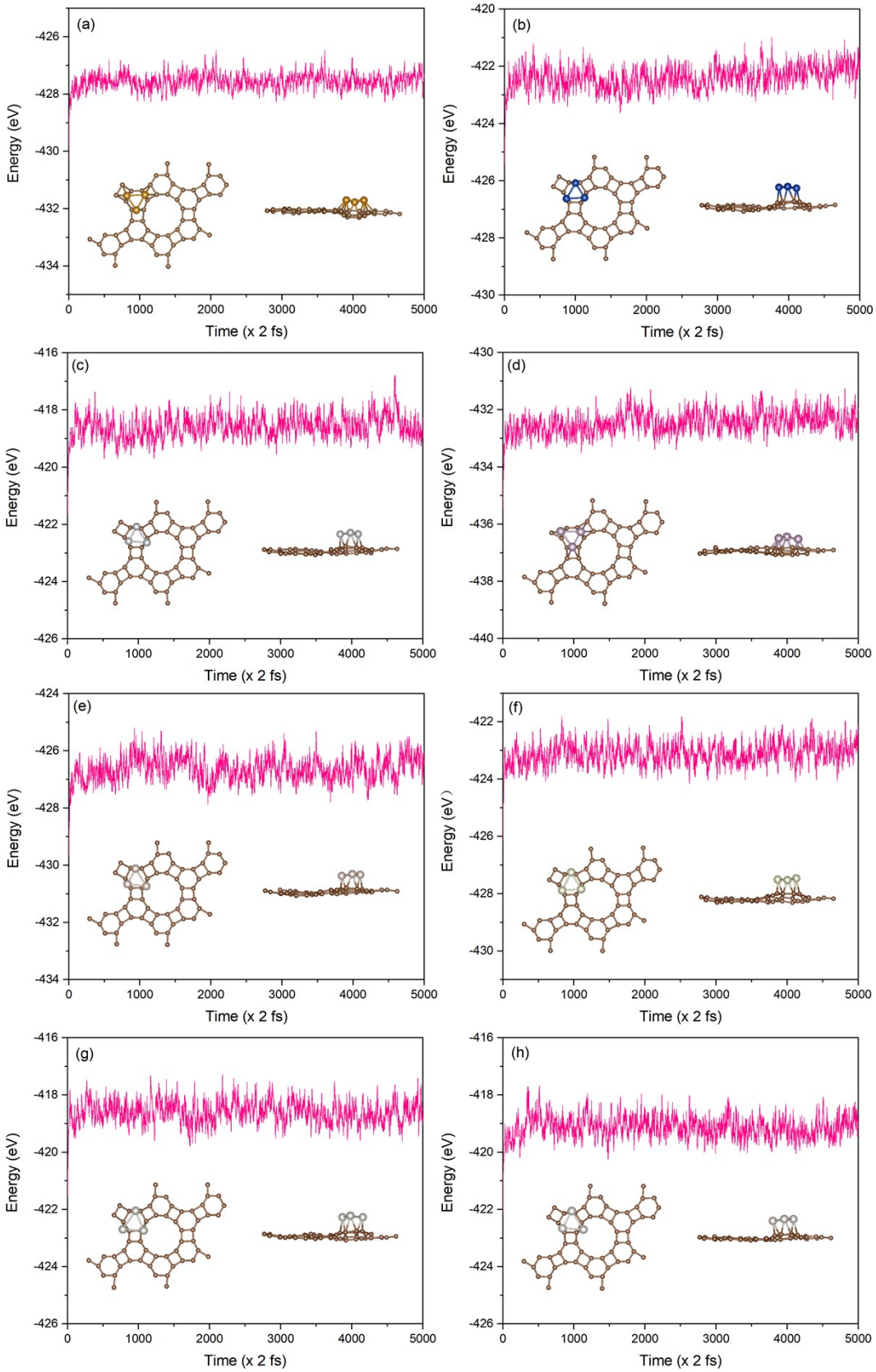

Fig. S2. AIMD simulations run at 300 K for (a) Fe_3@GP, (b) Co_3@GP, (c) Ni_3@GP, (d) Mo_3@GP, (e) Ru_3@GP, (f) Rh_3@GP, (g) Pd_3@GP and (h) Pt_3@GP.

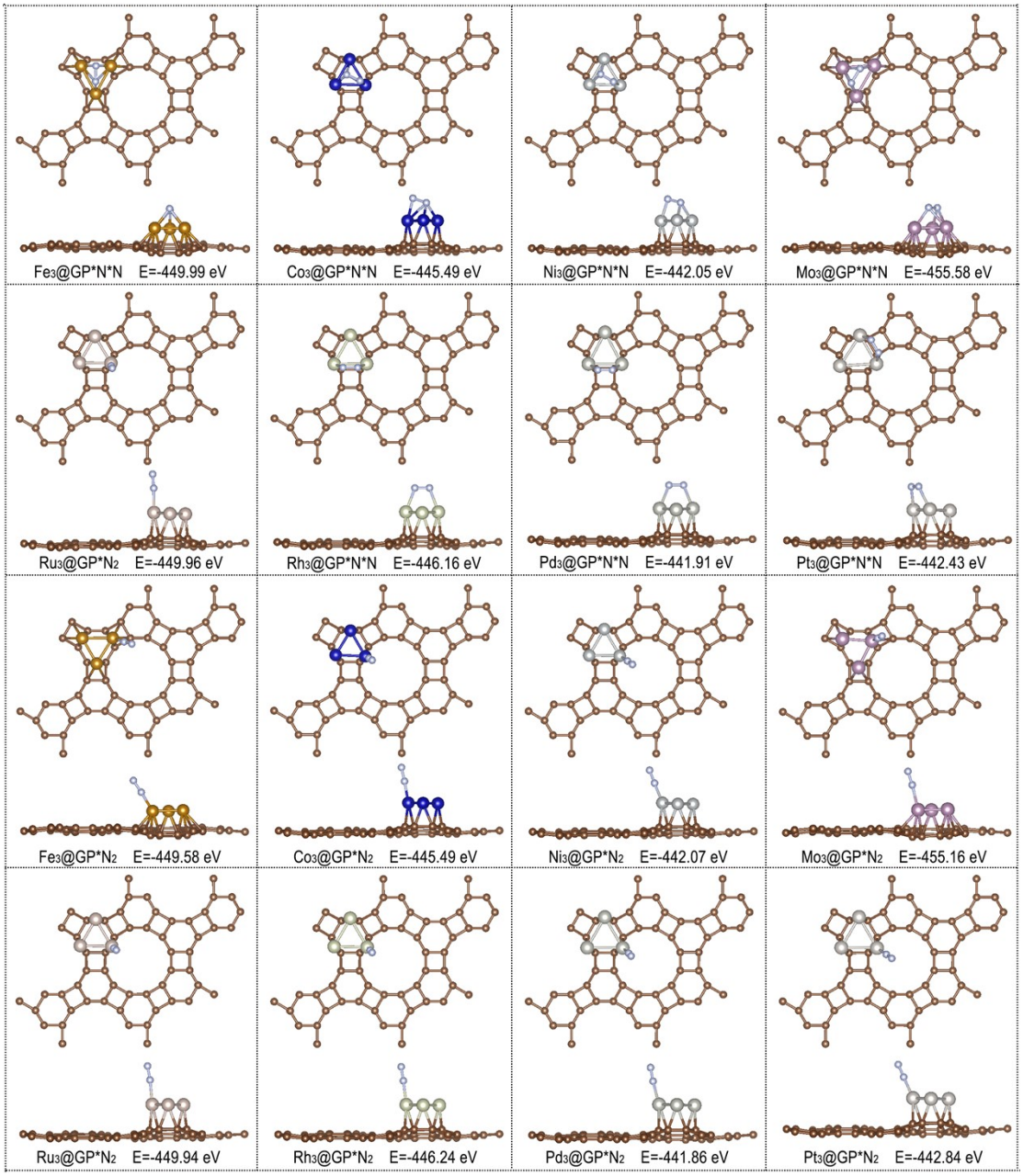

Fig. S3. The configurations of N_2 adsorption on TM_3@GP systems.

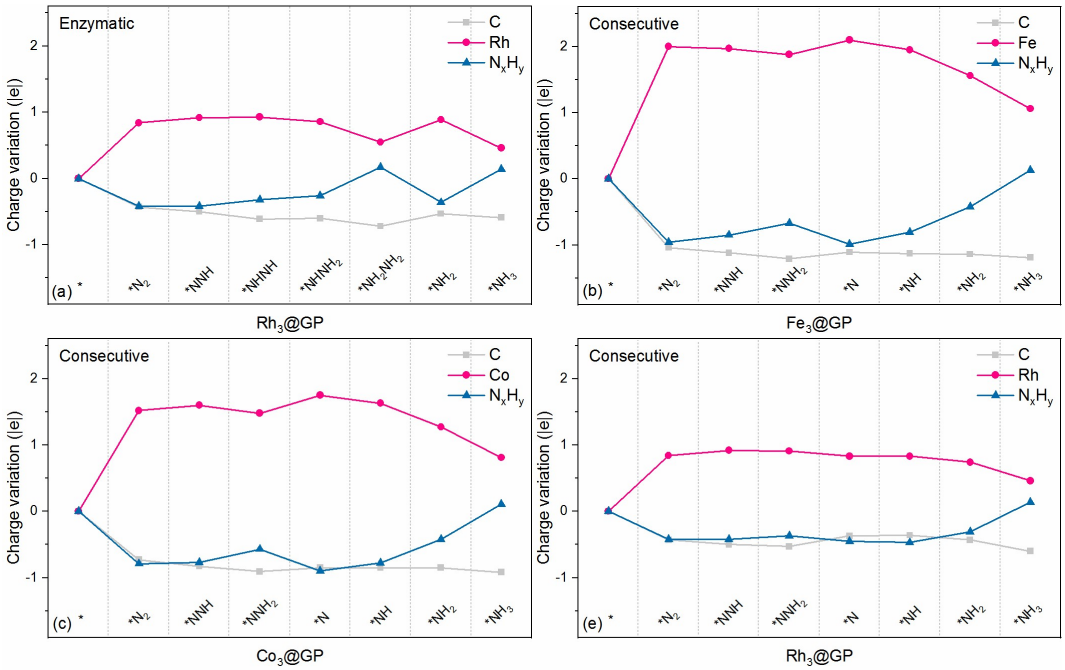

Fig. S4. Bader charge transfer during the (a) enzymatic pathway of Rh_3@GP, consecutive pathway of (b) Fe_3@GP, (c) Co_3@GP and (d) Rh_3@GP.

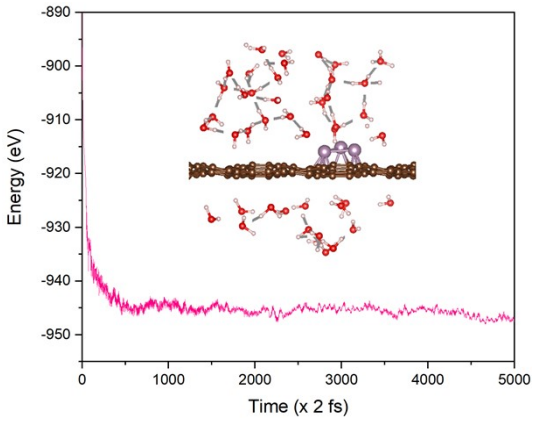

Fig. S5. AIMD simulations run at 300 K for Mo_3@GP in water environment.

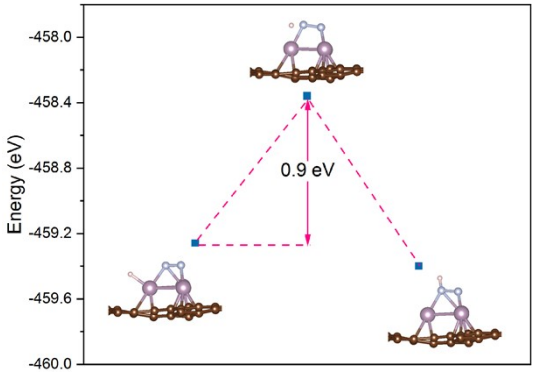

Fig.S6. Kinetic barrier from the *H + *N*N to *N*NH on Mo_3@GP.

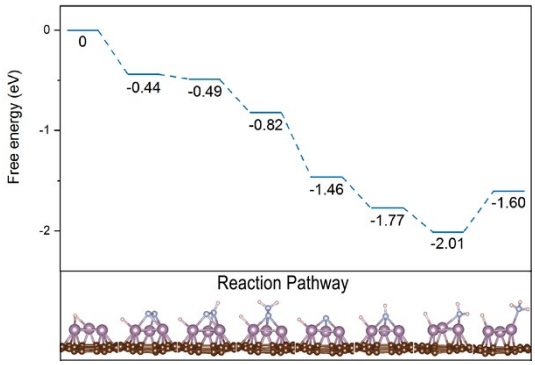

Fig. S7. The NRR process of H-terminated Mo_3@GP by consecutive pathway.

Table S1. Fractional Coordinates of Mo_3@GP.

CONTCAR

1.00000000000000

13.5082998276000001 0.0000000000000000 0.0000000000000000

6.7529881567999999 11.6989702353999991 0.0000000000000000

0.0749937988000000 -0.0288168372000000 19.7285370562000004

C Mo

48 3

Direct

0.2713085338385107	0.0773767369336980	0.4102711727663714
0.2715842316210381	0.1778478817972970	0.4104552784227321
0.1616080147224922	0.0777168840342749	0.4031832276684181
0.4357870727502246	0.2408258498261842	0.4084848135900022
0.4365098847762365	0.3488899204533934	0.3997693028894641
0.3342502855156004	0.2410270336764291	0.4098519252671104
0.0605279973636933	0.1785476590481795	0.3983881631067653
0.1619811203959177	0.2874027222229855	0.4037076031493691
0.0607261139222597	0.2881212367316013	0.3986801787689992
0.2249609266674674	0.3487673348935934	0.4022575673567492
0.3359758239918317	0.4492729993374059	0.3896154294267611
0.2246118732933000	0.4498577779697586	0.3906034047405329
0.7717271269454700	0.0778912654489607	0.4009235790406402
0.7720121604607016	0.1785925374701074	0.3958823444278174
0.6626048373520242	0.0775677268227639	0.4080741292534690
0.9356898774934648	0.2413161887664743	0.3922615719188899
0.9359167642019065	0.3508284273457013	0.3925346463480123
0.8343785839970735	0.2413720392330816	0.3912992155463075
0.5615273774189157	0.1782237703404320	0.4079737183710227
0.6621050043334746	0.2882272380490133	0.3953717822855705
0.5615781216545828	0.2873789431941106	0.4004987755478810
0.7248008341971264	0.3509584651822555	0.3906993933016904
0.8346540601631758	0.4522853686134423	0.3915231378579831
0.7249901806324948	0.4522970247104255	0.3906469298531690

0.2730568062998753	0.5733595163663165	0.3788023767813516
0.2741028067043573	0.6791392204202148	0.3795132639374412
0.1636633045929852	0.5724100927993362	0.3776453353617419
0.4374840569639029	0.7410298208791837	0.4001639953738875
0.4353766597276982	0.8501418067598319	0.4092675823043625
0.3366581734549795	0.7406224944615157	0.3887125222555089
0.0573181334885287	0.6789702751205532	0.3785313715698133
0.1641901144270453	0.7889850666330317	0.3806430031491154
0.0585348722656458	0.7882293117846620	0.3805761145653772
0.2250396175663608	0.8518937696397932	0.3899344793539856
0.3336228038382281	0.9516132527969796	0.4098795400495504
0.2247319063149251	0.9531326215879581	0.4017397011670731
0.7720845687462459	0.5773746977401468	0.3964948473417843
0.7714093672773082	0.6785316856175722	0.4022107657896184
0.6624631306060462	0.5774277235419125	0.3956148389149229
0.9345300199727961	0.7405057744316211	0.3911773212437066
0.9344003218961301	0.8516740326036875	0.3909950871878514
0.8332415372724757	0.7410840970966569	0.4021275029983493
0.5618842481608868	0.6785732740917383	0.4006663765397946
0.6618801698764576	0.7883454559564297	0.4094298855987895
0.5612309281840909	0.7882859941932130	0.4088338622387473
0.7256132382824524	0.8505345093511716	0.4100001385061963
0.8338876644205404	0.9526511179195101	0.4006115140921477
0.7256786908578993	0.9519399490616509	0.4088767012116173
0.2199166689744961	0.5669260671436238	0.4846931514254849
0.2354045445069191	0.7461327795260965	0.4843611314725456
0.0551301416117377	0.7316615363739948	0.4857596756635006

Table S2. Averaged bond lengths between TM-TM, averaged bond lengths between TM-C, Bader charge dispersion of TM_3@GP, binding energies and cohesive energies of TM_3@GP.

Name	d_{TM-TM}/Å	d_{TM-C}/Å	q_{TM3} /|e|	q_{GP} /|e|	E_b/eV	E_{coh}/eV
Fe_3@GP	2.33	2.12	1.05	-1.05	-8.46	-4.28
Co_3@GP	2.29	2.03	0.72	-0.72	-8.49	-4.39
Ni_3@GP	2.37	2.00	0.62	-0.62	-8.51	-4.44
Mo_3@GP	2.43	2.22	1.47	-1.47	-10.16	-6.82
Ru_3@GP	2.47	2.08	0.66	-0.66	-11.05	-6.74
Rh_3@GP	2.61	2.08	0.46	-0.46	-10.19	-5.75
Pd_3@GP	2.84	2.14	0.33	-0.33	-6.35	-3.89
Pt_3@GP	2.72	2.12	0.04	-0.04	-9.6	-5.84

Table S3. The ΔG (H), ΔG (N_2-side on), ΔG (N_2-end on) , ΔG (*N*NH) and ΔG (*NNH) of TM_3@GP.

Name	ΔG (H) /eV	ΔG (H) (on GP)/eV	ΔG (*N*N) /eV	d_{N-N}/Å	ΔG ($*N_2$) /eV	d_{N-N}/Å	ΔG (*N*NH) /eV	ΔG (*NNH) /eV
GP	-	0.71	3.36	1.26	0.29	1.11	-	-

Fe_3@GP	-0.20	0.52	-0.72	1.27	-0.36	1.14	0.25	0.98
Co_3@GP	-0.53	1.04	-0.62	1.23	-0.64	1.14	0.48	1.11
Ni_3@GP	-0.76	1.00	-0.84	1.22	-0.90	1.14	0.72	1.38
Mo_3@GP	-0.74	0.40	-1.10	1.34	-0.76	1.14	-0.07	-
Ru_3@GP	-0.37	1.02	-	1.14	-0.81	1.14	-	1.09
Rh_3@GP	-0.12	0.90	-0.57	1.17	-0.66	1.13	0.54	1.14
Pd_3@GP	-0.13	1.10	-0.62	1.16	-0.63	1.13	1.28	1.71
Pt_3@GP	-0.70	1.06	-0.54	1.18	-0.99	1.13	-	1.33

Table S4. Zero-point and entropic corrections to the free energy of the gas phase and the adsorbed species along different catalysts.

Name	E/eV	E_{ZPE}/eV	TS/eV	G/eV
H_2	-6.76565715	0.268608	0.4019062	-6.89895535
N_2	-16.62627336	0.149570	0.59182775	-17.06853111
NH_3	-19.54133424	0.909892	0.5951074	-19.22654964
GP	-413.37	0	0	-413.37
Fe_3@GP	-432.12	0	0	-432.12
Co_3@GP	-427.74	0	0	-427.74
Ni_3@GP	-424.07	0	0	-424.07
Mo_3@GP	-437.30	0	0	-437.30
Ru_3@GP	-432.01	0	0	-432.01
Rh_3@GP	-428.48	0	0	-428.48
Pd_3@GP	-424.16	0	0	-424.16
Pt_3@GP	-424.74	0	0	-424.74
Fe_3@GP (Enzymatic pathway)				
*N*N	-449.99	0.18561	0.099618	-449.904008
*N*NH	-453.52	0.50382	0.085801	-453.101981
*NH*NH	-457.36	0.823844	0.094946	-456.631102
NHNH_2	-460.95	1.168633	0.108435	-459.889802
*NH_2*NH_2	-466.41	1.340669	0.234737	-465.304068
*NH_2	-449.41	0.698205	0.083244	-448.795039
*NH_3	-452.87	1.015197	0.142056	-451.996859
Co_3@GP (Enzymatic pathway)				
*N*N	-445.49	0.18042	0.124327	-445.433907
*N*NH	-448.82	0.501535	0.086518	-448.404983
*NH*NH	-452.87	0.802983	0.130019	-452.197036
NHNH_2	-456.43	1.138509	0.159026	-455.450517
*NH_2*NH_2	-461.98	1.346543	0.226595	-460.860052
*NH_2	-444.47	0.63491	0.119075	-443.954165
*NH_3	-448.52	1.002118	0.146887	-447.664769
Mo_3@GP (Enzymatic pathway)				
*N*N	-455.58	0.186673	0.073783	-455.46711
*N*NH	-459.4	0.499624	0.084625	-458.985001
*NH*NH	-463.03	0.820132	0.093553	-462.303421
NHNH_2	-466.39	1.15969	0.124865	-465.355175

*NH_2*NH_2	-472.74	1.361142	0.2027	-471.581558
*NH_2	-454.99	0.691956	0.086646	-454.38469
*NH_3	-458.37	1.003909	0.138416	-457.504507
Rh_3@GP (Enzymatic pathway)				
*N*N	-446.16	0.186399	0.14298	-446.116581
*N*NH	-449.42	0.50363	0.111444	-449.027814
*NH*NH	-453.19	0.811338	0.12861	-452.507272
NHNH_2	-457.04	1.151873	0.143378	-456.031505
*NH_2*NH_2	-460.53	1.472276	0.1366	-459.194324
*NH_2	-445.46	0.695031	0.082305	-444.847274
*NH_3	-449.36	1.011009	0.127279	-448.47627
Fe_3@GP (Consecutive pathway)				
*N*N	-449.99	0.18561	0.099618	-449.904008
*N*NH	-453.52	0.50382	0.085801	-453.101981
NNH_2	-457.34	0.852902	0.09843	-456.585528
*N	-441.58	0.101384	0.022644	-441.50126
*NH	-446.11	0.388591	0.038932	-445.760341
*NH_2	-449.38	0.697339	0.08454	-448.767201
*NH_3	-452.89	1.020663	0.20222	-452.071557
Co_3@GP (Consecutive pathway)				
*N*N	-445.49	0.18042	0.124327	-445.433907
*N*NH	-448.82	0.501535	0.086518	-448.404983
NNH_2	-452.86	0.847563	0.104114	-452.116551
*N	-436.94	0.100298	0.023561	-436.863263
*NH	-441.13	0.366355	0.045842	-440.809487
*NH_2	-445.06	0.694582	0.085133	-444.450551
*NH_3	-448.53	0.999984	0.141344	-447.67136
Mo_3@GP (Consecutive pathway)				
*N*N	-455.58	0.186673	0.073783	-455.46711
*N*NH	-459.4	0.499624	0.084625	-458.985001
NNH_2	-463.12	0.84702	0.09983	-462.37281
*N	-447.63	0.097551	0.02521	-447.557659
*NH	-451.36	0.373562	0.04213	-451.028568
*NH_2	-455.1	0.694807	0.08389	-454.489083
*NH_3	-458.43	1.013529	0.135641	-457.552112
Rh_3@GP (Consecutive pathway)				
*N*N	-446.16	0.186399	0.14298	-446.116581
*N*NH	-449.42	0.50363	0.111444	-449.027814
NNH_2	-452.66	0.827756	0.123964	-451.956208
*N	-436.08	0.077261	0.068644	-436.071383
*NH	-440.28	0.309819	0.085644	-440.055825
*NH_2	-445.12	0.659192	0.134675	-444.595483
*NH_3	-449.35	1.011403	0.125413	-448.46401