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

Table S1. The **s**pecial bond length of P-P bond and P-Fe bond of Fe-P.

Bond	Length (Å)	Bond	Length (Å)
$Fe\text{-}P_1$	2.39	$P_3\text{-}P_4$	2.23
$Fe\text{-}P_2$	2.08	$P_4\text{-}P_5$	2.23
$Fe\text{-}P_4$	2.16	$P_4\text{-}P_7$	2.96
$Fe\text{-}P_6$	2.08	$P_5\text{-}P_6$	2.20
$Fe\text{-}P_7$	2.12	$P_7\text{-}P_8$	2.23
$P_1\text{-}P_2$	2.27	$P_7\text{-}P_{11}$	2.23
$P_1\text{-}P_6$	2.31	$P_8\text{-}P_9$	2.27
$P_2\text{-}P_3$	2.20	$P_{10}\text{-}P_{11}$	2.26

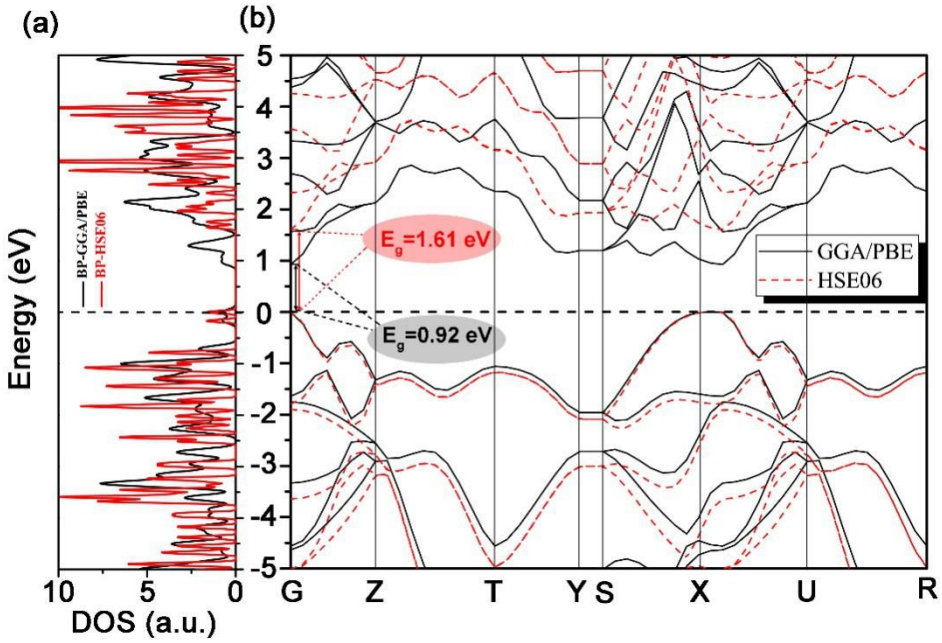

Figure S1. Density of states (a) and band structure (b) of P. Both the GGA and HSE06 functionals were used to calculate the electronic properties. The Fermi level is set to zero.

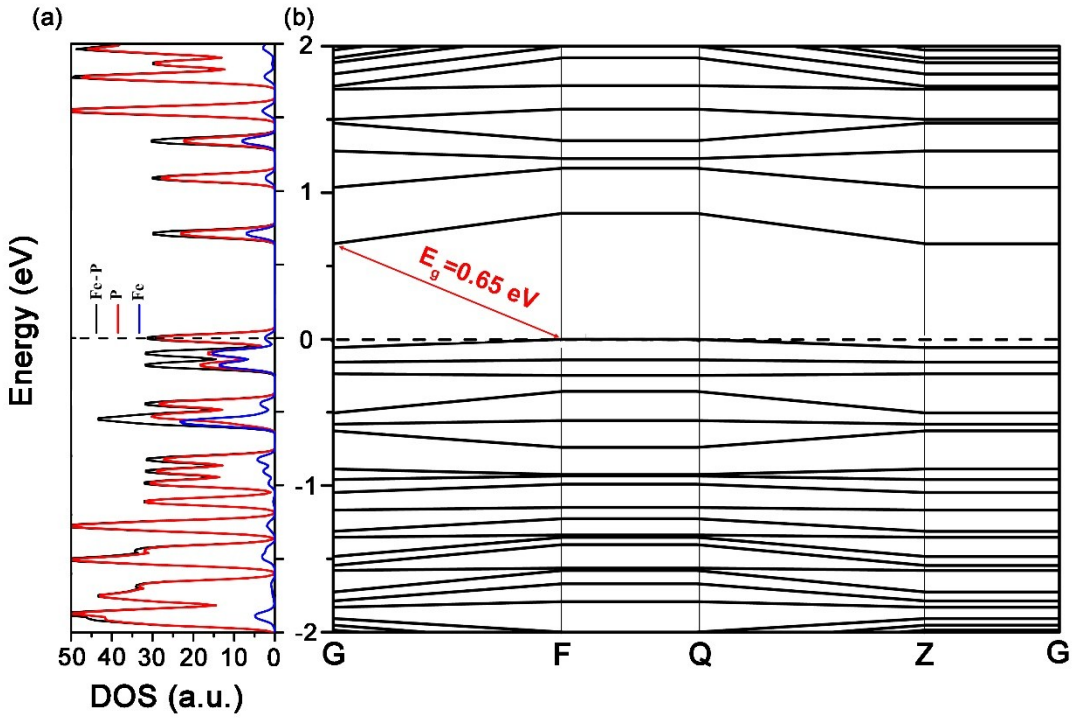

Figure S2. Density of states (a) and band structure (b) of Fe-P. The same electronic properties of Fe-P in both GGA and HSE06 functionals. The Fermi level is set to zero.

Table S2. The Mulliken population analysis of Fe-P.

Atom	Charges (e)	atom	Charges (e)
Fe	0.18	P6	0.03
P1	-0.12	P7	-0.07
P2	0.04	P8	-0.03
P3	0.03	P9	0.00
P4	-0.07	P10	0.00
P5	0.03	P11	-0.03

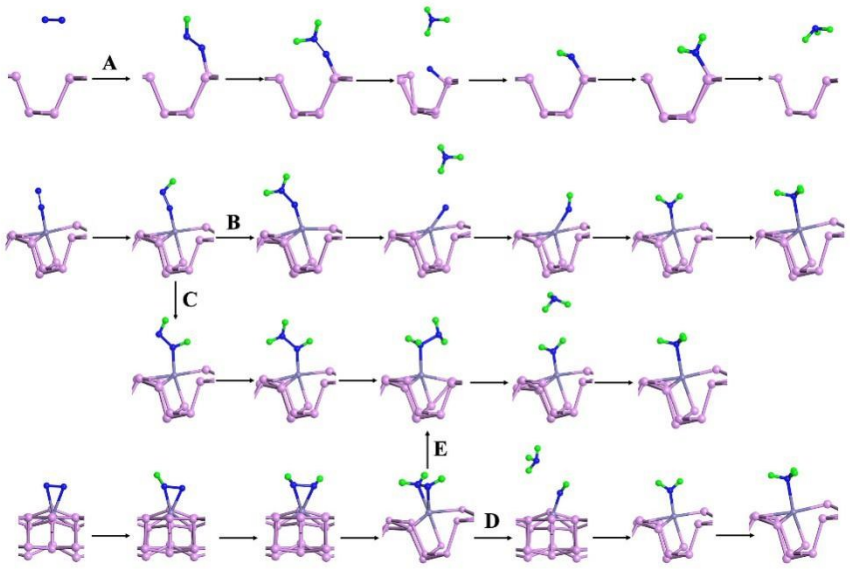

Figure S3. The optimized structures of each step in the Dis-P (A), Dis-Fe-P (B), Alt-Fe-P (C), Enz^1-Fe-P (D), and Enz^2-Fe-P (E) pathways, respectively.

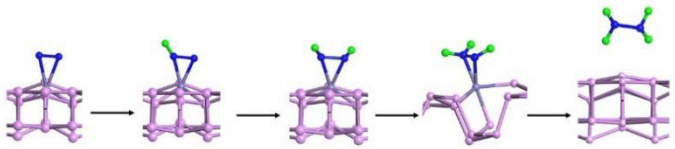

Figure S4. The optimized structures of each step in the emission of the intermediate product N_2H_4, respectively.

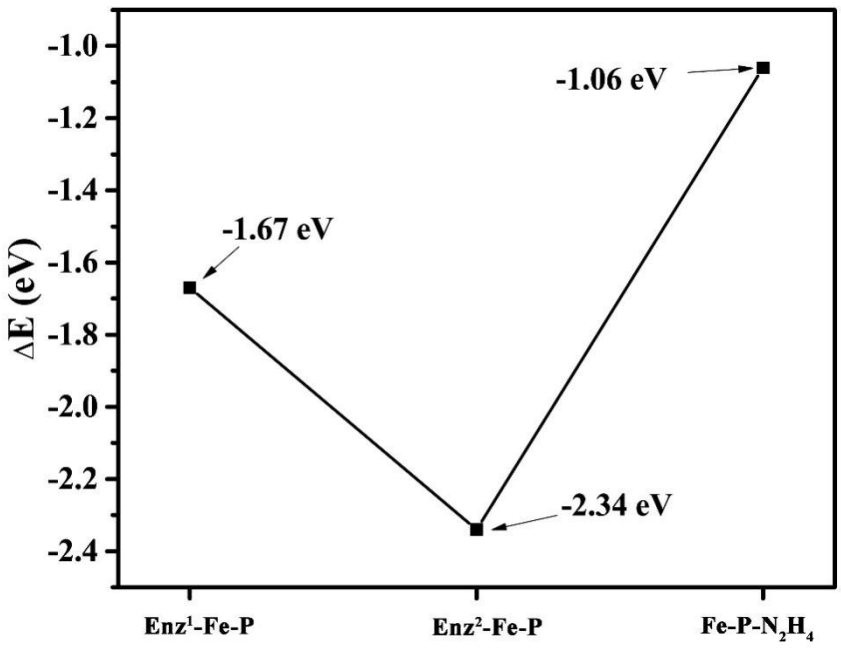

Figure S5. Reaction energy of the fifth step in the Enz pathway, which converted NH_2-NH* to NH_2-NH_2, NH*+NH_3 and H_2N-H_2N*, respectively.

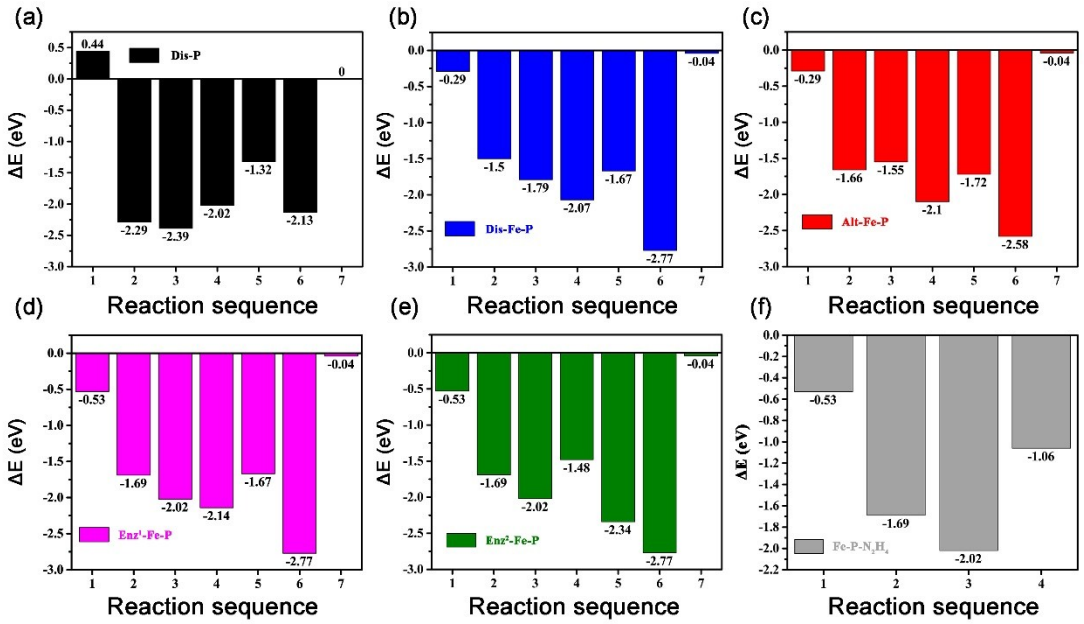

Figure S6. The reaction energies in each step (a) Dis-P, (b) Dis-Fe-P, (c) Alt-Fe-P, (d) Enz^1-Fe-P, (e) Enz^2-Fe-P, respectively.

Table S3. The N-N bond length (Å) of the adsorbed N_2 in the various reaction pathways (Dis-P, Dis-Fe-P, Alt-Fe-P, Enz^1-Fe-P and Enz^2-Fe-P, respectively)

steps	0	1	2	3	4	5	6
Dis-P	1.15	1.15	1.32	1.42	3.52	--	--
Dis-Fe-P	1.15	1.17	1.24	1.30	3.46	--	--
Alt-Fe-P	1.15	1.17	1.24	1.29	1.36	1.48	3.75
Enz^1-Fe-P	1.15	1.19	1.26	1.36	1.41	1.48	3.75
Enz^2-Fe-P	1.15	1.19	1.26	1.36	1.41	3.75	--

Table S4. The Mulliken charge of the three moieties (mole is equal to molecule, P, Fe, respectively)

	Dis-P		Dis-Fe-P			Alt-Fe-P			Enz^1-Fe-P			Enz^2-Fe-P		
steps	**mol**	**P**	**mol**	**P**	**Fe**	**mol**	**P**	**Fe**	**mol**	**P**	**Fe**	**mol**	**P**	**Fe**
1	0.00	-0.02	-0.23	0.3	-0.23	-0.23	-0.08	0.3	-0.24	-0.05	0.26	-0.24	-0.05	0.26
2	-0.59	0.59	-0.24	0.38	-0.24	-0.24	-0.14	0.38	-0.28	-0.15	0.42	-0.28	-0.15	0.42
3	-0.66	0.65	-0.13	-0.21	0.33	-0.2	-0.18	0.39	-0.51	0.1	0.41	-0.51	0.1	0.41
4	-1.12	1.14	-0.83	0.44	0.4	-0.04	-0.34	0.38	-0.03	-0.31	0.33	-0.03	-0.31	0.33
5	-0.72	0.71	-0.73	0.39	0.34	0.04	-0.31	0.27	-0.27	-0.07	0.39	0.04	-0.31	0.27
6	-0.26	0.24	-0.3	-0.12	0.44	-0.27	-0.07	0.39	-0.3	-0.12	0.44	-0.27	-0.07	0.39
7	-0.02	-0.08	0.07	-0.34	0.29	-0.05	-0.16	0.19	0.07	-0.34	0.29	-0.05	-0.16	0.19

in the five reaction pathways.