Supporting Information for

The Effective Regulation of Heterogeneous N-heterocyclic Carbenes: Structures, Electronic Properties and Transition Metal Adsorption

Wei Liu[a,†,], Jingchao Sun[a,†], Yunhao Xie[a], Liang Chen[b,a], and Jing Xu[a,*]*

[a] *College of Optical, Mechanical and Electrical Engineering, Zhejiang A&F University, Lin'an, Zhejiang, 311300, P.R. China*

[b]*School of Physical Science and Technology, Ningbo University, Ningbo, Zhejiang, 315211, P.R. China*

[†]These authors contributed equally to this work.

Email: jingxu@zafu.edu.cn; weiliu@zafu.edu.cn

Table S1. The lattice constants of the 16 NCMs, the average bond lengths of the carbene carbon atoms to the adjacent nitrogen atoms in the NHC and CAAC five-membered ring fragments (C2 NHC-N, C2 CAAC-N), "—" represents no data.

Structure	a (Å)	b (Å)	γ (°)	C2 NHC-N (Å)	C2 CAAC-N (Å)
3T-3:0	7.94	7.00	90.00	1.40	—
3T-2:1	7.92	7.15	89.89	1.40	1.39
3T-1:2	8.00	7.13	89.78	1.42	1.41
3T-0:3	8.09	7.12	89.96	—	1.40
3H-3:0	7.79	7.79	120.00	1.39	—
3H-2:1	7.76	7.83	119.84	1.39	1.40
3H-1:2	7.88	7.90	120.06	1.41	1.38
3H-0:3	7.95	7.95	120.00	—	1.42
4T-4:0	10.90	8.20	90.00	1.41	—
4T-3:1	11.02	8.22	90.00	1.41	1.42
4T-2:2	10.94	8.30	89.42	1.40	1.40
4T-1:3	11.00	8.34	89.11	1.41	1.41
4T-0:4	11.24	8.26	89.32	—	1.43
4H-4:0	11.06	9.41	118.40	1.41	—
4H-3:1	11.27	9.37	118.91	1.40	1.41
4H-2:2	11.52	9.29	119.62	1.42	1.41

Table S2. Detailed adsorption energies of 16 NCMs and nitrogen-doped graphene (T/H-$N_{3/4}$-G) on 3d (Fe, CO, Ni, Cu), 4d (Ru, Rh, Pd) and 5d (Ir, Pt, Au) transition metals.

TM / Structure	Fe	Co	Ni	Cu	Ru	Rh	Pd	Ir	Pt	Au
T-N_3-G	-4.23	-4.40	-4.51	-3.14	-6.04	-4.22	-2.35	-3.97	-2.86	-1.13
3T-3:0	-5.53	-6.14	-6.49	-4.61	-8.18	-6.44	-4.22	-7.42	-6.00	-2.82
3T-2:1	-6.75	-7.57	-7.46	-5.78	-9.61	-7.63	-5.04	-8.59	-6.88	-4.09
3T-1:2	-7.54	-8.56	-8.33	-6.19	-11.21	-9.00	-6.05	-9.92	-8.09	-4.49
3T-0:3	-8.27	-8.79	-8.59	-6.14	-11.24	-9.62	-6.28	-10.62	-8.41	-4.73
H-N_3-G	-4.28	-4.36	-4.49	-3.12	-6.13	-4.12	-2.26	-3.99	-2.74	-1.20
3H-3:0	-6.32	-6.80	-7.07	-4.72	-8.79	-7.12	-4.88	-8.07	-6.73	-3.05
3H-2:1	-7.21	-8.03	-8.00	-6.30	-10.17	-8.42	-5.80	-9.35	-7.70	-4.64
3H-1:2	-8.13	-8.70	-8.65	-6.51	-11.57	-9.38	-6.44	-10.31	-8.36	-5.02
3H-0:3	-8.66	-9.33	-8.85	-6.48	-11.63	-10.35	-6.89	-11.31	-8.92	-5.15
T-N_4-G	-6.52	-7.63	-7.84	-4.76	-8.09	-7.57	-5.64	-8.45	-7.64	-3.34
4T-4:0	-8.87	-9.44	-7.55	-4.86	-10.19	-9.25	-6.63	-10.78	-9.26	-4.77
4T-3:1	-9.02	-9.63	-9.15	-4.87	-11.86	-11.07	-8.22	-12.65	-10.89	-6.19
4T-2:2	-9.16	-9.49	-9.80	-6.81	-11.83	-10.87	-8.95	-12.52	-11.58	-7.05
4T-1:3	-9.58	-9.86	-10.11	-7.73	-12.10	-11.11	-9.20	-12.83	-11.92	-8.50
4T-0:4	-9.88	-10.15	-10.38	-8.01	-12.38	-11.33	-9.49	-13.14	-12.30	-8.89
H-N_4-G	-6.74	-7.93	-8.18	-5.11	-8.37	-7.90	-6.02	-8.83	-8.06	-3.36
4H-4:0	-7.42	-8.00	-7.78	-5.21	-10.62	-9.54	-6.85	-11.05	-9.43	-4.81
4H-3:1	-7.83	-8.28	-6.68	-5.60	-10.78	-9.94	-7.51	-11.47	-10.04	-5.53
4H-2:2	-8.37	-8.71	-8.85	-6.04	-11.22	-10.19	-8.06	-11.88	-10.64	-6.43

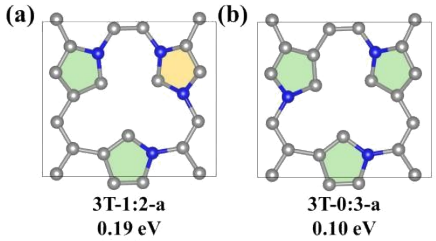


Fig. S1 The 3T structure with higher energy. (a) 3T-2:1-a, 0.19 eV higher energy than 3T-2:1. (b) 3T-2:1-b, 0.10 eV higher energy than 3T-2:1. The yellow and cyan regions represent NHC and CAAC fragments, respectively. Gray and blue balls represent C and N atoms, respectively.

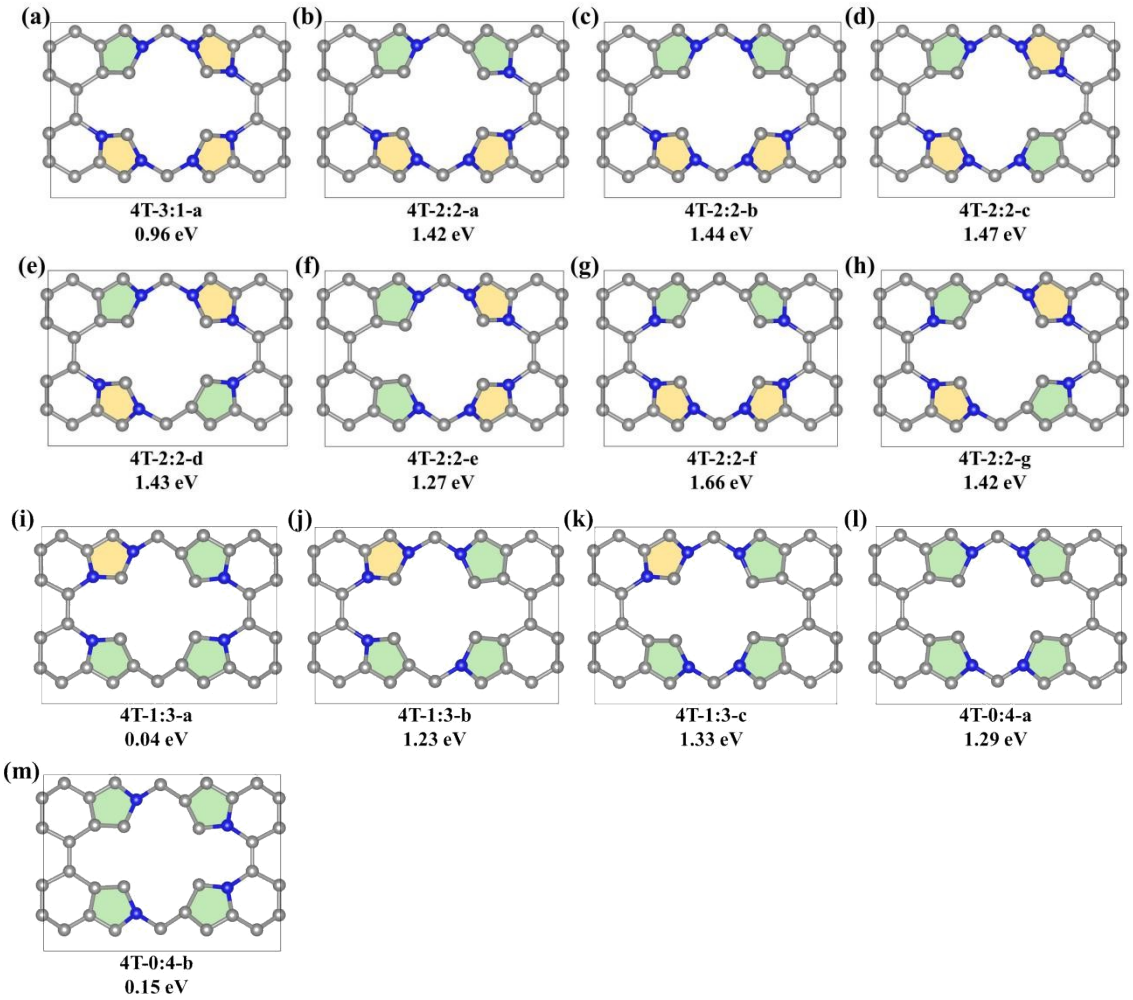


Fig. S2 The 4T structure with higher energy. (a) 4T-3:1-a, with 0.96 eV higher energy than 4T-3:1, (b)~(h) are 4T-2:2-a, 4T-2:2-b, 4T-2:2-c, 4T-2:2-d, 4T-2:2-e, 4T-2:2-f, 4T-2:2-g, with 1.42, 1.44, 1.47, 1.43, 1.27, 1.66, 1.42 eV higher energy than 4T-2:2, respectively. (i)-(k) for 4T-1:3-a, 4T-1:3-b, 4T-1:3-c, respectively, with energies 0.04,

1.23, 1.33 eV higher than 4T-1:3. (l)-(m) for 4T-0:4-a, 4T-0:4-b, respectively, with energies higher than 4T-0:4 1.29, 0.15 eV, respectively. The yellow and cyan regions represent NHC and CAAC fragments, respectively. Gray and blue balls represent C and N atoms, respectively.

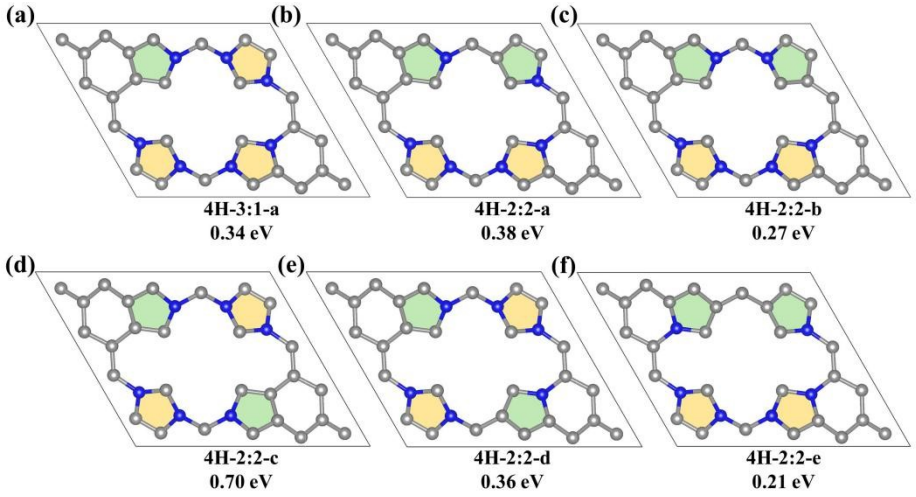


Fig. S3 The 4H structures with higher energy. (a) 4H-3:1-a, with 0.34 eV higher energy than 4T-3:1, (b)~(f) 4H-2:2-a, 4H-2:2-b, 4H-2:2-c, 4H-2:2-d, 4H-2:2-e, with 0.38, 0.27, 0.70, 0.36, 0.21 eV higher energy than 4H-2:2, respectively. The yellow and cyan regions represent NHC and CAAC fragments, respectively. Gray and blue balls represent C and N atoms, respectively.

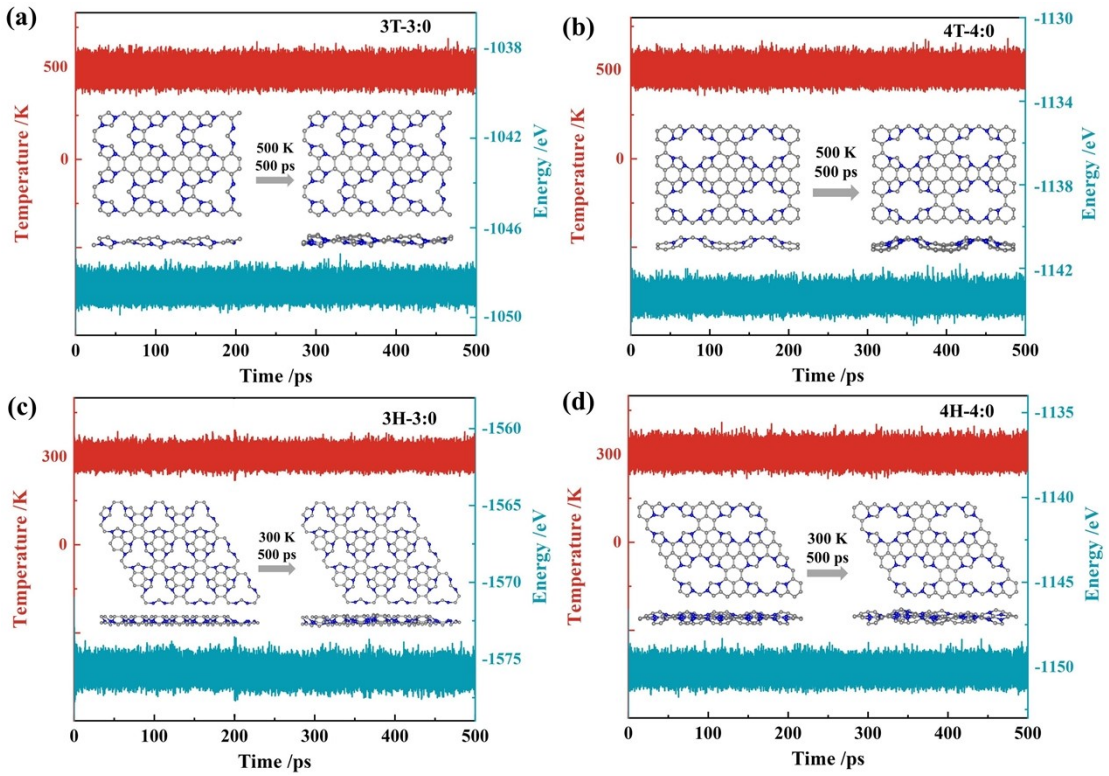
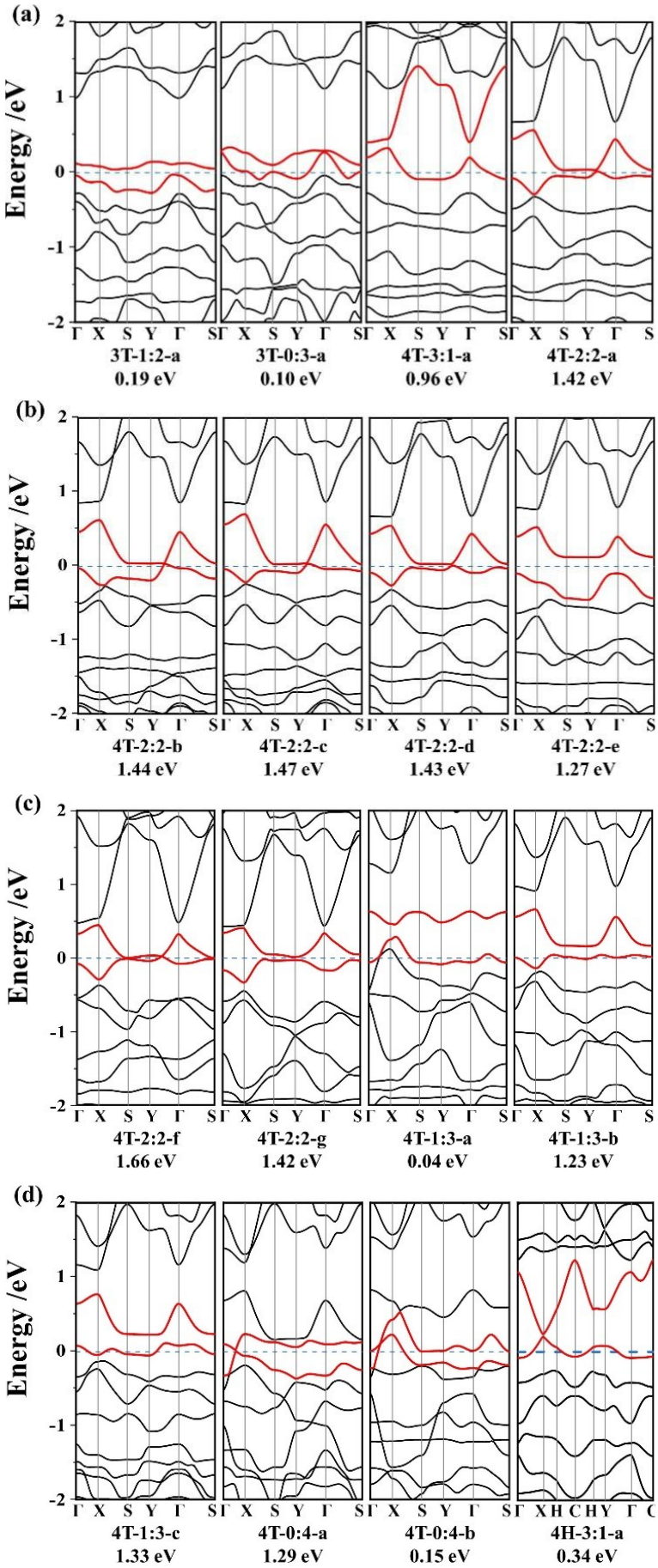


Fig. S4 The energy and temperature variations of the (a) 3T-3:0 and (b) 4T-4:0 structures in the 500 K AIMD simulation. The energy and temperature variations of the (c) 3H-3:0 and (d) 4H-4:0 structures in the 300 K AIMD simulation. The inset illustrates the top and side views of the structures after the 500 ps AIMD simulation. Gray and blue balls represent C and N atoms, respectively.


(a)
Energy /eV
2
1
0
-1
-2
Γ X S Y Γ S
3T-1:2-a
0.19 eV
3T-0:3-a
0.10 eV
4T-3:1-a
0.96 eV
4T-2:2-a
1.42 eV
(b)
Energy /eV
4T-2:2-b
1.44 eV
4T-2:2-c
1.47 eV
4T-2:2-d
1.43 eV
4T-2:2-e
1.27 eV
(c)
Energy /eV
4T-2:2-f
1.66 eV
4T-2:2-g
1.42 eV
4T-1:3-a
0.04 eV
4T-1:3-b
1.23 eV
(d)
Energy /eV
4T-1:3-c
1.33 eV
4T-0:4-a
1.29 eV
4T-0:4-b
0.15 eV
4H-3:1-a
0.34 eV

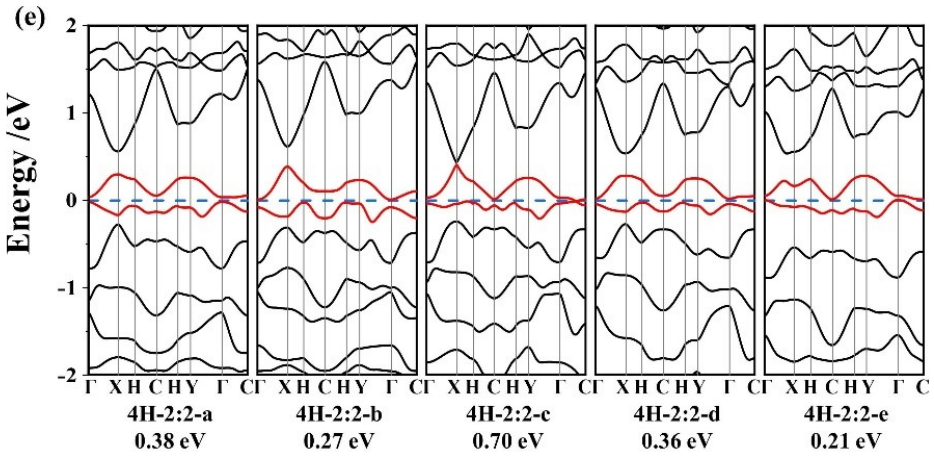


Fig. S5 The energy band structures of the NCMs with higher energy was calculated using the PBE method. The red lines indicate CB and VB. The Fermi level of PBE is set to 0 eV, marked by the blue dashed line (a) The energy band structures of 3T-1:2-a, 3T-0:3-a, 4T-3:1-a, 4T-2:2-a; (b) the energy band structures of 4T-2:2-b, 4T-2:2-c, 4T-2:2-d, 4T-2:2-e, (c) the energy band structures of 4T-2:2-f, 4T-2:2-g, 4T-1:3-a, 4T-1:3-b structure, (d) the energy band structures of 4T-1:3-c, 4T-0:4-a, 4T-0:4-b, 4H-3:1-a, (e) the energy band structures of 4H-2:2-a, 4H-2:2-b, 4H-2:2-c, 4H-2:2-d, 4H-2:2-e.

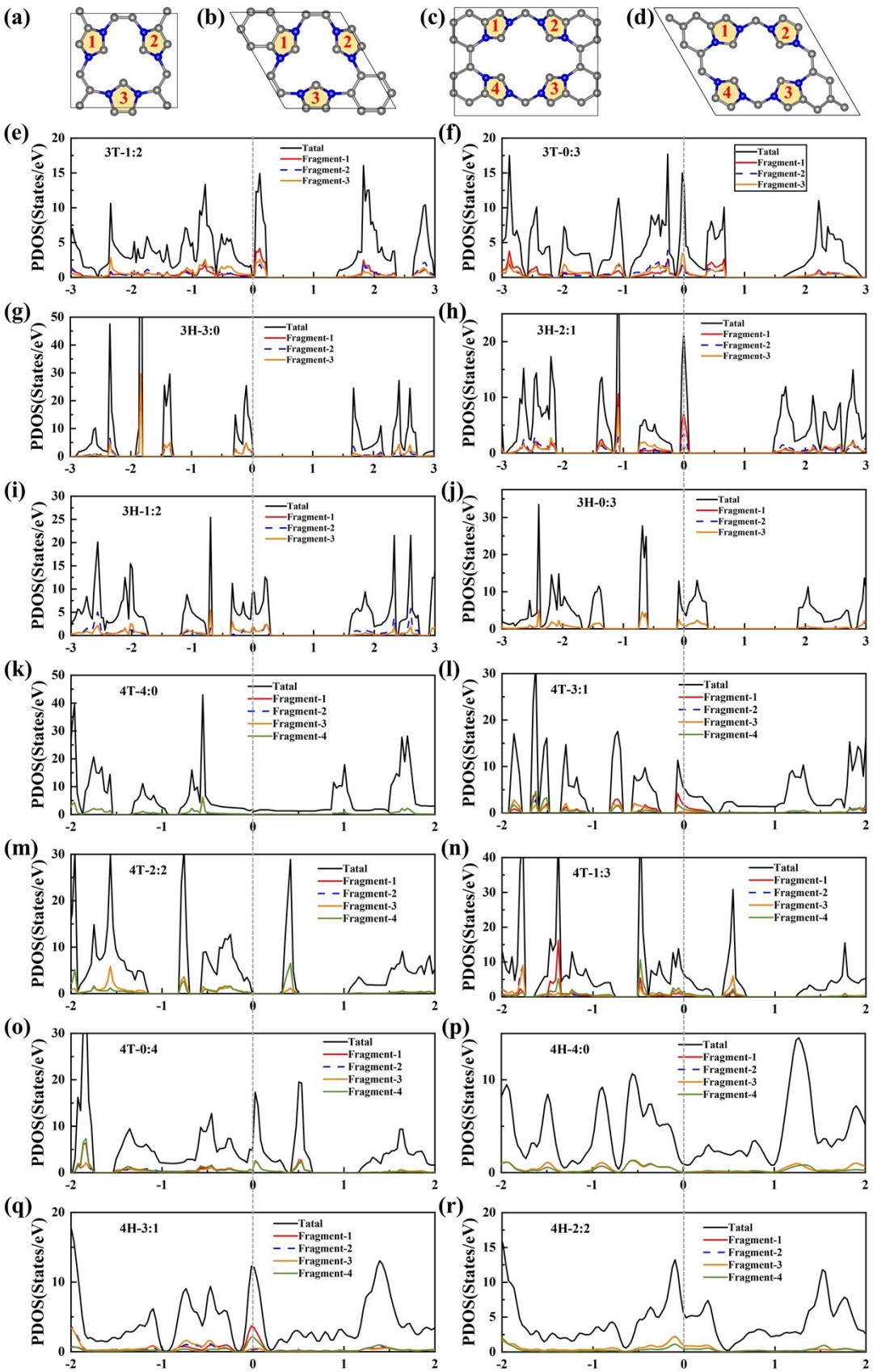


Fig. S6 The schematic diagrams of (a) 3T, (b) 3H, (c) 4T, and (d) 4H structures, with NHC and CAAC fragments sequentially labeled. Gray and blue balls represent C and

N atoms, respectively. (e)~(j) TDOS and PDOS for 3T-1:2, 3T-0:3, 3H-3:0, 3H-2:1, 3H-1:2, 3H-0:3, 4T-4:0, 4T-3:1, 4T-2:2, 4T-1:3, 4T-0:4, 4H-4:0, 4H-3:1, 4H-2:2, respectively. Black solid lines represent the TDOS, and colored lines represent the PDOS of fragments.

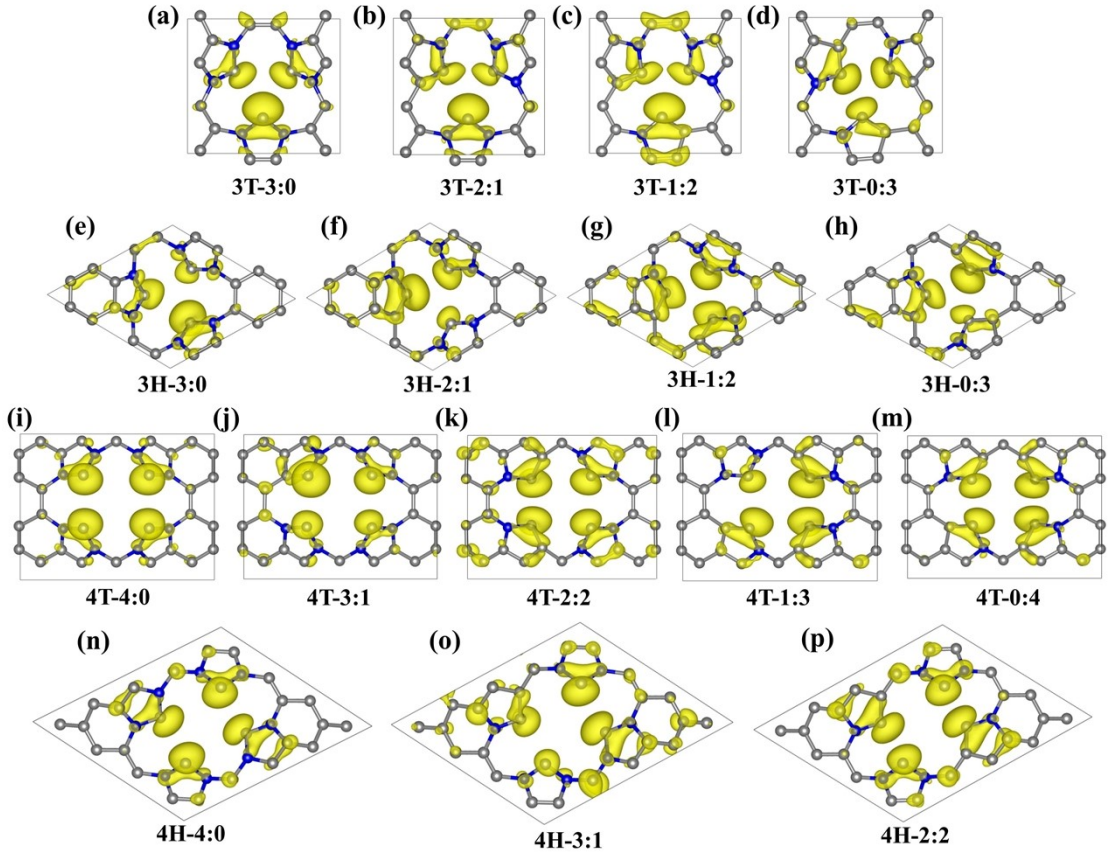


Fig. S7 Partial charge density at Γ-point of the 2nd band below the Fermi level for (a)3T-3:0, (b)3T-2:1, (c)3T-1:2, (d)3T-0:3. Partial charge density at Γ-point of the 2nd band below the Fermi level for (e)3H-3:0, (f)3H-2:1, (g)3H-1:2, (h)3H-0:3. Partial charge density at Γ-point of the 2nd band below the Fermi level for (i)4T-4:0, (j)4T-3:1, (k)4T-2:2, (l)4T-1:3, (m)4T-0:4. Partial charge density at Γ-point of the 2nd band below the Fermi level for (n)4H-4:0, (o)4H-3:1, (p)4H-2:2, the isosurface level is 0.005 e/Å^3. Gray and blue balls represent C and N atoms, respectively.

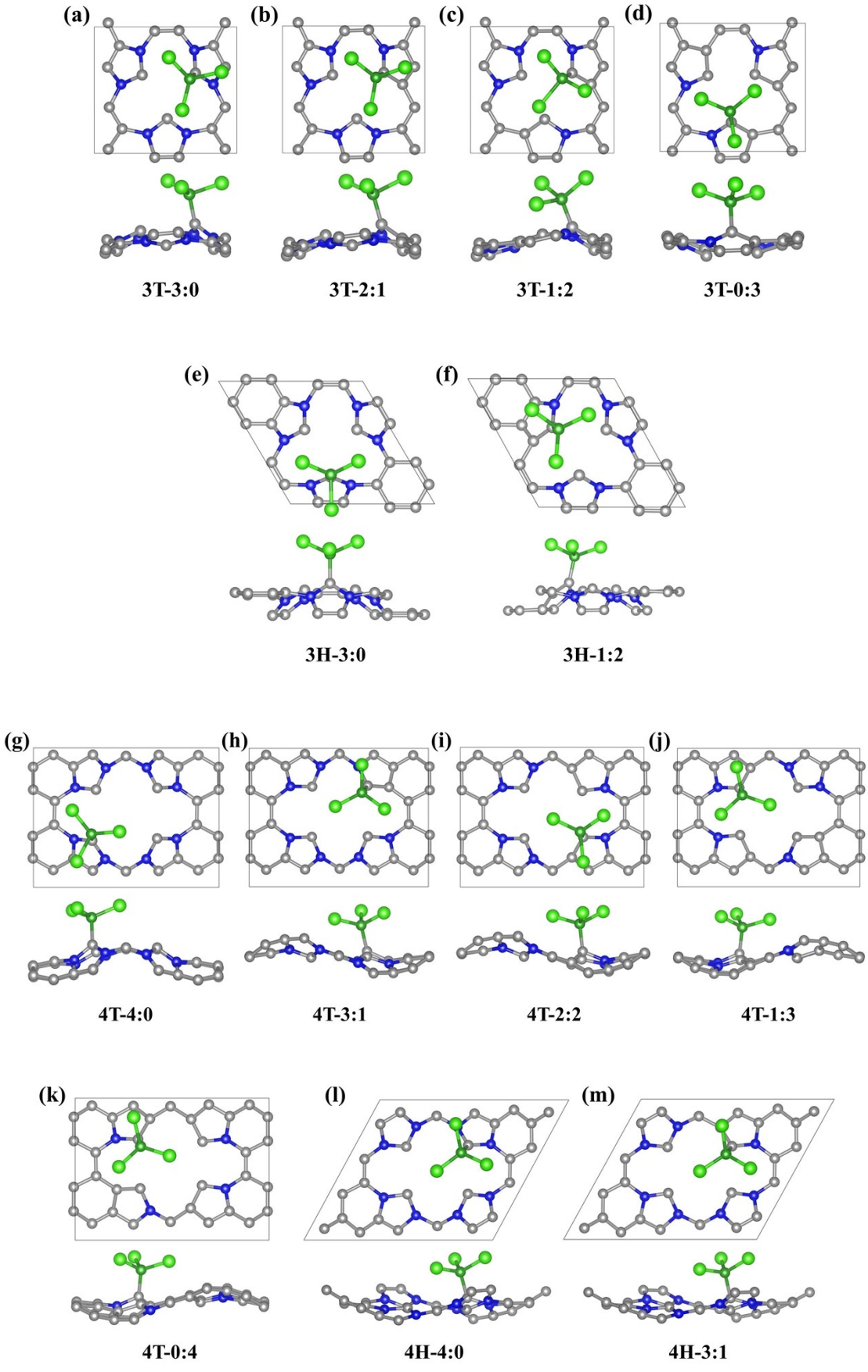
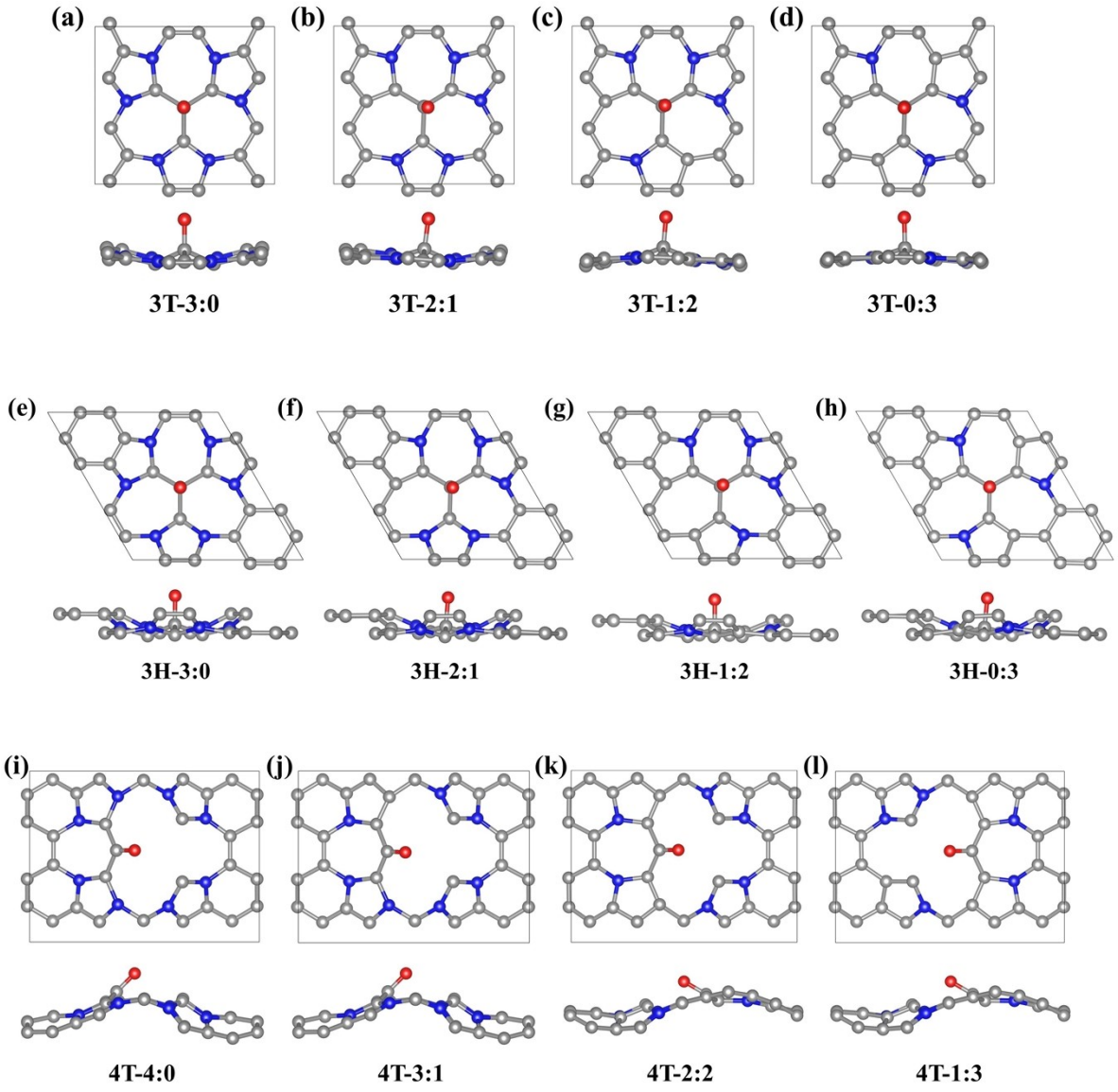


Fig. S8 Top and side view of NCMs adsorbed BCl_3. (a)~(d) are the adsorption structures

of 3T-3:0, 3T-2:1, 3T-1:2, 3T-0:3, respectively, (e)~(f) are the adsorption structures of 3H-3:0, 3H-1:2, respectively, (g)~(k) are the adsorption structures of 4T-4:0, 4T-3:1, 4T-2:2, 4T-1:3, 4T-0:4, respectively, (i)~(m) are the adsorption structure diagrams of 4H-4:0, 4H-3:1, respectively. Gray, blue, dark green and light green balls represent C, N, B, and Cl atoms, respectively.



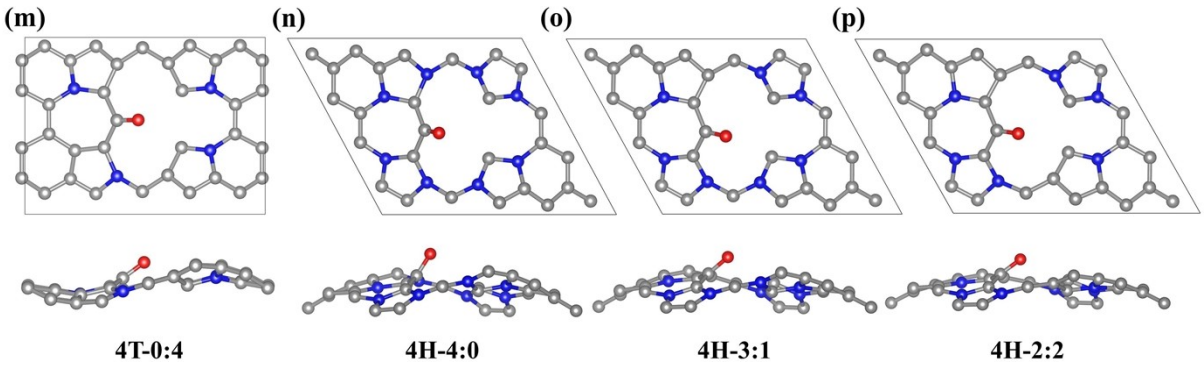


Fig. S9 Top and side view of NCMs adsorbed CO. (a)~(d) are the adsorption structures of 3T-3:0, 3T-2:1, 3T-1:2, 3T-0:3, respectively, (e)~(h) are the adsorption structures of 3H-3:0, 3H-2:1, 3H-1:2, 3H-0:3, respectively, (i)~(m) are the adsorption structures of 4T-4:0, 4T-3:1, 4T-2:2, 4T-1:3, 4T-0:4, respectively, (n)~(p) are the adsorption structure diagrams of 4H-4:0, 4H-3:1, 4H-2:2, respectively. Gray, blue, and red balls represent C, N, and O atoms, respectively.

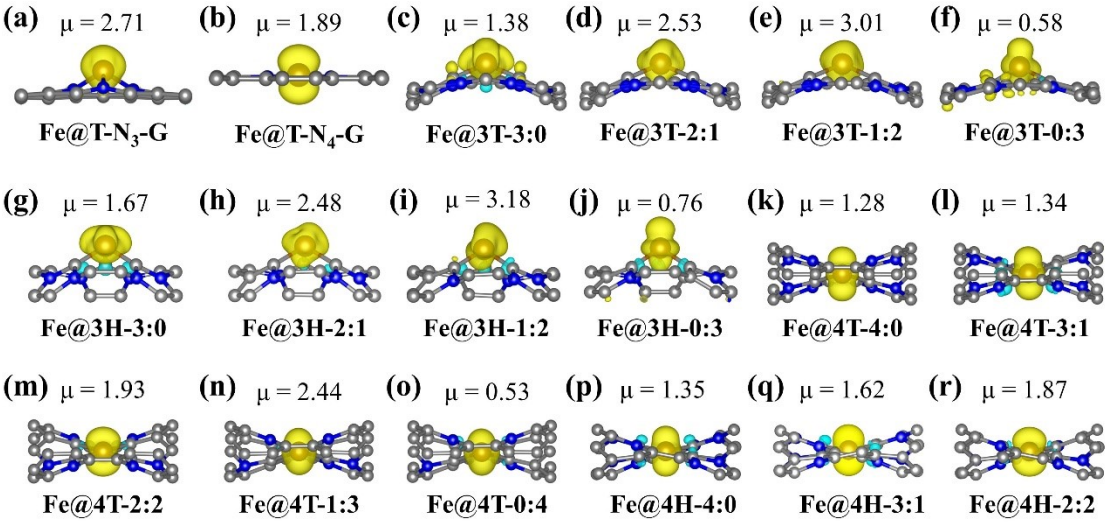


Fig. S10 The spin-resolved density figures of Fe adsorbed on (a) ~ (b) T-N_3-G, T-N_4-G, (c) ~ (f) 3T-3:0, 3T-2:1, 3T-1:2, 3T-0:3, (g) ~ (j) 3H-3:0, 3H-2:1, 3H-1:2, 3H-0:3, (k)~(o) 4T-4:0, 4T-3:1, 4T-2:2, 4T-1:3, 4T-0:4, and (p)~(r) 4H-4:0, 4H-3:1, 4H-2:2. The isosurface level is set to be 0.009 e/Å^3, and μ presents the spin magnetic moment of Fe atom. Gray and blue balls represent C and N atoms, respectively.