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

Supporting Information

Band Structure Engineering of Fluorine-Passivated Graphdiyne Nanoribbons via Doping with BN Pairs for Overall Photocatalytic Water Splitting

Junkang Xu, Qiang Wan, Zhonghui Wang, and Sen Lin*

State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350002, China

*Correspondence and requests for materials should be addressed to S. L. slin@fzu.edu.cn

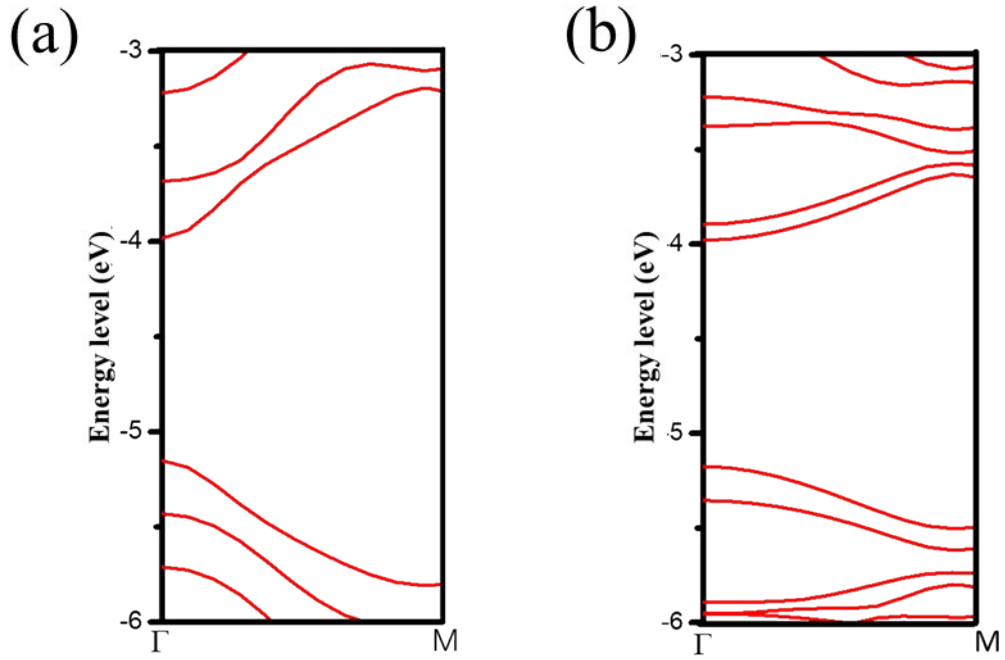


Fig S1 Electronic band structures of hydrogen-passivated GDYNRs (a) H_AC-GDYNR1 and (b) H_ZZ-GDYNR1 obtained by the PBE method. All energy levels are referenced to the vacuum level, which is set to zero.

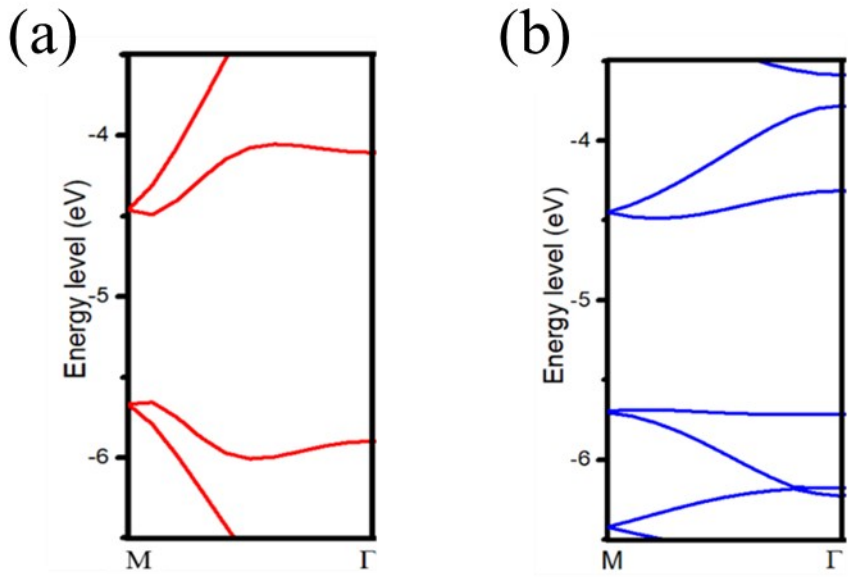


Fig S2 Electronic band structures of (a) F_AC-GDYNR2 and (b) F_ZZ-GDYNR2 obtained by the PBE method. The density of the charge carriers responsible for transport (i.e., the VBM states for holes and the CBM states for electrons) are shown at the right sides of figures. All energy levels are referenced to the vacuum level, which is set to zero.

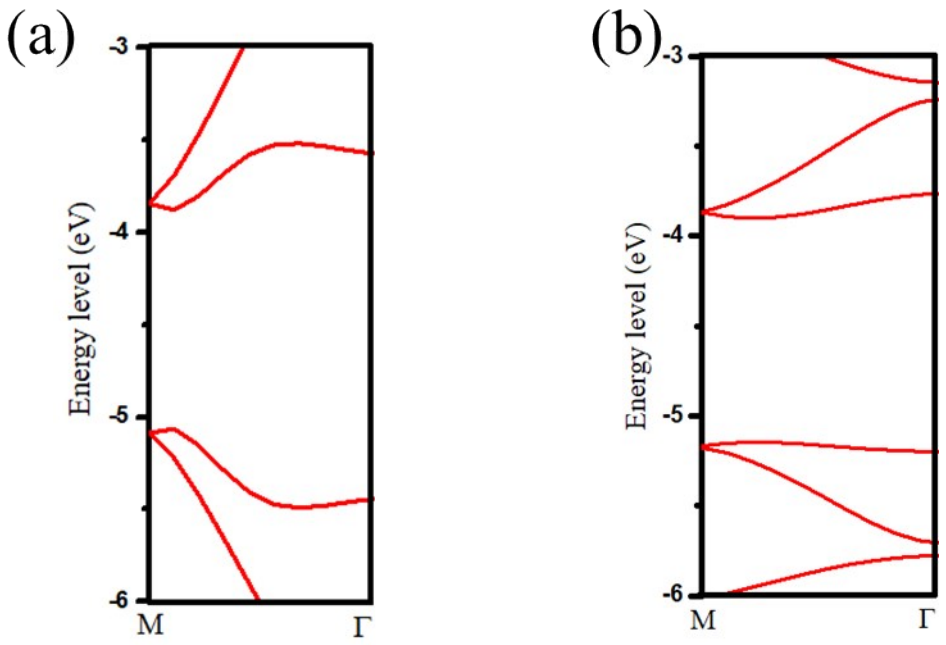


Fig S3 Electronic band structures of (a) H_AC-GDYNR2 and (b) H_ZZ-GDYNR2 obtained by the PBE method. All energy levels are referenced to the vacuum level, which is set to zero.

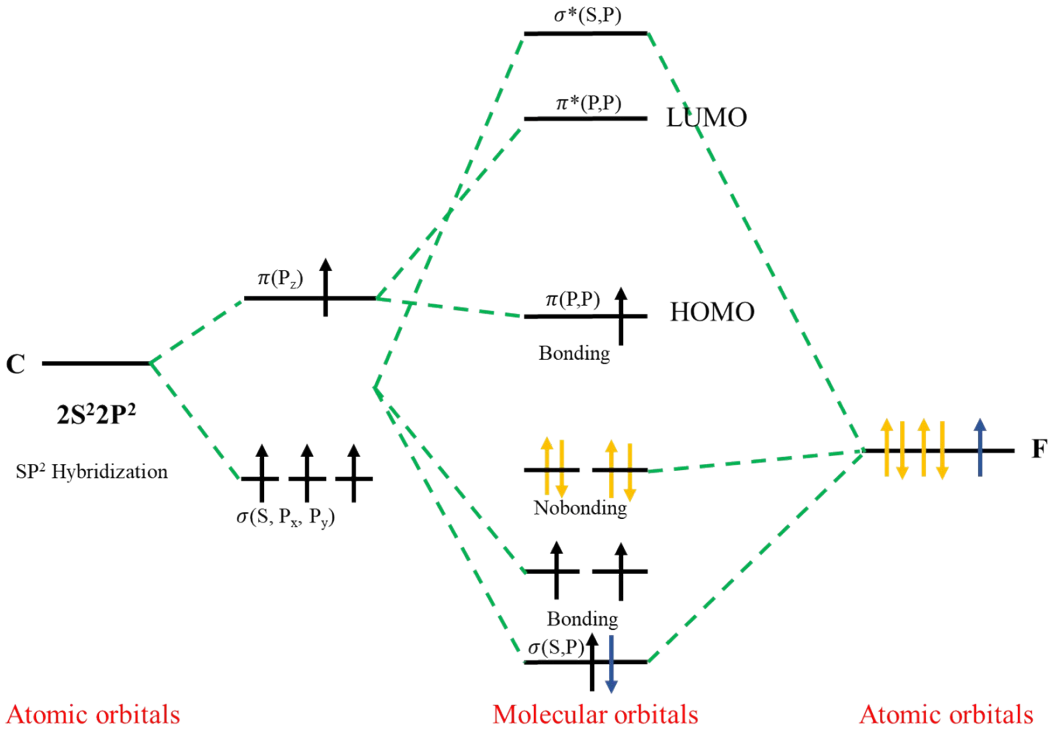


Fig S4. Schematic illustrating the hybrid molecular orbitals of C-C and C-F bonds in F_ZZ-GDYNR1 as an example. Here, s, p, p_x, p_y, and p_z represent the atomic orbitals, while σ, π and σ∗, π* represent the bonding and antibonding molecular orbitals, respectively.

Table S1. VBM and CBM band positions and band gap energies of F_GDYNRs with and without and B, N co-doping (see **Figs 1** and **4**). All results were obtained by the HSE06 method.

GDYNRs	VBM (eV)	CBM (eV)	Band gap (eV)
F_ZZ-GDYNR1	−5.70	−4.54	1.8
F-9BN_ZZ-GDYNR1	−6.20	−3.40	2.8
F-10BN_ZZ-GDYNR1	−6.31	−3.41	2.9
F_AC- GDYNR1	−5.70	−4.70	1.0
F-7BN_AC-GDYNR1	−6.10	−4.01	2.1
F-8BN_AC-GDYNR1	−6.00	−4.00	2.0
F_AC-GDYNR2	−5.75	−4.50	1.25
F-4BN_AC-GDYNR2	−6.29	−3.59	2.7
F_ZZ-GDYNR2	−5.70	−4.50	1.20
F-1BN_ZZ-GDYNR2	−6.12	−4.22	1.9
F-3BN_ZZ-GDYNR2	−6.26	−4.16	2.1

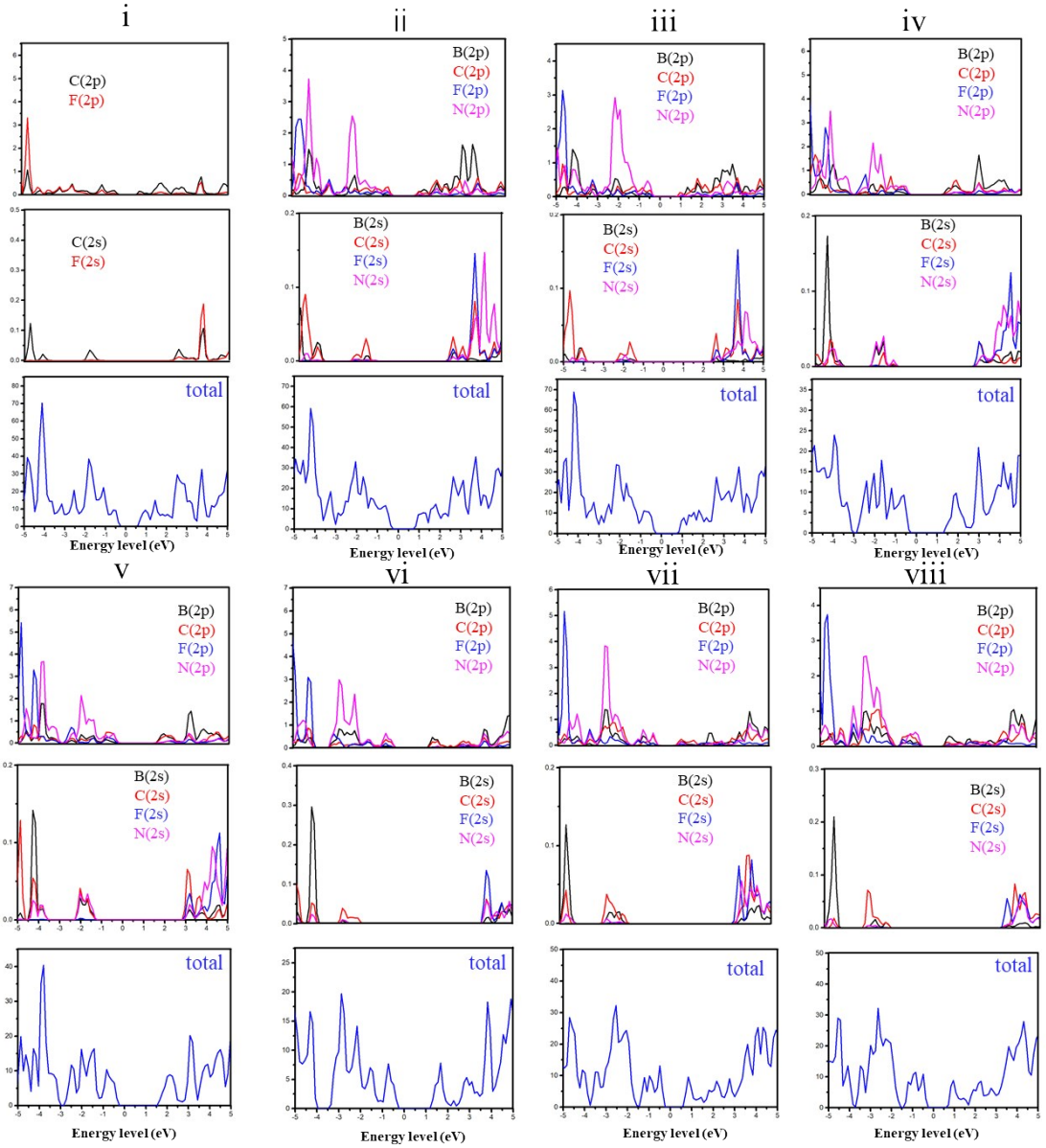


Fig S5. Projected density of state (PDOS) plots associated with boron (black), carbon (red), fluorine (blue), and nitrogen (pink) atoms, along with their totals for various F_GDYNRs with and without and B, N co-doping (see **Figs 1** and **4**). The Fermi level is set to zero.

Thermodynamics of water splitting

The micro kinetic process of water splitting reaction is modeled with the approach used by Nørskov and coworkers,[1, 2] which has been recently applied to two dimensional carbon nitride monolayer.[3] Two half reaction equations, i.e. OER and HER, are listed as below:

In the aqueous solution, the OER process generally involves four-electron oxidation steps, which can be written as:

$$H2O + * \rightarrow OH* + H+ + e- \quad (A)$$

$$OH* \rightarrow O* + H+ + e- \quad (B)$$

$$O*+ H2O \rightarrow OOH* + H+ + e- \quad (C)$$

$$OOH* \rightarrow * + H^{+} + O2 + e- \quad (D)$$

Or O-O coupling:

$$O*+ H2O \rightarrow OH* + O* + H+ + e- \quad (H)$$

$$OH* + O* \rightarrow H^{+} + OO* + e- \quad (N)$$

$$OO* \rightarrow * + O2 \quad (M)$$

Where * denotes the adsorption site, OH*, O* and OOH* denote the adsorbed intermediates.

$$\Delta G(A) = G(OH^{*}) + 0.5 * G(H_2(g)) - G(H_2O(l)) - G(*) - \Delta G_U - \Delta G_{PH}$$

$$\Delta G(B) = G(O^{*}) + 0.5 * G(H_2(g)) - G(OH^{*}) - \Delta G_U - \Delta G_{PH}$$

$$\Delta G(C) = G(OOH^{*}) + 0.5 * G(H_2(g)) - G(H_2O(l)) - G(O*) - \Delta G_U - \Delta G_{PH}$$

$$\Delta G(D) = G(*) + 0.5 * G(H_2(g)) + G(O_2(g)) - \Delta G_U - \Delta G_{PH}$$

$$\Delta G(H) = G(OH^{*}) + G(O^{*}) + 0.5 * G(H_2(g)) - G(H_2O(l)) - G(O*) - \Delta G_U - \Delta G_{PH}$$

$$\Delta G(N) = G(OO*) + 0.5 * G(H_2(g)) - G(O^{*}) - G(OH^{*}) - \Delta G_U - \Delta G_{PH}$$

$$\Delta G(M) = G(*) + G(O_2(g)) - G(OO*) - \Delta G_U - \Delta G_{PH}$$

Meanwhile, the HER process with two-electron pathways, including a fast ptoton/electron transfer step and a fast hydrogen release step, can be written as:

$$* + H+ + e- \rightarrow H* \quad (E)$$

$$H* + H+ + e- \rightarrow *+ H2 \quad \text{(F)}$$

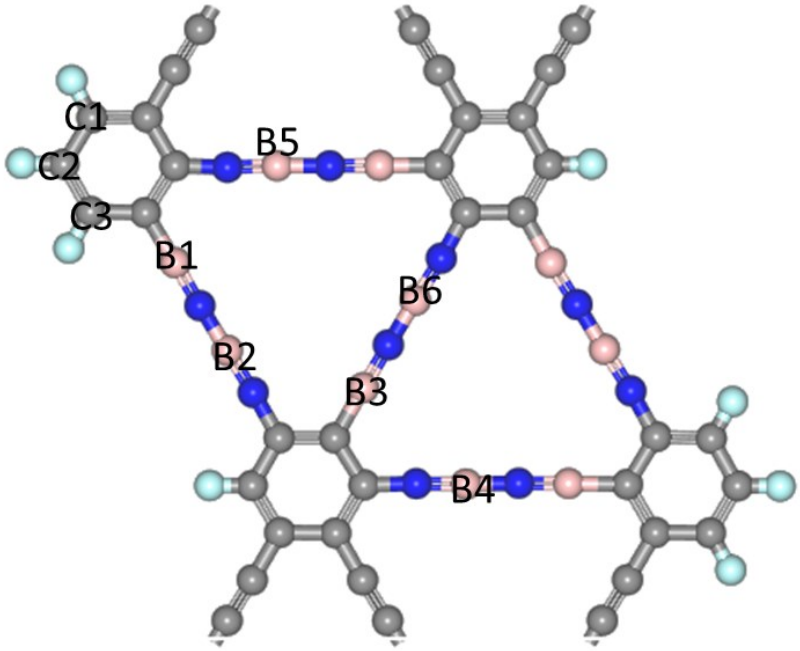
Where * denotes the adsorption site, H* denote the adsorbed intermediates.

$$\Delta G(E) = G(H^*) - 0.5 * G(H_2(g)) - G(*) - \Delta G_U + \Delta G_{PH}$$

$$\Delta G(F) = G(*) + G(H_2(g)) - G(H^*) - 0.5 * G(H_2(g)) - \Delta G_U + \Delta G_{PH}$$

Here, the values of TS and ZTP are 0.67 and 0.56 eV for H_2O, 0.41 and 0.27 eV for H_2, 0.64 and 0.10 eV for O_2, respectively. The ΔG of full reaction, *i.e.*$2H_2+ O_2 \rightarrow 2H_2O$, is set to 4.92 eV. Note that the total free energy here is -14.57 eV for H_2O molecule with PBE+D2 method. For $H_2$and O_2, these values are -6.91 and -10.40 eV, respectively.

Table S2. Values of ΔG obtained for the rate-determining steps of water oxidation and hydrogen reduction half reactions with different adsorption sites on the photocatalyst based on F-10BN_ZZ-GDYNR1 at pH = 7. The most active sites for the two reactions are given in bold font. These results indicate that the water oxidation and hydrogen reduction reactions can proceed spontaneously only at sites B_1 and C_3, respectively.

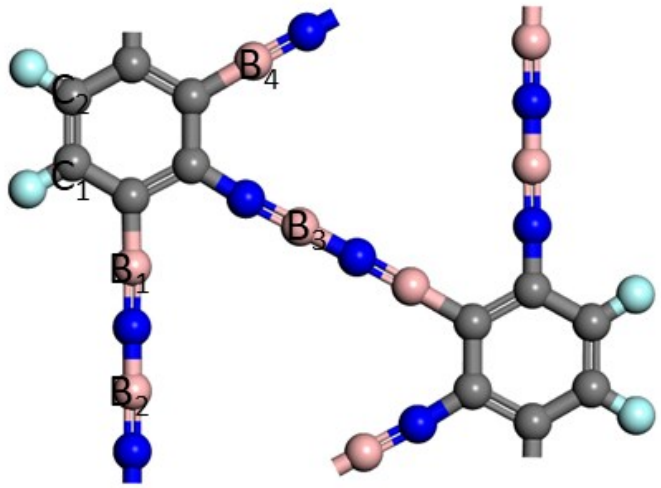


Adsorption site	C_1 (eV)	C_2 (eV)	C_3 (eV)	B_1 (eV)	B_2 (eV)	B_3 (eV)	B_4 (eV)	B_5 (eV)	B_6 (eV)
Water Oxidation	3.31	2.97	3.30	**1.73**	1.76	3.24	2.39	1.77	3.9
Hydrogen Reduction	0.69	0.74	**0.64**	0.98	0.91	1.08	1.03	1.02	0.97

Table S3. Zero point energy (*ZPE*), product of temperature and entropy (*TS*), absorption energy (*E*), and Gibbs free energy (*G*) of the various species involved in the water splitting reaction on F-10BN_ZZ-GDYNR1 at *T* = 298.15 K.

Species (ev)	*ZPE* (eV)	*TS* (eV)	*E* (eV)	*G* (eV)
H_2	0.29	0.41	−6.77	−6.91
H_2O	0.57	0.67	−14.47	−14.57
O*	0.12	0	−505.74	−505.62
OH*	0.91	0	−511.55	−510.64
OOH*	0.93	0	−515.52	−514.59
OH-O*	0.40	0	-515.07	-514.67
OO*	0.16	0	-510.57	-510.41
*	0	0	−500.07	−500.07
H*	0.24	0	−503.20	−502.96

Table S4. Values of ΔG obtained for the rate-determining steps of water oxidation and hydrogen reduction half reactions with different adsorption sites on the photocatalyst based on F-8BN_AC-GDYNR1 at pH = 7. The most active sites for the two reactions are given in bold font. These results indicate that the water oxidation and hydrogen reduction reactions can proceed spontaneously only at sites B_3 and C_2, respectively.



Adsorption site	C_1 (eV)	C_2 (eV)	B_1 (eV)	B_2 (eV)	B_3 (eV)	B_4 (eV)
Water Oxidation	2.90	2.30	2.31	1.82	**1.52**	4.01
Hydrogen Reduction	1.46	**1.09**	1.45	1.46	1.5	1.63

Table S5. Energy components of the various species involved in the water splitting reaction on F-8BN_AC-GDYNR1 at T = 298.15 K.

Species	*ZPE* (eV)	*TS* (eV)	*E* (eV)	*G* (eV)
H_2	0.29	0.41	−6.77	−6.91
H_2O	0.57	0.67	−14.47	−14.57
O*	0.12	0	−252.95	−252.83
OH*	0.91	0	−259.06	−258.15
OOH*	0.93	0	−262.94	−262.01
*	0	0	−247.25	−247.25
H*	0.24	0	−249.86	−249.62

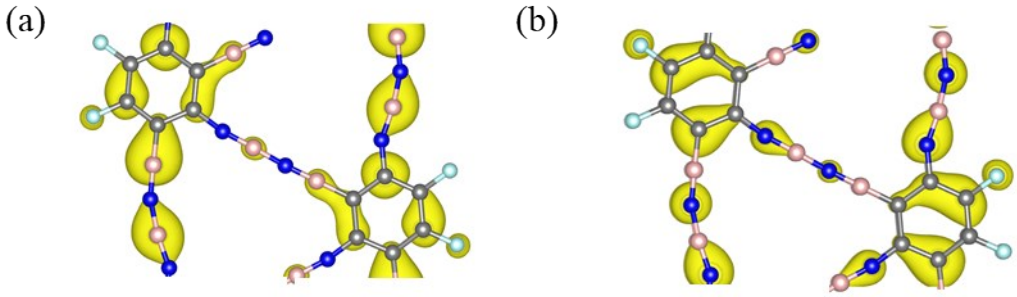


Fig S6. Charge density plots of the CBM (a) and the VBM (b) for the F-10BN_ZZ-GDYNR1 monolayer systems respectively illustrated in Figures 4 (i)

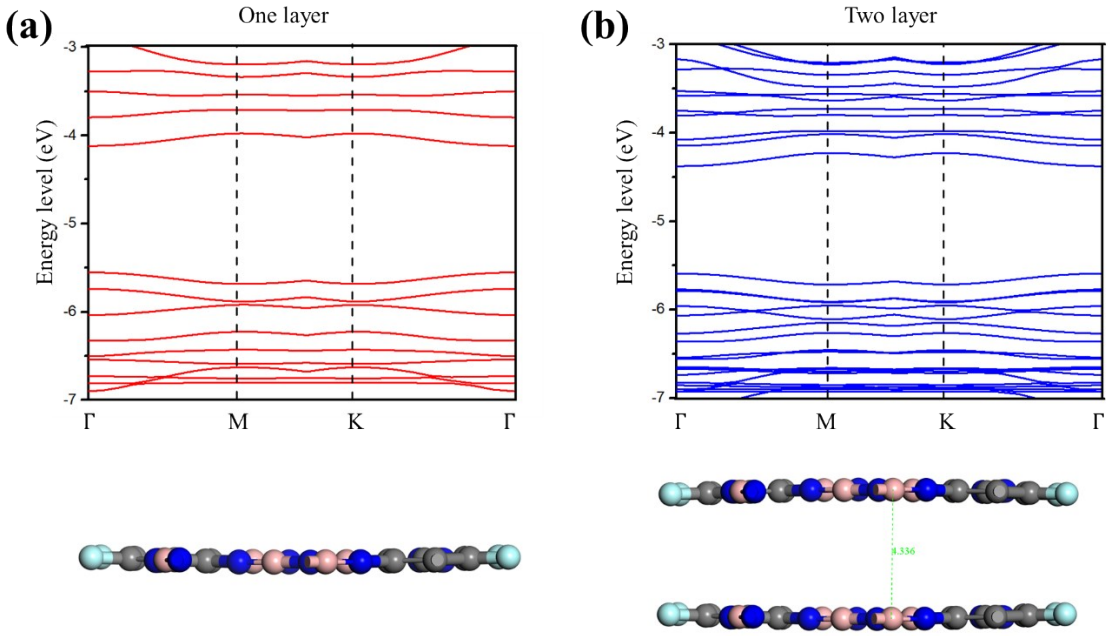


Fig S7. The calculated band structures of F-4BN_AC-GDYNR1 (a) without and (b) with stacking.

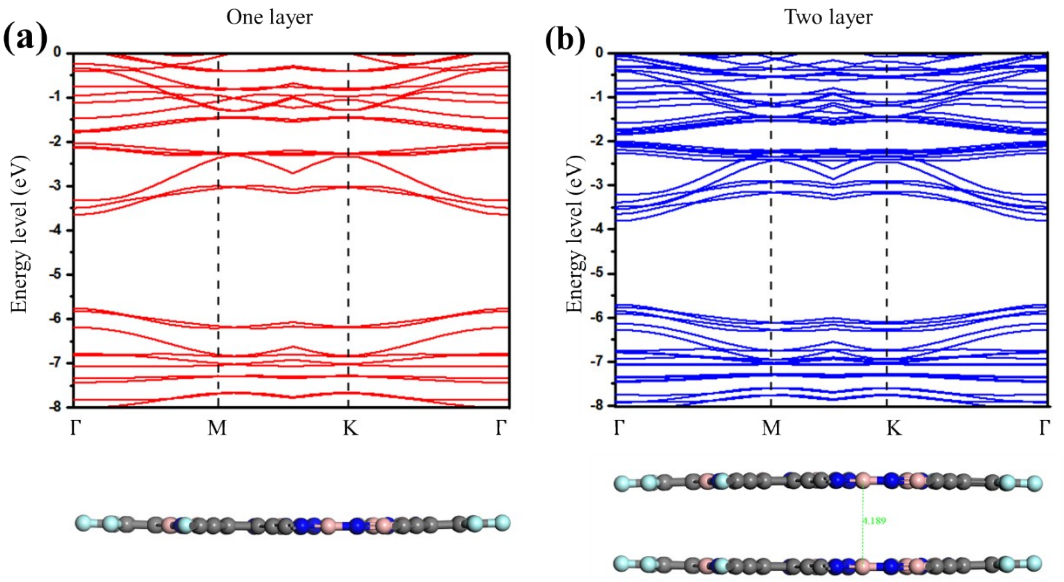


Fig S8. The calculated band structures of F-10BN_ZZ-GDYNR1 (a) without and (b) with stacking.

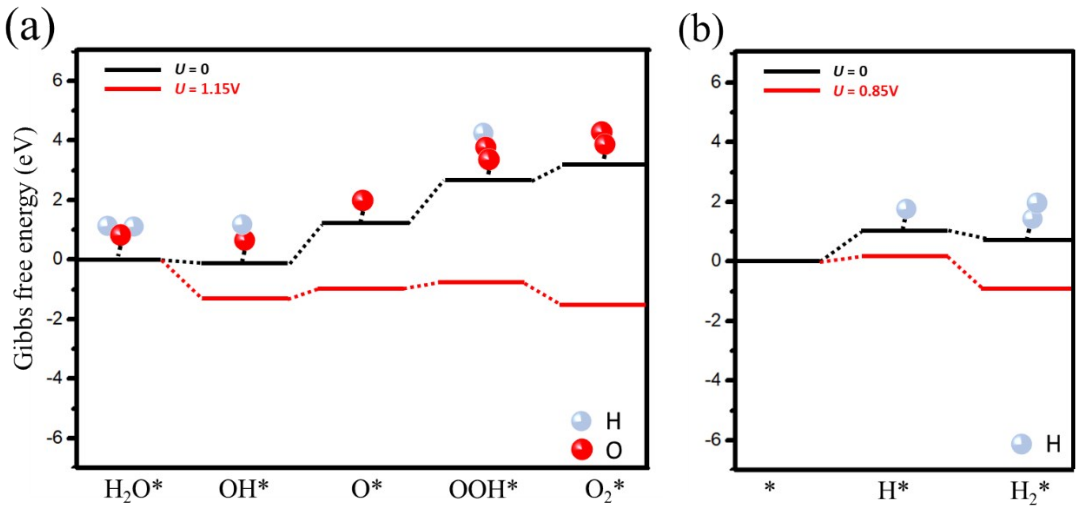


Fig S9. Reaction steps of **(a)** the OER and **(b)** the HER on F-8BN_AC-GDYNR1 under different electrode potentials *U* referenced to the SHE at pH = 7.

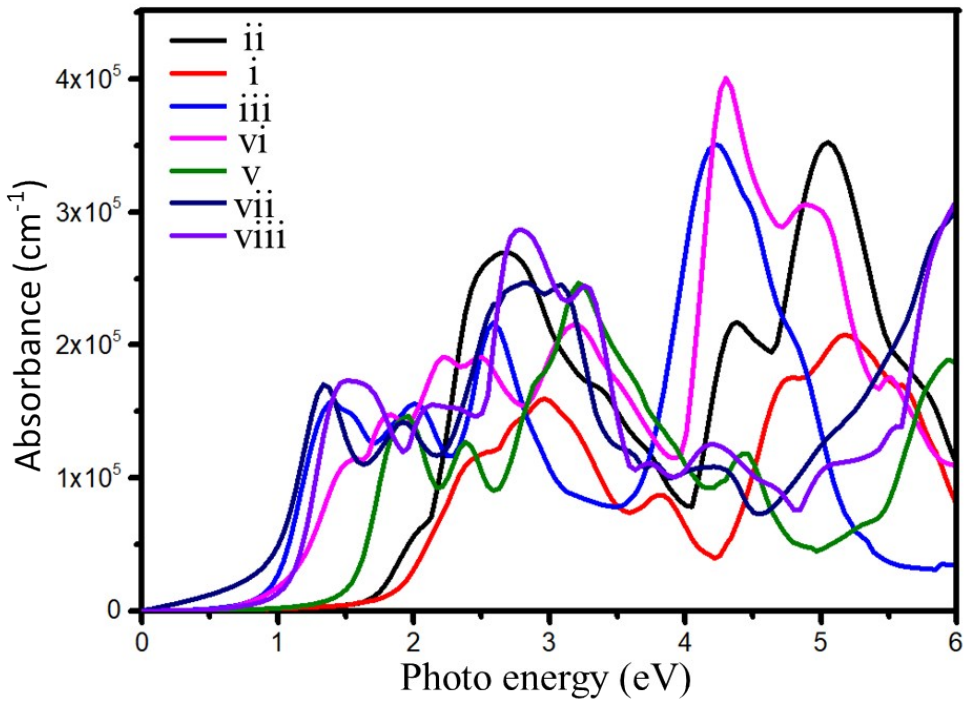


Fig S10. Optical absorption spectra of various F_GDYNRs with and without B, N co-doping (see **Figs 1** and **4**).

References

[1] Á. Valdés, Z.-W. Qu, G.-J. Kroes, J. Rossmeisl, J.K. Nørskov, *J. Phys. Chem. C 112*(2008) 9872-9879.

[2] J. Rossmeisl, Z.-W. Qu, H. Zhu, G.-J. Kroes, J.K. Nørskov, *J. Electroanal. Chem. 607*(2007) 83-89.

[3] J. Wirth, R. Neumann, M. Antonietti, P. Saalfrank, *Phys. Chem. Chem. Phys. 16*(2014) 15917-15926.