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

Electronic Supplementary Information (ESI)

A Simple Molecular Design for Tunable Two-Dimensional Imine Covalent Organic Frameworks for Optoelectronic Applications

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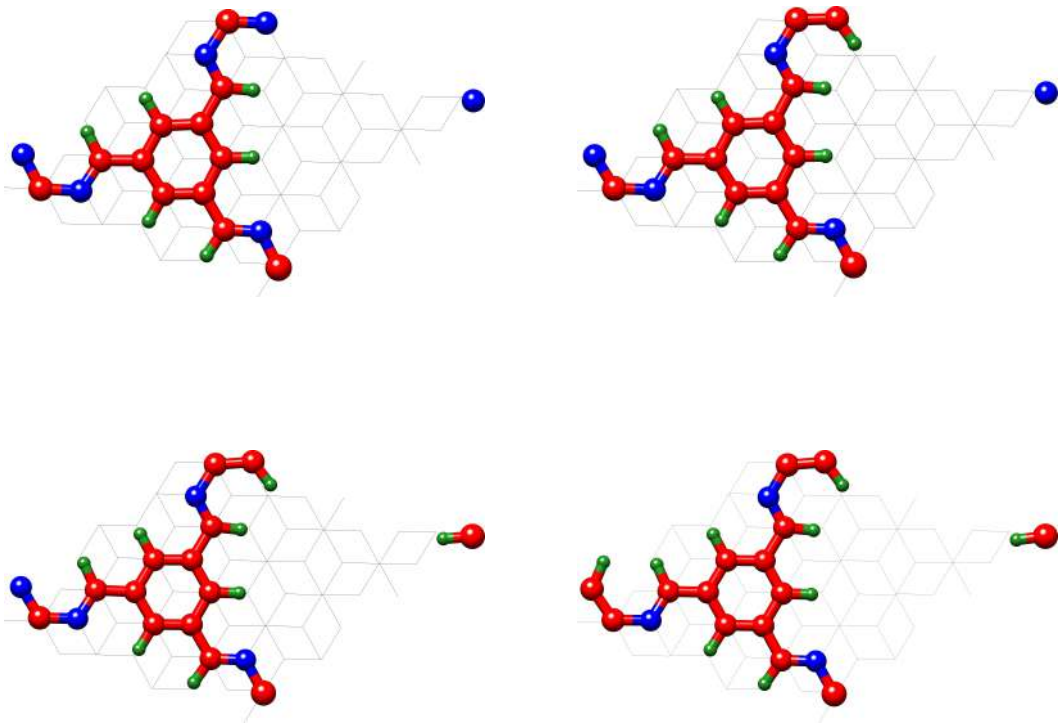

Fig. 1 Theoretically optimized structure of different 2D COFs on HOPG. Red, blue and green represents elements like carbon, nitrogen, hydrogen, respectively in 2D COF sheet. The HOPG sheet is shown as wired network.

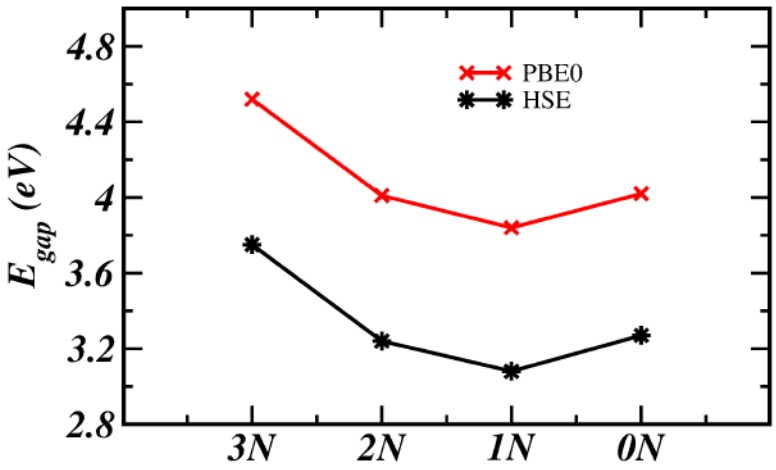

Fig. 2 Variation in bandgap of 2D COFs with nitrogen percentage calculated using hybrid functionals.

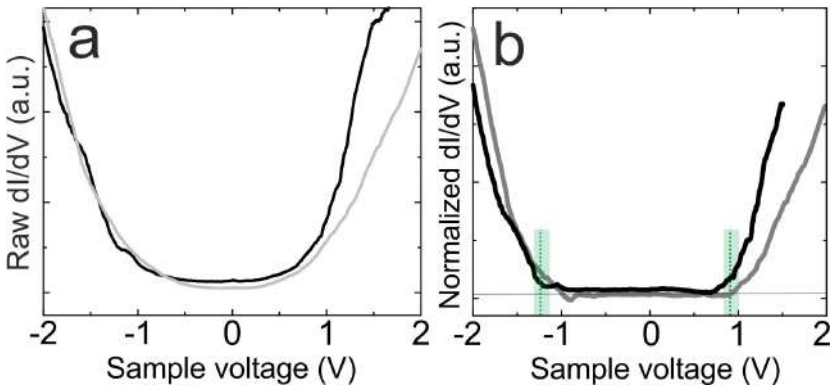

Fig. 3 (a) The raw differential conductivity (dI/dV) obtained on 2N COF on HOPG. (b) Normalized dI/dV obtained by subtracting graphite contribution form raw dI/dV. Dashed green lines in the normalized dI/dV show the valance band maximum and conduction band minimum.

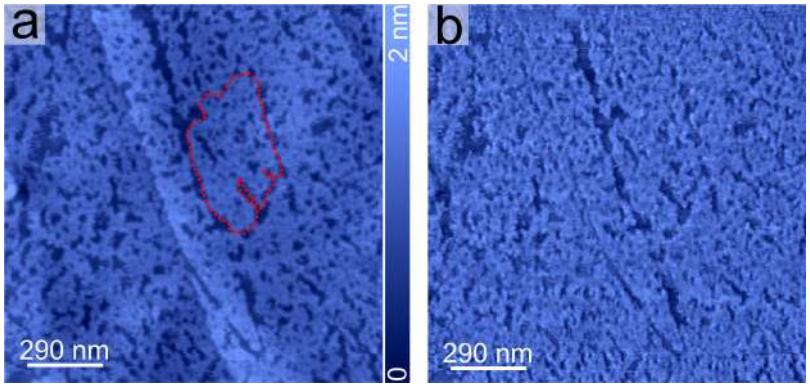

Fig. 4 Constant force AFM topograph (a)and phase image (b) of 2N-COF prepared from TCA (Benzene-1,3,5-tricarboxaldehyde) and PTA (pyrimidine-2,4,6-triamine). The bright regions correspond to COF (marked by red dashed line) and the dark blue depicts graphite.

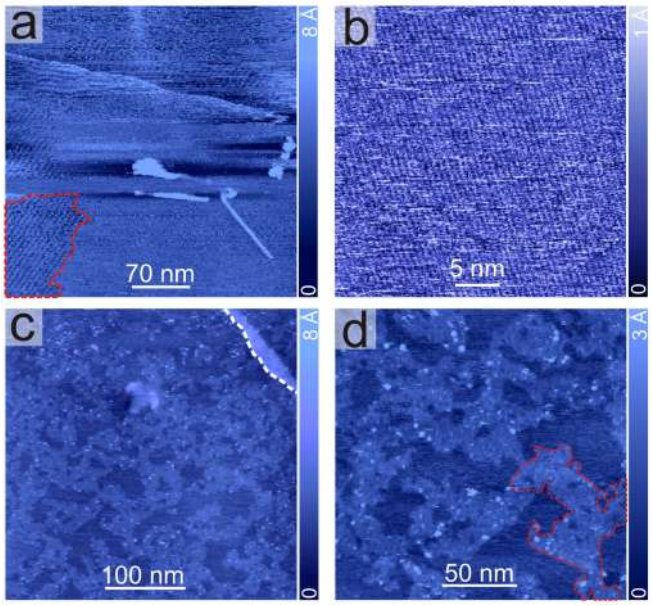

Fig. 5 STM topographs of 2N-COF obtained from two independent regions. Typically two types of domains are observed; uniform smooth domains typically of a few hundreds of nm large (a,b) and fractal-like growth with small domains interconnected (c,d). Area marked with red dashed line in (a) shows a single domain of 2N-COF. The periodic line like feature (marked with red dashed lines) inside the domain corresponds to the molecular level contrast of COF (Figure S4b). The inter line spacing is $\sim$6.2 Å, which corresponds to half of the unit cell parameter of the 2N-COF obtained from calculations. Bright regions in (c) represent 2D-COF (marked with red dashed lines) and dark blue regions corresponds to graphite. Further zoom of (c) is shown in (d).

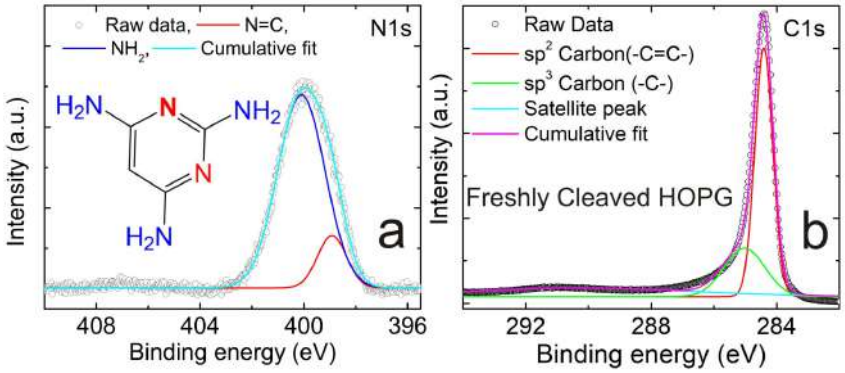

Fig. 6 X-ray photoelectron spectroscopy (XPS) recorded on the thin film of 2,4,6- pyrimidine- triamine, PTA (a) and on freshly cleaved HOPG. N1s region of PTA shows two major resonances corresponding to -N=C- (imine) and -NH2 (amine) nitrogen. Amine nitrogen is the major contribution as expected from the stoichiometry (see structure of PTA in the inset). C1s band shows major resonances corresponding to SP2 carbon.

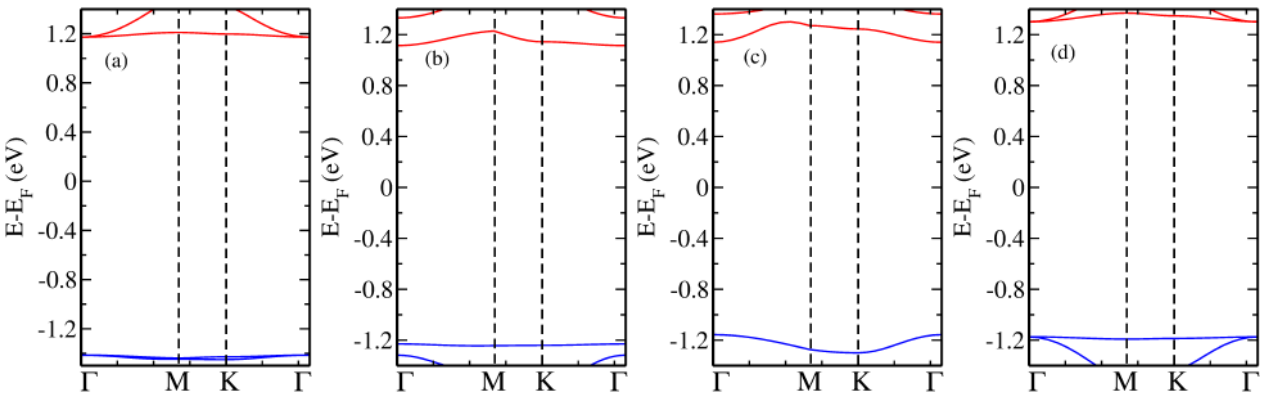

Fig. 7 Zoom in view of the band structure of (a–d) freely-standing 2D COFs from 3N to 0N calculated using PBE+D2 functional, respectively.

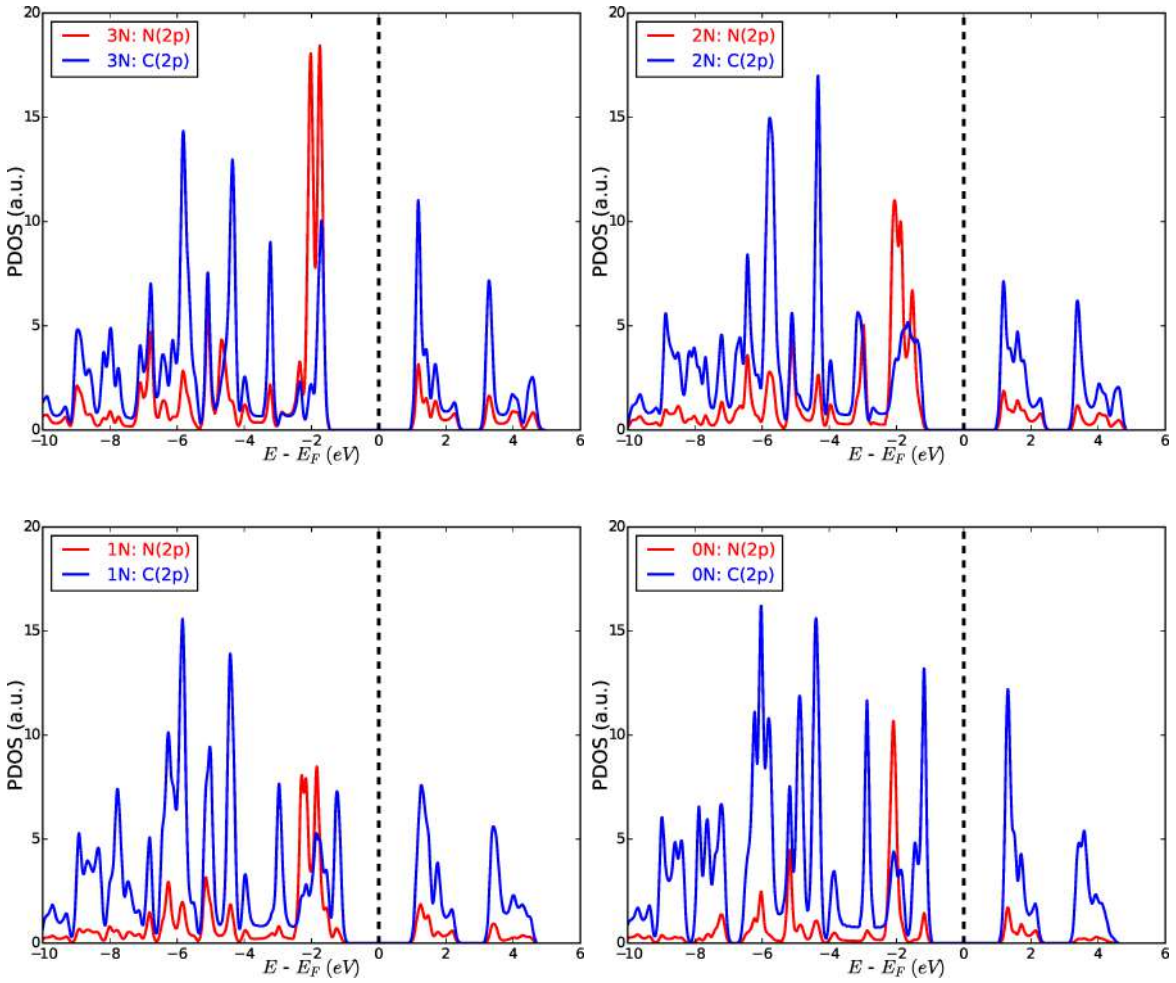

Fig. 8 Partial density of states (PDOS) of 2D COFs from 3N to 0N calculated using BLYP+D2 functional.

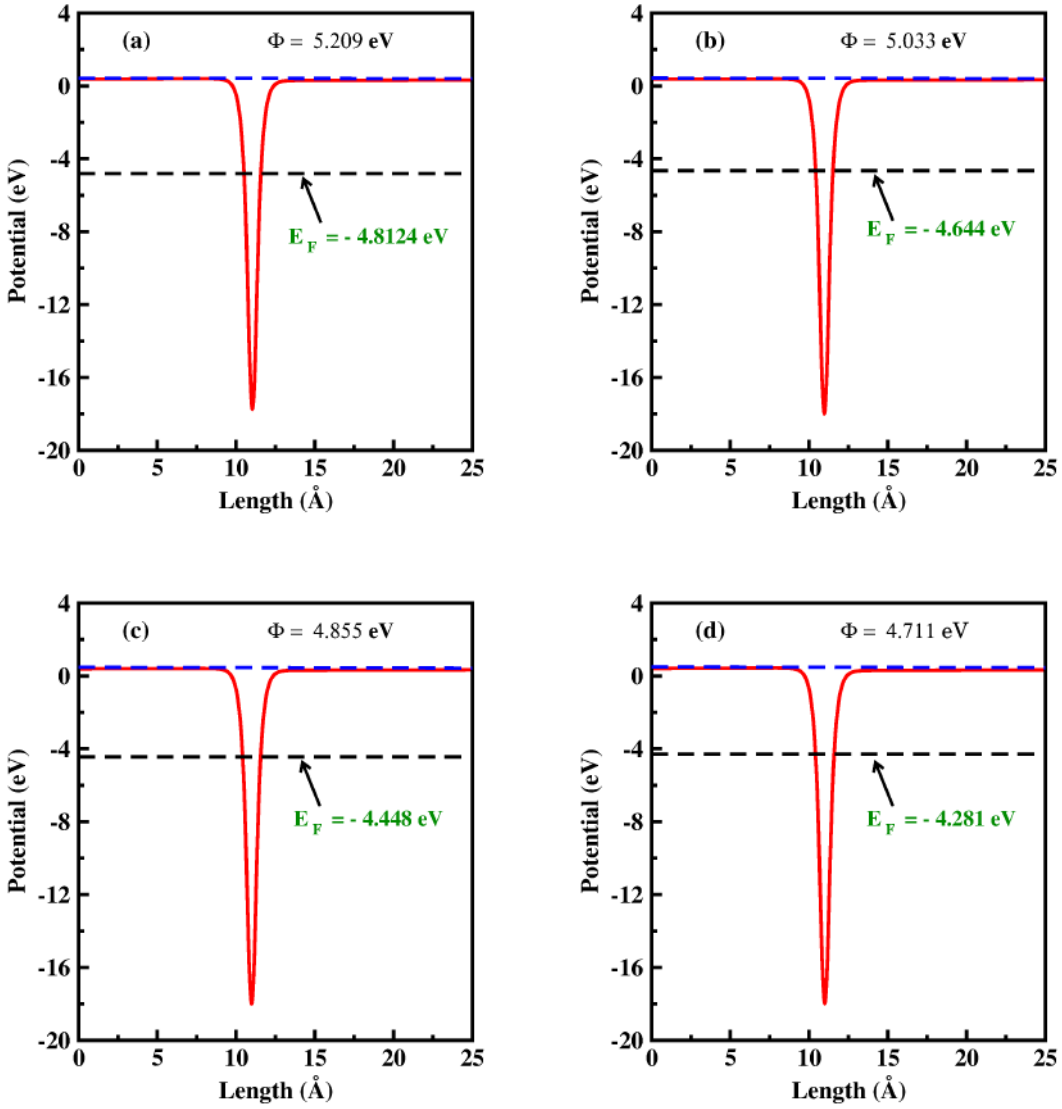

Fig. 9 Work function of 2D-COFs from 3N to 0N calculated using PBE+D2 functional. The work function was determined by calculating the average electrostatic vacuum potential of a 2D-COF and then subtracting from it the Fermi energy. Also, in the figure, the red line represents the average electrostatic vacuum potential, black line denotes the Fermi energy, and blue line corresponds to the work function.

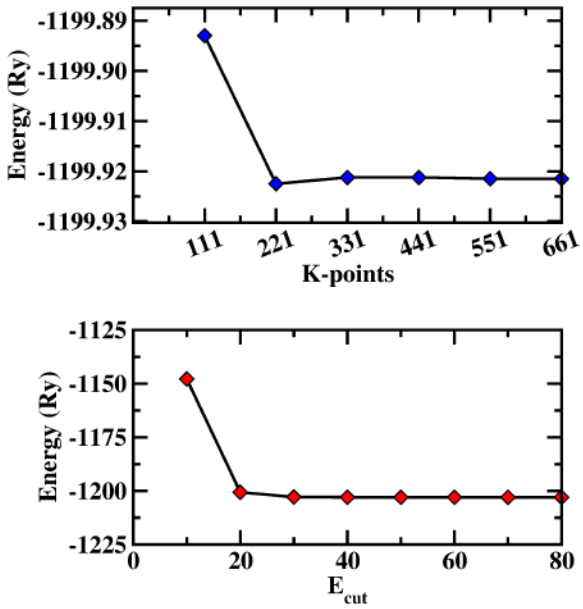

Fig. 10 Benchmark calculation for 2D COFs to obtain the optimized Ecut and k-points.

Optimized coordinates

0N-COF

TITLE 0N-COF

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