

Computational prediction of structure and electronic properties of monolayer and few-layer 2D polyimide covalent organic frameworks

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In contrast to similar and more established groups of materials, such as zeolites and metal organic frameworks, covalent organic frameworks (COFs) are distinctively built only from organic elements – carbon, oxygen, hydrogen, and often nitrogen or boron. They create light, mechanically rigid and chemically inert networks which have many advantages but also create issues with developing large-scale films or membranes because of low solubility and processability [1]. Together with a lack of strong coordination bonds, which direct the design and synthesis in case of frameworks that contain transition metal ions, it has slowed the progress in COF synthesis and characterization. Recently though, more robust design strategies have led, e.g., to first reports of bulk produced and single-crystal 2D COFs [2]. With the possibility in sight of controllable synthesis of monolayer and few-layer frameworks, they are on the path to becoming interesting candidates for integration in optoelectronic devices, similar to other layered 2D materials. Meanwhile, the rigidity and low solubility of COF that have hampered their development are becoming their valuable traits in device integration.

Imide COFs [3] in particular exemplify these characteristics by containing sp^2 carbon and a fair amount of enamine ($-C-N-$) instead of imine ($-C=N-$) bonds, both of which stabilize the crystal structure [1]. Here, we report the results of DFT calculations of such materials in the form of monolayers and AA and AB-stacked multilayers. We find the multilayers to be stable and with varying electronic properties. In particular, the finite band gap exhibited by every structure (monolayer and stacked) is sensitive to atomic arrangement of the atoms.

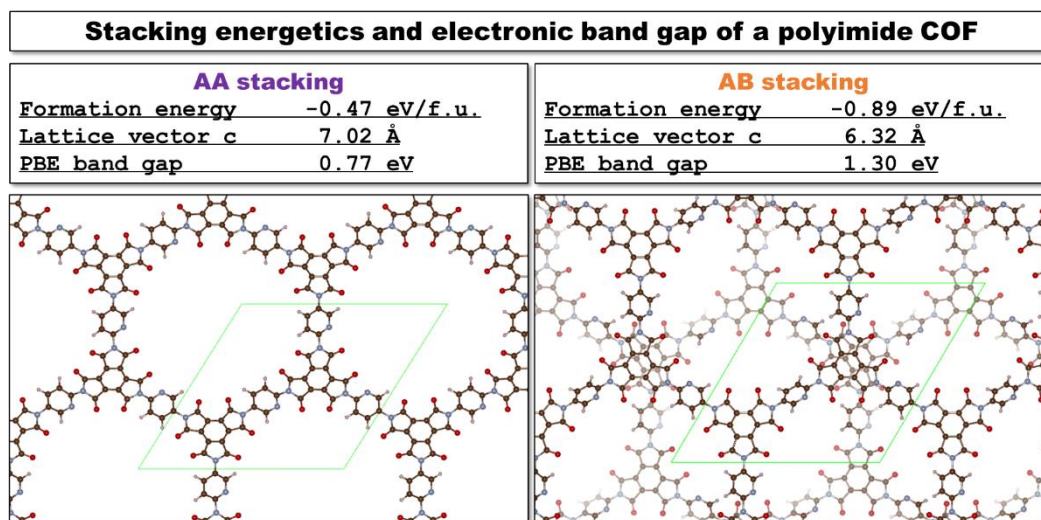


Figure 1: Formation energies (with respect to the flat monolayer), c lattice vector (out-of-plane) lengths, and PBE band gaps of AA and AB stacked polyimide COFs. The unit cell comprised of a monolayer relaxed towards a minimum with significant torsion (between 37 - 45 deg) against outer rings. The relaxed monolayer exhibits an energy lowering of -0.25 eV per formula unit (f.u., $C_{13}N_3O_4H_3$). The PBE band gap of the monolayer varies between 1.02 (flat) and 1.68 eV (relaxed).

[1] S. Kandambeth, K. Dey, R. Banerjee, *J. Am. Chem. Soc.* **141**, 1807–1822 (2019)

[2] A. M. Evans et al., *Science* **361**, 52–57 (2018)

[3] H. Veldhuizen, A. Vasileiadis, M. Wagemaker, T. Mahon, D.P. Mainali, L. Zong, S. Zwaag, A. Nagai, *J. Polym. Sci. Part A: Polym. Chem.* **57** 2373-2377 (2019)