Supporting Information: Unveiling the Effects of Nitrogen Incorporation and Stacking Sequences on the Electronic Structure of Imine-Based 2D Covalent Organic Frameworks

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S1: DFT optimized geometry of 5N-imine-COF

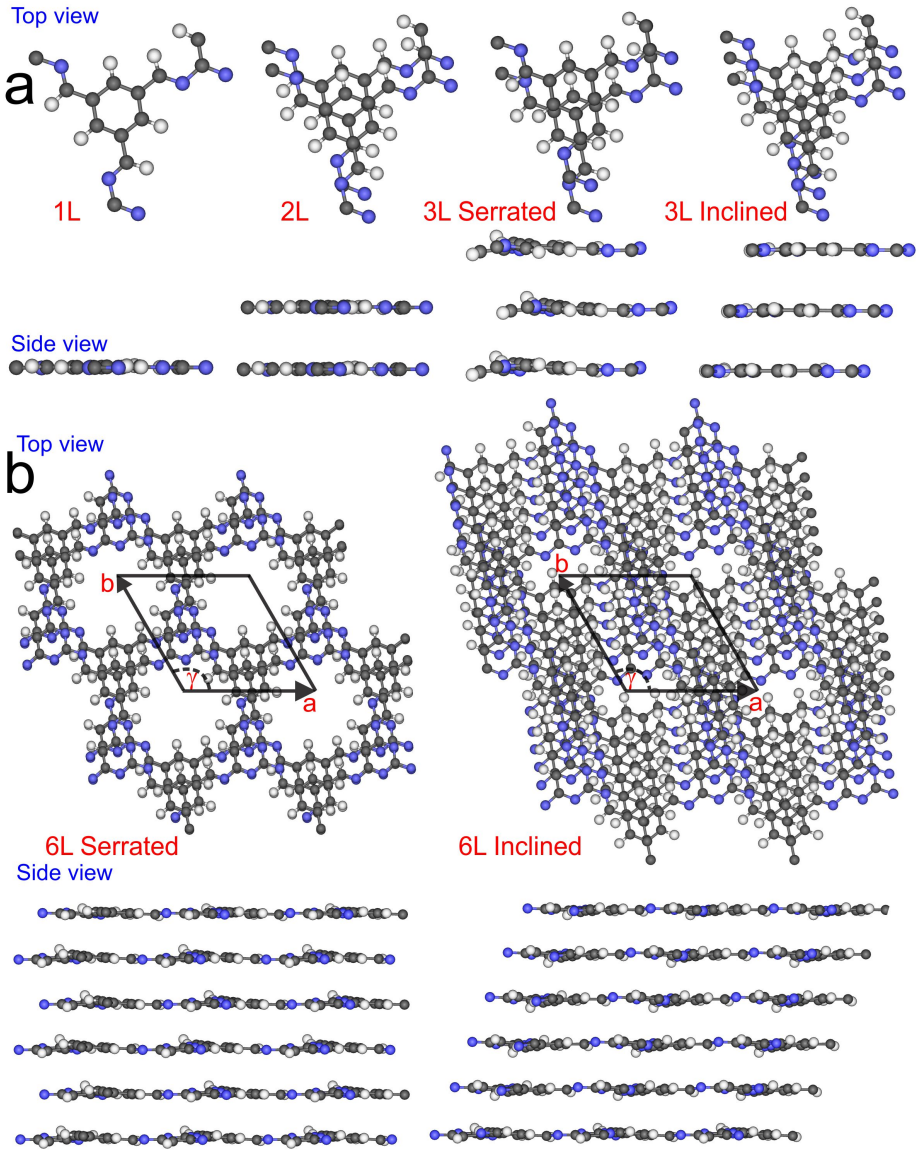

Figure 1: (a) Top and side view of the optimized unit cell of 5N-imine-COF for 1L, 2L, 3L *serrated* and 3L *inclined*. (b) Top and side view of 2 × 2 cell of 6L *serrated* and 6L *inclined* stacking of 5N-imine-COF adapted from optimized geometry (DFT). **a**, **b** and γ are the lattice parameters. Side view is projected along **a** lattice vector.

S2: DFT optimized geometry of 6N-imine-COF

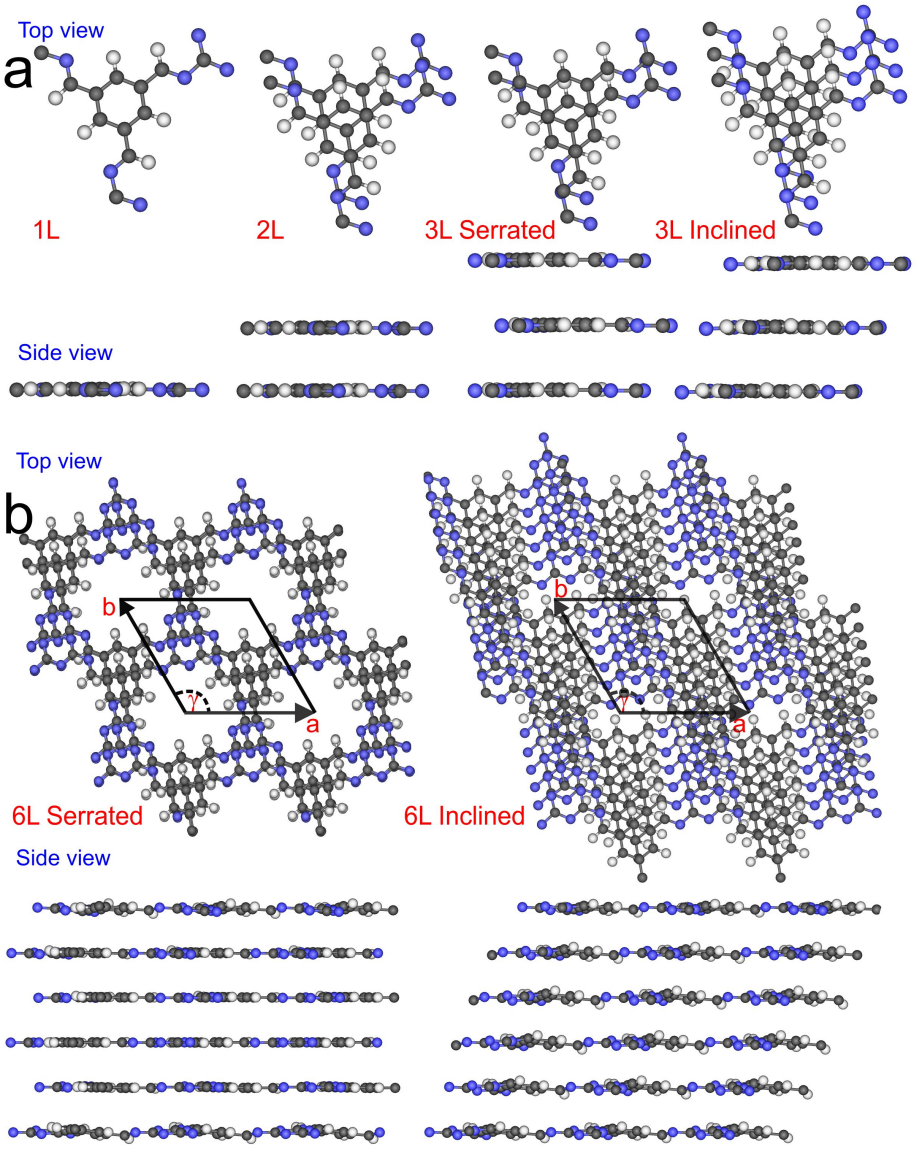

Figure 2: (a) Top and side view of the optimized unit cell of 6N-imine-COF for 1L, 2L, 3L *serrated* and 3L *inclined*. (b) Top and side view of 2 × 2 cell of 6L *serrated* and 6L *inclined* stacking of 6N-imine-COF adapted from optimized geometry (DFT). **a**, **b** and γ are the lattice parameters. Side view is projected along **a** lattice vector.

S3: Inter-layer cohesive energies of different imine-COFs

Table 1: The inter-layer cohesive energies for 3N-, 5N-, and 6N-imine-COFs in *serrated* and *inclined* stacking. More negative cohesive energies indicate stronger inter-layer interaction. Energies are reported in eV.

Layer number	Stacking type	Inter-layer cohesive energy (eV)
	3N-imine-COF	
1L	–	0.0000
2L	–	-0.2651
3L	*Serrated*	-0.3617
3L	*Inclined*	-0.3694
6L	*Serrated*	-0.4620
6L	*Inclined*	-0.4753
	5N-imine-COF	
1L	–	0.0000
2L	–	-0.2587
3L	*Serrated*	-0.3930
3L	*Inclined*	-0.3533
6L	*Serrated*	-0.4906
6L	*Inclined*	-0.4880
	6N-imine-COF	
1L	–	0.0000
2L	–	-0.2993
3L	*Serrated*	-0.3957
3L	*Inclined*	-0.3974
6L	*Serrated*	-0.4696
6L	*Inclined*	-0.5293

S4: pDOS of 3N-imine-COF

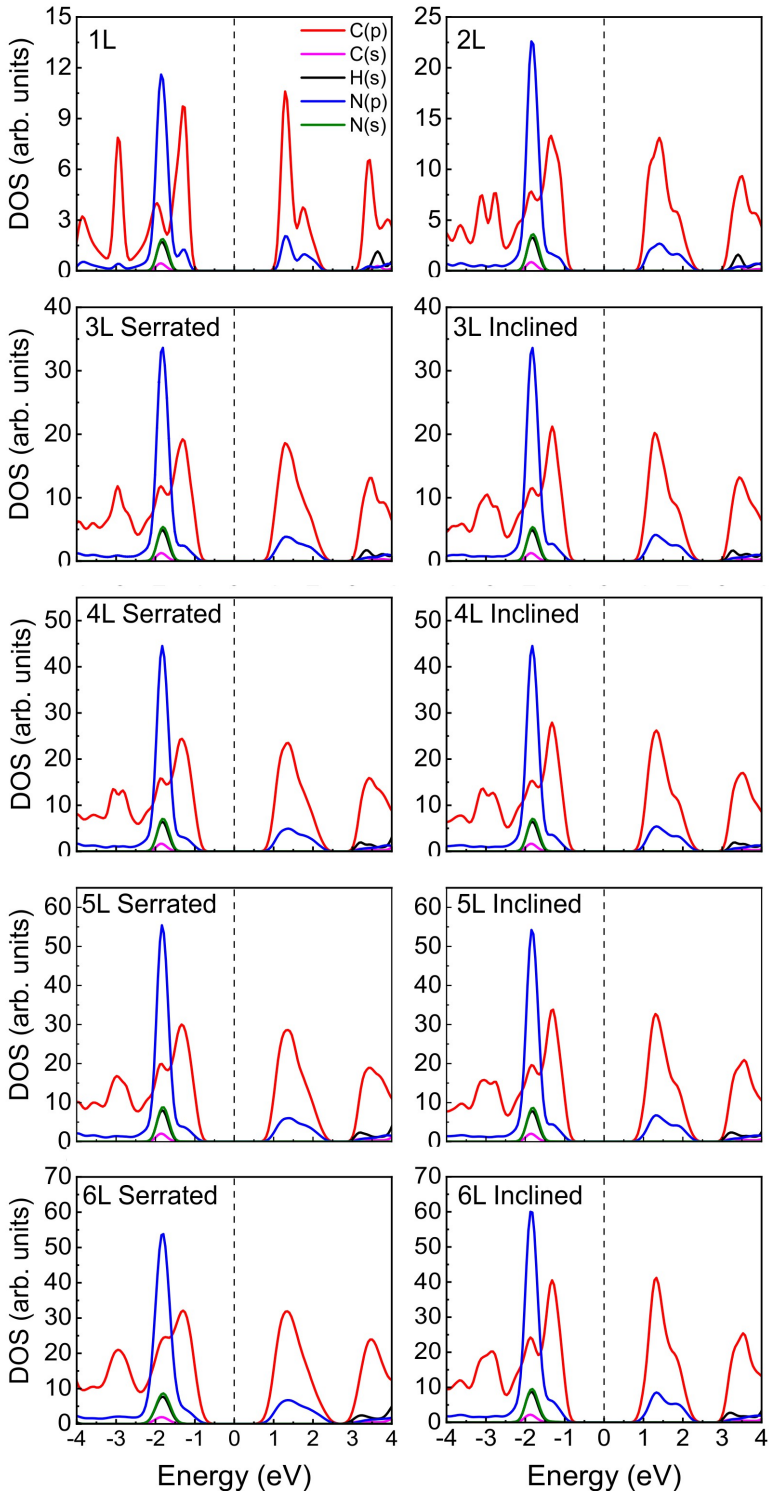

Figure 3

The partial density of states (pDOS) analysis for different layer thickness and stacking types (*serrated* and *inclined*) of 3N-imine-COF. Various atomic contributions, C(p) (red lines), C(s) (magenta lines) , H(s) (black lines), N(p) (blue lines), N(s) (green lines) are included in the pDOS. The frontier bands are mainly contributed by the C(p) and N(p) orbitals. This indicate that the frontier bands are mainly π-type and are localized across the frame work of the 3N-imine-COF. The VBM and CBM has proportional contribution (proportional to the number of carbon and nitrogen in the unit cell) from the N(p) and C(p) orbitals as expected. Except for broadening no major change is observed for the bands as a function of layer thickness.

S5: pDOS of 5N-imine-COF

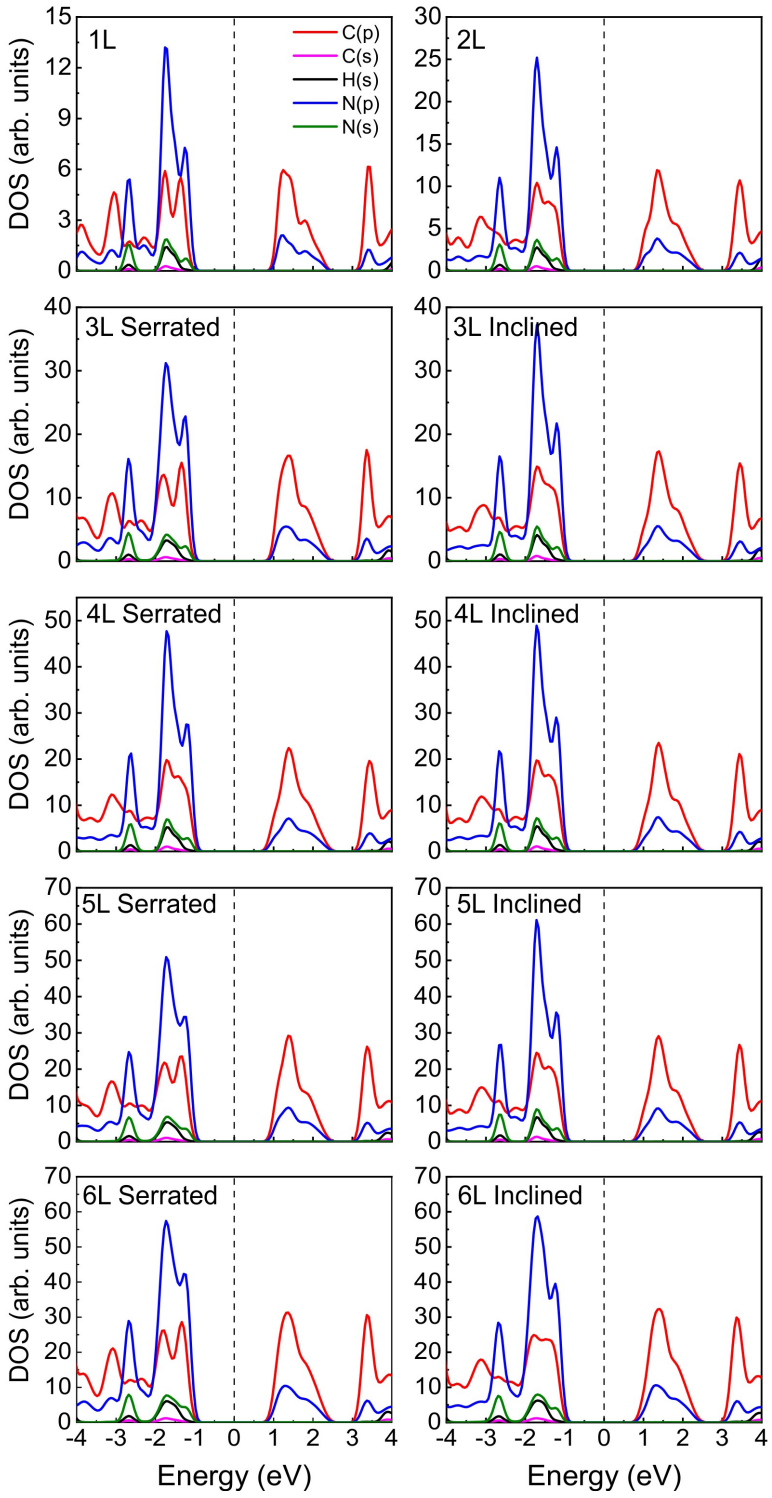

Figure 4

The partial density of states (pDOS) analysis for different layer thickness and stacking types (*serrated* and *inclined*) of 5N-imine-COF. Various atomic contributions, C(p) (red lines), C(s) (magenta lines) , H(s) (black lines), N(p) (blue lines), N(s) (green lines) are included in the pDOS. The pDOS of the 1L exhibits distinct feature characteristic of a 2D semiconductor. The frontier bands are mainly contributed by the C(p) and N(p) orbitals. The VBM is primarily composed of N(p) and C(p) orbitals, with the N(p) contribution being dominant. This shows that the density of additional nitrogen in the unit cell is contributing to the density of the VB. The CBM shows a proportional contribution from both C(p) and N(p) orbitals. The nature of the frontier bands indicates that the frontier bands are mainly π-type and is localized across the framework of the 5N-imine-COF. As the layer thickness increases the bands get broader.

S6: pDOS of 6N-imine-COF

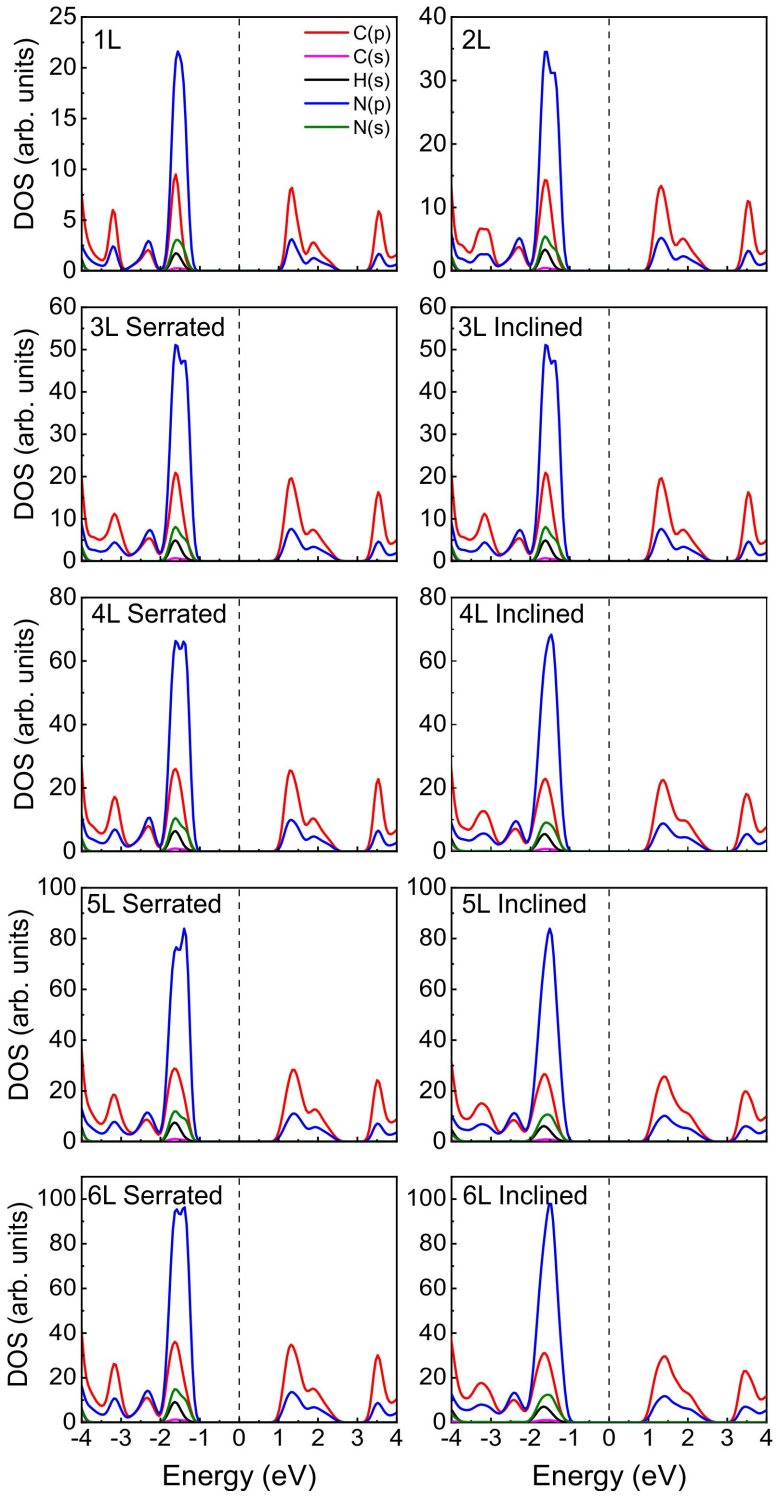

Figure 5

The partial density of states (pDOS) analysis for different layer thickness and stacking types (*serrated* and *inclined*) of 6N-imine-COF. Various atomic contributions, C(p) (red lines), C(s) (magenta lines) , H(s) (black lines), N(p) (blue lines), N(s) (green lines) are included in the pDOS. The pDOS of the 1L exhibits distinct feature characteristic of a 2D semiconductor. The frontier bands are mainly contributed by the C(p) and N(p) orbitals. The VBM is primarily composed of N(p) and C(p) orbitals, with the N(p) contribution being dominant. The density of the N(p) in the VBM is further increased compared to that of 5N-imine-COF. This is in line with the additional nitrogen atom in 6N-imine-COF. This shows that the density of additional nitrogen atoms in the unit cell is contributing to the density of VB. The CBM shows a proportional contribution from both C(p) and N(p) orbitals. This indicates that the frontier bands are mainly π-type and is localized across the framework of the 6N-imine-COF.

S7: Charge density for 5L and 6L of 3N-imine-COF

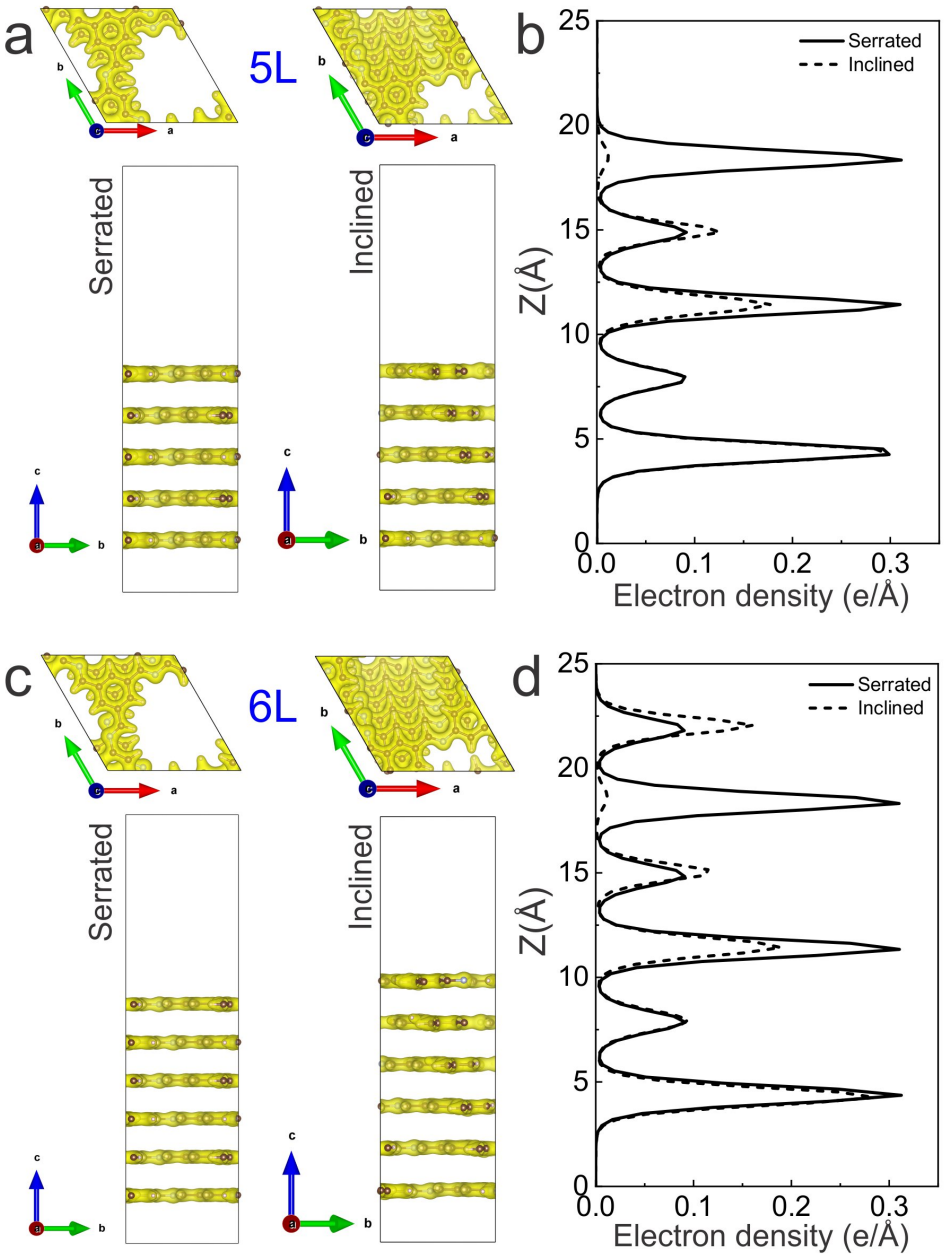

Figure 6: Top and side view of the charge density for 5L (a) and 6L (c) of 3N-imine-COF. Charge density for both *serrated* and *inclined* type stacking is shown. One dimensional charge density profile taken through the center and across the planes of 5L (b) and 6L (d) *serrated* and *inclined* type stacking.

S8: Charge density for 5L and 6L of 5N-imine-COF

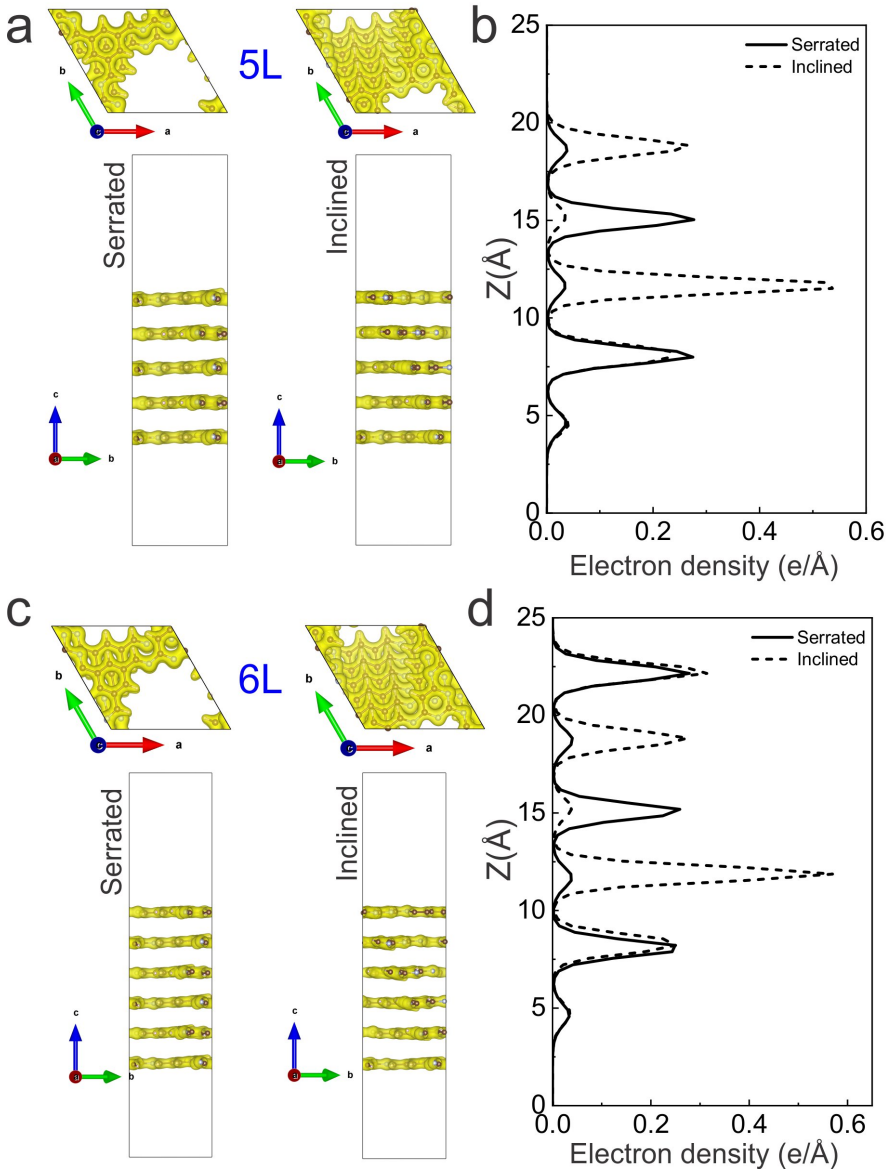

Figure 7: Top and side view of the charge density for 5L (a) and 6L (c) of 5N-imine-COF. Charge density for both *serrated* and *inclined* type stacking is shown. One dimensional charge density profile taken through the center and across the planes of 5L (b) and 6L (d) *serrated* and *inclined* type stacking.

S9: Charge density for 5L and 6L of 6N-imine-COF

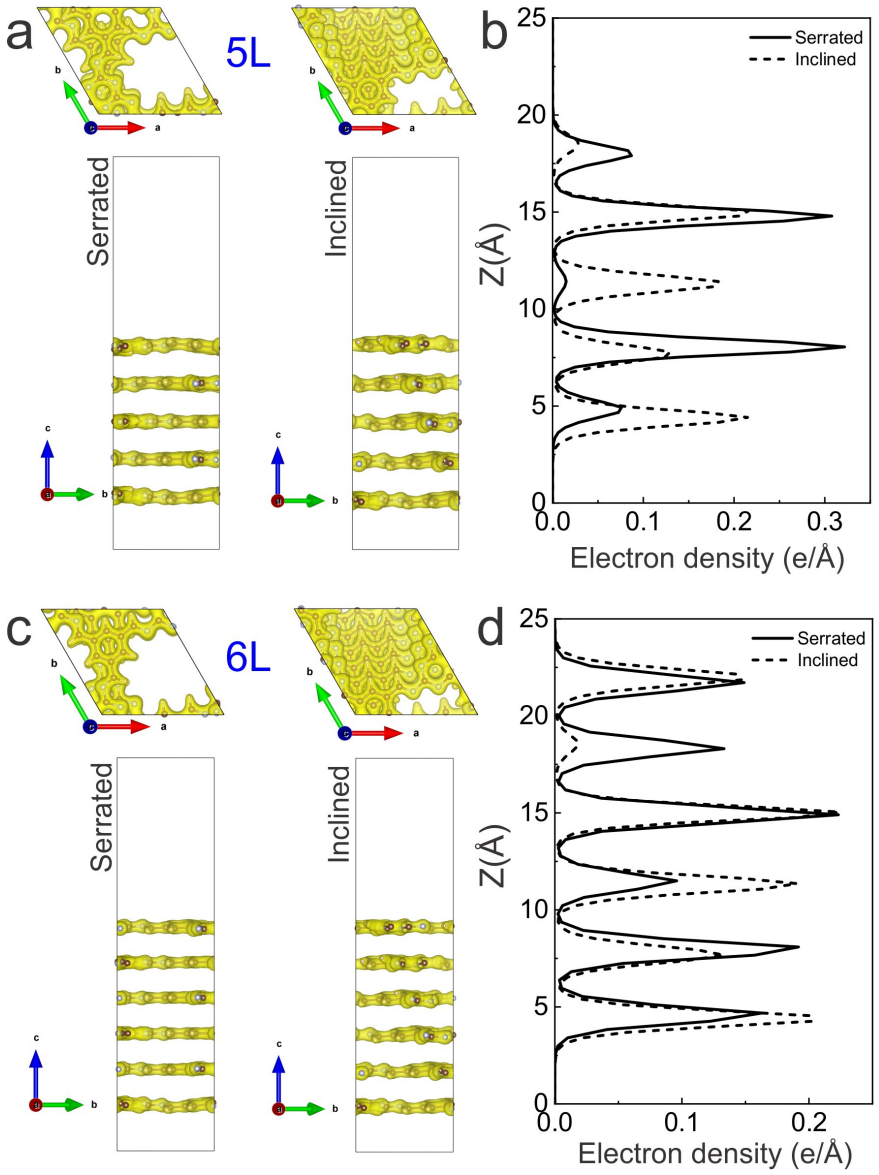

Figure 8: Top and side view of the charge density for 5L (a) and 6L (c) of 6N-imine-COF. Charge density for both *serrated* and *inclined* type stacking is shown. One dimensional charge density profile taken through the center and across the planes of 5L (b) and 6L (d) *serrated* and *inclined* type stacking.

S10: Isosurface of frontier bands of 6L 3N-imine-COF

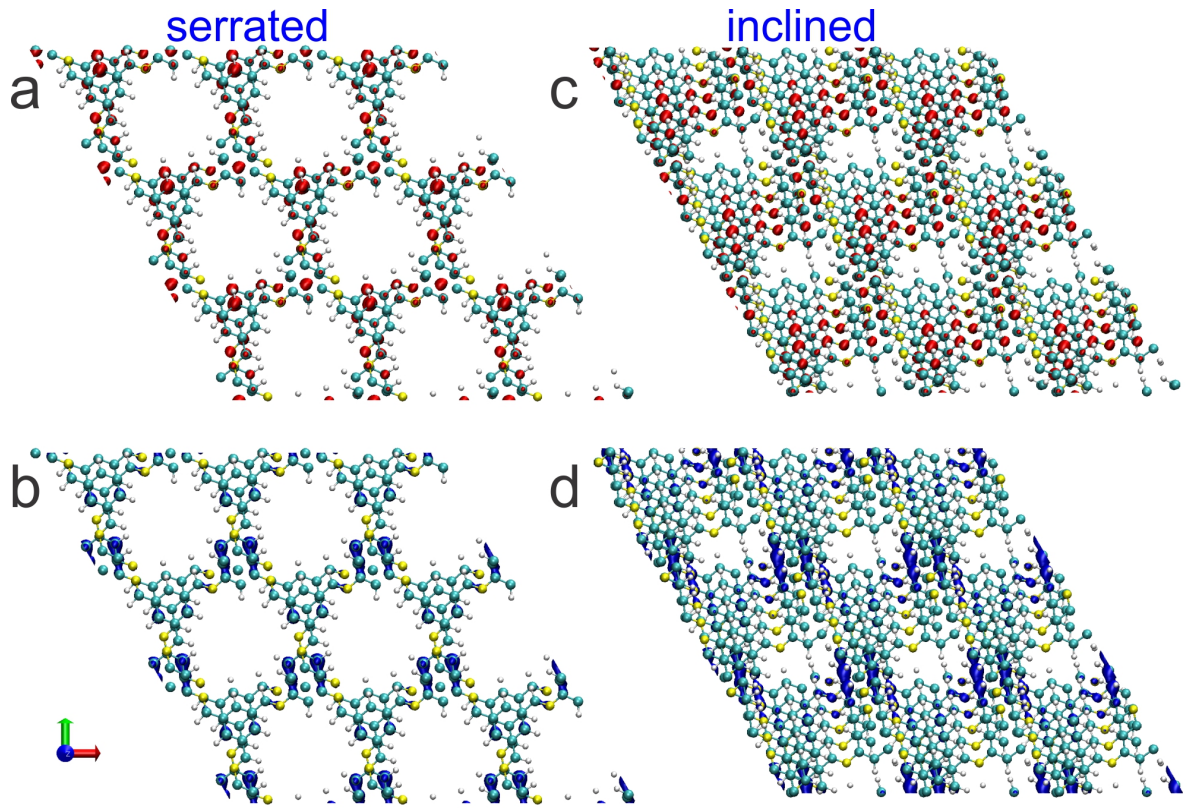

Figure 9: Isosurface of frontier bands of 6L 3N-imine-COF with different stacking types. Conduction band minimum (CBM) (a) and valence band maximum (VBM) (b) for *serrated* stacking, and CBM (c) and VBM (d) for *inclined* stacking. The CBM and VBM are shown in red and blue, respectively, highlighting the variation in charge distribution for different stacking arrangements.

S11: Isosurface of frontier bands of 6L 5N-imine-COF

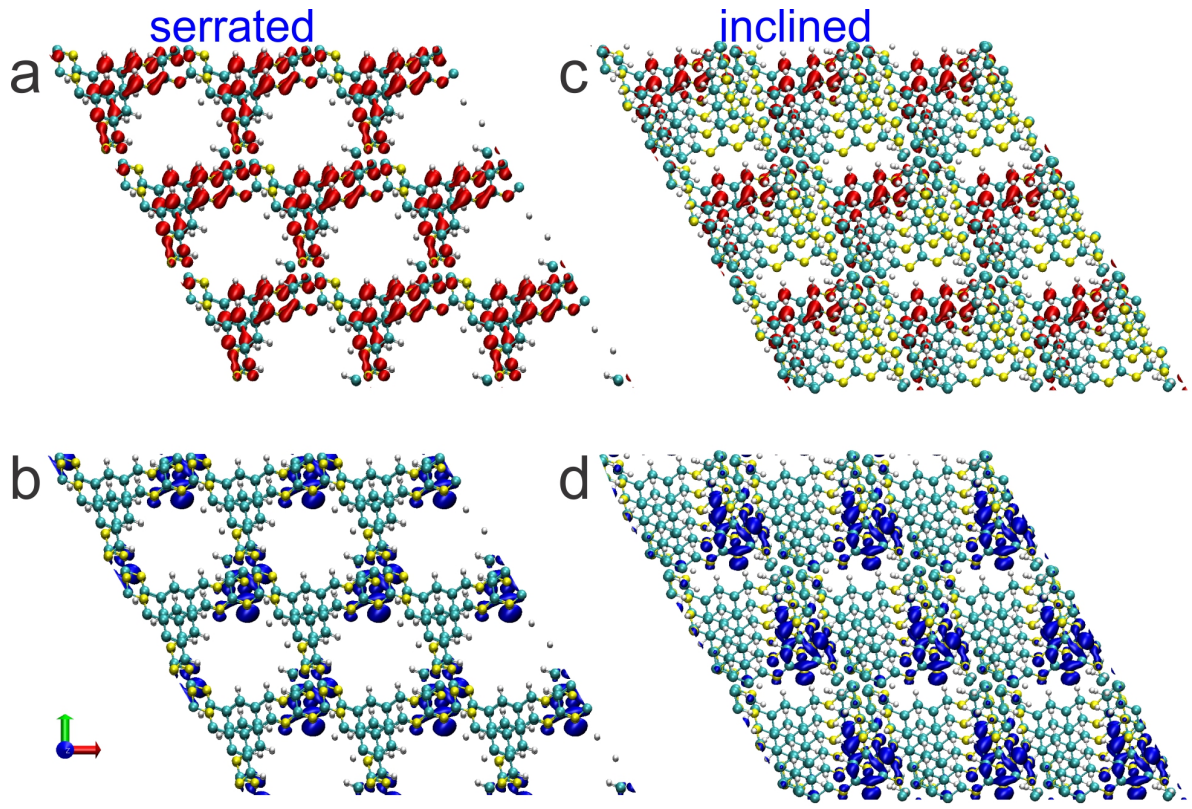

Figure 10: Isosurface of frontier bands of 6L 5N-imine-COF with different stacking types. Conduction band minimum (CBM) (a) and valence band maximum (VBM) (b) for *serrated* stacking, and CBM (c) and VBM (d) for *inclined* stacking. The CBM and VBM are shown in red and blue, respectively, highlighting the variation in charge distribution for different stacking arrangements.

S12: Isosurface of frontier bands of 6L 6N-imine-COF

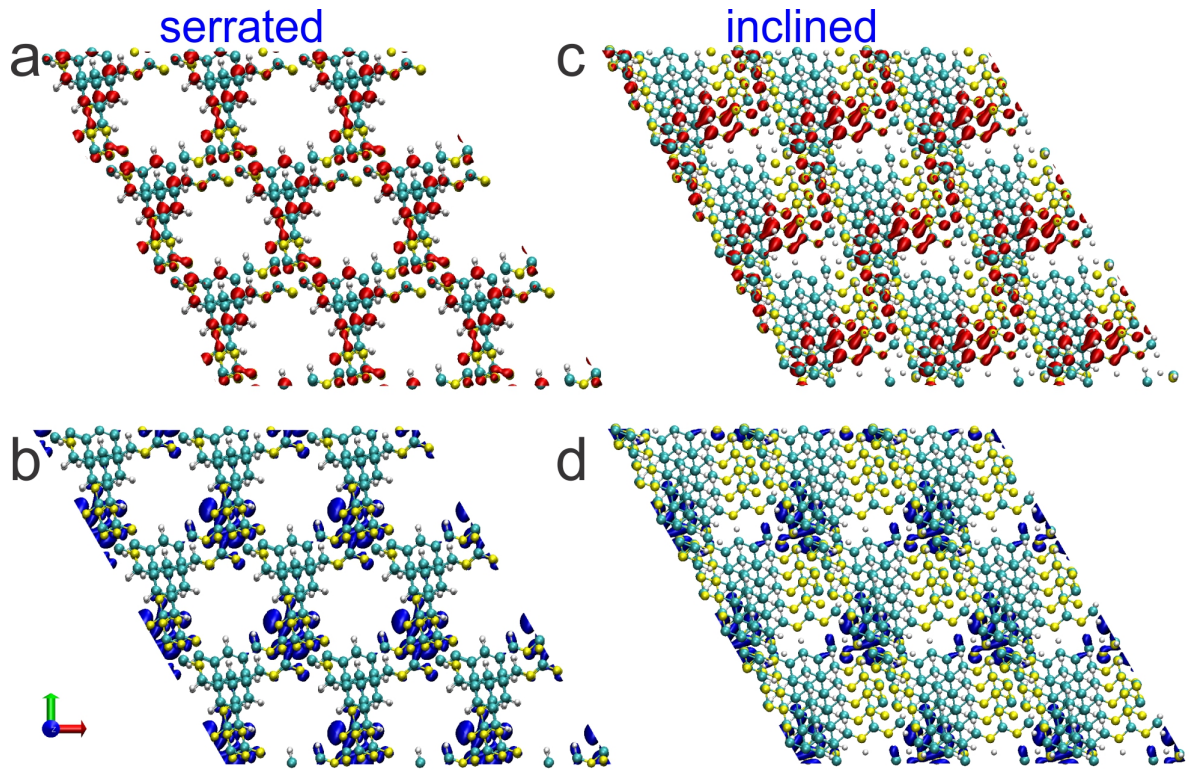

Figure 11: Isosurface of frontier bands of 6L 6N-imine-COF with different stacking types. Conduction band minimum (CBM) (a) and valence band maximum (VBM) (b) for *serrated* stacking, and CBM (c) and VBM (d) for *inclined* stacking. The CBM and VBM are shown in red and blue, respectively, highlighting the variation in charge distribution for different stacking arrangements.