# Mechanisms for Engineering Highly Anisotropic Conductivity in a Layered Covalent Organic Framework

## Supplementary Information

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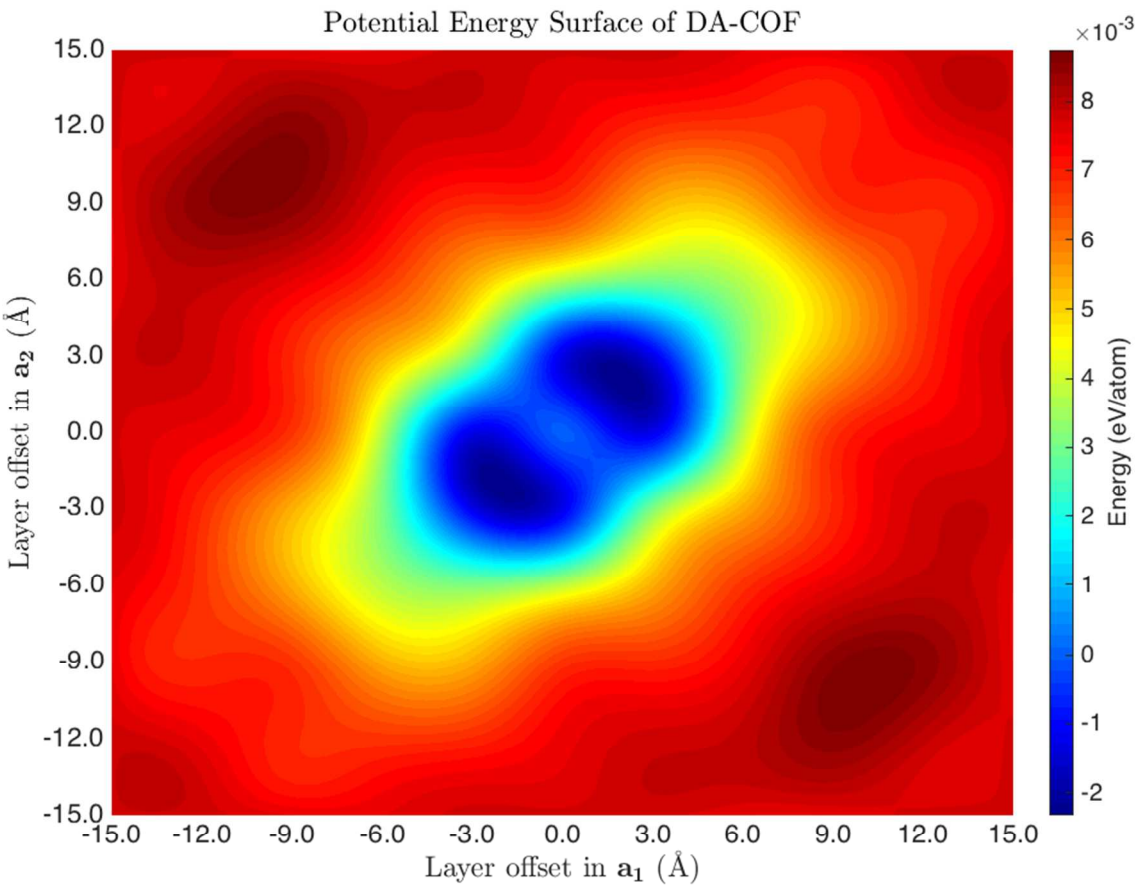
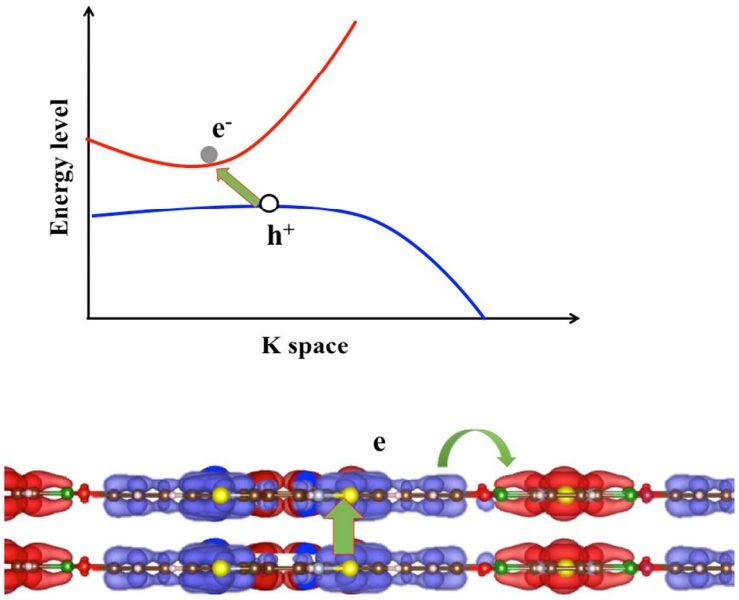
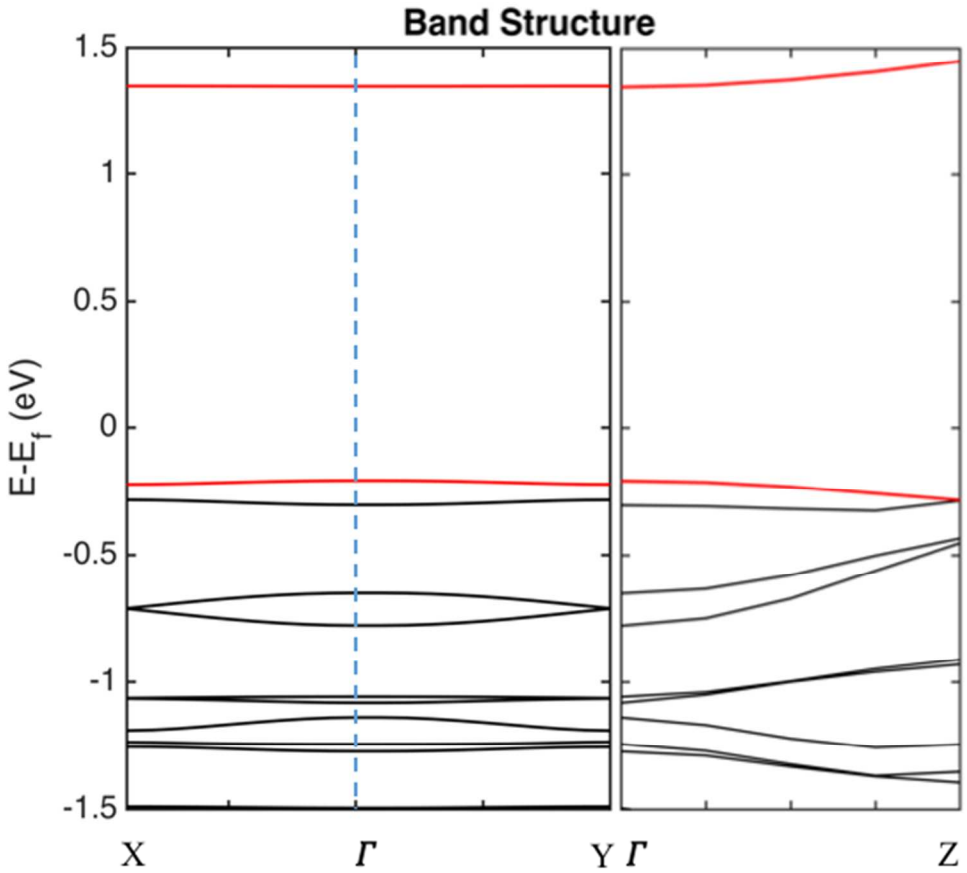
# Supplementary Figures



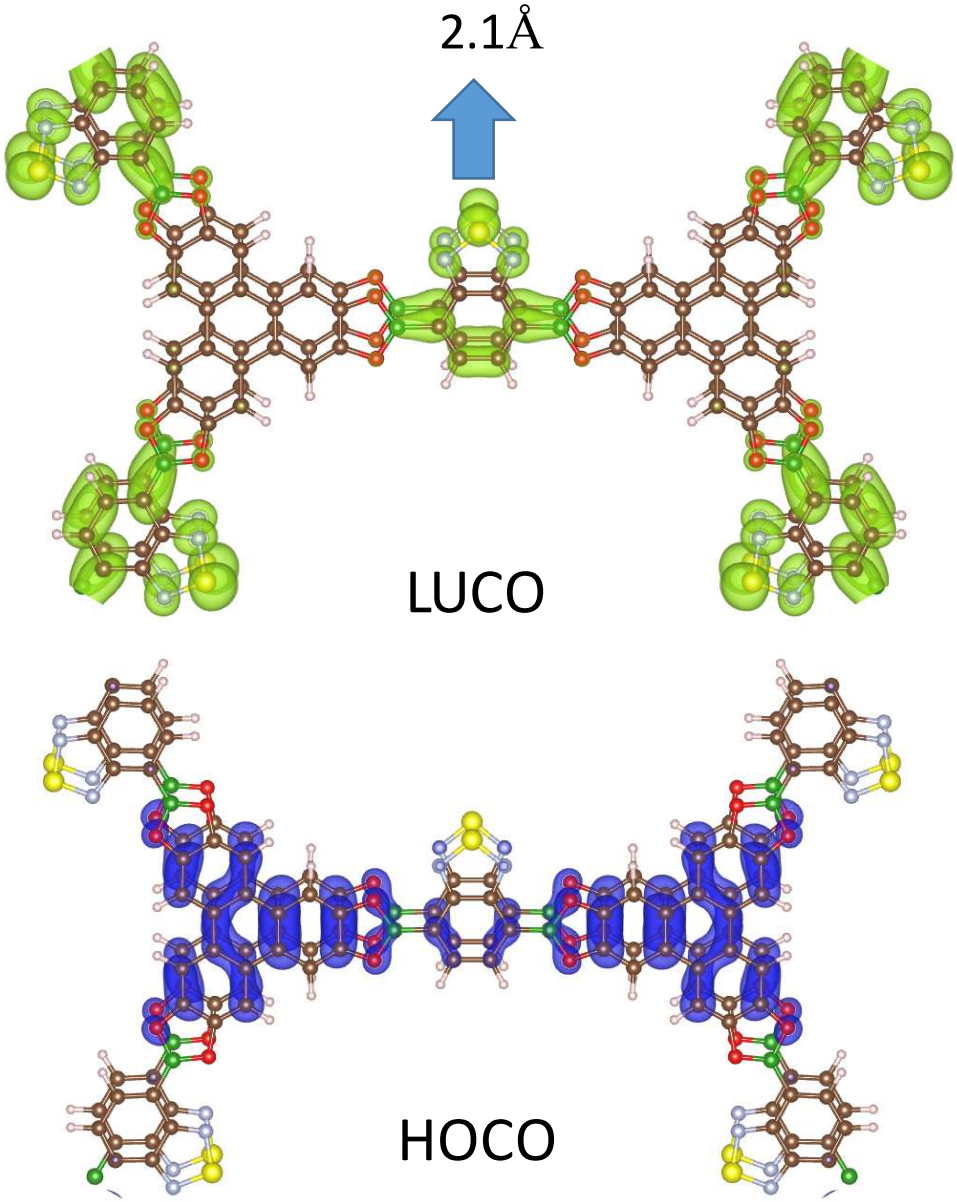

***Supplementary Figure S1*** *Potential energy surface of different stacking shifts along* $\boldsymbol{a_1}$ *and* $\boldsymbol{a_2}$ *direction with respect to a fixed monolayer. Two local minima can be found as shown in figure of this gamma surface, which correspond to a shift of 2.1 Å along both the* $\boldsymbol{a_1}$ *and* $\boldsymbol{a_2}$ *directions.*



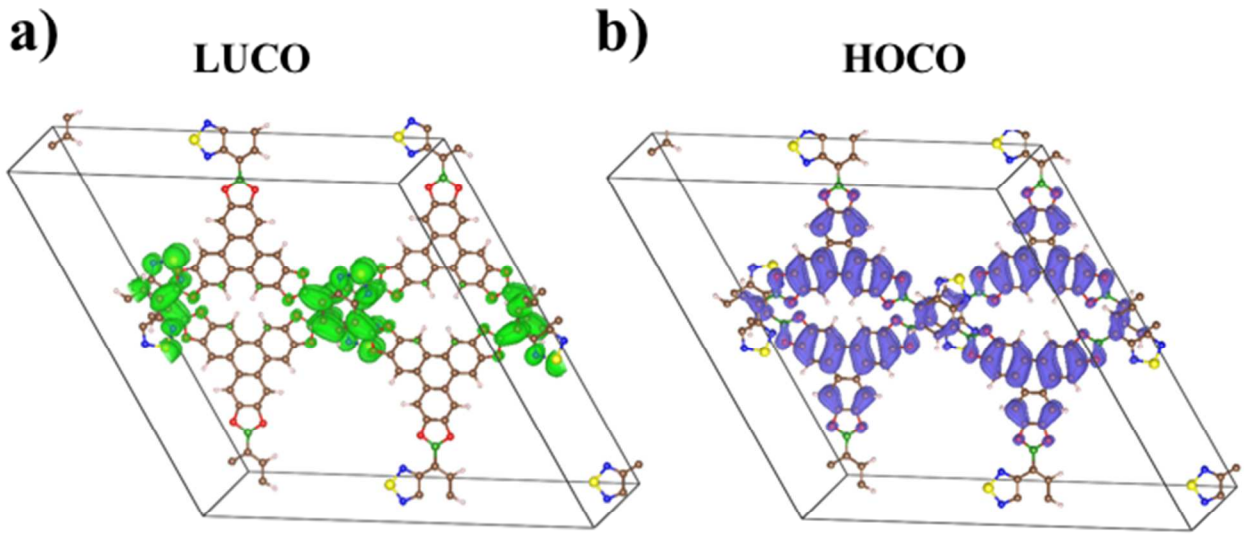

***Supplementary Figure S2*** *Schematic depiction of interlayer hopping in DA-COF, where electrons ($e^-$) and holes ($h^+$) locate at D and A parts, respectively. The excitation leads to hopping of carriers along vertical direction.*




***Supplementary Figure S3*** *Band structure of eclipsed AA-stacked DA-COF with space group P1.*[1] *The Fermi levels are aligned to zero.*




***Supplementary Figure S4*** *HOCO-LUCO plot of eclipsed AA stacking with 2.1 Å offset, which has the minimum energy. Less π –overlap between adjacent 2D layers has been observed.*




***Supplementary Figure S5*** *Schematic drawing of DA-COF with AB stacking where little overlap of a) HOCO and b) LUCO orbitals do not support a vertical carrier conduction.*

## Supplementary Discussion

In order to better understand the relationship between different stacking configurations and the conductivity, we first performed calculations for AB, AA, and eclipsed AA stackings. The AB stacking has much higher energy compared to the other two stacking sequences, and are therefore excluded from the discussion below. The energy difference between AA and eclipsed AA stackings are shown in the potential energy surface (or gamma surface) in Fig. S1, which indicates a minimum energy configuration when the top layer is shifted with respect to the

bottom layer by about 2.1 Å along both $\mathbf{a_1}$ and $\mathbf{a_2}$, respectively. This agrees well with previous work.[2] We then performed band structure calculations for this particular low-energy eclipsed AA stacking configuration and calculated its carrier effective masses along the Γ-X/Y (almost in-plane) and Γ-Z (vertical) directions (see Table 1). The carrier effective masses along the vertical direction is significantly smaller than those in the basal plane, implying that the conduction mainly occurs along the vertical direction. This is similar to the result in the AA stacking, since the eclipse here is relatively moderate.

It is worth mentioning that the energy difference between AA and eclipsed AA stacking configurations is relatively small, whereas the eclipse stacking is harmful for columnar conductivity. The carrier effective masses along the vertical direction is significantly smaller than those in the basal plane, implying that the conduction mainly occurs along the vertical direction. This is similar to the result in the AA stacking, since the eclipse here is relatively moderate. We thus expect further experimental and theoretical studies that aim at stabilizing the AA stacking in order to achieve higher carrier mobility in the columnar channel.

## Supplementary References


(1) Setyawan, W.; Curtarolo, S. High-Throughput Electronic Band Structure Calculations: Challenges and Tools. *Comput. Mater. Sci.* **2010**, *49*, 299–312.

(2) Feng, X.; Chen, L.; Honsho, Y.; Saengsawang, O.; Liu, L.; Wang, L.; Saeki, A.; Irle, S.; Seki, S.; Dong, Y.; et al. An Ambipolar Conducting Covalent Organic Framework with Self-Sorted and Periodic Electron Donor-Acceptor Ordering. *Adv. Mater.* **2012**, *24*, 3026–3031.