Engineering Flat and Dispersive Bands in 2D Layered COFs via Interlayer Stacking and Donor-Acceptor Strategy

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Abstract

Covalent organic frameworks (COFs) are an emergent class of two-dimensional (2D) crystalline organic materials that exhibit unique electronic, optical, and transport properties. In this study, we employ density functional theory (DFT) and the multiparticle Holstein formalism (MHF) to investigate the electronic structure and two-dimensional coherence of polarons in donor-acceptor COFs as a function of interlayer stacking arrangement. We show that simple modifications in the interlayer stacking arrangement have a profound impact on the transport properties, which can range from metallic behavior with vanishing band gap to highly localized states having completely flat bands. The extent of charge delocalization is found to be sensitive to the type of stacking arrangement and the precise arrangement of the donor and acceptor fragments within the COF structure. The results from the DFT calculations are consistent with MHF-based simulations, demonstrating that stacking-induced interlayer interactions facilitate better in-plane charge delocalization. As a consequence, we find that interlayer interactions help circumvent defect-induced trap states to enhance overall charge delocalization. Based on these analyses, we conclude that interlayer stacking can be exploited to guide the design of new 2D layered COF structures with potential applications in organic electronics.
Introduction

The discovery of 2D covalent organic frameworks (COFs) in 2005 has sparked renewed interest in organic electronics research. Due to a range of unique advantages such as morphological precision and positional control of diverse functional building blocks, COFs have received widespread research interest for a broad range of applications, including gas adsorption and separation, sensing, catalysis, energy conversion and storage. More recently, building upon the success of D-A copolymers for device applications, there have been reports of the synthesis of several donor-acceptor (D-A) COFs. For example, D-A copolymers have achieved record power conversion efficiencies (17.3%) and hole mobilities as high as 10 cm$^2$ V$^{-1}$ s$^{-1}$ have been reported, thus making them ideal candidates for field-effect transistors (FETs). In a similar vein, the incorporation of donor and acceptor building blocks has been found to modulate the optoelectronic properties of various COF structures, thus demonstrating the potential of COFs in photoelectric and photocatalytic applications.

Tailoring COFs with the aforementioned targeted properties requires a deeper understanding of the factors influencing charge transport processes. Charge transport in COFs is a multi-scale process that involves many aspects of the COF microstructure, from molecular-scale charge transfer events to nano-scale intra- and inter-framework polaron/charge delocalization. In this context, 2D layered COFs are formed from the self-assembly of the molecular layers via interlayer π-stacking interactions. The manner in which the layers stack largely impacts the electronic and transport properties of COFs. Interlayer stacking interactions are governed by several factors such as monomer structure and planarity, crystallinity, stacking configuration (e.g., eclipsed vs. staggered vs. random), and hydrogen bonding. Different stacking arrangements such as cofacial vs. slip-stacked configurations directly influence the degree and extent of charge/energy transfer along the π-stacks. Although slipped and inclined stacking are usually the energetically preferred stacking patterns, various stacking patterns can be achieved under appropriate chemical and
thermodynamic conditions.\textsuperscript{30,36,42} Common forms of interlayer stacking patterns, which are ubiquitous in most D-A COF structures, are the eclipsed and staggered forms. In the eclipsed configuration, $\pi$-stacking maintains an “in-phase” registry where the donors and acceptors in one layer are positioned adjacent to the donors and acceptors in the neighboring layer, respectively. The staggered arrangement instead exhibits an “out of phase” registry, where the donors in one layer line up adjacent to the acceptors in the neighboring layer. Since there are few prior computational reports,\textsuperscript{35,37,38,43–45} we employ density functional theory (DFT) and simulations based on the multiparticle Holstein formalism (MHF) to investigate the influence of interlayer stacking on the electronic and transport properties of layered D-A COFs.

Due to remarkable photo-induced charge transfer and long-lived charge separation,\textsuperscript{22} we chose $\text{D}_{\text{CuPc}}$-$\text{A}_{\text{PyrDi}}$-COFs as a representative model COF system for this study. In our recent studies, we have introduced the three-dimensional MHF model to investigate the effects of defects, domain size, chemical doping, and topological connectivity on the charge transport properties of COFs.\textsuperscript{26,46,47} Based on the agreement with available measurements of mid-infrared spectra, we were able to gain fundamental insights and proposed new design strategies for the synthesis of 2D COFs with improved conductivity.\textsuperscript{26} In this study, we combine the MHF model with DFT calculations of layered D-A COFs to investigate the sensitivity of charge delocalization to stacking patterns. Our goal is to identify and establish connections between DFT calculations of the electronic structure and MHF-based analyses of photophysical and charge transport properties to determine correlations between molecular stacking and the extent of energy/charge transport efficiency in layered COFs.
Methodology

Electronic Structure

Electronic structure calculations were performed at the DFT level using the Vienna ab initio simulation package (VASP). The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional of the generalized gradient approximation (GGA) was adopted in all DFT calculations. The core electrons were treated by the projector augmented wave (PAW) pseudopotential. A plane-wave basis set with an energy cutoff of 400 eV was used in all calculations. The convergence criteria for energy and force were set to $1 \times 10^{-4}$ eV and 0.03 eV Å$^{-1}$, respectively. The electron spin polarization was applied in systems containing Cu(II) since the electronic configuration of the Cu(II) is [Ar]3d$^9$ and, therefore, every Cu(II) atom has an unpaired spin. Monkhorst-Pack $k$-meshes of $1 \times 1 \times 1$ and $1 \times 1 \times 3$ $k$-point grids were used for structural optimization, and $3 \times 3 \times 1$ and $3 \times 3 \times 9$ $k$-point grids were used for electronic structure calculations, for the monolayer and multi-layered D-A COF unit cells, respectively. For the molecular donor and acceptor building blocks, $\Gamma$ point $k$-point grid was used for the electronic calculations. A vacuum space of more than 15 Å along the $c$ direction was set for the monolayer unit cell to avoid spurious interactions between the periodic replicas. The empirical correction by Grimme with the Becke-Johnson damping (D3(BJ)) was applied in the multilayered systems, to describe the van der Waals interactions. It is known that the PBE functional, and any functional developed within GGA, systematically underestimates band gaps. However, the objective of this study is to investigate how the electronic, magnetic, and transport properties for different stacking arrangements evolve compared to a monolayer structure. Although the reported band gap values may not be an exact representation of the actual systems, the trends reported in this study provide useful insights into how interlayer stacking can be used to engineer the electronic and transport properties in D-A COFs. Visualization and post-processing were carried out using VESTA and VASPKIT.
Multiparticle Holstein Formalism

We used the MHF model introduced in our previous studies\textsuperscript{26,46,62} to investigate intra- and inter-framework polaron coherence in D-A COFs as a function of interlayer stacking. Within the MHF model, which considers electronic coupling, electron-phonon coupling, and defects on equal footing, the D-A COF is treated as a sequence of donor and acceptor fragments with a periodic variation of the local HOMO energies. In the vector subspace containing a single hole in a one-dimensional lattice with an alternate arrangement of donor and acceptor fragments, the complete Hamiltonian for single polarons in a disordered COF structure is given by

\[ H_{total} = H_{FH} + H_{D-A} + H_{disorder} \]  

where \( H_{FH} \) is defined as

\[ H_{FH} = \sum_n E_n |n\rangle \langle n| + \sum_{m,n} t_{m,n} \{ |m\rangle \langle n| + |n\rangle \langle m| \} \]

\[ + \omega_{vib} \sum_n b_n^+ b_n + \lambda \omega_{vib} \sum_n (b_n^+ b_n + \lambda)|n\rangle \langle n| \]  

In Eq. 2, the first term represents the local hole energy, while the transfer integral, \( t_{m,n} \), in the second term governs the transport of the polaron in the lattice. Upon electronic excitation, polarons in \( \pi \)-conjugated organic molecules strongly couple to the vinyl stretching or aromatic-quinoidal vibrational mode, \( \omega_{vib} \), in the 1200-1500 cm\(^{-1}\) range. The last two terms in Eq. 2 account for the vibronic couplings, where the operator \( b_n^+ \) (\( b_n \)) creates (annihilates) a vibrational quantum of energy on the \( n^{th} \) unit in the ground state (\( S_0 \)) of the corresponding potential energy well. The Huang-Rhys factor (\( \lambda^2 \)) represents the geometric relaxation energy experienced by a single repeat unit upon ionization (in units of \( \hbar \omega_{vib} \)).

The second term in Eq. 1 represents the local hole energy with the even and odd units
associated with the acceptors and donors, respectively, where $H_{D_A}$ is defined as

$$H_{D_A} = \frac{\Delta}{2} \sum_n (-1)^n |n\rangle \langle n|$$  \hspace{1cm} (3)

The local energies of the HOMO orbitals alternate between the donor and acceptor units: $\frac{\pm \Delta}{2}$ is assigned for the donors and $\frac{-\Delta}{2}$ for the acceptors. The difference in the HOMO energies between the donor and acceptor fragments is referred to as $\Delta$. As in our previous studies,\textsuperscript{62} we assume $\hbar \omega_{\text{vib}}$ and $\lambda^2$ to be the same in both donors and acceptors to be consistent with the vibronic terms in Eq. 2. The Huang Rhys factor is set to one for the simulations.

Disorder in $\pi$-stacked organic molecules such as COFs arises due to an inhomogeneous polarizing environment surrounding the hole, which includes variations in the nearest-neighbor $\pi$-stacking distances, intramolecular torsional angles within the framework backbone, and spatially varying local electric fields. The various forms of disorder induce random changes in the hole energy, for a hole located at site $n$. In our model, all these sources of disorder are accounted for phenomenologically and the disorder Hamiltonian, $H_{\text{disorder}}$, is given by

$$H_{\text{disorder}} = \sum_{n=1}^{M} \Delta_n d_n^+ d_n$$  \hspace{1cm} (4)

where $\Delta_n$ is selected randomly from a Gaussian distribution of width $\sigma$.

## Results and Discussion

### Structural Models

Fig. 1 shows the DFT-optimized structures of the DCuPc-A$_2$PyrDI COF monolayer, eclipsed, and staggered stacking arrangements along with the high symmetry $k$-point pathways in the first Brillouin zone (highlighted in orange). Our calculated lattice parameters (reported in the caption of Fig. 1) are in good agreement with previously reported values.\textsuperscript{22} It should be
noted that the optimized structures reported in Ref. 22 were obtained at the DFTB level of theory, which is possibly the reason for the small differences found with our PBE-D3(BJ)-optimized geometries.

**Electronic Structure Calculations**

In this section, we investigate the evolution of the intra- and inter-framework electronic properties of D$_{\text{CuPc}}$-A$_{\text{PyrDI}}$ COFs as a function of interlayer stacking arrangements. As a starting point, we characterize the electronic properties of the individual donor and acceptor
building blocks.

**Donor and acceptor building blocks:** Fig. 2 shows the frontier molecular orbitals (MOs) of the isolated Cu(II) phthalocyanine donor, $D_{\text{CuPc}}$, and pyromellitic diimide acceptor, $A_{\text{PyrDI}}$, which have $D_{4h}$ and $D_{2h}$ symmetry, respectively. The shifted energy levels between the spin-up (-4.75 eV) and spin-down (-3.82 eV) configurations (labeled “mid-gap Cu” in Fig. 2) are primarily induced by the Cu(II) center. This can be confirmed by analyzing the partial density of states (PDOS) in Fig. 3 as well as the symmetry associated with the

Figure 2: PBE-optimized geometry structure of the donor ($D_{\text{CuPc}}$) and acceptor ($A_{\text{PyrDI}}$) along with the evaluated spin-up (orange) and spin-down (purple) energy levels of the frontier MOs. The non-spin-polarized frontier MOs of $A_{\text{PyrDI}}$ are shown in blue. The MO symmetries are shown in parentheses. The $E_{\text{gx}}$ and $E_{\text{gy}}$ orbitals are named due to their nodal planes lying along the $y$ and $x$ axes, respectively.
Figure 3: PBE-D3(BJ)-evaluated spin-polarized band structures and density of states (DOS) of the D_{CuPc}-A_{PyrDI}-COFs. (a) monolayer, (b) eclipsed, (c) staggered I, and (d) staggered II. The orange and purple band structures on the left and right columns in each sub-figure correspond to the spin-up and down configurations, respectively. The left and right parts of the middle column in each subfigure show the corresponding spin-polarized total and PDOS from C, N, O, and Cu. The bands in cyan near the Fermi level represent the mid-gap bands with predominant contributions from the Cu(II) centers as indicated by the PDOS. The Fermi level is set to zero and indicated by the black horizontal dashed line.

two mid-gap states, $B_{1g}$, which matches the symmetry of the $3d_{x^2-y^2}$ orbital from the Cu center. For the donor building block, the highest occupied molecular orbital (HOMO, singly degenerate) and lowest unoccupied molecular orbitals (LUMOs, doubly degenerate) exhibit slightly different energies ($\approx 0.01$ eV) between the spin-up and spin-down configurations due to spin polarization induced by the unpaired electron of Cu(II). The energies of the frontier MOs suggest that the predominant contributions to the valence (VB) and conduction (CB) bands of the D-A system originate from the individual donor and acceptor building blocks, respectively, which can be confirmed by analyzing the partial charge distributions in the CBs and VBs that are shown in Fig. 4.

**Monolayer:** The band structure of the 2D COF monolayer (Fig. 3a) exhibits flat
bands for the (doubly degenerate) bottom CBs and top VB along the Γ-X-M-Γ (i.e. intra-framework) directions. This implies that both electrons and holes have infinite effective masses ($m^*$) and are highly localized within the COF monolayer (see the Supporting Information for more details). The partial charge distribution in Fig. 4a shows that the contributions to the VB and CBs are indeed dominated by the donor ($D_{\text{CuPc}}$) and acceptor ($A_{\text{PyrDI}}$) building blocks, respectively. More specific details regarding the partial charge distribution can be found in Fig. S1 of the Supporting Information. The monolayer is semiconducting and displays direct band gaps of 0.50 eV and 0.21 eV for the spin-up and spin-down configurations, respectively. The lower band gap for the spin-down configuration is due to the appearance of a mid-gap state induced by Cu(II). Spin polarization due to the presence of the unpaired electron in Cu(II) results in the formation of flat bands having energies 0.70 eV and -0.10 eV for the spin-up and spin-down configurations, respectively (Fig. 3a). The monolayer exhibits a magnetization of $\sim 1\mu_B$, which can also be confirmed by inspection of the band structure and PDOS shown in Fig. 3a.

**Eclipsed stacking:** For the eclipsed stacking (Fig. 1b), the bottom CBs within the COF plane (i.e., along the Γ-X-M-Γ direction in Fig. 3b) display flat bands which are consistent with our analyses of the 2D monolayer (Fig. 3a). However, the VBs (at $\sim$0.46 eV) within the plane (Γ-X-M-Γ) become more dispersive compared to the monolayer (see Fig. S3 and S4 of the Supporting Information for more details). This difference can be understood by analyzing the partial density distribution of the VB at the Γ point (VB@Γ) in Fig. 4b and at the X point (VB@X) in Fig. S4 of the Supporting Information. This observation suggests that stacking-induced interlayer interactions potentially enhance charge delocalization within the plane resulting in more dispersive bands and lighter hole effective masses compared to the monolayer. Despite the VBs being more dispersive compared to the monolayer, the presence of Cu(II) centers is detrimental to charge transport. The appearance of highly flat mid-gap states due to the presence of unpaired electrons in the Cu(II) centers modifies the band gap and, therefore, affects the transport properties of the system.
Figure 4: Partial charge distribution in the CBs (yellow) and VBs (blue) at Γ of the D_{CuPc-A_{PyrDI}}-COFs. (a) monolayer, (b) eclipsed, (c) staggered I, and (d) staggered II. The unit cell boundaries are indicated by the dashed lines. More details can be found in the Supporting Information.
In contrast to the flat CBs within the plane, the bands near the Fermi level along the $c$ direction ($\Gamma$ to $Z$) are significantly dispersive (Fig. 3b). The bands crossing the Fermi level along the $\Gamma$-$Z$ direction for spin-up and spin-down configurations suggest metallic behavior, both exhibiting zero band gap. The corresponding $m^*$ is calculated to be 0.929 $m_0$ (spin-up) and 0.896 $m_0$ (spin-down), respectively, suggesting lighter and more delocalized charge carriers (both electrons and holes) along this direction as compared to the in-plane directions. The enhanced delocalization of the charge carriers along the out-of-plane stacking direction primarily arises due to effective $\pi$-overlap of the frontier orbitals and resonant electronic interactions between the donors and acceptors in the adjacent layers (Fig. 4b). The dispersion along the $\Gamma$-$Z$ direction can be confirmed by analyzing the partial charge distribution of the CBs, which originates mostly from the $\pi$ orbitals of the C and O atoms located on the acceptors, allowing the charges to efficiently transfer between layers. Our analysis, therefore, suggests that the highly anisotropic transport characteristics including metallic behavior can be achieved via eclipsed stacking arrangements in 2D layered COFs. The eclipsed stacking exhibits semiconducting behavior within the COF plane, displaying a reduced band gap of 0.34 eV for both spin-up and spin-down configurations due to the presence of mid-gap states. Eclipsed stacking also displays a negligible magnetization of 0.0009 $\mu_B$ per unit cell, suggesting pairing up of all the spins. This is due to the close proximity (3.36 Å) of the two Cu(II) centers in the unit cell.

**Staggered I:** Unlike eclipsed stacking, in staggered I stacking (Fig. 1c), the donors line up adjacent to the acceptors in the neighboring layers. Due to the lower symmetry of the staggered I stacking ($D_{2h}$ symmetry) compared to monolayer and eclipsed stacking ($D_{4h}$ symmetry), there is a change in the high symmetry $k$-paths along the in-plane directions shown in Fig. 1c. The band structure (Fig. 3c) near the Fermi level along the in-plane direction (i.e., along $\Gamma$-X-S-Y-$\Gamma$) displays completely flat CBs, with the partial charge distribution being localized on the acceptors (Fig. 4c). More details about the nature of the VBs and CBs can be found in Supporting Information (Fig. S5). However, similar to the eclipsed stacking,
the VBs become more dispersive as shown in Fig. 3c. The dispersive nature and associated enhancement in charge (hole) transport originate from interlayer interactions, which can be appreciated by looking at the delocalized partial charge distribution induced by the donor from the neighboring layer (Fig. 4c). However, this is not the case for the CBs which are dominated by the acceptors (Fig. 4c), primarily due to the highly localized LUMO of the acceptor (Fig. 2).

While the eclipsed stacking displays metallic behavior and a vanishing band gap due to resonant electronic interactions between the VBs and CBs in neighboring layers, the presence of flat CBs along the Γ-Z direction (inter-plane) in the staggered I stacking is a direct consequence of minimal wavefunction overlap between the frontier orbitals of donors and acceptor fragments in the adjacent layers. The flatness of the CBs corresponds to states localized on the acceptors, with negligible overlap (see Fig. 4c) of the partial charge distribution between neighboring components, either in the intra- or inter-plane directions. Unlike the CBs, the more dispersive VBs result in effective masses of $m^*_h$ of -4.715 $m_0$ (spin-up) and -4.854 $m_0$ (spin-down), respectively, which are heavier compared to those calculated for the eclipsed stacking. This implies that the relative arrangement of donors and acceptors in neighboring layers has a profound impact on the extent of anisotropic through-space and through-bond electron and hole transport. The staggered I stacking exhibits semiconducting behavior with calculated band gaps of 0.36 eV for spin-up configuration and a reduced band gap of 0.15 eV for spin-down configuration due to the appearance of mid-gap defect states that are predominantly contributed by the Cu(II) centers and neighboring N atoms (see Fig. S5 of the Supporting Information). The calculated magnetization is $\sim2.0 \mu_B$ per unit cell, indicating that the two unpaired electrons from the Cu(II) centers remain unpaired in the staggered I stacking, primarily due to their large separation ($\sim18.0$ Å).

**Staggered II:** Slipping one layer relative to the neighboring layer results in a new stacking arrangement referred to as staggered II stacking where the donors are positioned on top of the central pores in the neighboring layers (Fig. 1d) and the acceptors in the neighboring
layers lie adjacent to each other. Due to this specific stacking arrangement, the lower VBs contributed by the donors along the Γ-Z direction (i.e., the π-stacking direction) in staggered II stacking are flat (Fig. 3d). However, the CBs along the Γ-Z direction are dispersive due to effective overlap of the frontier orbitals of the acceptor fragments in the neighboring layers (see the partial charge distribution in the CBs shown in Fig. S6 of the Supporting Information). Staggered II stacking exhibits anisotropic transport behavior, with metallic behavior along the stacking direction and localized charge carriers within the plane. The bands near the Fermi level are dispersive and cross the Fermi level (Fig. 3d) suggesting delocalized electrons along Γ-Z and a fraction of delocalized holes. Additionally, the higher CBs are dispersive while the lower VBs are highly flat along Γ-Z. Staggered II stacking, therefore, demonstrates quasi single-carrier-type behavior along the interlayer direction, with delocalized electrons and mostly localized holes. Apart from modifying the interlayer stacking arrangement, it is also possible to modify the Fermi level either by fine-tuning the externally applied electric fields or via chemical doping \(^{63-65}\) to obtain fully single-carrier-type (either electron or hole) charge transport characteristics for applications in unipolar transistors or FETs. While the band gap for the spin-down configuration of the staggered II stacking is 0.71 eV, the appearance of mid-gap states due to the presence of the Cu(II) centers slightly above the Fermi level (Fig. 3d) results in a reduced band gap of 0.05 eV for the spin-up configuration. Finally, as a consequence of the even larger distance (\(\sim25.5\) Å) between the two Cu(II) centers in the unit cell, the electrons of the Cu(II) centers remain unpaired, as in the staggered I stacking. This results in a magnetization of \(\sim1.8\) \(\mu_B\) per unit cell.

**Effect of Interlayer Stacking on Intra- and Inter-framework Polaron Coherence**

In this section we investigate the intra- and inter-framework coherence numbers in 2D layered COFs having eclipsed and staggered interlayer stacking arrangements. Intra-framework and inter-framework polaron coherence numbers refer to the number of coherently connected
Figure 5: (a) Schematic illustration of the eclipsed and staggered stacking geometries with the donor and acceptor units distinguished as red and blue rectangles. (b) Schematic showing the offset of the energies of the HOMO orbitals (Δ) of the donor and acceptor (black) fragment units which is referred to as the HOMO alternation energy. Simulated polaron coherence numbers for the two stacking geometries polarized along the (c) intraframework and (d) interframework directions.

repeat units over which the polaron is spatially delocalized. For our analysis, we utilize the MHF adapted to polarons in polymers and COFs as described in our previous studies.\textsuperscript{26,46,47,66} We construct 2D D-A COF structures where the COF backbone is taken to be along the $x$-axis (in-plane) and the $\pi$-stacked layers are along the $y$-axis (out-of-plane) (Fig. 5a). As demonstrated in our previous studies,\textsuperscript{26,46,62,67,68} individual chromophores or building blocks can be successfully treated in a coarse-grained approximation. For our simulations, we only retain the local HOMO level for every repeat unit similar to our previous studies.\textsuperscript{26,46,66} The neighboring HOMOs for the adjacent repeat units along both the COF backbone and the $\pi$-stacked frameworks are electronically coupled through the hole transfer integral, $t_h$. $t_h$ has contributions from two components where $t_{\text{intra}}$ ($t_{\text{inter}}$) governs intraframework (inter-framework) delocalization of the hole. Hence, electronic coupling induces three-dimensional delocalization of the hole within the COF structure. In this section, our
ultimate goal is to have a qualitative understanding of how polaron coherence is impacted by the two extreme forms of stacking arrangement such as eclipsed and staggered. More specifically, we plan to investigate how the polaron coherence numbers or the extent of charge delocalization is affected by the difference in the HOMO energies of the donor and acceptor fragments ($\Delta$).

Polaron coherence describing hole delocalization can be defined as the range over which the polaron maintains a wave-like property and is given by

$$C_P(r) \equiv \langle \Psi_G | \sum_R d_R^d d_{R+r} \Psi_G \rangle$$

(5)

In Eq. 5, $R = (m, n)$ is a dimensionless position vector. In the limit when $r = 0$, the coherence function reduces to unity, $C_P[(0, 0)] = 1$, since $\sum_R d_R^d d_R$ is the operator for the total number of holes, which is taken to be unity. The total number of coherently connected repeat units, $N_{coh}$, is derived from the coherence function, and is given by

$$N_{coh} = \sum_r |C_P(r)|$$

(6)

which reduces to unity in the limit of a strongly localized or trapped polaron. From the coherence function in Eq. 5, one can also determine the intra-framework ($L_{intra}$) and inter-framework ($L_{inter}$) coherence lengths which are given by

$$L_{intra}/d_{intra} = \left\{ \sum_{r \in in-plane} |C_P(r)| \right\} - 1$$

(7)

$$L_{inter}/d_{inter} = \left\{ \sum_{r \in out-of-plane} |C_P(r)| \right\} - 1$$

(8)

Here, $d_{intra}$ ($d_{inter}$) refers to the distance between the neighboring units along the intra-framework (inter-framework) direction.

In our coarse-grained models (Fig. 5a), each layer in the eclipsed and stacking arrange-
ments consists of ten repeat units along the intra-framework direction and has four \( \pi \)-stacked layers in the inter-framework direction (\( \pi \)-stacking direction). To investigate the sensitivity of polaron/charge delocalization to the interlayer stacking arrangement, we report the intra-framework and inter-framework polaron coherence numbers for the eclipsed and staggered stackings as a function \( \Delta \), where \( \Delta \) is the difference in the HOMO energies of the donor and acceptor fragments. For our simulations of the polaron coherence numbers reported in Figs. 5c,d, we used an inhomogeneous disorder width having a standard deviation of \( \sigma = 0.3 \) eV. This value of disorder width was successful in quantitatively reproducing the polaron-induced infrared lineshapes in TANG COF in our previous study.\(^{26}\) We used 1000 disorder configurations, which were shown to be sufficient to obtain converged coherence numbers.\(^{26}\) The intra-framework and inter-framework charge transfer integrals were set to 0.4 eV and 0.1 eV, respectively. Since we are only interested in exploring the relative difference in the polaron coherence numbers as a function of stacking arrangement, it is important to note that the absolute values of the nearest-neighbor charge transfer integrals are irrelevant in our study, since the relative difference in the coherence numbers is independent of the absolute values of intra-framework and inter-framework charge transfer integrals. Similarly, the results of our simulations are also independent of the absolute values of the HOMO energies of the donor and acceptor fragments. Unlike in Fig. 5c, where the simulated intra-framework polaron coherence numbers converge to similar values for both eclipsed and staggered stackings, the origin of much larger coherence along the \( \pi \)-stacking direction for the eclipsed configuration shown in Fig. 5d can be traced back to the resonant donor-donor and acceptor-acceptor electronic couplings. The greater delocalization of the hole along the stacking axis in the eclipsed stacking can therefore be correlated to a much more dispersive band along the stacking axis.

In the previous sections, we showed that the completely flat bands along the intra-framework direction in the monolayer become dispersive in the eclipsed and staggered stacking. To understand the origin of stacking-induced interlayer interactions, we constructed
Figure 6: Schematic illustration of (a) 3D COF structure with no defects and (b) 3D COFs with $\sigma = 0.3$ eV (c) calculated intra-framework coherence numbers as a function of inter-framework coupling.

3D COF structures as schematically shown in Fig. 6a,b. In our coarse-grained 3D models, each layer consists of five units along the $x$ and $y$ directions and three $\pi$-stacked layers. Our analysis starts with considering a hypothetical scenario where the inter-framework electronic coupling ($t_{\text{inter}}$) and inhomogeneous static disorder are neglected. $t_{\text{inter}} = 0$ implies that the movement of the hole is restricted such that the hole can only delocalize along the intra-framework direction, with no delocalization of the hole along the $\pi$-stacked columns. Gradual increase in the $t_{\text{inter}}$ value is representative of better $\pi$ orbital overlap, therefore, resulting in more efficient delocalization of the hole along the $\pi$-stacking direction. In the absence of disorder, the black curve in Fig. 6c indicates that the calculated intra-framework coherence numbers display slight improvement when $t_{\text{inter}} = 0.20$ eV compared to when $t_{\text{inter}} = 0.0$ eV. This analysis suggests that inter-framework interactions facilitate more efficient delocalization of the hole along the intra-framework direction. Interestingly, in a realistic scenario where inhomogeneous static disorder ($\sigma$) is incorporated in our modeling, the calculated intra-framework coherence numbers for $t_{\text{inter}} = 0.20$ eV show significant gradual improvement and converge to a larger number compared to when $t_{\text{inter}} = 0.0$ eV (see red curve in Fig. 6c). This implies that interlayer interactions have the potential to circumvent defect-induced trap sites and facilitate enhanced delocalization of the charge carriers.
along the intra-framework direction. This observation sheds light on why flat bands become dispersive upon $\pi$-stacking.

Conclusions

We employed DFT calculations and MHF simulations on a model D-A COF ($D_{\text{CuPc}}-A_{\text{PyrDI}}$) to demonstrate that different interlayer stacking arrangements (i.e., eclipsed, staggered I, and staggered II) can be exploited to significantly modify the electronic, magnetic, and transport properties of layered COFs. In particular, due to resonant donor-donor and acceptor-acceptor electronic interactions along the stacking direction, the eclipsed stacking displays metallic behavior with a vanishing band gap. In sharp contrast to the eclipsed stacking, staggered I stacking exhibits localized charge carriers along both in-plane and out-of-plane directions. The origin of this difference can be traced back to the different arrangements of the donors and acceptor building blocks. Unlike the eclipsed configuration, where the donor and acceptor building blocks in the neighboring layers are positioned adjacent to each other, the morphology of the staggered I stacking is quite distinct, with one donor being surrounded by four acceptors. Along with eclipsed stacking, metallic behavior along the out-of-plane direction was also achieved via staggered II stacking. We believe that if the stacking-induced band dispersion is larger than the in-plane band gap, the CBs and/or VBs can cross the Fermi level, resulting in metallic behavior. However, if the stacking-induced band dispersion is smaller than the in-plane band gap, the system remains semiconducting or insulating, with a smaller bandgap along the stacking direction compared to the in-plane directions. Based on this observation, we hypothesize that metallic charge transport along the interlayer direction can be potentially achieved in low bandgap 2D layered COFs (and possibly in 2D MOFs too). In addition, our findings indicate that the staggered II stacking displays quasi single-carrier-type behavior with delocalized electrons and primarily localized holes. This suggests the potential of this stacking arrangement for applications in FETs with fine-tuned
band structures.

To corroborate the observations from the electronic structure calculations, we constructed 2D coarse-grained COF structures with eclipsed and staggered stackings to investigate the extent of in-plane and out-of-plane charge/polaron delocalization as a function of the difference between the HOMO energies of the donors and acceptor units. By performing MHF-based simulations on the 2D coarse-grained COF structures, we demonstrated that the extent of charge delocalization (or polaron coherence) is sensitive to the type of stacking. The simulated intra-framework coherence numbers were found to converge to similar values for the two stacking arrangements due to similar arrangements of the donor and acceptor fragments along the intra-framework direction. However, as the difference between the HOMO energies of the donors and acceptors increases, the simulated inter-framework coherence numbers were found to converge to a larger number for the eclipsed stacking compared to the staggered stacking. This analysis highlights that the extent of inter-framework charge delocalization is sensitive to the type of stacking arrangement.

Our analyses suggest that both the interlayer stacking and the precise arrangement of donors and acceptor building blocks can be exploited to engineer the functionalization of 2D layered COFs for applications in organic electronic devices. Furthermore, the combination of DFT calculations and MHF simulations unambiguously demonstrates that intra-layer delocalization of the charge carriers within the plane can be enhanced by stacking-induced interlayer interactions. Importantly, our analyses also suggest that interlayer interactions can help circumvent defect-induced trap states which, in turn, can greatly improve overall charge delocalization in 2D layered COF structures.

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**Supporting Information Available**

Detailed discussions of effective mass, electronic band structures, and partial charge densities.
References


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