# SUPPORTING INFORMATION for

# Understanding the origin of serrated stacking motifs in

# planar two-dimensional covalent organic frameworks

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# 1. Methodological details

Please note that all input and the most important output files of all calculations can be found on the NOMAD database at: https://dx.doi.org/10.17172/NOMAD/2021.02.15-1

Thus, the details on all parameters and settings that have been employed during the calculations can be found there.

# 1.1. Overview of basis functions used in FHI-Aims

**Table S1.** Basis functions that have been used for all calculations performed with FHI-AIMS. The abbreviations read as follows: H(nl,z), where H refers to hydrogen-like basis functions, n is the main quantum number, l denotes the angular momentum quantum number, and z denotes an effective nuclear charge which scales the radial function in the defining Coulomb potential.<sup>1</sup>

	Н	С	В	0	Ν	Zn
Minimal	1s	[He]+2s2p	[He]+2s2p	[He]+2s2p	[He]+2s2p	[Ar]+4s3p3d
Tier 1	H(2s,2.1)	H(2p,1.7)	H(2p,1.4)	H(2p,1.8)	H(2p,1.8)	H(2p,1.7)
	H(2p,3.5)	H(3d,6)	H(3d,4.8)	H(3d,7.6)	H(3d,6.8)	H(3s,2.9)
		H(2s,4.9)	H(2s,4)	H(3s,6.4)	H(3s,5.8)	H(4p,5.4)
						H(4f,7.8)
						H(3d,4.5)
Tier 2	H(1s,0.85)	H(3p,5.2)	H(4f,7.8)	H(3p,6.2)	H(3p,5.8)	
	H(2p,3.7)	H(3s,4.3)	H(3p,4.2)	H(3d,5.6)	H(1s,0.8)	
	H(2s,1.2)	H(3d,6.2)	H(3s,3.3)	H(1s,0.75)	H(3d,4.9)	
	H(3d,7)	H(4f,9.8)	H(5g,11.2)	H(4f,11.6)		
		H(5g,14.4)	H(3d,5.4)	H(5g,17.6)		

## 1.2. Determination and optimization of individual COF-structures

Let us note some general aspects before we describe the details how the individual structures of the considered COFs have been obtained. First of all, we grouped the systems into two categories: category (A) comprises COF-1, for which reliable experimental lattice parameters are available<sup>2</sup> and category (B) which comprises COF-5, Zn-Por, NH-Por, and HBC-COF. This categorization was employed, as for several of the materials in category (B) no complete set of experimental lattice parameters is available. Therefore, for these materials all unit cell parameters (in-plane parameters and cell-heights) had to be determined. In the following we will first describe how the unit cells of the materials falling under category (B) were constructed. Further, we will discuss category (A), i.e. COF-1 with the experimental lattice parameters of the systems. Then we will describe how the shifted (or displaced) structures have been obtained.

# 1.2.1 Construction of the unit cells for COF-5, NH-Por, Zn-Por, and HBC-COF

The unit cell parameters of these systems were obtained following a two-step procedure. In a first step (1), the in-plane lattice parameters were calculated and then in a next step (2), based on these in-plane parameters, the optimal stacking distance for the cofacial arrangement was evaluated. The main reason for this stepwise procedure was to obtain a cofacial arrangement, avoiding shifts of consecutive layers in a full geometry optimization. These would be energetically favorable, as discussed in the main manuscript. In detail, we performed the following steps:

- (1) The optimal in plane lattice parameters for the individual COFs were evaluated by considering a COF monolayer (4x4x1 k-point grid for COF-5 and HBC-COF and 6x6x1 for NH-Por and Zn-Por, total energy converged within less than 1 meV, individual layers were decoupled quantum-mechanically by a vacuum of 40 Å and electrostatically by using a dipole correction) and gradually shrinking the lateral unit cell size while keeping the initial symmetry. For each unit cell size, all atomic positions were relaxed<sup>†</sup> and the total energy was calculated. These data were fitted with a Birch-Murnaghan equation of state<sup>3</sup> to obtain the equilibrium in-plane lattice parameters.
- (2) The obtained in-plane unit cell parameters and the atomic positions of the relaxed monolayer are then used for constructing the bulk structure of each COF. These unit cells contain two consecutive layers (A and B) in stacking direction, where these layers are cofacially stacked at an initial distance of 4 Å. This stacking distance then was varied within a range of ±0.75 Å in steps of 0.25 Å. For COF-5, Zn-Por, and NH-Por single point calculations were performed to get the total energy of the system for each stacking distance. For the only non-planar COF considered here, HBC-COF, the atomic positions were relaxed at each stacking distance and from these relaxations the total energy was obtained. During these relaxations, the planar hexabenzocoronene-core was fixed with respect to in-plane displacements. This relaxation step was necessary, as especially the phenylene groups of individual HBC-COF-layers can twist. Now, based on the total energy as a function of displacement, we identified the minimum and calculated additional data points (single-point calculations for COF-5, Zn-Por, and NH-Por and geometry relaxations for HBC-COF) around this minimum with ±0.125 Å variation. All data points were then fitted with a Birch-Murnaghan equation of state and the minimum of that fit was used as the optimal stacking distance of layers A and B.

Finally, the atomic positions of the COFs in the obtained unit cells were relaxed. In order to avoid interlayer shifts, the in-plane positions of 2 atoms contained in the planar core of the individual systems were fixed. These planar cores are the triphenylene units in COF-5, the porphyrins in Zn-Por and NH-Por and the hexabenzocoronene in HBC-COF.

<sup>&</sup>lt;sup> $\dagger$ </sup> For all geometry relaxations the convergence criterion was set to 0.01 eV/Å. This means that all atomic positions were relaxed until the largest force component on any of the atoms was below this value.

Note that this procedure was employed to construct the unit cell for the cofacial arrangement of the individual COFs. These structures and unit cells then serve as the starting points for finding the systems with the lowest total energy. Details how this was done can be found below in section 1.2.4.

Further note that the cofacial arrangement of COF-366 was constructed following a similar procedure as described for HBC-COF. The only difference is that in the case of COF-366 all coordinates of the porphyrin core were fixed during the determination of the stacking distance at cofacial arrangement. The linking groups were relaxed for each stacking distance, as it was the case for HBC-COF. Considering the HBC-COF only the in-plane coordinates were fixed.

# 1.2.2 Construction of the unit cell for COF-1

COF-1 is the system at the heart of our investigations. For this system the unit cell has been constructed in two ways (i) and (ii). Type (i) was constructed by employing the experimental lattice parameters (in-plane: a=b=15.420 Å and stacking distance z=3.328 Å) reported in literature.<sup>2</sup> Type (ii) relied on relaxed unit cell parameters following the relaxation procedure outlined in section 1.2.1.<sup>‡</sup> Essentially all data for COF-1 in the main manuscript were obtained for the system built from the experimental lattice parameters. Therefore, we start by describing the optimization procedure for this system.

For type (i) the bulk structure of COF-1 was constructed by first optimizing the positions of all atoms in isolated monolayers (setting the unit cell height perpendicular to the layers to 40.0 Å and employing a 6x6x1 k-grid). Then these layers were stacked at the experimental interlayer distance<sup>2</sup> of 3.328 Å with the unit cell of COF-1 containing two layers in stacking direction (layers A and B, see Figure 1 of main manuscript). This allows displacing these layers along directions parallel to the xy-plane.

# 1.2.3 Stacking distances of COF-1 at cofacial and shifted layer arrangements

To investigate the energies as a function of interlayer displacement for constant stacking distance, one can simply displace consecutive layers along the respective direction and then calculate the energies. When considering also changes of the stacking distance one has to optimize this distance at each displacement. This was done in the following way:

One of the two layers in the unit cell was displaced along the considered shift direction, while the stacking distance was kept at the initial value of 3.328 Å. This stacking distance then was varied within a range of  $\pm 0.50$  Å in steps of 0.25 Å for the shifted arrangement. The total energies of these structures were calculated in single-point calculations. Based on the obtained energies the minimum was identified and additional data points were calculated around this

<sup>&</sup>lt;sup>‡</sup> It was found that for COF-1 optimizing the in-plane lattice parameters results in smaller lattice constants of a=b=15.126 Å but does not change the trends and the relative ratios of the effects studied – see section 2.1.. These optimized in-plane lattice parameters are in good agreement with previous computational studies.<sup>16</sup>

minimum with  $\pm 0.125$  Å variation. Then the total energies as a function of the stacking distance were fitted using a Birch-Murnaghan equation of state and the minimum of that fit determines the optimal stacking distance. Here, the positions of the atoms within individual layers correspond to those when relaxing isolated monolayers. That this has hardly any impact on the results will be shown in sections 2.1 and 2.2.

## 1.2.4 Finding the optimal structures of COF-5, NH-Por, Zn-Por, HBC-COF, and COF-1

To find the layer arrangement with the lowest energy for all the COFs considered in this work, we performed geometry relaxations as follows: The obtained cofacial structures were used as a starting point with the two layers in the unit cell somewhat shifted relative to each other to avoid starting the geometry relaxation from a saddle point. In the optimizations then all atomic positions were allowed to relax together with the unit cell vector in stacking direction.

For COF-1, both systems, the one with the unit cell constructed from the experimental lattice parameters and the one possessing optimized in-plane parameters together with the optimized stacking distance for the cofacial arrangement were considered. In the main manuscript, in section "3.5 Additional Layered COFs" we include the data for the optimized parameters to stay consistent with the data for COF-5, NH-Por, Zn-Por, and HBC-COF reported in that section of the main manuscript. Here, in section 2.2 of this Supporting Information we compare the absolute energies (including the energy contributions) obtained for the two unit cells ((i) and (ii)) of COF-1. There one can see that especially the differences in these energies are rather small. Furthermore, the trends are in excellent agreement no matter whether unit cell (i) or (ii) are considered for COF-1, which suggests that the exact details on how the geometry is obtained is of only minor relevance.

## 2. Additional data

#### 2.1. Relative energies of COF-1 in a fully optimized unit cell

Figure S1 shows the evolution of the relative energies as a function of the displacement parallel to a pore wall for COF-1 with unit cell parameters taken from the optimized cell (rather than from the experimental one).

For each displacement the optimal stacking distance was determined using the procedure outlined in section 1.2.3. Now, considering the evolution of the energies in Figure S1 and comparing them to Figure 3 of the main manuscript one observes that the data agree. Only minor numerical differences can be seen. Thus, one can conclude that optimizing in the inplane lattice parameters does not impact the qualitative behavior, i.e. the trends, of the relative energies of the system.



Figure S1. Relative energies of COF-1 with optimized in-plane lattice parameters. Consecutive layers are shifted along a direction parallel to a pore wall and the stacking distance is relaxed at each displacement. (a) Comparison of total energy to the (electronic) interaction energy and the vdW energy (b) Decomposed terms of the electronic interaction energy. The energy values for 0.0 Å displacement are reported in Table S2.

#### 2.2. Comparison of absolute energies of COF-1 for cofacial and optimal arrangement

The absolute energies for a cofacial and the optimal arrangement of COF-1 layers have been obtained for unit cells (i) and (ii). Here (i) is the system with the experimental in-plane lattice parameters and (ii) denotes the system with the relaxed in-plane parameters. The obtained data are reported in Table S2.

The interlayer stacking distances show hardly any difference when comparing COF-1 with the experimental and the optimized in-plane lattice parameters. When considering the total and the interaction energies, we find that the system with the relaxed in-plane lattice parameters yields lower values, i.e. it is more stable. Dealing with the individual contributions to the interaction energy, a similar behavior can be found for the attractive vdW and electrostatic energies, the relaxed system consistently yields lower values (larger magnitudes, more negative). This trend is also found for the repulsive term comprising Pauli repulsion with orbital rehybridization. The effect, however, is different, as here the relaxed system is slightly destabilized by this energy contribution.

More important, however, is the comparison of the changes in these energies when comparing the optimal layer arrangement to the cofacial one. These values can be found in the last two columns of Table S2. For the change of the stacking distance we find that it decreases by 0.26 (0.27) Å for the experimental and the relaxed unit cells of COF-1. Similarly to this small difference between the two unit cells also the total energies change by almost the same value of -0.866 (0.861) eV. Also for the interaction and the van der Waals energies such negligible differences between unit cells (i) and (ii) are found. For the electrostatic energy contribution, these differences become somewhat larger, but still remain small. To summarize, there are

small numerical differences when looking at the trends of the energies. Nevertheless, the trends of the energies prevail.

**Table S2.** Energies and structural parameters (displacement vectors, stacking distances) of COF-1 with the experimental and the optimized in-plane lattice parameters. z ... stacking distance,  $E_{total}$  ... total energy per unit cell,  $\Delta E_{int}$  ... interaction energy,  $\Delta E_{vdW}$  ... vdW energy contribution,  $\Delta E_{elstat}$  ... electrostatic energy contribution,  $\Delta E_{Pauli,orb}$  ... Pauli repulsion with orbital rehybridization; The stacking distances as well as the energies are given for the cofacial and the optimal arrangement for each COF.

		COF-1 COF-1		$\Delta$ (optimal-	-cofacial)	
unit cell		experimental	relaxed	experimental	relaxed	
	cofacial	3.64	3.62	0.27	0.26	
Z/A	optimal	3.37	3.36	-0.27	-0.20	
E / N	cofacial	-70443.278	-70443.846	0.966	0.961	
E <sub>total</sub> / ev	optimal	-70444.144	-70444.707	-0.800	-0.801	
	cofacial	-1954	-2036	916	-809	
$\Delta E_{int} / Ine v$	optimal	-2770	-2845	-810		
AE /maV	cofacial	-2770	-2863	522	527	
$\Delta E_{vdW}$ / meV	optimal	-3302	-3390	-332	-327	
AE / may	cofacial	-386	-416	754	729	
$\Delta E_{elstat}$ / meV	optimal	-1140	-1154	-734	-/38	
$\Delta E_{Pauli,orb} / meV$	cofacial	1202	1243	470	156	
	optimal	1672	1699	470	430	

#### 2.3. Gaussian Process Regression: Model uncertainty and training data

As described in the main manuscript, the potential energy surface, PES, of COF-1 was obtained employing Gaussian Process Regression, GPR. A distinct advantage of GPR is that a model uncertainty,  $\sigma$ , can be obtained. As already described in the main manuscript our model (constant kernel times a radial basis function kernel (RBF) kernel) was trained on 80 randomly chosen data points and later 39 additional data points were added to the training data, in order to decrease the model uncertainty. These additional training data points were placed at positions with large model uncertainties. In Figure S2a the calculated potential energy surface (PES) can be seen, where all training data points (80 initial points plus 39 additional ones) are shown as black dots. The PES is the same as in Figure 2, albeit shown for a somewhat different plotting range. The main reason is to include all training data in the visualization. This is important for points with a radius/amplitude larger than 6 Å, as they were included in the training of our model. Figure S2b displays the corresponding model uncertainty. It can be seen that for the entire range of shifts that was considered, the model error is well below 60 meV. Especially for values of x and y smaller than 5 Å, this uncertainty is even well below 25 meV. Importantly, for displacements, where we find the global minimum of the total energy, the model uncertainty is even below 8 meV.



Figure S2. Panel (a) shows the potential energy surface for COF-1 calculated using Gaussian Progress Regression together with the considered training data (black dots). In panel (b) one can see the model uncertainty within the considered range of xy-shifts. The black dash dotted lines denote the amplitude of the displacements in terms of a radius. The white lines are located at 60° and indicate the six-fold symmetry of the system.

#### 2.4. Results for COF-1 for shifts perpendicular to a pore wall

In addition to the calculations of the interaction energy for interlayer shifts parallel to a pore wall, we also considered shifts of COF-1 layers along a direction perpendicular to the pore wall. For such shifts the interaction energy and the van der Waals energy have been determined for systems with a constant interlayer stacking distance and with optimized stacking distances. Considering the data for constant interlayer stacking distances in Figure S3a we find that the overall trend of the interaction energy for shifts parallel to the pore wall is also recovered here.

Again the interaction energy  $\Delta E_{int}$  has its highest value for the cofacial arrangement and exhibits a pronounced minimum at displacements around 1.75 Å. Comparing the total energies for the minima found for shifts parallel to the pore wall from the main manuscript and the direction considered here, it can be seen that the minimum for shifts perpendicular to the pore walls is ~40 meV higher in energy.

Furthermore, comparing the results for optimized interlayer stacking distances, we find that the overall trends are also similar. Again, the minimum found along direction **2** is slightly higher in energy (~50 meV) than the one found along direction **1**. Like for the constant interlayer stacking distance, a local minimum in the interaction energy is observed for displacements around 3.5 Å. However, this minimum is significantly higher in energy (~200 meV) than the observed minima at shifts of 1.75 Å.



Figure S3. Interaction and van der Waals energy for shifts of consecutive COF-1 layers along a direction perpendicular to the pore walls. In panel (a) the data for a system with constant interlayer stacking distance (3.328 Å) are shown. Panel (b) shows the energies for systems with stacking distances optimized at each displacement. The energies are given per unit cell containing two layers and are aligned to their respective values at cofacial arrangement. Energy values at 0.0 Å displacement for constant interlayer stacking distance:  $\Delta E_{int}$ =-1290 meV,  $\Delta E_{int,elec}$ =2257 meV,  $\Delta E_{vdW}$ =-3547 meV,  $\Delta E_{electrostatic}$ =-1344 meV,  $\Delta E_{Pauli,orb}$ =3601 meV,  $E_{total}$ =-70442.671 eV; Energy values at 0.0 Å displacement for optimized interlayer stacking distance:  $\Delta E_{int}$ =-1957 meV,  $\Delta E_{int,elec}$ =812 meV,  $\Delta E_{vdW}$ =-2769 meV,  $\Delta E_{elstat}$ =-385 meV,  $\Delta E_{Pauli,orb}$ =1197 meV,  $E_{total}$ =-70443.275 eV;

## 2.5. Comparison of van der Waals corrections many body dispersion interactions vs. the

#### **Tkatchenko-Scheffler scheme**

In this section we test, whether the observed trends (presented in the main manuscript) of the interaction energy as well as those of the individual energy contributions show any qualitative changes when treating the dispersion interactions by employing a many body dispersion (MBD) interaction scheme.<sup>4-6</sup> Within MBD, the system is described by a number of harmonic oscillators which are centered at the positions of the atoms. These oscillators are determined by polarizabilities which stem from the ground state electron density of the considered system. Based on these polarizabilities the MBD Hamiltonian is constructed. In order to determine the MBD energy correction, the obtained Hamiltonian is diagonalized. Such an MBD energy correction scheme is implemented in FHI-aims and has been employed to obtain data for a cofacial arrangement of COF-1 and for a shifted layer arrangement with a displacement of 1.75 Å. The in-plane lattice constants reported in literature have been used, see Methods section of main text. The interlayer stacking distance was optimized employing the MBD scheme and additionally we also kept it constant at the literature stacking distance. The obtained data can be found in Table S3 for the calculations with many body dispersion interactions and in Table S4 for the Tkatchenko-Scheffler scheme, vdW<sup>TS,7</sup> What is important for the investigations presented in the main manuscript are the changes in the energies that are induced by interlayer shifts. Therefore, we can focus our considerations on these changes presented in Tables S3 and S4 (see the rows named "diff"). For the constant interlayer stacking distance we find that the deviations in the energy-shift differences between MBD and TS are negligible. For layer arrangements with optimized interlayer stacking distances, we find that MBD yields larger stacking distances compared to TS; also the difference between the stacking distance for cofacial and displaced structures are larger for MBD. Nevertheless, considering the changes in the interaction energy and the individual contributions, one finds that the overall trends are qualitatively the same for MBD and TS also when the stacking distance is optimized. This suggests that the trends presented in the main manuscript are not massively affected by the employed dispersion correction scheme.

constant interlayer stacking distance									
shift / Å	$\Delta E_{int} / meV$	$\Delta E_{vdW}$ / meV	$\Delta E_{elstat} / meV$	$\Delta E_{Pauli,orb}$ / meV	z/Å				
0.0	-463	-2720	-1344	3601	2 2 2 9				
1.75	-1927	-2565	-1297	1935	5.526				
diff / meV	-1464	155	47	-1666	0.0				
	oľ	otimized interla	yer stacking di	stance					
0.0	-1393	-1886	-182	675	3.778				
1.75	-1973	-2398	-982	1407	3.415				
diff / meV	-580	-512	-800	732	-0.363				

*Table S3.* Interaction energy ad individual contributions when employing many body dispersion, MBD, corrections to the energy.

1			00						
constant interlayer stacking distance									
shift / Å	$\Delta E_{int} / meV$	$\Delta E_{vdW}$ / meV	$\Delta E_{elstat} / meV$	$\Delta E_{Pauli,orb}$ / meV	z/Å				
0.0	-1290	-3547	-1344	3601	2 2 2 9				
1.75	-2751	-3389	-1297	1936	3.328				
diff/meV	-1461	158	47	-1665	0.0				
	oľ	otimized interla	yer stacking di	stance					
0.0	-1957	-2769	-385	1197	3.636				
1.75	-2760	-3339	-1207	1786	3.350				
diff/meV	-803	-570	-822	589	-0.286				

**Table S4.** Interaction energy and individual contributions when employing the pairwise dispersion correction scheme by Tkatchenko and Scheffler,  $vdW^{TS}$ .

#### 2.6. Electronic band structure evaluated with a hybrid functional

For the constant interlayer stacking distance we also calculated the electronic bands employing the hybrid functional HSE06.<sup>8,9</sup> There, we find that the evolutions of the valence band shows good agreement comparing PBE and HSE06 results (compare Figure 5 and Figure S4). Nevertheless, the bandwidths obtained with HSE06 are somewhat larger (VBW=2045 meV (1835 meV) for cofacial and VBW=1165 meV (1038 meV) for the shifted arrangement when calculated with the HSE06 (PBE) functional) and the effective mass is somewhat smaller for HSE06 (m<sup>\*</sup>=0.55 (0.85) m<sub>e</sub> for cofacial and m<sup>\*</sup>=1.13 (1.31) m<sub>e</sub> for the shifted arrangement again for HSE06 (PBE)).



Figure S4. Electronic band structure of COF-1 for cofacial (a) and minimum arrangements (b) shifted by 1.75 Å parallel to a pore wall for constant interlayer stacking distance. The band structures have been calculated using the PBE (solid red lines) functional and the hybrid HSE06 (dashed black lines) functional.

# 2.7. Distance weighted histograms for COF-1

For rationalizing the evolution of the vdW interactions reported in the main manuscript we calculated histograms that show the number of atoms within a certain distance interval, i.e. that are within a sphere of a particular radius. This number of atoms was then weighted with the individual distance to the power of -6. This  $1/R^6$  weight is inspired by terms that are included in typical pairwise vdW corrections. In Figure S5 the data for COF-1 shifted along the edge of the pores and relaxed interlayer stacking distances is shown. Figure S6 shows the data for the system without relaxed stacking distance.

Figure S5 shows that when optimizing the stacking distance the low distance fraction increases for displacements up to 1.75 Å. This trend is perfectly in line with the vdW interactions becoming more attractive in this range of displacements. For constant stacking distance, one observes that for layer displacements up to 1.75 Å only minor changes in the histogram appear, which correlates with the almost constant vdW interaction for that range. For larger displacements significant changes are observed, which is again consistent with the vdW interactions showing larges changes for such layer arrangements.



Figure S5. Histogram showing the number of atoms found within a certain interlayer distance interval and weighted by this distance to the power of -6 ( $\#atoms/(r^6)$ ) for COF-1 with optimized stacking distance. At each layer displacement such a histogram is created. One can see that the low distance contributions to this weighted number of atoms increase for displacements up to 1.75 Å, which is perfectly in line with the vdW interactions becoming more attractive in this region.



Figure S6. Histogram showing the number of atoms found within a certain interlayer distance interval and weighted by this distance to the power of -6 ( $\#atoms/(r^6)$ ) for COF-1 with constant stacking distance. At each layer displacement such a histogram is created. For layer displacements up to 1.75 Å one can sees only little changes in the histogram, which correlated with the almost constant vdW interaction for that range. For larger displacements, significant changes are observed, again perfectly consistent with the vdW showing large changes for such layer arrangements.

#### 2.8. Comparison of total energy and interaction energy for COF-1

In Figure S7 one can see the evolution of the total energy and that of the interaction energy for COF-1 shifted along direction 1 with optimized stacking distances for each displacement. Both energies are aligned to their respective values for the cofacial arrangement. One can see that these energies essentially evolve in parallel and that only minor numerical differences occur. The reason why these energies do not coincide is that for each displacement the stacking distance and, thus, the unit cell vector along that direction, changes and so also the energies of fragments A and B (entering the determination of  $\Delta E_{int}$ ) vary. Nevertheless, two energy curves show a excellent qualitative agreement.



Figure S7. Comparison of the evolution of the total energy (grey triangles and line) and the interaction energy (red squares and line) for COF-1 shifted along direction 1 with optimized stacking distances. Energies at cofacial arrangement:  $\Delta E_{int}$ =-1957 meV,  $E_{total}$ =-70443.275 eV;

#### 2.9. Relative energies of COF-5

In Figure S9 one can see the relative evolution of the energies of COF-5 as a function of displacements along a shift direction parallel to the edges of the pore, analogous to direction 1 of COF-1. For each displacement the stacking distance of consecutive COF-5 layers was optimized. Considering the evolution of the interaction energy we find that it exhibits a minimum at a displacement of around 1.5 Å, which is similar to COF-1. For both COFs, cofacial arrangements are energetically unfavorable and driving forces exist pushing these systems towards shifted layer arrangements. Decomposing the interaction energy into individual contributions comprising vdW interactions, electrostatic interactions and Pauli repulsion plus orbital rehybridization we find that their evolution shown in Figure S9b shows again very similar behavior compared to COF-1 (see Figure 6 of the main manuscript). Electrostatic and vdW interactions become more attractive upon layer displacements up to 1.5 Å and then, for larger displacements they become weaker again. The repulsion term (Pauli repulsion plus orbital rehybridization), on the contrary, gets more repulsive in the range of displacements where vdW and electrostatic contributions became more attractive. The sum of the changes in the vdW and the electrostatic interactions are larger than those of the repulsion, thus, they determine the formation of the minimum at the shifted layer arrangement of 1.5 Å.



Figure S9. (a) Relative energies of COF-5 as a function of the displacement for shifts along a direction parallel to one of the pore walls. The interlayer stacking distance was optimized at each displacement. Absolute energy values at 0.0 Å displacement:  $\Delta E_{int,elec}=1779$  meV,  $\Delta E_{vdW}=-8483$  meV,  $\Delta E_{elstat}=-1446$  meV,  $\Delta E_{Pauli,orb}=3225$  meV,  $\Delta E_{int}=-5238$  meV

#### 2.10. Stacking motif of graphite

In the main manuscript it was found that especially for HBC-COF the energetically favorable arrangement shows a packing motif of the C atoms of the hexabenzocoronene core which is largely reminiscent to that of graphite (CCDC 918549).<sup>10</sup> Therefore, we considered two stacking motifs of graphite, eclipsed AA-stacking and the energetically favorable serrated arrangement, and determined the relative energetics for these situations. The stacking distance was held constant for both systems. The structures of the considered systems are shown in Figure S10. For performing a decomposition of the interaction energy in analogy to the COFs in the main manuscript we had to consider graphene flakes stacked like graphite. This is due to the semi-metallic character of the individual graphene layers that are stacked when forming graphite. Nevertheless, the interaction energy for graphite and the considered flakes shows a consistent behavior. The energy contributions obtained from the decomposition of the system consisting of periodically stacked graphene flakes are shown in Table S5. They reveal a behavior reminiscent to COF-1 when considering a constant stacking distance. Pauli repulsion acts as the major driving force scompared to the COFs are at work.

The employed k-grids comprise 20x20x8 k-points for graphite and 3x3x6 k-points for the flakes.

<i>Table S5.</i> Energies of graphite and graphene flakes stacked similar to graphite. $E_{total}$ total
energy per unit cell, $\Delta E_{int}$ interaction energy, $\Delta E_{vdW}$ $vdW$ energy contribution, $\Delta E_{elstat}$
electrostatic energy contribution, $\Delta E_{Pauli,orb}$ Pauli repulsion with orbital rehybridization ;
The energies are given for the cofacial and the optimal arrangement for the two graphite
systems. A decomposition is only available for the system constructed from graphene flakes.

1	1				1 0	
		graphite	graphite flake		l-cofacial)	
$E_{total} / eV$	cofacial	-4148.8606	-312093.7544	0.053	2 071	
	optimal	-4148.9135	-312097.7253	-0.033	-3.971	
$\Delta E_{int}$ / meV	cofacial	-252	-15702	52	2071	
	optimal	-305	-19673	-35	-39/1	
	cofacial	-344	-22803	10	61	
$\Delta E_{vdW}$ / mev	optimal	-354	-22867	-10	-04	
$\Delta E / m a V$	cofacial	/	-6247	1	601	
$\Delta E_{elstat}$ / IIIe v	optimal	/	-5556	/	091	
$\Delta E_{Pauli,orb} / meV$	cofacial	/	13348	/	4508	
	optimal	/	8750	/	4398	



*Figure S10. Energetically favorable stacking motif of (a) graphite, (b) periodically stacked graphite flakes, and (c) the HBC-COF. Colors of the atoms: C ... grey, N ... blue, H ... white;* 

#### 2.11. Electronic band structures of COF-5 and HBC-COF

The electronic band structures of COF-5 and HBC-COF have been evaluated for the cofacial and the energetically favorable serrated arrangement. The corresponding plots are shown in Figures S11 and S12.

Let us start by considering the data for COF-5. From the electronic band structures plotted for the region around the valence and conduction bands of the material one can see quite some differences when comparing the cofacial arrangement to the energetically favorable serrated stacking motif. First of all, it is observed the width of the valence band is decreased for the shifted arrangement. This in turn leads to an increase of the effective mass as already discussed in the main manuscript. Moreover, one can see that the valence band maximum, which is originally located at  $\Gamma$  for the cofacial arrangement, is shifted to M, and K respectively. Considering these points we find that the effective masses are even larger (4.39 m<sub>0</sub> for M- $\Gamma$ and >13 m<sub>0</sub> for K- $\Gamma$ ). However, the energy difference between the VBM at M and the Gamma point is only ~10 meV. Therefore, as the Gamma point is very close in energy to the VBM, one might also consider this point and the respective bands along a direction parallel to the  $\pi$ stacking of the COF-layers (as done in the main manuscript). Additionally, one can see that the band-gap increases from the cofacial arrangement to the shifted one. From HSE06 calculations we find that this increase from 2.0 eV to 2.6 eV.

For HBC-COF, one can see a very similar behavior compared to COF-5.



Figure S11. Electronic band structure of COF-5 for the cofacial (a) arrangement and the energetically favorable, shifted arrangement (b). A zoom into the region of the valence band is shown in the bottom panel.



Figure S12. Electronic band structure of HBC-COF for the cofacial (a) arrangement and the energetically favorable, shifted arrangement (b). A zoom into the region of the valence band is shown in the bottom panel. Like for COF-5 one can also see an increase in the HOMO-LUMO gap, however, for the larger HBC-COF we did not perform HSE06 calculations and thus refrain from reporting actual numbers.

# 2.12. Additional stacking motifs of COF-1

In addition to the considered stacking motifs presented in the main manuscript, we also considered AB-type stacking for COF-1 when optimizing the stacking distance. Furthermore, a more "exotic" type of stacking, ABC-type, which has been reported recently,<sup>11</sup> has also been considered. For a more direct comparison between cofacial stacking and the ABC stacking motif we also considered a 3 layer system exhibiting AA-stacking, the AAA system. The corresponding data are presented in Table S6 and the structures are shown in Figure S13. From the total energy per layer for AB and ABC stacking motifs we find that these arrangements are energetically favorable with respect to cofacial AA-stacking. However, it is important to note that these arrangements are significantly higher in energy than the serrated stacking motif identified as the energetically favorable structure in the main manuscript. Regarding the individual energy terms we can note that AB and ABC stacking come along with a significant reduction of the attractive vdW and electrostatic interactions. For the structures discussed in Ref 11 it seems that ABC stacking is largely driven by steric interactions, which are of no relevance for COF-1. They certainly become important for non-planar systems like COF-366. These systems might even get kinetically trapped at a specific stacking motif which is not the energetically most favorable one.

**Table S6.** Energies per layer and structural parameters (displacement vectors, stacking distances) of COF-1 exhibiting different stacking motifs: AA, AB, ABC, and AAA. The stacking distance was held constant and optimized.  $z \dots$  stacking distance,  $E_{total} \dots$  total energy per unit cell,  $\Delta E_{int} \dots$  interaction energy,  $\Delta E_{vdW} \dots vdW$  energy contribution,  $\Delta E_{elstat} \dots$  electrostatic energy contribution,  $\Delta E_{Pauli,orb} \dots$  Pauli repulsion with orbital rehybridization; The stacking distances as well as the energies are given for the cofacial and the optimal arrangement for each COF.

		AA	AB	AAA	ABC
z / Å	constant	3.328	3.328	3.328	3.328
	optimal	3.636	3.019	/	3.043
$E_{total} / eV$	constant	-35221.3355	-35221.6448	-35221.3355	-35221.6201
	optimal	-35221.6376	-35221.7452	/	-35221.7060
$\Delta \Sigma / m a V$	constant	-645	-954	-726	-1011
$\Delta E_{int} / IIIe v$	optimal	-978	-999	/	-1089
AE /maV	constant	-1774	-965	-1859	-1021
$\Delta E_{vdW}$ / me v	optimal	-1385	-1195	/	-1258
AE /maV	constant	-620	-215	-643	-207
$\Delta E_{elstat} / meV$	optimal	-672	-558	/	/
$\Delta E_{Pauli,orb}$ / meV	constant	1749	226	1776	217
	optimal	1079	754	/	/



Figure S13. Structures of COF-1 exhibiting AB-type stacking (a) and ABC-type stacking with a top view in (b) and a perspective view in (c). The A and B layers have been colored in blue and purple for better visibility.

## 2.13. Electronic band structures of NH-Por and Zn-Por at PBE and HSE06 level

The electronic band structures for the two porphyrin based COFs NH-Por (see Figures S14 and S15) and Zn-Por (Figures S16 and S17) have been calculated at the semi-local GGA level by employing the PBE functional. In order to get a more accurate prediction of the band gap we also employed the hybrid functional HSE06. Based on the HSE06 calculations we find that an indirect gap of around 0.5 eV opens for the serrated stacking motif. This suggests that there appears a metal-to-semiconductor transition between the cofacial arrangement and the energetically favorable serrated stacking motif.



Figure S14. Electronic band structure of NH-Por COF. for the cofacial (a) arrangement and the energetically favorable, shifted arrangement (b). A zoom into the region of the valence band is shown in the bottom panel. One can see that for the serrated arrangement that already at the PBE level a small indirect gap of around 0.2 eV opens.



Figure S15. Electronic band structure of NH-Por COF calculated at the HSE06 level for the cofacial (a) arrangement and the energetically favorable, shifted arrangement (b). One can see that for the serrated arrangement a small indirect gap of around 0.5 eV opens.



Figure S16. Electronic band structure of Zn-Por COF. for the cofacial (a) arrangement and the energetically favorable, shifted arrangement (b). A zoom into the region of the valence band is shown in the bottom panel. One can see that for the serrated arrangement that already at the PBE level a small indirect gap of around 0.2 eV opens.



Figure S17. Electronic band structure of Zn-Por COF calculated at the HSE06 level for the cofacial (a) arrangement and the energetically favorable, shifted arrangement (b). One can see that for the serrated arrangement a small indirect gap of around 0.5 eV opens.

### 2.13 Porosity of the considered COFs

In order to quantitatively assess the porosity of the various structures presented here, various characteristic measures have been calculated utilizing the Zeo++ code (version 0.2.2).<sup>12</sup> Using this package, the pore sizes were analyzed in terms of three different pore diameters by means of a Voronoi decomposition:<sup>13</sup> the diameter of the largest included sphere (regardless of whether the associated pore is also accessible for this sphere or not), D1, the largest free sphere (i.e. the largest sphere that fits in the narrowest pore or channel), D2, and the largest included sphere along the path of the free sphere, D3. Beyond those diameters (non-)accessible surface areas, (N)ASAs, and (non-)accessible volumes, (N)AVs, were calculated from a Monte Carlosampling approach (using 106 sampling points per atom for the (N)ASA calculations, and 106 sampling points per unit-cell for the (N)AV calculations) which randomly samples spheres in the unit-cell and discards all those ones overlapping with each other or with the atoms so that the total surface area can be estimated from the non-discarded probing spheres. For this statistical determination of the ASA, three probe radii were used (1.32 Å, 1.86 Å, and 1.92 Å), which are typically used to resemble the average radius of a helium atom, a nitrogen molecule and an argon atom approximated as a sphere.<sup>14,15</sup>

**Table S7.** Volume per unit-cell, V, and mass density,  $\rho$ , of the studied systems as well as the calculated diameters of the largest included spheres,  $D_1$ , the largest free sphere,  $D_2$ , and the largest included sphere along the path of the free sphere,  $D_3$ . Here, and in the following tables cofacial and shifted refer to systems that were considered in section 3.5 of the main manuscript. Thus, these systems are constructed following the procedure described in section 1.2.1 and 1.2.4 of this Supporting Information.

		COF-1	COF-5	COF-366	HBC-COF	Zn-Por	NH-Por
$\mathbf{V}$ / $\mathbf{\hat{X}}$ 3	cofacial	1435	5646	5609	5637	1305	1305
$\mathbf{v} / \mathbf{A}^{\mathbf{v}}$	shifted	1333	5337	5032	5347	1218	1225
a / 1	cofacial	0.900	0.547	0.516	0.803	1.186	1.024
ρ / kgm <sup>s</sup>	shifted	0.969	0.579	0.575	0.847	1.270	1.091
	cofacial	9.48	23.95	19.98	12.00	7.83	7.80
$D_1 / A$	shifted	8.49	22.85	19.71	11.35	6.97	7.02
	cofacial	8.92	23.72	19.68	11.55	7.18	7.16
$D_2 / A$	shifted	7.87	22.62	19.61	11.04	6.21	6.26
D <sub>3</sub> / Å	cofacial	9.47	23.95	19.98	12.00	7.83	7.80
	shifted	8.49	22.85	19.71	11.35	6.97	7.02

**Table S8.** Characteristics quantifying the porosity of the studied systems calculated with a probe radius of 1.32 Å (resembling He). (N)ASA...(Non-)Accessible Surface Area, (N)AV...(Non-)Accessible Volume. The AV fraction corresponds to the ratio of the AV per unit-cell and the total volume per unit-cell. Relative changes for the ASA per volume between cofacial and shifted stacking are given in brackets.

		COF-1	COF-5	COF-366	HBC-COF	Zn-Por	NH-Por
ASA per unit-cell /	cofacial	204	635	685	831	178	177
Å <sup>2</sup>	shifted	183	611	598	792	161	162
ASA per volume /	cofacial	1420	1125	1221	1475	1366	1359
$m^2 \text{cm}^{-3}$	shifted	1372	1146	1189	1481	1323	1320
		(3.4 %)	(-1.7 %)	(2.6 %)	(-0.4 %)	(3.2 %)	(2.9%)
ASA per mass /	cofacial	1577	2057	2367	1836	1152	1328
$m^2g$	shifted						
8		1416	1980	2068	1748	1042	1210
NASA per unit-	cofacial	0	0	0	0	0	0
cell / Å <sup>2</sup>	shifted	0	0	0	0	0	0
AV per unit-cell /	cofacial	284	2986	2723	1616	169	168
Å <sup>3</sup>	shifted						
		238	2759	2384	1423	134	136
AV fraction	cofacial	0.198	0.529	0.486	0.287	0.129	0.129
	shifted	0.178	0.517	0.474	0.266	0.110	0.111
AV per mass /	cofacial	0.22	0.97	0.94	0.36	0.11	0.13
$cm^3g^{-1}$	shifted						
0		0.18	0.89	0.82	0.31	0.09	0.10
NAV per unit-cell	cofacial	0	0	0	0	0	0
/ Å <sup>3</sup>	shifted	0	0	0	0	0	0

**Table S9.** Characteristics quantifying the porosity of the studied systems calculated with a probe radius of 1.86 Å (resembling  $N_2$ ). (N)ASA...(Non-)Accessible Surface Area, (N)AV...(Non-)Accessible Volume. The AV fraction corresponds to the ratio of the AV per unit-cell and the total volume per unit-cell. Relative changes for the ASA per volume between cofacial and shifted stacking are given in brackets.

		COF-1	COF-5	COF-366	HBC-COF	Zn-Por	NH-Por
ASA per unit-cell /	cofacial	150	567	611	698	110	109
Å <sup>2</sup>	shifted						
		137	551	540	650	96	97
ASA per volume /	cofacial	1046	1005	1090	1238	843	838
$m^2 cm^{-3}$	shifted	1026	1033	1074	1216	792	791
		(1.9 %)	(-2.8 %)	(1.5 %)	(1.8 %)	(6.0 %)	(5.6 %)
ASA per mass /	cofacial	1162	1838	2114	1541	711	818
$m^2g$	shifted						
		1058	1785	1868	1435	623	725
NASA per unit-	cofacial	0	0	0	0	0	0
cell / Å <sup>2</sup>	shifted	0	0	0	0	0	0
AV per unit-cell /	cofacial	190	2663	2374	1206	92	92
Å <sup>3</sup>	shifted						
		152	2447	2076	1034	67	68
AV fraction	cofacial	0.132	0.472	0.423	0.214	0.071	0.070
	shifted	0.114	0.459	0.412	0.193	0.055	0.056
AV per mass /	cofacial	0.15	0.86	0.82	0.27	0.06	0.07
$cm^3g^{-1}$	shifted						
		0.12	0.79	0.72	0.23	0.04	0.05
NAV per unit-cell	cofacial	0	0	0	0	0	0
/ Å <sup>3</sup>	shifted	0	0	0	0	0	0

**Table S10.** Characteristics quantifying the porosity of the studied systems calculated with a probe radius of 1.926 Å (resembling Ar). (N)ASA...(Non-)Accessible Surface Area, (N)AV...(Non-)Accessible Volume. The AV fraction corresponds to the ratio of the AV per unit-cell and the total volume per unit-cell. Relative changes for the ASA per volume between cofacial and shifted stacking are given in brackets.

		COF-1	COF-5	COF-366	HBC-COF	Zn-Por	NH-Por
ASA per unit-cell /	cofacial	146	561	605	686	105	104
Å <sup>2</sup>	shifted	122	546	525	()7	02	02
		132	546	535	63/	92	92
ASA per volume /	cofacial	1015	994	1078	1218	803	799
$m^2 cm^{-3}$	shifted	994	1023	1063	1192	753	753
		(2.1 %)	(-2.9 %)	(1.4 %)	(2.1 %)	(6.2 %)	(5.8 %)
ASA per mass /	cofacial	1127	1819	2091	1516	677	780
$m^2g$	shifted						
8		1025	1767	1849	1408	593	690
NASA per unit-	cofacial	0	0	0	0	0	0
cell / Å <sup>2</sup>	shifted	0	0	0	0	0	0
AV per unit-cell /	cofacial	181	561	605	686	105	104
Å <sup>3</sup>	shifted						
		144	546	535	637	92	92
AV fraction	cofacial	0.126	0.466	0.417	0.206	0.066	0.065
	shifted	0.108	0.452	0.406	0.186	0.051	0.051
AV per mass /	cofacial	0.14	0.85	0.81	0.26	0.06	0.06
$cm^3 q^{-1}$	shifted						
8		0.11	0.78	0.71	0.22	0.04	0.05
NAV per unit-cell	cofacial	0	0	0	0	0	0
/ Å <sup>3</sup>	shifted	0	0	0	0	0	0

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