Supporting Information

Enforcing Extended Porphyrin J-Aggregate Stacking in Covalent Organic Frameworks

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Table of contents

1 Materials and methods S2
2 Syntheses S3
3 Simulations S4
4 X-Ray diffraction S11
5 IR spectroscopy S13
6 UV-Vis and fluorescence spectroscopy S15
7 Time correlated single photon counting S18
8 Differential pulse voltammetry and optical bandgap of the starting materials S21
9 Solid-state nuclear magnetic resonance S24
10 References S25

Abbreviations

BET Brunauer-Emmett-Teller
DFT density functional theory
HOMO highest occupied molecular orbital
IRF instrument response function
LUMO lowest unoccupied molecular orbital
OMe 2,5-dimethoxybenzene-1,4-dicarboxaldehyde
1P terephthalaldehyde
2P 4,4'-biphenyldicarboxaldehyde
Por 5,10,15,20-tetrakis(4-aminophenyl)porphyrin
QSDFT quenched solid density-functional theory
SHE standard hydrogen electrode
TT thieno[3,2-b]thiophene-2,5-dicarboxaldehyde
Section 1: Materials and methods

Unless stated otherwise, all reactions were performed in oven-dried glassware under a positive pressure of Ar. All reagents and solvents were sourced from commercial suppliers and used without further purification. Solvents were, unless provided under inert gas, degassed and saturated with argon prior to use. Thiено[3,2-b]thiophene-2,5-dicarboxaldehyde (TT) and 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (compound 1) were acquired from Sigma Aldrich and PorphyChem, respectively.

**Magic angle spinning (MAS) solid state nuclear magnetic resonance (ssNMR)** spectra were recorded using a Bruker Avance III 500 spectrometer.

**Infrared (IR) spectra** were recorded on a Perkin Elmer Spectrum BX II FT-IR system and a Thermo Scientific Nicolet™ 6700 FT-IR spectrometer in transmission mode. IR data are reported in wavenumbers (cm\(^{-1}\)).

The **nitrogen sorption** isotherm was recorded on a Quantachrome Autosorb 1 at 77 K in a pressure range from \(p/p_0 = 0.001\) to \(0.98\). Prior to the measurement of the sorption isotherm, the sample was heated for 24 h at 120°C under turbomolecular pump vacuum. For the evaluation of the surface area, the BET model was applied between 0.05 and 0.2 \(p/p_0\). The calculation of the pore size distribution was done using the QSDFT equilibrium model with a carbon kernel for cylindrical pores on the adsorption branch. The Connolly surface area differs from the experimental data usually due to the non-ideal composition and structure of the COF sample. Grain boundaries and the displacement of COF layers may lead to defects in the crystalline structure and to blocked pores and thus lower experimental values. Adsorbed molecular fragments may also decrease the accessible surface area.

**Powder X-ray diffraction (PXRD)** measurements were performed using a Bruker D8 Discover with Ni-filtered Cu K\(_\alpha\) radiation and a LynxEye position-sensitive detector.

**Transmission electron microscopy (TEM)** measurements were performed on a probe-corrected FEI Titan Themis 60-300 kV (FEI Company/Thermo Fisher Scientific Inc., USA) electron microscope equipped with a Super-X windowless EDX (four quadrant SDD EDX detection) and a X-FEG high-brightness gun with monochromator (energy spread <0.2 eV). **Scanning electron microscopy (SEM)** measurements were performed on a FEI Helios NanoLab G3 UC electron microscope (FEI Company/Thermo Fisher Scientific Inc., USA) with a X-MaxN EDX detector (Oxford Instruments, UK). The samples were mounted on sample carriers with a sticky carbon support and sputtered with carbon on a Bal-Tec MED 020 coating system.

**UV-Vis spectra** were recorded using a Perkin-Elmer Lambda 1050 spectrometer equipped with a 150 mm integrating sphere. **Diffuse reflectance** spectra were collected with a Praying Mantis (Harrick) accessory and were referenced to barium sulfate powder as white standard.

**Photoluminescence (PL)** measurements were performed using a home-built setup consisting of a Horiba Jobin Yvon iHR 320 monochromator equipped with a photomultiplier tube and a liquid N\(_2\)-cooled InGaAs detector. The samples were illuminated with a pulsed (83 Hz) 365 nm or 405 nm LED at a light intensity of 500 mW cm\(^{-2}\).

Time-resolved PL measurements were acquired using a **time correlated single photon counting (TCSPC)** setup (FluoTime 300, PicoQuant GmbH). The samples were photo-excited using lasers with suitable wavelengths according to the sample absorption, i.e. 378 nm, 403 nm or 507 nm wavelength (LDH-P-C-375, LDH-P-C-405, and LDH-P-C-510, respectively, all from PicoQuant GmbH) pulsed at 500 kHz, with a pulse duration of \(~100\) ps and fluence of \(~300\) nJ/cm\(^2\)/pulse. The samples were exposed to the pulsed light source set at 3 μJcm\(^{-2}\)/pulse fluence for \(~10\) minutes prior to measurement to ensure stable sample emission. The PL was collected using a high-resolution monochromator and photomultiplier detector assembly (PMA-C 192-N-M, PicoQuant GmbH).

**Differential pulse voltammetry (DPV)** was measured using 50 μM solutions of the starting materials in acetonitrile or in a mixture of acetonitrile and dioxane (8 Vol%), with 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte and 0.1 mM ferrocene as internal reference. Measurements were performed with a Metrohm Autolab PGSTAT302N potentiostat, using Pt wires as the working electrode and counter electrode and a saturated Ag/AgCl reference electrode (Sigma Aldrich, 0.197 V vs. SHE). The potential window was from \(-1.8\) V up to \(1.4\) V with a modulation amplitude of 0.005 V, modulation time of 0.05 s and an interval time of 0.5 s.
**Section 2: Syntheses**

The reaction conditions for all COF syntheses were optimized in a screening program concerning solvents, solvent ratio, concentration and volume of the acid, temperature and reaction time.

**TT-Por COF**

For the synthesis of TT-Por COF, 13.5 mg of 5,10,15,20-(tetra-4-aminophenyl)porphyrin, further mentioned as compound 1 (0.02 mmol, 1 equiv.) and 7.9 mg of thieno[3,2-b]thiophene-2,5-dicarboxaldehyde, further referred to as TT (0.04 mmol, 2 equiv.) were added to a 10 mL Schott culture tube with screw cap and dispersed in a solvent mixture of benzyl alcohol, o-dichlorobenzene and 6 M acetic acid (30:10:4 v:v:v, 550 µL). The tube was placed in an oven at 120 °C for 72 h. After the time had elapsed, the reaction mixture was allowed to cool down to room temperature and the resulting powder was then collected by filtration through a Hirsch funnel. After washing the product three times with dry 1,4-dioxane, it was dried under vacuum, followed by CO2-extraction to furnish TT-Por COF as a black powder at a high yield of 75%.

Elemental analysis (calculated, found for C$_{60}$H$_{36}$NaS$_{4}$): C (72.41, 68.68), H (3.44, 3.86), N (11.26, 10.14), S (12.89, 11.12).

**COF-366**

13.5 mg compound 1 (0.02 mmol, 1 equiv.) and 5.36 mg of terephthalaldehyde (0.04 mmol, 2 equiv.) were dispersed in a solvent mixture of benzyl alcohol, mesitylene and 6 M acetic acid (10:20:3 v:v:v, 550 µL) in a 10 mL Schott culture tube with screw cap. The tube was heated in an oven at 120 °C for 72 h. After cooling down, the product was isolated by filtration, followed by three washing cycles with 1,4-dioxane. The dark purple product was dried under reduced pressure, followed by CO2-extraction to furnish COF-366 as a brownish, black powder at a high yield of 76%.

Elemental analysis (calculated, found for C$_{60}$H$_{36}$NaS$_{4}$): C (82.74, 79.99), H (4.40, 4.73), N (12.86, 12.81).

**OMe-Por COF**

6.74 mg compound 1 (0.01 mmol, 1 equiv.) and 5.82 mg of 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (0.02 mmol, 2 equiv.) were dispersed in a solvent mixture of benzyl alcohol, mesitylene and 6 M acetic acid (49:49:2 v:v:v, 510 µL) in a 10 mL Schott culture tube with screw cap. The tube was heated in an oven at 100 °C for 2 h and then heated at 120 °C for 72 h. After cooling down, the product was isolated by filtration, followed by CO2-extraction to furnish OMe-Por as a brownish, black powder at a high yield of 71%.

Elemental analysis (calculated, found for C$_{64}$H$_{56}$Na$_{2}$O$_{4}$): C (77.56, 77.22), H (4.68, 4.96), N (11.31, 11.90).

**2P-Por COF**

6.74 mg compound 1 (0.01 mmol, 1 equiv.) and 4.20 mg of 4,4’-biphenyldicarboxaldehyde (0.02 mmol, 2 equiv.) were dispersed in a solvent mixture of 1,4-dioxane, mesitylene and 6 M acetic acid (58:29:12 v:v:v, 570 µL) in a 10 mL Schott culture tube with screw cap. The tube was heated in an oven at 70 °C for 2 h and then heated at 120 °C for 72 h. After cooling down, the product was isolated by filtration, followed by three washing cycles with mesitylene. The dark purple product was dried under reduced pressure, followed by CO2-extraction to furnish 2P-Por COF as a brownish, black powder at a high yield of 69%.

Elemental analysis (calculated, found for C$_{72}$H$_{68}$Na$_{2}$): C (84.52, 82.40), H (4.53, 4.70), N (10.95, 9.58).
Section 3: Simulations

To determine the crystal structure of the obtained products, a powder diffraction pattern was calculated based on a simulated crystal structure. The unit cell was constructed using the Materials Studio software and optimized by force field calculations. Due to the non-planar porphyrin building block, the unit cell is limited to a triclinic P1 symmetry in the case of a stacked staircase structure and to P4 symmetry for an eclipsed arrangement. The comparison of the calculated pattern with the experimental data identified the obtained structure as staircase stacked TT-Por COF.

DFT calculations were performed using Vienna Ab initio Simulation Package (VASP)\(^1\) code, which employs a plane-wave basis set and the projector augmented-wave method\(^2\). The applied Perdew-Burke-Ernzerhof exchange-correlation functional\(^3\) was supplemented by the D3 van der Waals correction\(^4\) (including Becke-Johnson damping)\(^5\) to take dispersive forces into account. The energy cutoff for the plane-wave basis-set was set to 415 eV. The Brillouin zone (BZ) was sampled by 2\(\times\)2\(\times\)6 Monkhorst-Pack k-point grids\(^6\). Electronic structures and geometries converged below 1\(\times\)10\(^{-7}\) eV and 0.01 eVÅ\(^{-1}\) with respect to total energies and forces acting on ions, respectively.

All semiempirical calculations were performed in the EMPIRE program. The unit cell was optimised in the way of manual scan over each of 6 transition vectors while the structure was optimised within each point of this scan. The last 3 vectors are particulary important, as they are defining interlayer distance and a split visible in XRD data. These values are also affected the strongest by varying of Hamiltonian and switching the Grimme correction on and off.

Optimized structures within the optimized unit cell are listed in Tables S1 and S3.

Force-field-based simulated annealing was performed using Dreiding force-field\(^7\) in LAMMPS computational package.\(^8\) Supercells were built as 10\(\times\)10\(\times\)10 and 5\(\times\)5\(\times\)40 unit cells. Calculations included relaxation, MD at constant temperature 300 K for 1 nanosecond (timestep 1 femtosecond) and 5 time gradual heating and cooling from 300 K to 800 K and back in 2 millions steps during 2 nanoseconds. Thus, the total length of the annealing simulation is 10 nanoseconds. Each of the annealed structures was kept one nanosecond longer in MD simulation under the constant temperature to ensure that total energy did not decrease or significant geometry shifts did not occur, respectively. XRD data for these structures were computed with 2Theta values in the range from 2.0° to 45°, with the most interesting area (2-8°) plotted in the main text of the article. Heating to higher temperature as well as more rapid cooling were tested on the smaller supercells. Among the obtained snapshots we found structures with very significant slicing of one layer or blocking of few layers with respect to the rest of the layers. This results in additional XRD peaks that are different for each structure with this kind of defects and do not occur in experimental patterns. However, experimental spectra have a significantly higher level of noise than predicted from simulation described above, thus this kind of defects has not to be excluded.

Table S1: Cell parameters from experiment and different levels of simulation

| Cell parameter | X-Ray | DFT | Semiempirics |
|----------------|-------|-----|--------------|
| \(a\) (Å)      | 27.96 | 27.41 | 27.20        |
| \(b\) (Å)      | 27.92 | 27.46 | 27.17        |
| \(c\) (Å)      | 4.51  | 4.57  | 4.48         |
| \(\alpha\) (°) | 113.83| 111.41| 115.39       |
| \(\beta\) (°)  | 79.04 | 80.85 | 79.71        |
| \(\gamma\) (°) | 96.0  | 94.34 | 95.70        |

Table S2: Calculated energies of optimized TT-Por COF

| Energy           | Value     |
|------------------|-----------|
| Total energy     | -750.82 eV|
| D3 energy        | -7.37 eV  |

Table S3: xyz-coordinates of optimized structures

| PBE-D3          | AM1-D3     |
|-----------------|------------|
| H 3.513296467   | 24.902945380 | 2.806906687 | 2.806906687 | 1.426674 | -0.738334 |
| H 5.964908645   | 24.976642310 | 2.818532626 | 0.258639937 | -1.614292 | 1.521637 |
| H 2.344030758   | 4.759690262  | 0.258639937 | 0.208028521 | 0.208028521 | 0.208028521 |
Table S4: Calculated total energy and lattice parameters of TT-Por COF in a geometry with an initial interlayer spacing of 15 Å and fixed unit cell volume.

| Total energy | -749.01 eV |
| D3 energy    | -5.14 eV   |
| Cell parameters |
| a            | 27.39 Å   |
| b            | 27.33 Å   |
| c            | 15.13 Å   |
| α            | 95.33     |
| β            | 89.91     |
| γ            | 90.97     |

Table S5: xyz-coordinates of optimized TT-Por COF with an initial interlayer spacing of 15 Å and fixed unit cell volume.

| H    | 4.086719378 | 24.974673068 | 13.657355127 |
| H    | 6.552029911 | 25.073286238 | 13.763414277 |
| H    | 2.303563290 | 4.764899127  | 0.192741405  |
| H    | 4.354965306 | 3.032670135  | 0.035755019  |
| H    | 5.008682382 | 1.383198924  | 1.954315181  |
| H    | 7.496477123 | 1.488642858  | 2.063566559  |
| H    | 15.278989379 | 0.568933542  | 1.932382834  |
| H    | 22.080276764 | 1.894045991  | 1.122464308  |
| H    | 19.614897566 | 1.795883601  | 1.016710743  |
| H    | 23.863019134 | 22.103757903 | 14.586350353 |
| H    | 21.811590102 | 23.836020471 | 14.743680850 |
|   |   |   |   |
|---|---|---|---|
| C | -0.903900708 | 22.213305320 | 15.314886826 |
| C | 25.139342857 | 23.936819090 | 14.664740271 |
| C | 23.410433610 | 25.398400525 | 14.746470471 |
| C | 23.918468676 | 23.185159459 | 14.746470471 |
| C | 22.870071188 | 24.070762174 | 14.715785712 |
| C | 21.207546065 | 26.507541600 | 14.726665313 |
| C | 20.557432172 | 25.891572840 | 13.641421271 |
| C | 19.170617175 | 25.838010095 | 13.572977779 |
| C | 18.373949921 | 26.364592269 | 14.605628040 |
| C | 0.351164045 | 5.543565713 | 14.354000213 |
| C | 0.512765269 | 4.163805142 | 14.266172317 |
| C | 0.306955956 | 8.359149758 | 15.122887093 |
| C | 0.038265299 | 9.768690908 | 15.182720057 |
| C | 0.848276851 | 10.792509622 | 14.700016864 |
| C | 0.269383054 | 12.056536311 | 14.924840182 |
| C | 24.930360767 | 0.623843778 | 14.386153830 |
| C | 25.884065811 | 3.887463511 | -0.577282166 |
| C | 24.149678988 | 1.849967874 | 14.268449382 |
| C | 25.038595027 | 2.877360545 | 14.321246747 |
| C | 26.929408641 | 6.134308026 | -0.442988463 |
| C | 26.288781751 | 6.715260905 | 0.666546439 |
| C | 26.113434885 | 8.090813090 | 0.756795699 |
| C | 26.596970282 | 8.945261287 | -0.252339535 |
| C | 22.690345046 | 26.607878898 | 14.774749801 |
| C | 3.476186549 | 0.260743219 | 0.004753447 |
| C | 1.236242899 | 26.244764014 | 0.393162740 |
| C | 0.282529776 | 22.981221874 | 15.356330122 |
| C | 2.016931589 | 25.018668989 | 0.510607173 |
| C | 1.128034590 | 23.991285422 | 0.457593263 |
| C | -0.762939166 | 20.734403122 | 15.221740055 |
| C | -0.122422840 | 20.153619916 | 14.112018455 |
| C | 0.052809340 | 18.778016927 | 14.021500717 |
| C | -0.430677148 | 17.923423272 | 15.030559401 |
| C | 25.815214389 | 21.324969982 | 0.424289280 |
| C | 25.653741509 | 22.704697449 | 0.512404351 |
| C | 25.859130844 | 18.509575967 | -0.345151797 |
| C | 26.127698572 | 17.100051697 | -0.405287758 |
| C | 25.317616003 | 16.076168896 | 0.077280441 |
| C | 25.896464355 | 14.812092117 | -0.147639360 |
| N | -0.197400221 | 16.554493921 | 14.889561225 |
| N | 0.369996165 | 24.350847563 | 15.331555743 |
| N | 26.363566087 | 10.314255952 | -0.111594330 |
| N | 25.796583804 | 2.517832581 | -0.552271668 |
| N | 16.988613366 | 26.288902878 | 14.451427879 |
|   |   |   |   |
|---|---|---|---|
| N | 24.781404233 | 25.265751514 | 14.727375113 |
| N | 9.177885794  | 0.580670926  | 0.328719438  |
| N | 1.385180036  | 1.602911543  | 0.051938061  |
| S | 12.112636043 | 0.573239863  | 1.049393164  |
| S | 14.054013678 | 26.296360574 | 13.730918783 |
| S | 25.441828346 | 13.178624228 | 0.185850480  |
| S | 0.724068631  | 13.690059338 | 14.591470175 |
|   | 27.3522114645 | +1.2093273530 | -0.6872402161 |
|   | -1.6593806253 | 27.2731628462 | 0.4267892610  |
|   | 0.4741983004  | -1.6140519556 | 15.0395126815 |
Section 4: X-Ray diffraction

COF-366 was analyzed via PXRD, revealing a crystalline framework.

Figure S1. Experimental PXRD data (black dots) of the COF-366. Pawley refinement (red line) using the P1 symmetric structure model shown on the right provides a very good fit to the experimental pattern (difference shown in light grey). The simulated crystal structure of COF-366 (grey line) is in good agreement with the experimental and the refined data, respectively. Differences in the peak intensities, in particular the altered intensity ratios between lower- and higher-angle reflections, may be caused by small oligomeric fragments trapped in the large COF pores (the attenuation of peak intensities due to this will be strongest at small 2θ angles).

OMe-Por COF and 2P-Por COF was analyzed via PXRD, revealing a crystalline framework.

Figure S2. Experimental PXRD data (black dots) of the OMe-Por COF. Pawley refinement (red line) using the P1 symmetric structure model shown on the right provides a very good fit to the experimental pattern (difference shown in light grey). The simulated crystal structure of OMe-Por COF (grey line) is in good agreement with the experimental and the refined data, respectively. Differences in the peak intensities, in particular the altered intensity ratios between lower- and higher-angle reflections, may be caused by small oligomeric fragments trapped in the large COF pores (the attenuation of peak intensities due to this will be strongest at small 2θ angles).
Figure S3. Experimental PXRD data (black dots) of the 2P-Por COF. Pawley refinement (red line) using the P1 symmetric structure model shown on the right provides a good fit to the experimental pattern (difference shown in light grey). The simulated crystal structure of 2P-Por COF (grey line) is in reasonable agreement with the experimental and the refined data. Differences in the peak intensities, in particular the altered intensity ratios between lower- and higher-angle reflections, may be caused by small oligomeric fragments trapped in the large COF pores (the attenuation of peak intensities due to this will be strongest at small 2θ angles).
Section 5: IR spectroscopy

The successful formation of the imine-linked TT-Por COF was confirmed by Fourier transform infrared (FTIR) spectroscopy. Consistent with previously reported COFs, the appearance of the characteristic C=N stretching mode at 1581 cm\(^{-1}\) indicates the coupling of the monomers via imine bonds (Figure S4). The lack of the aldehyde Fermi double resonance at 2841 and 2755 cm\(^{-1}\) as well as the aldehyde C=O stretching vibration at 1652 cm\(^{-1}\) suggests the complete consumption of the starting material TT-dialdehyde. Furthermore, the attenuation of the characteristic C-N stretching mode at 1285 cm\(^{-1}\) indicates the absence of the second starting material porphyrin-tetraphenylamine.\(^{9,10}\)

![Figure S4](image)

**Figure S4.** (a) IR spectra of TT-Por COF (blue), thienothiophene monomer (dark yellow) and porphyrin monomer (magenta), measured as powder. (b) Enlargement of the region of interest.

![Figure S5](image)

**Figure S5.** (a) IR spectra of OMe-Por COF (cyan), porphyrin monomer (magenta) and 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (orange). (b) Enlargement of the region of interest.

Furthermore, the successful synthesis of OMe-Por COF, COF-366 and 2P-Por COF was confirmed by FTIR spectroscopy. As seen in the spectra (Figure S5-S7), the lack of the aldehyde Fermi double resonance between 2750 cm\(^{-1}\) and 2850 cm\(^{-1}\) as well as the aldehyde C=O stretching vibration at 1669 cm\(^{-1}\), 1686 cm\(^{-1}\) and 1686 cm\(^{-1}\), respectively, suggests the complete consumption of the starting dialdehyde material (terephthalaldehyde, 2,5-dimethoxybenzene-1,4-dicarboxaldehyde and 4,4'-biphenyldicarboxaldehyde, respectively). Additionally, the attenuation of the characteristic C-N stretching mode at 1252 cm\(^{-1}\), 1285 cm\(^{-1}\), and 1284 cm\(^{-1}\), respectively, indicates the absence of the second starting material compound 1. The appearance of the C=N stretching mode at 1594 cm\(^{-1}\), 1564 cm\(^{-1}\), and 1572 cm\(^{-1}\), respectively, is characteristic for the formation of imine bonds within the COF material and indicates the successful Schiff base reaction of the monomers.\(^{9,10}\)
Figure S6. (a) IR spectra of COF-366 (green), porphyrin monomer (magenta) and terephthalaldehyde (gray). (b) Enlargement of the region of interest.

Figure S7. (a) IR spectra of 2P-Por COF (red), porphyrin monomer (magenta) and 4,4'-biphenyldicarboxaldehyde (light gray). (b) Enlargement of the region of interest.
Section 6: UV-Vis and fluorescence spectroscopy

Absorption spectra of the starting materials, TT-Por COF, COF-366, OMe-Por COF and 2P-Por COF (Figure S8) were collected from solid samples in diffuse reflection mode and transferred into absorption spectra by applying the Kubelka Munk equation:

\[ \frac{K}{S} = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \]

with \( K \) = Absorption Coefficient, \( S \) = the Scattering Coefficient, \( R_{\infty} \) = reflectance of sample with infinite thickness. 27

Figure S8. (a) UV-Vis spectra of TT-Por COF (blue) and the corresponding starting materials compound 1 (Por, magenta) and thienothiophene (TT, dark yellow). (b) UV-Vis spectra of OMe-Por COF (cyan) and the corresponding starting materials compound 1 (Por, magenta) and 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (OMe, orange). (c) UV-Vis spectra of COF-366 (green) and the corresponding starting materials compound 1 (Por, magenta) and terephthalaldehyde (1P, gray). (d) UV-Vis spectra of 2P-Por COF (red) and the corresponding starting materials compound 1 (Por, magenta) and 4,4'-biphenyldicarboxaldehyde (2P, light gray). Diffuse reflectance spectra measured for the respective powders dispersed in BaSO₄.
Figure S9. Tauc plot for absorption spectra (black) obtained with Kubelka-Munk function of the TT-Por COF and the linear fit for a direct band gap (red).

Figure S10. (a) Absorption (dark yellow) and PL ($\lambda_{exc} = 365$ nm, black) spectra of the TT starting material measured as solid. (b) Absorption (magenta) and PL ($\lambda_{exc} = 365$ nm, black) spectra of compound 1 measured as solid. Diffuse reflectance spectra measured for the respective powders dispersed in BaSO$_4$. 
Figure S11. (a) Optical absorption (OMe: orange, TT: dark yellow, 2P: light gray, 1P: gray) and PL ($\lambda_{exc} = 365$ nm, black) spectra of the starting materials. (b) Absorption (magenta) and PL ($\lambda_{exc} = 365$ nm, black) spectra of the compound 1. The absorbance of the compounds was measured in a 50 µM solution in dioxane.

Figure S12. Optical absorption spectra measured as diffuse reflectance of the solid and converted with the Kubelka Munk equation, and PL ($\lambda_{exc} = 365$ nm, black) spectra of TT-Por COF (a), OMe-Por COF (b), COF-366 (c) and 2P-Por COF (d).
Section 7: Time correlated single photon counting

The tri-exponential fit of the TCSPC histogram for TT-Por COF revealed long decay times of 4.90 ns (16.4%) and also two fast components with lifetimes of 0.55 ns (38.1%) and 0.15 ns (45.5%). Quenching by the imine bond weakens the PL intensity compared to the starting materials. Internal conversion involving bond rotation results in the deactivation of the singlet excited state which is primarily the reason for PL quenching in imines.11,12

Figure S13. (a) PL decay of TT-Por COF excited at 378 nm and measured at the maximum of the PL emission at 800 nm. (b) PL decay of OMe-Por COF excited at 408 nm and measured at the maximum of the PL emission at 735 nm. (c) PL decay of COF-366 excited at 378 nm and measured at the maximum of the PL emission at 735 nm. (d) PL decay of 2P-Por COF excited at 408 nm and measured at the maximum of the PL emission at 743 nm. Experimental decay: blue (TT-Por), dark cyan (OMe-Por), green (1P-Por) and red (2P-Por) dots, tri-exponential fit of the decay: cyan line, instrument response function: gray dots.

When comparing the lifetimes it is obvious that the TT-Por COF reveals the longest PL decay. In addition, the fractional intensity of the longest lifetimes is, with 16.4%, significantly higher for the TT-Por COF than the fractional intensities of OMe-Por COF, COF-366 and 2P-Por COF. Hence, the optoelectronic behavior of the TT-Por COF seems to be substantially different, which is attributed to different structural features indicated by the distinct peak splitting in the XRD data for the TT-Por COF compared to the other three COFs.
Table S6. PL decay times of TT-Por COF, OMe-Por COF, COF-366 and 2P-Por COF. The given errors are uncertainties from the fit and hence do not reflect the real time-resolution of the setup. The latter is limited by the laser pulse duration of around 100 ps.

|          | τ / ns | error / ns | fractional intensity / % |
|----------|--------|------------|---------------------------|
| TT-Por   | τ₁     | 4.9 ± 0.3  | 16.4                      |
|          | τ₂     | 0.55 ± 0.02| 38.1                      |
|          | τ₃     | 0.150 ± 0.006| 45.5                    |
| OMe-Por  | τ₁     | 3.2 ± 0.2  | 5.5                       |
|          | τ₂     | 0.60 ± 0.01| 37.9                      |
|          | τ₃     | 0.175 ± 0.003| 56.6                    |
| COF-366  | τ₁     | 1.74 ± 0.09| 6.5                       |
|          | τ₂     | 0.31 ± 0.01| 19.1                      |
|          | τ₃     | 0.066 ± 0.001| 74.4                    |
| 2P-Por   | τ₁     | 2.9 ± 0.2  | 7.5                       |
|          | τ₂     | 0.63 ± 0.01| 35.1                      |
|          | τ₃     | 0.121 ± 0.003| 57.4                  |

The PL lifetime was also measured for the two starting materials TT and (1) by illumination at 405 nm and 508 nm, respectively, with a pump fluence of ~0.99 nJ cm⁻²; the emission was monitored at the maximum of the PL emission at 550 nm for TT and at 800 nm for (1).
Figure S14. (a) PL decay of compound (1) excited at 508 nm and measured at the PL maximum at 800 nm. (b) PL decay of TT linker excited at 405 nm and measured at the PL maximum at 550 nm. All samples were measured as solids. Experimental decay: black dots, tri-exponential fit of the decay: red line, instrument response function: gray line.

Table S7: PL decay times of the starting materials (1) and TT, measured as solids. The given errors are uncertainties from the fit and hence do not reflect the real time-resolution of the setup. The latter is limited by the laser pulse duration of around 100 ps.

|          | \( \tau \) / ns | error / ns | fractional intensity / % |
|----------|-----------------|------------|--------------------------|
| Compound (1) | \( \tau_1 \) | 1.01 ± 0.02 | 47.7                     |
|          | \( \tau_2 \) | 0.365 ± 0.006 | 52.3                     |
| TT       | \( \tau_1 \) | 2.31 ± 0.06 | 37.3                     |
|          | \( \tau_2 \) | 0.42 ± 0.01 | 62.7                     |

Furthermore, TCS PC measurements were performed for the starting materials in dilute solutions of dioxane (50 \( \mu \)M), in which the monomers exist as individual molecules and intermolecular interactions can be neglected. It can be observed that the two starting materials TT and (1) observed as solvated molecules in dilute solutions have very long PL decay times, which when aggregated in a solid reduce to the order of 1 ns. This was also reported for porphyrin derivatives, which reveal shorter lifetimes when a J-aggregate behavior of the porphyrin stacks in the solid phase exists. When embedding (1) in a COF, the decay lifetimes far exceed those of the solid compound (1), but do not reach the PL lifetimes of the individual molecules in dilute solution.
Figure S15: (a) PL decay of compound (1) in dilute solutions of dioxane (50 µM) excited at 508 nm and measured at the maximum of the PL emission at 680 nm. (b) PL decay of TT in dilute solutions of dioxane (50 µM) excited at 378 nm and measured at the maximum of the PL emission at 495 nm. Experimental decay: black dots, tri-exponential fit of the decay: red line.

Table S8: PL decay times of the COF starting materials (1) and TT in dilute solutions of dioxane (50 µM). The given errors are uncertainties from the fit and hence do not reflect the real time-resolution of the setup. The latter is limited by the laser pulse duration of around 100 ps.

| Compound (1) | \( \tau \) / ns | error / ns | fractional intensity / % |
|--------------|------------------|------------|--------------------------|
| \( \tau_1 \) | 9.05             | ±0.02      | 100.0                    |
| \( \tau_2 \) | 0.987            | ±0.007     | 78.9                     |
| TT           | \( \tau_1 \)     | 4.04       | ±0.06                    | 21.1                     |
|              | \( \tau_2 \)     | 0.987      | ±0.007                   | 78.9                     |

Section 8: Differential pulse voltammetry and optical HOMO-LUMO gap of the starting materials

Differential pulse voltammetry was performed to obtain the energy levels of the HOMO from the different starting materials (Figure S16). The monomers were analyzed in dilute solutions of dioxane (50 µM) such that the starting materials exist as individual molecules, and interactions with other molecules are minimized. As a result, the measurement reveals the HOMO level of the solvated molecule. To identify the LUMO, Tauc plots were generated from the UV-Vis spectra (Figure S17) leading to the energy levels displayed in Figure S18.
Figure S16. DPV measurements of the starting materials referenced to ferrocene (at 0.0 V). (a) TT, (b) OMe, (c) 1P, (d) 2P and (e) compound 1 (Por).

Figure S17. Tauc plots generated from optical absorption spectra obtained with Kubelka-Munk data of the starting materials and linear fits for direct band gaps (red). (a) TT, (b) OMe, (c) 1P, (d) 2P and (e) compound 1 (Por).
Figure S18. DPV measurements of the starting materials and the corresponding HOMO-LUMO gaps lead to the exact positions of the HOMO (red) and LUMO (blue) of the monomers. The linear monomers (a) TT, (b) OMe, (c) 1P and (d) 2P are compared to the tetragonal porphyrin unit (compound 1, Por).
Section 9: Solid-state nuclear magnetic resonance

The formation of the imine bonds in the COF can be confirmed by solid-state nuclear magnetic resonance (ssNMR). In the $^{13}$C solid-state NMR only the carbons next to protons can be seen due to the cross-polarization. In the spectrum only four main broad peaks are clearly visible but there are some shoulders that can be attributed to other signals (Figure S19). The peak at 146 ppm can be attributed to C4 in the imine bonds arising from COF formation. For the TT unit only C5 is visible, appearing in the spectrum at 140 ppm. Furthermore, the phenyl carbons C2 and C3 are observed around 119 ppm and the side peak at 123 ppm. The carbons of the tetrapyrrrole subunit are summarized under C1 and can be found at 131 ppm and the shoulder at 133 ppm.

Figure S19: $^{13}$C ssNMR of TT-Por COF measured with cross polarization to enhance signal from $^{13}$C. Inset visualizes the different carbon species in the framework.
Section 10: References

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