Supporting Information

Oligothiophene-Bridged Conjugated Covalent Organic Frameworks

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Table of contents

A  Methods . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . S2
B  Building block syntheses . . . . . . . . . . . . . . . . . . . . . . . S3
C  COF syntheses . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . S13
D  NMR spectra of the building blocks . . . . . . . . . . . . . . . . . S14
E  HRMS analysis of the building blocks . . . . . . . . . . . . . . . . . S20
F  IR spectroscopy . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . S21
G  UV-VIS-NIR spectroscopy . . . . . . . . . . . . . . . . . . . . . . . . S22
H  PL spectroscopy . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . S23
I  Time-correlated single photon counting . . . . . . . . . . . . . . . . S24
J  Transmission electron microscopy . . . . . . . . . . . . . . . . . . . S25
K  Py-a4TMe COF XRD . . . . . . . . . . . . . . . . . . . . . . . . . . . . S26
L  Nitrogen sorption of the Py-a4TMe COF . . . . . . . . . . . . . . . S26
M  References . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . S27

Abbreviations

Ac  acetyl
Bn  benzyl
dba  trans,trans-dibenzylideneacetone
DCB  1,2-dichlorobenzene
DCE  1,2-dichloroethane
DCM  dichloromethane
DFT  density functional theory
DMF  N,N-dimethylformamide
DMSO  dimethyl sulfoxide
dppp  1,3-bis(diphenylphosphino)propane
EI  electron ionization
eq.  equivalents
Et  ethyl
HRMS  high resolution mass spectroscopy
IRF  instrument response function
NBS  N-bromosuccinimide
PL  photoluminescence
PXRD  powder X-ray diffraction
rt  room temperature
TCSPC  time-correlated single photon counting
TEM  transmission electron microscopy
TFP  tri(2-furyl)phosphine
THF  tetrahydrofuran
A. Methods

**Nuclear magnetic resonance** (NMR) spectra were recorded on Bruker AV 400 and AV 400 TR spectrometers. Chemical shifts are expressed in parts per million (δ scale) and are calibrated using residual (undeuterated) solvent peaks as an internal reference (1H-NMR: CDCl3: 7.26, DMSO-d6: 2.50, DMF-d7: 8.03; 13C-NMR: CDCl3: 77.16, DMSO-d6: 39.52, DMF-d7: 163.15). Data for 1H NMR spectra are reported in the following way: chemical shift (δ ppm) (multiplicity, coupling constant/Hz, integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, or combinations thereof.

High resolution electron ionization (EI) **mass spectra** (MS) were recorded with a Thermo Finnigan MAT 95 instrument.

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

The **structure models of the COFs** were built using the Forcite module of the Accelrys Materials Studio software package. For each COF structure, we applied the space group with the highest possible symmetry, taking into account the rotation of the phenylenes versus the pyrene core. Structure refinements using the Pawley method were carried out as implemented in the Reflex module of the Materials Studio software. Pseudo-Voigt peak profiles were used, and peak asymmetry was corrected using the Finger-Cox-Jephcoat method. A crystallite domain size of 100 nm along a, b and c, and lattice strain parameters of 0.5%, 0.5% and 0.2% along a, b, c, respectively, were assumed throughout the refinements. The asymmetric linear building blocks were treated as a superposition of both possible orientations, both having 50% occupancy.

**DFT-based geometry optimizations** were performed with the CASTEP code using the generalized-gradient-approximation PBE functional. The energy cutoff for the planewave basis set was set to 310.0 eV, ions were represented with ultra-soft pseudopotentials and k-point sampling was performed with a 1x1x4 Monkhorst-Pack grid (1x1x2 for the Py-a4T COF double layer). The correction scheme of Tkatchenko and Scheffler was used to account for dispersion interactions.

The **nitrogen sorption isotherms** were recorded on a Quantachrome Autosorb 1 at 77 K in a pressure range from $p/p_0 = 0.001$ to 0.999. For the evaluation of the surface area, the BET model was applied between 0.069 and 0.132 $p/p_0$. The pore size distribution was calculated from the adsorption branch using a QSDF model with a carbon kernel for cylindrical pores.

**Transmission electron microscopy** (TEM) was performed on an FEI Titan Themis instrument equipped with a field emission gun operated at 300 kV.

**Infrared** (IR) spectra were recorded on a Perkin Elmer Spectrum BX II FT-IR system equipped with a diamond attenuated total reflection unit.

**UV-VIS-NIR spectra** were recorded using a Perkin-Elmer Lambda 1050 spectrometer equipped with a 150 mm integrating sphere and photomultiplier tube (PMT) and InGaAs detectors. **Diffuse reflectance spectra** were collected with a Praying Mantis (Harrick) accessory and were referenced to barium sulfate powder as white standard. The specular reflection of the sample surface was removed from the signal using apertures that allow only light scattered at angles > 20° to pass.

**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 N2-cooled InGaAs detector. The samples were illuminated with a 378 nm diode laser (pulse power 0.99 nJ cm−2, pulse rate 40 MHz).

**Time-correlated single photon counting** (TCSPC) measurements were performed using a PicoQuant FluoTime 300 spectrometer equipped with a 378 nm picosecond diode laser (pulse power 0.99 nJ cm−2, pulse rate 40 MHz).
B. Building block syntheses

All reactions were performed in oven-dried glassware under argon atmosphere using standard Schlenk techniques. Reagents and solvents were obtained in high purity grades from commercial suppliers and used as received.

3-butylthiophene (1)

A solution of BuMgCl (2.0 M in THF, 100 mmol, 1.25 eq.) was slowly added to a solution of 3-bromothiophene (13.0 g, 80 mmol, 1.0 eq.) and Ni(dppp)Cl₂ (867 mg, 1.6 mmol, 2 mol%) in 120 mL THF. During the addition, the reaction mixture was maintained at room temperature by a water bath. After stirring at 30 °C overnight, the reaction mixture was quenched by the addition of 50 mL of 2M HCl, extracted with Et₂O, washed with brine, dried over MgSO₄, and concentrated under reduced pressure. Vacuum distillation (10⁻¹ mbar, 35°C) furnished the title compound as a colorless liquid (8.02 g, 57.2 mmol, 71%).

¹H NMR (400 MHz, CDCl₃): 7.24 (dd, \( J = 4.9, 2.9 \text{ Hz}, 1\text{H} \)), 6.94 (dd, \( J = 4.9, 1.3 \text{ Hz}, 1\text{H} \)), 6.93 – 6.91 (m, 1H), 2.67 – 2.62 (m, 2H), 1.66 – 1.57 (m, 2H), 1.42 – 1.31 (m, 2H), 0.93 (t, \( J = 7.3 \text{ Hz}, 3\text{H} \)).
2-bromo-3-butylthiophene (2)

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\begin{align*}
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N-bromosuccinimide (10.7 g, 60 mmol, 1.05 eq.) was added to a solution of compound 1 (8.02 g, 57.2 mmol, 1.0 eq.) in 60 mL CHCl₃. The reaction mixture was cooled to 0 °C, followed by the addition of 60 mL glacial acetic acid. The solution was allowed to warm to room temperature over the course of several hours and stirred for 2 d in the dark. The slightly yellow solution was poured onto 200 mL H₂O, extracted with DCM, washed with saturated NaHCO₃ solution, dried over MgSO₄, and concentrated under reduced pressure. High vacuum distillation (10⁻³ mbar, 33°C) furnished the title compound as a colorless liquid (11.2 g, 51.1 mmol, 89%).

\(^1\)H NMR (400 MHz, CDCl₃): 7.18 (d, \(J = 5.6\) Hz, 1H), 6.80 (d, \(J = 5.6\) Hz, 1H), 2.60 – 2.55 (m, 2H), 1.61 – 1.52 (m, 2H), 1.41 – 1.31 (m, 2H), 0.94 (t, \(J = 7.3\) Hz, 3H).

3,3'-dibutyl-2,2'-bithiophene (3)[1]

A Grignard reagent, prepared by sonication of compound 2 (1.10 g, 5.0 mmol, 1.1 eq.), 1,2-dibromoethane (939 mg, 5.0 mmol, 1.1 eq.) and Mg (243 mg, 10 mmol, 2.2 eq.) in 14 mL of dry Et₂O, was slowly added to a solution containing compound 2 (986 mg, 4.5 mmol, 1.0 eq.) and Ni(dppp)Cl₂ (81 mg, 0.15 mmol, 3 mol%) in 21 mL of dry Et₂O. The reaction mixture was heated to reflux for 20 h. Upon completion, the reaction was quenched by the addition of EtOH and a few droplets of 2M HCl, and concentrated under reduced pressure. The crude product was purified via column chromatography (silica gel, heptane), yielding the title compound as a colorless oil (772 mg, 2.77 mmol, 62%).

\(^1\)H NMR (400 MHz, CDCl₃): 7.29 (d, \(J = 5.2\) Hz, 2H), 6.97 (d, \(J = 5.2\) Hz, 2H), 2.53 – 2.48 (m, 4H), 1.58 – 1.49 (m, 4H), 1.34 – 1.23 (m, 4H), 0.86 (t, \(J = 7.3\) Hz, 6H).

\(^{13}\)C NMR (101 MHz, CDCl₃): 142.4, 128.9, 125.4, 33.0, 28.6, 22.6, 14.1.

5,5'-dibromo-3,3'-dibutyl-2,2'-bithiophene (4)

Compound 3 (772 mg, 2.77 mmol, 1.0 eq.) was dissolved in 6 mL CHCl₃ and cooled to 0 °C. N-bromosuccinimide (1.04 g, 5.82 mmol, 2.1 eq.) and glacial acetic acid (6 mL) were added and the solution was allowed to slowly warm up to room temperature. After stirring at room temperature for 2 d in the dark, the reaction mixture was poured onto H₂O, extracted with DCM, washed with saturated NaHCO₃ solution, dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, cyclohexane), yielding a colorless oil (1.17 g, 2.68 mmol, 97%).

\(^1\)H NMR (400 MHz, CDCl₃): 6.91 (s, 2H), 2.47 – 2.41 (m, 4H), 1.54 – 1.44 (m, 4H), 1.33 – 1.22 (m, 4H), 0.86 (t, \(J = 7.3\) Hz, 6H).

\(^{13}\)C NMR (101 MHz, CDCl₃): 143.9, 131.6, 129.0, 112.5, 32.8, 28.6, 22.5, 14.0.
3′,3″-dibutyl-[2,2′:5′,5″:2″,2‴-quaterthiophene]-5,5‴-dicarbaldehyde (s4T)

Following a procedure by Yang et al.,[2] compound 4 (1.08 g, 2.48 mmol, 1.0 eq.) was stirred with Pd(OAc)$_2$ (23 mg, 0.10 mmol, 4 mol%) and XPhos (57 mg, 0.12 mmol, 4.8 mol%) in 14 mL n-butanol until complete dissolution of the solids (ca. 15 min). Next, a solution containing CsOH·H$_2$O (1.42 g, 8.43 mmol, 3.4 eq.) in 3.5 mL H$_2$O was added, followed by the addition of 5-formyl-2-thienylboronic acid (1.16 g, 7.44 mmol, 3.0 eq.). The resulting mixture was stirred for 2 d at 35 °C. After completion, H$_2$O was added and the product was extracted with DCM, dried over MgSO$_4$ and concentrated under reduced pressure. Purification via column chromatography (silica gel, DCM) furnished the title compound as a bright red powder (697 mg, 1.40 mmol, 56%).

$^1$H NMR (400 MHz, CDCl$_3$): 9.86 (s, 2H), 7.67 (d, $J = 4.0$ Hz, 2H), 7.24 (d, $J = 3.9$ Hz, 2H), 7.23 (s, 2H), 2.59 – 2.51 (m, 4H), 1.63 – 1.52 (m, 4H), 1.38 – 1.27 (m, 4H), 0.89 (t, $J = 7.3$ Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$): 182.6, 146.9, 144.4, 141.9, 137.4, 136.1, 129.8, 127.8, 124.3, 32.9, 28.8, 22.6, 14.0.

HR-EI-MS: m/z 498.74 (M+, calculated for C$_{26}$H$_{26}$O$_2$S$_4$: 498.75).

3,3″-dibutyl-2,2′:5′,2″-terthiophene (5)[1]

A Grignard reagent, prepared by sonication of compound 2 (4.38 g, 20 mmol, 2.9 eq.), 1,2-dibromoethane (3.76 g, 20 mmol, 2.9 eq.) and Mg (972 mg, 40 mmol, 5.7 eq.) in 56 mL of dry Et$_2$O, was slowly added to a solution containing 2,5-dibromothiophene (1.69 g, 7.0 mmol, 1.0 eq.) and Ni(dppp)Cl$_2$ (325 mg, 0.6 mmol, 3 mol%) in 50 mL dry Et$_2$O. The reaction mixture was heated to reflux for 40 h. Upon completion, the reaction was quenched by the addition of 1M HCl (50 mL), extracted with DCM, washed with H$_2$O, dried over MgSO$_4$, and concentrated under reduced pressure. The crude product was purified via column chromatography (silica gel, heptane), yielding the title compound as a slightly yellow oil (2.47 g, 6.84 mmol, 98%).

$^1$H NMR (400 MHz, CDCl$_3$): 7.18 (d, $J = 5.2$ Hz, 2H), 7.06 (s, 2H), 6.94 (d, $J = 5.2$ Hz, 2H), 2.79 – 2.81 (m, 2H), 2.82 – 2.76 (m, 2H), 1.73 – 1.60 (m, 4H), 1.49 – 1.36 (m, 4H), 0.97 (t, $J = 7.4$ Hz, 3H), 0.94 (t, $J = 7.3$ Hz, 3H).

3,3″-dibutyl-5-formyl-2,2′:5′,2″-terthiophene (6)

A Vilsmeier reagent, prepared by the addition of POCl$_3$ (1.57 mg, 10.3 mmol, 1.5 eq.) to 6.5 mL of dry DMF at 0 °C, was added to a solution of compound 5 (2.47 g, 6.84 mmol, 1.0 eq.) in 96 mL DCE at 0 °C. The reaction mixture was stirred overnight at 70 °C. Subsequently, H$_2$O was added and the pH was adjusted to 8.5-9 with 1M NaOH. The product was extracted with DCM, dried over MgSO$_4$ and concentrated under reduced pressure. Purification via column chromatography (silica gel, DCM/n-hexane 3:2) furnished the product as a slightly yellow solid (1.95 g, 5.02 mmol, 73%).

$^1$H NMR (400 MHz, CDCl$_3$): 9.83 (s, 1H), 7.60 (s, 1H), 7.24 (d, $J = 3.8$ Hz, 1H), 7.22 (d, $J = 5.2$ Hz, 1H), 7.11 (d, $J = 3.8$ Hz, 1H), 6.96 (d, $J = 5.2$ Hz, 1H), 2.87 – 2.81 (m, 2H), 2.82 – 2.76 (m, 2H), 1.73 – 1.60 (m, 4H), 1.49 – 1.36 (m, 4H), 0.97 (t, $J = 7.4$ Hz, 3H), 0.94 (t, $J = 7.3$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): 182.7, 141.3, 140.5, 140.4, 140.4, 139.2, 138.6, 134.6, 130.4, 129.9, 127.9, 126.5, 124.6, 33.0, 32.6, 29.3, 29.2, 22.8, 22.7, 14.1, 14.1.
5-bromo-3,3''-dibutyl-5''-formyl-2,2':5',2''-terthiophene (7)

Compound 6 (1.95 g, 5.02 mmol, 1.0 eq.) was dissolved in 15 mL CHCl₃ and cooled to 0 °C. NBS (938 mg, 5.27 mmol, 1.05 eq.) and glacial acetic acid (15 mL) were added and the solution was allowed to slowly warm up to room temperature. After stirring at room temperature for 2 d in the dark, the reaction mixture was poured onto H₂O, extracted with DCM, washed with saturated NaHCO₃ solution, dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, DCM/cyclohexane 3:2), yielding an orange solid (2.20 g, 4.71 mmol, 94%).

1H NMR (400 MHz, CDCl₃): 9.83 (s, 1H), 7.60 (s, 1H), 7.22 (d, J = 3.8 Hz, 1H), 7.05 (d, J = 3.8 Hz, 1H), 6.92 (s, 1H), 2.85 – 2.79 (m, 2H), 2.76 – 2.70 (m, 2H), 1.73 – 1.56 (m, 4H), 1.49 – 1.33 (m, 4H), 0.96 (t, J = 7.3 Hz, 3H), 0.94 (t, J = 7.3 Hz, 3H).

13C NMR (101 MHz, CDCl₃): 182.7, 141.1, 140.9, 140.6, 139.1, 137.1, 135.2, 133.0, 131.4, 127.9, 126.9, 111.4, 32.9, 32.6, 29.3, 29.2, 22.7, 14.0, 14.0.

3,3''-dibutyl-[2,2':5',5'':2'',2'''-quaterthiophene]-5,5'''-dicarbaldehyde (a4T)

Following a procedure by Yang et al.,[2] compound 7 (2.20 g, 4.71 mmol, 1.0 eq.) was stirred with Pd(OAc)₂ (21 mg, 0.094 mmol, 2 mol%) and XPhos (54 mg, 0.113 mmol, 2.4 mol%) in 26.4 mL n-butanol until complete dissolution of the solids (ca. 15 min). Next, a solution containing CsOH·H₂O (1.58 g, 9.42 mmol, 2.0 eq.) in 6.6 mL H₂O was added. Subsequently, 5-formyl-2-thienylboronic acid (1.32 g, 8.48 mmol, 1.8 eq.) was added and the resulting mixture was stirred for 18 h at room temperature. After completion, H₂O was added and the product was extracted with CHCl₃, dried over MgSO₄ and concentrated under reduced pressure. Purification via column chromatography (silica gel, CHCl₃), followed by recrystallization from hot DCE furnished the title compound as a dark red microcrystalline powder (2.15 g, 4.29 mmol, 91%).

1H NMR (400 MHz, CDCl₃): 9.86 (s, 1H), 7.67 (d, J = 4.0 Hz, 1H), 7.60 (s, 1H), 7.26 (d, J = 3.8 Hz, 1H), 7.24 (d, J = 4.0 Hz, 1H), 7.20 (s, 1H), 7.16 (d, J = 3.9 Hz, 1H), 2.86 – 2.82 (m, 2H), 2.82 – 2.77 (m, 2H), 1.74 – 1.63 (m, 4H), 1.50 – 1.39 (m, 4H), 0.97 (t, J = 7.4 Hz, 3H), 0.97 (t, J = 7.3 Hz, 3H).

13C NMR (101 MHz, CDCl₃): 182.6, 146.7, 142.0, 141.6, 140.7, 140.5, 139.1, 137.4, 137.4, 135.5, 134.3, 131.9, 129.3, 128.0, 126.9, 124.4, 32.8, 32.6, 29.4, 29.3, 22.8, 22.7, 14.1, 14.0.

HR-EI-MS: m/z 498.73 (M⁺, calculated for C₂₆H₂₆O₂S₄: 498.75).

3,3''-dimethyl-2,2':5',2''-terthiophene (5Me)

A Grignard reagent, prepared by sonication of 2-bromo-3-methylthiophene (1.126 mL, 10.0 mmol, 2.9 eq.), 1,2-dibromoethane (0.862 mL, 10.0 mmol, 2.9 eq.), and Mg (477.7 mg, 19.6 mmol, 5.7 eq.) in 30 mL dry Et₂O was slowly added to a solution containing 2,5-dibromothiophene (389 µL, 3.5 mmol, 1.0 eq.) and Ni(dppp)Cl₂ (162.6 mg, 0.3 mmol, 3 mol%) in 20 mL dry Et₂O. The reaction mixture was heated to reflux for 40 h. Upon completion, the reaction was quenched by the addition of 30 mL 1 M HCl, extracted with DCM and washed with H₂O. The organic phase was then dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified via column chromatography (silica gel, pentane), yielding the title compound as a slightly yellow oil, which crystallized slowly (492 mg, 1.78 mmol, 51%).

1H NMR (400 MHz, CDCl₃): 7.15 (d, J = 5.1 Hz, 2H), 7.08 (s, 2H), 6.89 (d, J = 5.1 Hz, 2H), 2.42 (s, 6H).

13C NMR (101 MHz, CDCl₃): 136.7, 134.5, 131.9, 131.3, 126.2, 123.8, 15.9.
5-formyl-3,3''-dimethyl-2,2':5',2''-terthiophene (6Me)

A Vilsmeier reagent, prepared by the addition of POCl₃ (283 mg / 168 µL, 1.8 mmol, 1.3 eq.) to 1.343 mL of dry DMF, was added to a solution of compound 5Me (391.8 mg, 1.4 mmol, 1.0 eq.) in 28 mL DCE. The reaction mixture was stirred overnight at 70 °C. Subsequently, 50 mL H₂O was added and the pH was adjusted to 8.5-9 with 1 M NaOH. The product was extracted with DCM, dried over MgSO₄ and concentrated under reduced pressure. Purification via column chromatography (silica gel, chloroform) furnished the product as a slightly yellow solid (397 mg, 1.3 mmol, 92%).

¹H NMR (400 MHz, CDCl₃): 9.82 (s, 1H), 7.54 (s, 1H), 7.28 (d, J = 3.9 Hz, 1H), 7.19 (d, J = 5.1 Hz, 1H), 7.13 (d, J = 3.9 Hz, 1H), 6.91 (d, J = 5.1 Hz, 1H), 2.48 (s, 3H), 2.43 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): 182.5, 141.7, 140.5, 139.8, 139.0, 134.9, 134.9, 134.8, 131.8, 130.4, 127.8, 126.1, 124.2, 16.0, 15.7.

5-bromo-5''-formyl-3,3''-dimethyl-2,2':5',2''-terthiophene (7Me)

Compound 6Me (397 mg, 1.3 mmol, 1.0 eq.) was dissolved in a mixture of 12.5 mL CHCl₃ and 12.5 mL glacial acetic acid and cooled to 0 °C. N-bromosuccinimide (255 mg, 1.4 mmol, 1.1 eq.) was added in the dark and the solution was allowed to slowly warm up to room temperature. After stirring at room temperature for 3 d in the dark, the reaction mixture was poured onto H₂O, extracted with DCM, washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, gradient eluent: n-hexane with 2% - 25% EtOAc), yielding a bright yellow solid (438 mg, 1.14 mmol, 90%).

¹H NMR (400 MHz, CDCl₃): 9.82 (s, 1H), 7.54 (s, 1H), 7.26 (d, J = 4.0 Hz, 1H), 7.07 (d, J = 3.9 Hz, 1H), 6.88 (s, 1H), 2.47 (s, 3H), 2.37 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): 182.5, 141.3, 140.4, 140.1, 137.5, 135.4, 135.4, 135.0, 134.3, 131.9, 127.7, 126.5, 111.0, 16.0, 15.6.

3,3''-dimethyl-[2,2':5',5'':2'',2'''-quaterthiophene]-5,5'''-dicarbaldehyde (a4TMe)

Following a procedure by Yang et al.,² compound 7Me (232 mg, 0.6 mmol, 1.0 eq.) was stirred with Pd(OAc)₂ (2.71 mg, 0.012 mmol, 2 mol%) and XPhos (6.91 mg, 0.015 mmol, 2.4 mol%) in 3.4 mL n-butanol (ca. 15 min). Next, a solution containing CsOH-H₂O (203 mg, 1.21 mmol, 2.0 eq.) in 846 µL H₂O was added, followed by the addition of 5-formyl-2-thienylboronic acid (170 mg, 1.09 mmol, 1.8 eq.). The resulting mixture was stirred for 2 d at room temperature and 1 d at 50 °C. After completion, H₂O was added and the product was extracted with CHCl₃, washed with brine 3 times, dried over MgSO₄, and concentrated under reduced pressure. Purification via column chromatography (silica gel, chloroform/EtOAc 99:1) furnished the title compound as a bright red powder (205 mg, 0.494 mmol, 82%).

¹H NMR (400 MHz, CDCl₃): 9.86 (s, 1H), 9.83 (s, 1H), 7.67 (d, J = 4.0 Hz, 1H), 7.55 (s, 1H), 7.30 (d, J = 3.9 Hz, 1H), 7.23 (d, J = 4.0 Hz, 1H), 7.19 (d, J = 3.9 Hz, 1H), 7.18 (s, 1H), 2.49 (s, 3H), 2.45 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): 182.5, 146.6, 142.0, 141.2, 140.4, 140.2, 137.8, 137.5, 136.0, 135.8, 135.1, 133.9, 132.4, 130.6, 127.9, 126.7, 124.4, 16.1, 15.9.

HR-ESI-MS: m/z 414.56 (M⁺, calculated for C₂₀H₁₄O₂S₄: 414.57).
5-iodothiophene-2-carbaldehyde (8)[3]

Thiophene-2-carbaldehyde (2.24 g, 20 mmol, 1.0 eq.) was dissolved in 40 mL EtOH and heated to 50 °C. N-iodosuccinimide (4.95 g, 22 mmol, 1.1 eq.) and p-toluenesulfonic acid monohydrate (380 mg, 2 mmol, 10 mol%) were added and the resulting mixture was stirred at 50 °C in the dark for 10 min. After completion, 20 mL of 1 M aqueous HCl and 20 mL EtOAc were added. The organic layer was extracted with EtOAc, washed with saturated aqueous Na₂S₂O₃ and Na₂CO₃ solutions, dried over MgSO₄, and filtered through a cotton plug. All volatiles were removed under high vacuum, yielding a slightly yellow solid (4.57 g, 19.2 mmol, 96%).

¹H NMR (400 MHz, CDCl₃): 9.77 (s, 1H), 7.39 (s, 2H).
¹³C NMR (101 MHz, CDCl₃): 181.3, 149.8, 138.4, 137.1, 87.9.

5-(trimethylstannyl)thiophene-2-carbaldehyde (9)

A reaction mixture containing compound 8 (472 mg, 2.0 mmol, 1.0 eq.), hexamethylditin (786 mg, 2.4 mmol, 1.2 eq.), and Pd(PPh₃)₄ (116 mg, 0.1 mmol, 5 mol%) in 10 mL of dry toluene was heated to 85 °C for 24 h. After completion, the solution was concentrated under reduced pressure at room temperature to remove the solvent and most of the by-product. The product was purified by sublimation (10⁻³ mbar, 60°C), yielding the title compound as a white crystalline solid (264 mg, 0.96 mmol, 48%).

¹H NMR (400 MHz, CDCl₃): 9.94 (s, 1H), 7.83 (d, J = 3.5 Hz, 1H), 7.28 (d, J = 3.5 Hz, 1H), 0.42 (s, with Sn coupling, 9H).

5'-bromo-[2,2'-bithiophene]-5-carbaldehyde (10)

A reaction mixture containing 5'-bromo-[2,2'-bithiophene]-5-carbaldehyde (1.00 g, 3.66 mmol, 1.0 eq.), hexamethylditin (1.44 g, 4.4 mmol, 1.2 eq.), and Pd(PPh₃)₄ (208 mg, 0.18 mmol, 5 mol%) in 20 mL of dry toluene was heated to 85 °C for 24 h. After completion, all volatiles were removed under high vacuum at 40 °C. The brown residue was dissolved in toluene, washed with saturated aqueous KCl, dried over Na₂SO₄, passed through a neutral alumina plug and evaporated to dryness, yielding a yellow solid (920 mg, 2.58 mmol, 70%), which was used in the next step without further purification.

¹H NMR (400 MHz, CDCl₃): 9.85 (s, 1H), 7.66 (d, J = 4.0 Hz, 1H), 7.45 (d, J = 3.4 Hz, 1H), 7.24 (d, J = 4.0 Hz, 1H), 7.14 (d, J = 3.4 Hz, 1H), 0.41 (s, with Sn coupling, 9H).
5-butyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (11)\textsuperscript{[4,5]}

Thiophene-3,4-dicarboxylic acid (3.29 g, 19.1 mmol, 1.0 eq.) and 3 Å molecular sieve (~200 mg) were dispersed in 40 mL acetic anhydride and heated to 140 °C for 24 h. After cooling to room temperature, the solution was decanted and evaporated to dryness. The resulting light grey solid was dried under high vacuum and re-dissolved in 60 mL of dry toluene. Butylamine (2.01 g, 28.7 mmol, 1.5 eq.) was added, and the solution was heated to reflux for 24 h. All volatiles were removed under high vacuum, yielding a faint brownish powder. SOCl\textsubscript{2} (120 mL) was added and the mixture was heated to reflux (88°C) overnight. The SOCl\textsubscript{2} was distilled off at ambient pressure, leaving behind a dark crystalline solid. Purification via column chromatography (silica gel, DCM), followed by recrystallization from Et\textsubscript{2}O afforded the title compound as colorless platelets (3.06 g, 14.6 mmol, 77%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): 7.80 (s, 2H), 3.67 – 3.57 (m, 2H), 1.67 – 1.58 (m, 2H), 1.41 – 1.30 (m, 2H), 0.94 (t, \(J = 7.4\) Hz, 3H).

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): 162.8, 136.9, 125.6, 38.4, 30.7, 20.2, 13.8.

1,3-dibromo-5-butyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (12)\textsuperscript{[6]}

Compound 11 (2.64 g, 12.6 mmol, 1.0 eq.) was dissolved in a mixture of conc. H\textsubscript{2}SO\textsubscript{4} (18.9 mL) and trifluoroacetic acid (63 mL) at 0 °C. N-bromosuccinimide (6.73 g, 37.8 mmol, 3.0 eq.) was added and the reaction mixture was allowed to slowly warm to room temperature. After stirring in the dark for 2 d, the solution was poured onto H\textsubscript{2}O, extracted with CHCl\textsubscript{3}, dried over MgSO\textsubscript{4}, and concentrated under reduced pressure. The product was purified by column chromatography (silica gel, toluene/DCM/heptane 3:1:1), yielding a slightly yellow solid (3.18 g, 8.65 mmol, 69%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): 3.60 (t, \(J = 7.2\) Hz, 2H), 1.66 – 1.57 (m, 2H), 1.40 – 1.29 (m, 2H), 0.94 (t, \(J = 7.3\) Hz, 3H).

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): 160.5, 135.0, 113.1, 38.7, 30.5, 20.2, 13.7.

compound 13

A reaction mixture containing compound 12 (602 mg, 1.64 mmol, 1.0 eq.), compound 9 (451 mg, 1.64 mmol, 1.0 eq.), Pd(db\textsubscript{a})\textsubscript{2} (47 mg, 0.082 mmol, 5 mol%), and tri(2-furyl)phosphine (47 mg, 0.20 mmol, 12 mol%) in 20 mL dry toluene was heated to 85 °C for 48 h. After completion, all volatiles were removed under high vacuum at 50 °C. Purification via column chromatography (silica gel, CHCl\textsubscript{3}) yielded the title compound as a yellow solid (171 mg, 0.43 mmol, 26%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): 9.94 (s, 1H), 8.08 (d, \(J = 4.0\) Hz, 1H), 7.75 (d, \(J = 4.1\) Hz, 1H), 3.66 (t, \(J = 7.2\) Hz, 2H), 1.71 – 1.60 (m, 2H), 1.42 – 1.32 (m, 2H), 0.95 (t, \(J = 7.4\) Hz, 3H).
TPD-modified quaterthiophene (4TTPD)

A reaction mixture containing compound 13 (80 mg, 0.20 mmol, 1.0 eq.), compound 10 (86 mg, 0.24 mmol, 1.2 eq.), Pd(db)2 (12 mg, 0.020 mmol, 10 mol%), and tri(2-furyl)phosphine (12 mg, 0.050 mmol, 25 mol%) in 2 mL dry toluene was heated to 85 °C for 24 h. After completion, all volatiles were removed under high vacuum at 50 °C. Purification via column chromatography (silica gel, DCM), followed by recrystallization from DCE/Et2O afforded the title compound as an orange solid (89 mg, 0.174 mmol, 87%).

1H NMR (400 MHz, CDCl3): 9.94 (s, 1H), 9.90 (s, 1H), 8.19 (d, J = 4.0 Hz, 1H), 7.98 (d, J = 4.0 Hz, 1H), 7.77 (d, J = 4.0 Hz, 1H), 7.71 (d, J = 4.0 Hz, 1H), 7.36 (d, J = 4.0 Hz, 2H), 3.70 (t, J = 7.3 Hz, 2H), 1.74 – 1.64 (m, 2H), 1.46 – 1.35 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H).

13C NMR (101 MHz, CDCl3): 182.7, 182.6, 162.5, 162.3, 145.9, 144.9, 143.0, 140.6, 139.8, 137.3, 137.2, 136.8, 134.8, 133.1, 131.8, 131.6, 130.6, 129.8, 127.2, 125.6, 38.7, 30.7, 20.3, 13.8.

HR-El-MS: m/z 511.63 (M+, calculated for C24H17NO4S4: 511.64).

Figure S3. Synthesis of the 4TTT building block.

4-bromothiophene-3-carbaldehyde (14)

A solution of 3,4-dibromothiophene (5.4 g, 22.3 mmol, 1.0 eq.) in 15 mL of dry Et2O was cooled to -78 °C and n-BuLi (2.0 M in cyclohexane, 22.3 mmol, 1.0 eq.) was slowly added. After stirring for 15 min, DMF (1.63 g, 22.3 mmol, 1.0 eq.) was added. The reaction mixture was stirred for 3 h at -78 °C and then allowed to slowly warm to room temperature. H2O was added to quench the reaction, and the solution was extracted with DCM, dried over Na2SO4, and evaporated to dryness. Purification via high vacuum distillation (10⁻³ mbar, 65 °C) afforded the title compound as a faint yellowish, air-sensitive liquid (2.29 g, 12.0 mmol, 54%).

1H NMR (400 MHz, CDCl3): 9.95 (s, 1H), 8.15 (d, J = 3.4 Hz, 1H), 7.36 (d, J = 3.4 Hz, 1H).

13C NMR (101 MHz, CDCl3): 184.8, 137.7, 134.7, 125.2, 111.5.
ethyl thieno[3,4-b]thiophene-2-carboxylate (15)[7]

![Chemical Structure](image)

Ethyl mercaptoacetate (1.59 g, 13.2 mmol, 1.1 eq.) was added dropwise to a solution of compound 14 (2.29 g, 12.0 mmol, 1.0 eq.), K₂CO₃ (2.49 g, 18.0 mmol, 1.5 eq.), and CuO nanopowder (< 50 nm particle size, 28 mg, 0.36 mmol, 3 mol%) in 24 mL DMSO at 60 °C. The reaction mixture was stirred overnight at 60 °C. After completion, H₂O and brine were added, and the product was extracted with DCM. The combined organic phase was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. Purification via column chromatography (silica gel, DCM/heptane 2:1) yielded the title compound as a slightly yellowish powder (1.50 g, 7.08 mmol, 59%).

¹H NMR (400 MHz, CDCl₃): 7.70 (d, J = 0.8 Hz, 1H), 7.59 (d, J = 2.6 Hz, 1H), 7.28 (dd, J = 2.7, 0.8 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): 163.3, 146.1, 140.0, 140.0, 123.6, 116.7, 111.5, 61.8, 14.5.

ethyl 6-bromothieno[3,4-b]thiophene-2-carboxylate (16)[8]

Compound 15 (1.34 g, 6.31 mmol, 1.0 eq.) was dissolved in 45 mL DMF and stirred at 0 °C in the dark. A solution of N-bromosuccinimide (1.12 g, 6.31 mmol, 1.0 eq.) in 45 mL DMF was added over the course of 6 h via an addition funnel (approximately one drop every 10 s). Upon completion, the reaction mixture was allowed to warm up to room temperature over the course of 12 h. All volatiles were removed under reduced pressure. Purification via column chromatography (silica gel, CHCl₃/cyclohexane 1:1) afforded a slightly pink solid (1.68 g, 5.78 mmol, 92%). The product was found to be a 80:20 mixture of the 6-bromo- and the 4-bromothieno[3,4-b]thiophene-2-carboxylate that could not be separated at this stage.

¹H NMR (400 MHz, CDCl₃): 7.56 (d, J = 0.9 Hz, 1H), 7.24 (d, J = 0.9 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H).

Isomer: 7.66 (s, 1H), 7.52 (s, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): 162.7, 145.9, 140.8, 138.9, 122.5, 112.6, 102.8, 61.9, 14.3.

Isomer: 162.7, 145.3, 140.4, 124.2, 123.2, 118.0, 97.9, 61.8, 14.3.

compound 17

A reaction mixture containing compound 16 (730 mg, 2.5 mmol, 1.0 eq.), compound 9 (825 mg, 3.0 mmol, 1.2 eq.), Pd(dbä)₂ (144 mg, 0.25 mmol, 10 mol%), and tri(2-furyl)phosphine (145 mg, 0.625 mmol, 25 mol%) in 25 mL dry toluene was heated to 85 °C for 20 h. After completion, all volatiles were removed under high vacuum at 50 °C. Purification via column chromatography (silica gel, DCM/cyclohexane 5:1) afforded the title compound as a yellow-green solid (470 mg, 1.46 mmol, 58%). The product was found to be a 90:10 mixture of the 6-thienyl and 4-thienyl isomers.

¹H NMR (400 MHz, CDCl₃): 9.90 (s, 1H), 7.99 (d, J = 0.8 Hz, 1H), 7.73 (d, J = 4.0 Hz, 1H), 7.36 (d, J = 4.0 Hz, 1H), 7.33 (d, J = 0.8 Hz, 1H), 4.42 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): 182.4, 162.6, 145.3, 143.2, 142.4, 142.3, 141.3, 137.1, 126.8, 124.8, 122.9, 112.8, 62.0, 14.3.
Compound 18 (470 mg, 1.46 mmol, 1.0 eq.) was dissolved in 30 mL CHCl₃. N-bromosuccinimide (312 mg, 1.75 mmol, 1.2 eq.) was added and the resulting mixture was stirred at room temperature in the dark for 2 d. After completion, the solution was poured onto H₂O and extracted with DCM. The organic phase was dried over Na₂SO₄ and concentrated under reduced pressure. Purification via column chromatography (silica gel, DCM/cyclohexane 4:1) afforded the isomer-pure title compound as an orange solid (501 mg, 1.25 mmol, 86%). The 4-thienyl isomer is slightly slower on the column and thus could be fully removed from the product.

¹H NMR (400 MHz, CDCl₃): 9.91 (s, 1H), 7.96 (s, 1H), 7.71 (d, J = 4.0 Hz, 1H), 7.28 (d, J = 4.0 Hz, 1H), 4.42 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): 182.5, 162.4, 144.3, 143.0, 142.9, 142.8, 142.4, 137.2, 128.3, 125.2, 100.1, 62.4, 14.5.

TT-modified quaterthiophene (4TT)

A reaction mixture containing compound 18 (321 mg, 0.8 mmol, 1.0 eq.), compound 10 (343 mg, 0.96 mmol, 1.2 eq.), Pd(dba)₂ (46 mg, 0.08 mmol, 10 mol%), and tri(2-furyl)phosphine (46 mg, 0.20 mmol, 25 mol%) in 8 mL dry toluene was heated to 85 °C for 20 h. After completion, all volatiles were removed under high vacuum at 50 °C. Purification via column chromatography (silica gel, DCM), followed by precipitation from CHCl₃/Et₂O afforded the title compound as a deep red solid (266 mg, 0.517 mmol, 65%).

¹H NMR (400 MHz, CDCl₃): 9.92 (s, 1H), 9.89 (s, 1H), 8.03 (s, 1H), 7.75 (d, J = 4.1 Hz, 1H), 7.71 (d, J = 4.1 Hz, 1H), 7.39 (d, J = 3.8 Hz, 1H), 7.32 (d, J = 4.1 Hz, 1H), 7.29 (d, J = 4.0 Hz, 1H), 4.46 (q, J = 7.1 Hz, 2H), 1.46 (t, J = 7.2 Hz, 3H).

¹³C NMR data could not be recorded for this compound due to its low solubility.

HR-EI-MS: m/z 514.61 (M⁺, calculated for C₂₃H₁₄O₄S₅: 514.61).

1,3,6,8-tetrakis(4-aminophenyl)pyrene (Py)[9,10]

A reaction mixture containing 1,3,6,8-tetrabromopyrene (1482 mg, 2.86 mmol, 1.0 eq.), 4-aminophenylboronic acid pinacol ester (3010 mg, 13.7 mmol, 4.8 eq.), K₂CO₃ (2175 mg, 15.7 mmol, 5.5 eq.), and Pd(PPh₃)₄ (330 mg, 0.29 mmol, 10 mol%) in 32 mL 1,4-dioxane and 8 mL H₂O was heated to reflux (115 °C) for 3 d. After cooling to room temperature, H₂O was added. The resulting precipitate was collected via filtration and was washed with H₂O and MeOH. Recrystallization from 1,4-dioxane, followed by drying under high vacuum furnished the title compound, co-crystallized with approximately 1.5 dioxane molecules per formula unit, as a bright yellow powder (1792 mg, 2.56 mmol, 90%).

¹H NMR (400 MHz, DMSO-d₆): 8.13 (s, 4 H), 7.79 (s, 2 H), 7.34 (d, J = 8.4 Hz, 8 H), 6.77 (d, J = 8.5 Hz, 8 H), 5.30 (s, 8 H), 3.56 (s, 12 H, dioxane).

¹³C NMR (100 MHz, DMSO-d₆): 148.2, 137.1, 131.0, 129.0, 127.6, 126.7, 126.1, 124.4, 113.9, 66.3 (dioxane).
C. COF syntheses

All COF syntheses were performed under argon atmosphere in PTFE-sealed glass reaction tubes (6 mL volume). Solvents and acetic acid were obtained in high purity grade from commercial suppliers and were, unless shipped under argon, degassed and saturated with argon prior to use.

**Py-a4T COF**

1,3,6,8-tetrakis(4-aminophenyl)pyrene dioxane adduct (Py; 14.0 mg, 20 µmol, 1.0 eq.) and 3,3''-dibutyl-[2,2':5',5'':2'',2''''-quaterthiophene]-5,5''''-dicarbaldehyde (a4T; 20 mg, 40 µmol, 2.0 eq.) were filled into a reaction tube, followed by the addition of mesitylene (133 µL), BnOH (67 µL), and 6 M acetic acid (20 µL). The tube was sealed and the reaction mixture was heated at 120 °C for 4 d. After cooling to room temperature, the precipitate was collected by filtration and slowly dried in air for 24 h, yielding the **Py-a4T COF** as a dark red powder (19 mg, 64%).

Following the same synthesis protocol, but employing the s4T building block instead, did not lead to the formation of a crystalline network. Other solvent mixtures (mesitylene/dioxane, mesitylene/BnOH, DCB/dioxane, DCB/BnOH; ratios from 2:1 to 1:9) and concentrations were tested as well, but the resulting solids did not show any sign of long-range order.

**Py-a4TMe COF**

1,3,6,8-tetrakis(4-aminophenyl)pyrene dioxane adduct (Py; 14.0 mg, 20 µmol, 1.0 eq.) and 3,3''-dimethyl-[2,2':5',5'':2'',2''''-quaterthiophene]-5,5''''-dicarbaldehyde (a4TMe; 17 mg, 40 µmol, 2.0 eq.) were filled into a reaction tube, followed by the addition of mesitylene (333 µL), BnOH (167 µL), and 6 M acetic acid (50 µL). The tube was sealed and the reaction mixture was heated at 120 °C for 4 d. After cooling to room temperature, the precipitate was collected by filtration, slowly dried in an argon atmosphere overnight, and extracted with supercritical CO₂ for 2h, yielding the **Py-a4TMe COF** as a dark red powder.

**Py-4TTPD COF**

Py (7.0 mg, 10 µmol, 1.0 eq.) and the TPD-modified quaterthiophene (4TTPD; 10.2 mg, 20 µmol, 2.0 eq.) were filled into a reaction tube, followed by the addition of mesitylene (167 µL), 1,4-dioxane (333 µL), and 6 M acetic acid (50 µL). The tube was sealed and the reaction mixture was heated at 120 °C for 4 d. After cooling to room temperature, the precipitate was collected by filtration and slowly dried in air, yielding the **Py-4TTPD COF** as an orange powder.

**Py-4TTT COF**

Py (14.0 mg, 20 µmol, 1.0 eq.) and TT-modified quaterthiophene (4TTT; 20.6 mg, 40 µmol, 2.0 eq.) were filled into a reaction tube, followed by the addition of mesitylene (667 µL), BnOH (333 µL), and 6 M acetic acid (100 µL). The tube was sealed and the reaction mixture was heated at 120 °C for 4 d. After cooling to room temperature, the precipitate was collected by filtration and slowly dried in air for 24 h, yielding the **Py-4TTT COF** as a very dark purple powder (26 mg, 85%).
D. NMR spectra of the building blocks

$^1$H and $^{13}$C NMR spectra. Residual (undeuterated) solvent peaks are marked with asterisks.
E. HRMS analysis of the building blocks

Figure S4. Comparison between the theoretical (grey) and the experimental (colored) HR-EI-MS patterns of the four quaterthiophene-derived building blocks. The patterns correspond to the respective singly positively charged molecules ($M^+$).
F. IR spectroscopy

Figure S5. IR spectra of the building blocks and the quaterthiophene-based COFs.

Table S1. Assignments of the IR signals.

| Compound          | Wavenumber / cm⁻¹ | Vibration mode         |
|-------------------|-------------------|------------------------|
| Py                | 1276              | C-N stretching mode    |
|                   | 871               | N-H wag vibration      |
| a4T               | 1655              | C=O stretching vibration|
| Py-a4T COF        | 1580              | C=N stretching mode    |
| 4TTT              | 1659              | C=O stretching vibration|
| Py-4TT COF        | 1581              | C=N stretching mode    |
| 4T₁₆₀             | 1658              | C=O stretching vibration|
| Py-4T₁₆₀ COF      | 1578              | C=N stretching mode    |
G. UV‐VIS‐NIR spectroscopy

Figure S6. Comparison of the absorption spectra of the COF building blocks. (a) Transmission absorption spectra measured for 50 µM solutions in CHCl₃ (s4T, a4T, 4T_TPD, 4T_TT) or 1,4-dioxane (Py). (b) Corresponding diffuse reflectance spectra measured for the respective powders dispersed in BaSO₄.

Figure S7. Comparison of the absorption and diffuse reflectance spectra of the building blocks in solution, as a solid, and (for a4T, 4T_TPD, 4T_TT) incorporated into the pyrene-linked COF.

Figure S8. Tauc plots of the 4T-based COFs suggesting direct (Py-a4T and Py-4T_TT COFs) and indirect optical band gaps (Py-4T_TPD COF).
H. PL spectroscopy

Figure S9. PL spectra of the COF building blocks measured (a) as 50 µM solutions in CHCl₃ (s₄T, a₄T, 4Tₚاعدة, 4Tₜₜ) or 1,4-dioxane (Py), and (b) as solids. λₑₓᶜᵉˢ = 378 nm.

Figure S10. Comparison of the PL spectra of the building blocks in solution, as a solid, and (for a₄T, 4Tₚاعدة, 4Tₜₜ) incorporated into the pyrene-linked COF. λₑₓᶜᵉˢ = 378 nm.

Figure S11. Comparison of the relative PL intensities of the 4T building blocks and the corresponding COFs.
I. Time-correlated single photon counting

Figure S12. TCSPC traces of the building blocks (a) in 50 µM CHCl₃ solution and (b) as solids, recorded at their respective emission maximum. $\lambda_{exc} = 378$ nm. The lifetimes were obtained from exponential deconvolution fits (solid lines). For multi-exponential decays, the percentages in brackets denote the fraction of emitted photons that corresponds to the respective lifetime.

Figure S13. Comparison of the TCSPC traces of the building blocks in solution, as a solid, and (for $a4T$, $4T_{TPD}$, $4T_{TT}$) incorporated into the pyrene-linked COF.
**Figure S14.** High-resolution TEM image of the Py-a4T COF. The parallel-aligned pores are visible for a number of individual COF crystallites (visibility depends on crystal orientation relative to the electron beam).
Figure S15. (a) Experimental PXRD pattern (black dots) of the short-chain Py-a4TMe COF. Pawley refinement (red line) in the space group $C2/m$ provides an excellent fit to the experimental data. Inset, magnified view of the $2\theta > 10^\circ$ region. The simulated PXRD pattern (grey lines) based on the structure model shown in (b) agrees very well with the experimental and refined patterns of the framework. For the pattern simulation, the methyl groups were treated as a superposition of both possible orientations with 50% occupancy. The minimal differences in the peak intensities might stem from slight differences between the simulated and the actual COF structure. (b) The Py-a4TMe COF unit cell with the viewing direction normal to the $a$-$b$ plane (left) and along $b$ (right), and the Connolly surface calculated for a nitrogen-sized probe molecule.

L. Nitrogen sorption of the Py-a4TMe COF

Figure S16. (a) Nitrogen sorption isotherms recorded at 77 K. Two adsorption-desorption cycles were recorded using the same sample to test the stability of the framework. (b) QSDFT calculation using the adsorption branch yields a narrow pore size distribution with a maximum at 3.1 nm, in excellent agreement with the pore diagonal of 3.06 nm in the Py-a4TMe COF structure.

The Py-a4TMe COF is porous with a BET surface close to 1000 m$^2$ g$^{-1}$, and the maximum of the pore size distribution agrees very well with the pore diagonal when taking into account the methyl groups.

Due to the length and inherent flexibility of the 4T based building blocks, the frameworks described in this study are quite fragile. Thus, the COFs bearing longer alkyl chains have a tendency to deform as a response to the adsorption of probe molecules during the nitrogen sorption experiments, leading to inconsistent isotherms. The shorter chains of the Py-a4TMe COF, however, seem to reduce the forces onto the COF walls during the sorption cycle and therefore this COF yields consistent and reproducible sorption results (Figure S15).
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