Supporting Information

Fully Conjugated Tetraoxa[8]circulene-Based Porous Semiconducting Polymers

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Supporting Information
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Table of Contents

EXPERIMENTAL PROCEDURES ............................................................................................................ 3
MATERIALS AND INSTRUMENTATION ................................................................................................. 3
EXPERIMENTAL PROCEDURES ............................................................................................................ 4
RESULTS AND DISCUSSION ................................................................................................................. 8
\(^{13}\)C CP-MAS SOLID-STATE NMR ....................................................................................................... 8
FTIR KBR-PELLET IN TRANSMISSION MODE AND DRIFTS ................................................................. 9
RAMAN SPECTRA .................................................................................................................................. 10
POWDER X-RAY DIFFRACTION ............................................................................................................ 10
SCANNING ELECTRON MICROSCOPY ................................................................................................. 11
THERMOGRAVIMETRIC ANALYSIS ...................................................................................................... 12
ROUQUEROL AND BET PLOTS ............................................................................................................. 12
XPS SURVEY ......................................................................................................................................... 13
MATERIALS STUDIO SIMULATION OF THE PERFECT PTOC .............................................................. 15
EPR MEASUREMENT ............................................................................................................................. 16
CONDUCTIVITY MEASUREMENTS AND SUPPORTING CHARACTERIZATION ............................... 17
REFERENCES ......................................................................................................................................... 29
AUTHOR CONTRIBUTIONS .................................................................................................................. 29
Experimental Procedures

Materials and Instrumentation

All chemicals and solvents were purchased and used without any further purification. 1,8-Dihydroxy-9,10-anthraquinone (95%), aluminium(III)chloride (98.5%), sodium chloride (99.5%) and nitrobenzene (99%) were purchased from Acros Organics. Potassium carbonate (99%), dichloromethane (99%), magnesium sulfate, silica (60A, 35-70 micron), methanol, THF and hydrochloric acid (37%) were purchased from Fisher Chemicals. Dimethylethylammoniumnitrate (98.5%) were purchased from Sigma Aldrich. Acetone was purchased from Thomen Furler. Sodium hydroxide was purchased from Reactolab SA. N-bromosuccimimde was purchased from Fluorochem. Pyridine was purchased from Roth.

FTIR spectra were recorded on a PerkinElmer Frontier spectrometer equipped with a PIKE GladiATR module in the range of 4000-400 cm\(^{-1}\) at a scanning rate of 2 cm\(^{-1}\). Liquid phase NMR spectra were recorded on a Bruker Ascend 400 MHz spectrometer using deuterated solvents. CP-MAS \(^{13}\)C solid-state NMR spectra were recorded on a Bruker Avance Neo 400 MHz spectrometer using 7 kHz or 10 kHz spinning rate and a 5.0 s relaxation delay. PXRD patterns were recorded on a STOE STADI-P system using Cu Ka1 incident beam. The diffractograms were recorded between 2\(\theta\) 2-60\(^\circ\) and 0.015\(^\circ\)/step using a DECTRIS MYTHEN 1K detector. TGA analysis was recorded on a Mettler-Toledo TGA/DSC 3+ instrument using standard 70 \(\mu\)L alumina and 40 \(\mu\)L aluminium crucibles. The flowrate of the respective gas (nitrogen or air) was set to 10 mL/min and the heating rate was set to 5 °C/min for the 600 °C measurements under nitrogen and to 10 °C/min for the 1000 °C measurements under nitrogen or air. Nitrogen and CO\(_2\) sorption measurements were performed at 77 and 273 K, respectively, using Micromeritics 3Flex instrument, after evacuation of the samples at 363 K for 24 h. The pore size distribution was determined via NLDFT using carbon heterogeneous surface as model. Field emission SEM images were obtained using a TESCAN MIRA3. Prior to the SEM measurements, the samples were coated with 1.5 nm of gold using a Cressington 208HR sputter coater. RAMAN spectra were recorded on an Alpha 300R Raman microscope with a UHTS 300 spectrometer using 535 nm laser excitation. XPS measurements were performed at the MIT MRSEC (formerly the Center for Materials Science and Engineering, or CMSE) using a Physical Electronics PHI VersaProbe II X-ray photoelectron spectrometer equipped with a monochromatic Al anode X-ray source. The main chamber pressure was in the 10\(^{-10}\) Torr range. pTOC powder samples were pressed on copper tapes with full coverage. Survey spectra were collected from 0–1100 eV in binding energy (BE), with a resolution of 0.8 eV. High resolution spectra of C1s and O1s regions were collected with a resolution of 0.1 eV. BE calibration was carried out by shifting the adventitious carbon C1s peak to 284.8 eV. Deconvolution of the C1s spectra were conducted before BE calibration to find out the adventitious carbon C1s peak, given that the samples also contain significant amount of carbon. Gaussian-Lorentzian product function, with exponential tailing for asymmetrical peak shape if necessary, was used for the line shapes during fitting, which is commonly used for C1s and O1s. Valence-band XPS was measured at a resolution of 0.1 eV. DRIFTS measurements were performed on a Bruker Tensor 37 (MIR source and KBr beam splitter) with a mercury cadmium telluride (MCT, cooled with liquid nitrogen) detector utilizing the DiffusIR™ accessory (Pike Technologies). A sealable environmental chamber equipped with ZnSe window (Pike Technologies) was used. Samples were ground in air with dry potassium bromide (99.9%, Pike technologies) in a mortar and pestle to produce ~1 wt. pTOC mixtures. The data was averaged over 32 scans between 4000 – 600 cm\(^{-1}\) with the resolution of 4 cm\(^{-1}\). DRUV-Vis spectra between 200 and 2500 nm were collected on a Cary 5000i spectrophotometer, fitted with the UV-Vis DiffusIR accessory (Pike Technologies), at the scan rate of 200 nm/min under ambient conditions. A KBr baseline and a zero-background correction were collected prior to the sample measurements. Samples were prepared as described above for the DRIFTS measurements. Room temperature electrical conductivity measurements were carried out in an ambient atmosphere on pressed pellets using either the 2-probe or 4-probe setup described previously.\(^{11}\) For the 2-probe measurements, a home-made press was used, which has two probes that could be connected to source meter.\(^{11}\) Powder samples were transferred into a glass or PTFE tube and sandwiched between two stainless steel rod leads. The whole set-up was held by an IR press. For the 4-probe measurements, pressed pellets were prepared by adding sample powders into a 6 mm inner-diameter trapezoidal split sleeve pressing (Across International) and pressing the die set
Experimental Procedures

by a hydraulic pump (MTI corporation) for 1 min. The applied pressure was approximately 1 GPa. The pellet thicknesses were measured after the measurement using a micrometer (Mitutoyo). The resulting pellet was cut into a cuboid by a blade, and placed it onto a piece of dry glass slide with thermally conductive and electrically insulating grease (DuPont Krytox). Four parallel copper wire contacts were attached to the cuboid by carbon paste. The other end of the copper wire was pasted onto the glass slide by carbon paste. The device was mounted onto the sample chuck of a probe station (Janis Cryogenics ST-500) equipped with four micro-manipulators that allowed us to control the position of the probes with a resolution of 5 µm. Electrical contacts were made by gently pressing gold-plated tungsten probes (Janis 7B-100G) into the carbon paste that was on the glass slide. For both configurations, probes were connected to a sourcemeter (Keithley model 2450), either through normal wires for 2-probe or through triax cables (Keithley model 7078-TRX-10) for 4-probe. The chamber of the probe station was covered by a stainless-steel lid to keep the device in the dark. Linear I–V curves were obtained by (1) supplying the voltage and measuring the current for 2-probe configuration; (2) supplying the current and measuring the voltage for 4-probe configuration. At least three parallel measurements were conducted for each sample, and the conductivity values were averaged to give the average conductivity value. The light response was investigated using a four-probe configuration employing a 5 mW 650 nm laser. For the negative photoconductivity experiments, the samples were kept in a vial and irradiated for a specific amount of time – 1 h or 24 h for the actual experiments and stability evaluation respectively. **Variable temperature electrical conductivity data** were collected from 150 K to 375 K for pTOC-350, from 100 K to 375 K for pTOC-350-Iz using a home-built two-probe in situ screw press set-up described previously.[3] Electrical contacts were made by touching the short screw or the inner plate of the sample mounting chuck by gold-coated tungsten probes. Probes were connected to a sourcemeter (Keithley model 2450) through triax cables described above. Temperature was balanced by the heater of the probe station chuck and liquid nitrogen that were regulated by a temperature controller (Scientific Instruments 9700). All measurements were performed under dynamic vacuum (~10⁻⁵ Torr). I–V curves were collected by sweeping voltage while scanning temperatures with a step size of 5 K or 10 K and at least 30 minutes per step. Two I–V curves were measured for a given temperature to confirm the stability of temperature. The final measurement at each temperature was used to calculate the conductivity of the device. The **model structure** of pTOC was built by Materials Studio using Forcite module and the Universal forcefield, based on the crystal structure of molecular TOC (CCDC 887700). Ultra-fine level of calculation was employed. Reactions utilizing **microwave irradiation** were carried out in an Anton Paar Monowave 400 microwave reactor. Heating was performed as fast as possible while after reaching reaction temperature power was regulated by the system to keep temperature constant. **Electron paramagnetic resonance spectroscopy (EPR)** measurement was performed on pTOC-350 powder packed under nitrogen in a septum-sealed quartz tube using a Bruker EMX spectrometer equipped with an ER 4199HS cavity and Gunn diode microwave source at room temperature, with a microwave frequency of 9.37 GHz, power of 0.005 mW, and attenuation of 33.0 dB. The measurement was taken in perpendicular mode. Fitting and simulation of EPR spectrum was conducted using EasySpin (https://easyspin.org/). [1]

**Experimental Procedures**

![Experimental Procedures Diagram](image-url)
1,8-Dimethoxy-9,10-anthraquinone (1):
Procedure adapted from Rathore and coworkers.[4]
A 500 mL two-neck round bottomed flask was flushed with argon and charged with 1,8-di-hydroxy-9,10-anthraquinone (15.5 g, 64.5 mmol, 1 eq.) and K$_2$CO$_3$ (24.1 g, 174.2 mmol, 2.7 eq.) and acetone (400 mL) before heating to reflux for 30 minutes. Subsequently, dimethyl sulfate (15.26 mL, 161.3 mmol, 2.5 eq.) in acetone (50 mL) was slowly added over the course of 30 minutes. The obtained solution was subsequently refluxed for 48 h. After cooling to RT, the suspension was filtered, and the purple residue washed with 3x150 mL CH$_2$Cl$_2$. The combined organic phases were passed through silica and the pad was washed with 3x100 mL CH$_2$Cl$_2$. The solvents were removed under reduced pressure and the obtained residues were subsequently stirred in 2N NaOH for 30 minutes to remove residual dimethyl sulfate. Subsequently, the aqueous layers were extracted with CH$_2$Cl$_2$. After removing the solvents, the product was obtained as a yellow solid.
Yield: 15.8 g (91.3 %); yellow solid
$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.84 (dd, $J = 7.7$, 1.1 Hz, 1H), 7.64 (dd, $J = 8.4$, 7.7 Hz, 1H), 7.30 (dd, $J = 8.4$, 1.1 Hz, 1H), 4.01 (s, 3H).

1,8-Dimethoxyanthracene (2):
Procedure adapted from Rathore and coworkers.[4]
A 500 mL two-neck flask was flushed with argon and charged with 2 (5.00 g, 18.6 mmol, 1.00 eq.), 10% aq. NaOH (125 mL) and zinc powder (7.31 g, 111.8 mmol, 6.0 eq.). The obtained mixture was heated under vigorous stirring for 24 h. The suspension was filtered, and the filtrate washed with 3 x 100 mL water before drying under vacuum. The obtained yellow–grey precipitate was dissolved in CH$_2$Cl$_2$ (500 mL) and was passed through a short pad of silica before removing the solvents under reduced pressure. 
Yield: 3.9 g (89.6 %); yellow solid
$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 9.24 (d, $J = 1.0$ Hz, 1H), 8.31 (s, 1H), 7.56 (dq, $J = 8.6$, 0.8 Hz, 2H), 7.37 (dd, $J = 8.5$, 7.4 Hz, 2H), 6.73 (dd, $J = 7.5$, 0.8 Hz, 2H), 4.09 (s, 6H).

1,8-Dibromo-4,5-dimethoxyanthracene (3):
Procedure adapted from Rathore and coworkers.[4]
A 250 mL two-neck flask was flushed with argon and charged with 3 (1.0 g, 4.2 mmol, 1.0 eq.) in 50 mL CH$_2$Cl$_2$ before cooling to 0 °C with an ice bath. Subsequently, NBS (1.5 g, 8.6 mmol, 2.05 eq.) was added over 30 minutes and the solution was slowly allowed to warm to RT and was stirred for an additional 3 hours. After diluting the reaction mixture with CH$_2$Cl$_2$, the solution was washed with 2N NaOH (100 mL) and 3x150 mL water. The combined organic layers were dried over MgSO$_4$ and the solvents evaporated under reduced pressure. 
Yield: 1.1 g (66.2 %); green solid
$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 9.26 (d, $J = 0.9$ Hz, 1H), 9.01 (d, $J = 0.9$ Hz, 1H), 7.72 (d, $J = 8.1$ Hz, 2H), 6.63 (d, $J = 8.0$ Hz, 2H), 4.07 (s, 6H).

1,4,5,8-Tetramethoxyanthracene (4):
Procedure adapted from Rathore and coworkers.[4]
A 500 mL two-neck flask was flushed with argon and charged with methanol (200 mL). Freshly cut sodium (23.2 g, 1.01 mol, 100 eq.) was slowly added over the course of 1 hour. Towards the end of the addition the solution was heated to reflux before adding 3 (4.0 g, 10.1 mmol, 1.0 eq.), dry toluene (100 mL), MeOAc (9.52 g, 10.0 mL, 126.2 mmol, 12.5 eq.) and copper (I) bromide (1.4 g, 10.1 mmol, 1.0 eq.), successively. The obtained suspension was heated to reflux for 48 h. After cooling to RT, the solvents were removed under reduced pressure and the residue was carefully dissolved with CH$_2$Cl$_2$ (300 mL) and washed with 10% HCl followed by water (3x 200 mL). The organic layers were dried over MgSO$_4$ and the solvents evaporated under reduced pressure. The obtained solid was triturated with hot chloroform to afford 4 as a pale-yellow solid.
Yield: 1.8 g (59.7 %); pale-yellow solid

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 9.10 (s, 2H), 6.63 (s, 4H), 4.03 (s, 12H).

1,4,5,8-Anthracenetetrone (5):
Procedure adapted from Glöcklhofer and coworkers.[4b]
A 500 mL two-neck flask was charged with silica (50.0 g) before slowly adding ceric ammonium nitrate (23.3 g, 42.4 mmol, 5.5 eq.) dissolved in 37 mL of H$_2$O. The mixture was stirred till a yellow free-flowing solid was obtained. Subsequently, first 300 mL CH$_2$Cl$_2$ was added before adding 4 (2.3 g, 7.7 mmol, 1.0 eq.) dissolved in CH$_2$Cl$_2$ (50 mL) was added dropwise and stirred for 2 h. The obtained suspension was filtered, and the residues washed with CH$_2$Cl$_2$ (200 mL). The combined organic layers were dried over MgSO$_4$ and the solvents evaporated under reduced pressure. The obtained solid was purified via column chromatography with 4:1 CH$_2$Cl$_2$:hexanes as an eluent.

Yield: 1.35 g (73.5 %); red crystals
$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.82 (s, 2H), 7.14 (s, 4H).

Ionothermal synthesis of pTOC-350:
A 20 mL glass ampule was charged with ground sodium chloride (86.4 mg, 1.48 mmol, 1.76 eq.) before transferring to a glovebox. Subsequently, 5 (200.0 mg, 0.84 mmol, 1.00 eq.) and aluminum chloride (313.5 mg, 2.35 mmol, 2.8 eq.) were added and the ampule was evacuated to an internal pressure of 0.15 mbar for 45 min before flame-sealing the ampule. The mixture was heated to 350 °C for 72h or 120h. After cooling to RT the obtained black solid was stirred in a 1:1 mixture of water and methanol for 24h followed by 2N HCl for 48h. The solid was subsequently filtered using a POR4 fritted glass filter and washed with water, methanol, acetone, pyridine and THF. The polymer was subsequently stirred in a 1:1 water-ethanol mixture overnight followed by stirring in 2N HCl overnight. Finally, the polymers were filtered over a POR4 fritted glass, washed with water and acetone before being dried at 90 °C under vacuum.

Yield: 147 mg (88 %); black powder

pTOC-250 and -300 were synthesized by following same procedure at 250 and 300 °C, respectively.

Solvothermal synthesis of pTOCs:
A 20 mL microwave vial was charged with 5 (50.0 mg, 0.21 mmol, 1.00 eq.), aluminum chloride (39.2 mg, 0.29 mmol, 1.4 eq.) and nitrobenzene (5 mL) in a glovebox before heating to reaction temperature (100, 125, 150 and 175 °C) for 6 hours. After cooling to RT the obtained suspension was filtered over a POR4 fritted glass filter and subsequently washed with ethanol, 2N HCl, ethanol, pyridine and ethanol.

Yield: 0 g (0 %)

Solvothermal synthesis of TOC:
A 10 mL microwave vial was charged with previously sublimed naphthoquinone (100.0 mg, 0.63 mmol, 1.00 eq.), aluminum chloride (118.0 mg, 0.885 mmol, 1.4 eq.) and nitrobenzene (5 mL) in a glovebox before heating in a microwave to 60 °C for 1 hour. After cooling to RT the obtained suspension was filtered over a POR4 fritted glass filter and subsequently washed with ethanol, 2N HCl, ethanol, pyridine and ethanol.

Yield: 80.6 mg (91.0 %); yellow powder

Doping of pTOCs:
I$_2$ vapor doping: 10 mg of pTOCs placed in a 4 mL vial, and then this vial was placed into a 20 mL vial with 10 mg of I$_2$. The small vial left open, while the large vial was sealed. The vapor doping set-up kept at room temperature or elevated temperature for 6~12 hours.
KOH or HCl doping: To a 20 mL vial with 20 mg of pTOCs was added 5~10 mL of aqueous KOH or HCl solution. The vial was sealed and kept at room temperature overnight. The reaction mixture was then filtered and washed with DI water and acetone, and dried over air flow.

Post-synthetic modification of the unreacted carbonyl groups in pTOCs using Lawesson’s reagent:
In a N₂-filled glove box, 15 mg of pTOCs and 15 mg of Lawesson’s reagent were transferred into a 20 mL glass pressure tube, followed by the addition of 5 mL toluene. The pressure tube was then transferred out of the glove box and heated at 120 °C for 12 hours. After cooling down to room temperature, the reaction mixture was filtered and washed with toluene. The resulting black solid was dried under air flow.
Table S1 Reaction conditions of the attempted solvothermal conditions in nitrobenzene for the synthesis of pTOCs.

| eq. AlCl₃ | time [h] | Temperature [°C] |
|-----------|----------|------------------|
| a         | 1.4      | 1                | 60       |
| b         | 2.8      | 1                | 60       |
| c         | 2.8      | 2                | 60       |
| d         | 1.4      | 6                | 150      |
| e         | 1.4      | 6                | 125      |
| f         | 1.4      | 6                | 100      |
| g         | 2.8      | 6                | 100      |

Table S2 Reaction conditions of solvothermal reactions with different solvents and Lewis acids.

| Lewis acid | solvent | eq. Acid | time [h] | Temperature [°C] |
|------------|---------|----------|----------|------------------|
| h          | AlCl₃   | toluene  | 2.8      | 6                | 125       |
| i          | AlCl₃   | DMSO     | 2.8      | 6                | 125       |
| j          | BF₃-ΟEt₂ | dry ether| 100      | 72               | 40        |

Results and Discussion

\(^{13}\text{C CP-MAS Solid-State NMR}\)

![13C CP-MAS solid-state NMR spectra of TOC (purple) and pTOC-350 (blue). Side bands are indicated by symbols for TOC (*, +, -) and pTOC-350 (*). The spectrum of pTOC-350 shows a terminal/residual carbonyl peak indicated with "o" at 183 ppm](image-url)
FTIR KBr-Pellet in Transmission Mode and DRIFTS

Figure S2 Infrared spectroscopy of pTOCs, TOC and precursor. A) FTIR spectra of anthracene tetrone (orange), TOC (purple), pTOC-250 (black), pTOC-300 (green) and pTOC-350 (blue). Characteristic modes are highlighted in yellow (C=O stretch) and pink (C=C stretch). Obtained using KBR pellets in the transmission mode. B) Zoomed region of the pTOCs in the range of 2000 – 4000 cm⁻¹ with highlights of the C=O stretching modes. C) Zoomed ATR-IR spectrum of pTOC-350 in the range of 2000 – 6000 cm⁻¹ with highlights of the C-O stretching modes.

Figure S3 (A) DRIFTS of pTOC-250 (black), pTOC-300 (green) and pTOC-350 (blue). (B) DRIFTS normalized by the intensity of C=C stretching at ~1600 cm⁻¹, highlighting that the intensity of residual C=O stretching (marked by red dashed lines) decreased significantly from pTOC-250 to pTOC-350.
Raman Spectra

Figure S4 Raman spectra of pTOC-250 (black), pTOC-300 (green) and pTOC-350 (blue).

Powder X-ray Diffraction

Figure S5 Powder X-ray diffractograms of anthracene tetrone (orange), pTOC-250 (black), pTOC-300 (green) and pTOC-350 (blue).
Figure S6 SEM micrographs of A-C) pTOC-250, D-E) pTOC-300 and H-J) pTOC-350 at various magnifications.
Thermogravimetric Analysis

Figure S 7 Thermogravimetric analysis of (a) tetraoxa[8]circulene under air (blue) and nitrogen (black), (b) pTOC-350 under air (blue) and nitrogen (black) and (c) 1,4,5,8-anthracene tetrone under nitrogen.

Rouquerol and BET Plots

Figure S 8 A-C) Calculated Rouquerol plot for the pTOCs (Inset: enlarged plot) along with the pressure ranges used for the BET surface area calculations (pTOC-250 (black), pTOC-300 (green) and pTOC-350 (blue)). The pressure range where the Q(1–P/P₀) term increases continuously with P/P₀ for the surface area calculations (D-F). BET plot of the pTOCs obtained from N₂ isotherms at 77 K.
Figure S9 XPS survey spectra of pTOC-250 (A), pTOC-300 (B), pTOC-350 (C).

Table S3 Atomic compositions of pTOCs obtained by XPS survey spectra.

| Materials    | C At% | O At% | C/O ratio |
|--------------|-------|-------|-----------|
| pTOC-250     | 82.11 | 11.91 | 6.89      |
| pTOC-300     | 83.11 | 14.64 | 5.68      |
| pTOC-350     | 86.99 | 11.63 | 7.48      |

We note the presence of relatively weak signals of Si2p and Cl2p in the XPS survey spectrum. Whereas the Si can be explained by glass particles falling into the sample during opening the ampule, the Cl contamination comes from surface adsorption of Cl after the HCl washing that cannot be completely removed even after long washing/soaking.

Table S4 Deconvolution details of C1s XPS spectrum of pTOC-350.

| Name          | Position (eV) | FWHM (eV) | Line Shape | %Area |
|---------------|---------------|-----------|------------|-------|
| Adventitious carbon | 284.80         | 1.25      | LA(4.2, 9, 4) | 18.35 |
| C, C - C     | 285.52        | 2.04      | GL(30)     | 51.97 |
| C - O-C      | 286.72        | 2.62      | GL(30)     | 21.74 |
| C=O          | 289.95        | 2.62      | GL(30)     | 4.87  |
| π* - π*       | 291.43        | 3.00      | GL(30)     | 3.08  |

Table S5 Deconvolution details of C1s XPS spectrum of pTOC-300.

| Name          | Position (eV) | FWHM (eV) | Line Shape | %Area |
|---------------|---------------|-----------|------------|-------|
| Adventitious carbon | 284.85        | 1.59      | LA(4.2, 9, 4) | 6.04  |
| C, C - C     | 285.22        | 1.51      | A(0.35, 0.2, 0) GL(30) | 58.08 |
| C - O-C      | 286.67        | 1.96      | A(0.35, 0.2, 0) GL(30) | 24.27 |
| C=O          | 289.00        | 1.96      | A(0.35, 0.2, 0) GL(30) | 5.98  |
| π* - π*       | 291.41        | 2.87      | GL(30)     | 3.72  |

* A small C1s pre-peak at BE of 283.15 eV was needed for the deconvolution. * An asymmetric feature was needed for the line shape of (C-H, C-C), C-O-C, and C=O components in order to get a reasonable fit.

Table S6 Deconvolution details of C1s XPS spectrum of pTOC-250.

| Name          | Position (eV) | FWHM (eV) | Line Shape | %Area |
|---------------|---------------|-----------|------------|-------|
| Adventitious carbon | 284.80        | 1.00      | LA(4.2, 9, 4) | 14.09 |
| C, C - C     | 285.27        | 1.83      | GL(30)     | 53.54 |
| C - O-C      | 286.62        | 2.24      | GL(30)     | 22.57 |
| C=O          | 288.76        | 2.24      | GL(30)     | 6.22  |
| π* - π*       | 291.30        | 3.00      | GL(30)     | 3.58  |
### Table S7 Deconvolution details of O1s XPS spectrum of pTOC-350.

| Name       | Position (eV) | FWHM (eV) | Line Shape | %Area |
|------------|---------------|-----------|------------|-------|
| C=O        | 531.76        | 2.54      | GL(70)     | 13.14 |
| Surface O  | 533.17        | 2.54      | GL(70)     | 38.48 |
| C-O-C      | 533.85        | 2.54      | GL(70)     | 48.37 |
| Absorbed H$_2$O$^a$ | -         | -         | -          | -     |

$^a$ The BE of C=O peak is consistent with the literature values of aromatic C=O.

### Table S8 Deconvolution details of O1s XPS spectrum of pTOC-300.

| Name       | Position (eV) | FWHM (eV) | Line Shape | %Area |
|------------|---------------|-----------|------------|-------|
| C=O$^a$    | 531.80        | 1.79      | GL(70)     | 17.58 |
| Surface O  | 532.97        | 2.43      | GL(70)     | 40.05 |
| C-O-C      | 534.15        | 1.79      | GL(70)     | 36.76 |
| Absorbed H$_2$O | 537.28 | 3.00      | GL(70)     | 5.60  |

$^a$ The BE of C=O peak is consistent with the literature values of aromatic C=O.

### Table S9 Deconvolution details of O1s XPS spectrum of pTOC-250.

| Name       | Position (eV) | FWHM (eV) | Line Shape | %Area |
|------------|---------------|-----------|------------|-------|
| C=O$^a$    | 531.80        | 2.04      | GL(70)     | 25.17 |
| Surface O  | 532.97        | 2.01      | GL(70)     | 30.66 |
| C-O-C      | 534.15        | 2.04      | GL(70)     | 36.81 |
| Absorbed H$_2$O | 537.28 | 3.00      | GL(70)     | 7.35  |

$^a$ The BE of C=O peak is consistent with the literature values of aromatic C=O.

### Table S10 Area ratio analysis based on deconvolution of C1s and O1s XPS spectra.

| Materials   | (C-H,C-C)/C-O-C | C=O/C-O-C (C1s) | C=O/C=O-C (O1s) |
|-------------|-----------------|-----------------|-----------------|
| pTOC-250    | 2.37            | 0.276           | 0.684           |
| pTOC-300    | 2.39            | 0.246           | 0.478           |
| pTOC-350    | 2.39            | 0.224           | 0.272           |
Materials Studio Simulation of the Perfect pTOC

Figure S 10 Simulated structure of pTOC using Materials Studio (P4/mmm space group). (A) Layered structure of pTOC, a = b = 10.74 Å. (B) Stacking of pTOC layers, exhibiting an interlayer spacing of 3.42 Å.

Figure S 11 Connolly surface of the simulated structure of pTOC. The analysis showed that the actual pore diameter is around 5 Å. The gray lines represent the unit cell boundaries.

Regarding the difference of the single pore diameter shown in the theoretical model of perfect layered pTOC and the dual pore diameters determined by N₂ absorption measurements, we believe this is a piece of important evidence of our hypothesis that the actual structure is three-dimensionally (3D) connected, with localized planar structures exhibiting ~5 Å pore size. The 3D-like connectivity gives rise to the second main pore size that is larger with a 10 Å diameter. The actual 3D-like structure also accounts for the significantly higher surface area compared with the 2D layered-like simulated structure. We further note that the generation of 3D-connected structure and the amorphous nature is mainly due to the irreversibility of the cyclization reaction employed to synthesize the material.
Figure S 12 EPR spectrum of pTOC-350 at room temperature. The microwave frequency is 9.37 GHz, power is 0.005 mW, and attenuation is 10.0 dB. An isotropic organic radical signal at $g = 2.007$ is observed. Red dashed line is simulated EPR spectrum of an isotropic $S = \frac{1}{2}$ spin with $g = 2.007$ and Lorentzian line broadening (peak-to-peak (PP) line width equals to 0.5 mT).
Conductivity Measurements and Supporting Characterization

Figure S13 Typical linear I-V curves of two-probe (A-C) and four-probe (D) electrical conductivity measurements of pTOCs, suggesting ohmic contact for all devices. The contact resistance in the conductivity measurements of pTOCs has little influence on the final results, as suggested by the almost same conductivity values of two-probe and four-probe measurements of pTOC-350. The average electrical conductivities of pTOC-250, pTOC-300, and pTOC-350 are $1.7\times10^{-5}$ S/cm, $1.2\times10^{-5}$ S/cm, and $1.0\times10^{-6}$ S/cm. Inset of D shows the image of a typical four-probe device.
Figure S1 A typical I-V curve of two-probe electrical conductivity measurement of pTOC-350 synthesized by a 120h reaction. The average conductivity is $3.3 \times 10^{-6}$ S/cm, which is slightly higher than that of pTOC-350 synthesized over 72h.

Figure S15 I-V curve of two-probe electrical conductivity measurement of pTOC-350 synthesized by a 72h reaction. The sample was doped by soaking in saturated sodium chloride solution.

These measurements were conducted to prove that chloride ions are not acting as dopants in pTOCs. We hypothesize that the Cl could be 1) Cl$^-$ remaining in the framework, or 2) C–Cl moieties generated during synthesis as defects. Assuming hypothesis 1 is true, we performed conductivity measurements of pTOC-350 soaked in NaCl aqueous solution, which exhibit 2-probe electrical conductivity of $1.8 \times 10^{-7}$ S/cm. This value is slightly lower than that of pristine pTOC-350 ($1.0 \times 10^{-6}$ S/cm), and we thus prove that Cl$^-$, if present in the material, cannot promote charge transport of pTOCs. On the other hand, assuming the presence of C–Cl moieties, the in-plane π-conjugation will be significantly interrupted, leading to lower electrical conductivity. Therefore, we conclude that the presence of trace chlorine in pTOCs, being either chloride or organic chlorine, does not act as a doping agent and cannot promote charge transport of pTOCs.
Figure S16 Negative photoconductivity of another four-probe device of pTOC-350, exhibiting moderate to significant electrical conductivity drop upon light exposure.

Figure S17. High-resolution C1s (A) and O1s (B) XPS spectra of laser-exposed pTOC-350 and the corresponding deconvolutions.

Table S11. Deconvolution details of C1s XPS spectrum of pTOC-350 (laser exposed).

| Name            | Position (eV) | FWHM (eV) | Line Shape   | %Area |
|-----------------|---------------|-----------|--------------|-------|
| Adventitious carbon | 284.83        | 1.00      | LA(4.2, 9, 4) | 9.88  |
| C-H, C-C        | 285.20        | 1.53      | GL(30)       | 53.53 |
| C-O-C           | 286.66        | 1.84      | GL(30)       | 22.76 |
| C=O             | 288.52        | 1.53      | GL(30)       | 4.04  |
| π-π*            | 290.31        | 4.00      | GL(30)       | 9.79  |

Table S12. Deconvolution details of O1s XPS spectrum of pTOC-350 (laser exposed).

| Name            | Position (eV) | FWHM (eV) | Line Shape | %Area |
|-----------------|---------------|-----------|------------|-------|
| C=O<sup>a</sup> | 531.78        | 2.54      | GL(70)     | 13.16 |
| Surface O       | 533.09        | 2.54      | GL(70)     | 29.30 |
| C-O-C           | 534.10        | 2.54      | GL(70)     | 46.89 |
| Absorbed H<sub>2</sub>O<sup>b</sup> | 536.59      | 3.22      | GL(70)     | 10.65 |

<sup>a</sup> The BE of C=O peak is consistent with the literature values of aromatic C=O. <sup>b</sup> A peak of absorbed H<sub>2</sub>O is needed for fitting.
Figure S18. (A) DRUV-Vis spectra of pristine pTOC-350 and pTOC-350 exposed to laser. (B) Tauc plot of the DRUV-Vis spectrum of pTOC-350 exposed to laser. The dashed line is the linear fitting, revealing an optical band gap of 1.85 eV.

The absorption maximum exhibited no shift upon laser exposure, and the optical band gap also remained unchanged, indicating that the overall band structure of pTOC-350 undergoes little change upon laser exposure. The decreased intensity of absorption in the NIR range of pTOC-350 after laser exposure relative to that of the pristine material could presumably imply slight sample degradation upon prolonged exposure. However, the actual experiment with the laser was only a couple of minutes long and showed the biggest impact right after turning the laser on.

Figure S19 Typical I-V curves of two-probe electrical conductivity measurements of pTOC-250 (A) and pTOC-350 (B) after post-synthetic modification using Lawesson’s reagent (LR). The average electrical conductivities of pTOC-250 (LR) and pTOC-350 (LR) are 4.7×10⁻⁸ S/cm and 7.3×10⁻⁶ S/cm, respectively.
Figure S20 S2p XPS spectrum of pTOC-350 reacted with LR. The low signal intensity agrees well with the defect engineering.

Figure S21 O1s XPS spectrum of pristine pTOC-350 and pTOC-350 (LR). According to the O1s deconvolution of pTOCs, the lower intensity at lower BE of pTOC-350 (LR) indicates the decrease of residual carbonyl groups.
Figure S22 The comparison of DRIFTS of pristine pTOCs and pTOCs (LR). The decrease in the intensity of residual carbonyl moiety was observed along with the appearance of new peaks between 1200 cm$^{-1}$ and 800 cm$^{-1}$, which were tentatively assigned to C=S stretching modes.\cite{5}

Figure S23 I3d XPS spectrum of pTOC-350 doped with I$_2$. The presence of iodine was clearly seen even under ultrahigh vacuum (~10$^{-10}$ Torr), suggesting that the iodine-containing species present in the doped material indeed interact with the framework. Deconvolution of the I 3d5/2 region resulted in three components (65.5% : 27.8% : 6.7%). The species with BE of 619.05 eV has oxidation states lower than I$_2$, which normally shows a BE of 620.2±0.5 eV. We attribute this species to the product obtained after redox reaction between I$_2$ and pTOC-350 and/or I$_2$ molecules that are strongly interacting with the framework, given that previous literature has reported that I$_2$ chemisorbed on Ag surface also exhibited a BE of 619.3 eV. The component with a BE of 620.6 eV is assigned to trapped iodine. The broad peak with a BE of 623.4 eV is the result of satellite feature.
The typical I-V curves of two-probe electrical conductivity measurements of pTOC-350 doped with I₂ vapor at RT (A), and 50 °C (B). The average conductivity of pTOC-350 doped at 50 °C for 6 h and 18 h are $1.9 \times 10^{-4}$ S/cm and $5.1 \times 10^{-4}$ S/cm, respectively. (C) IV curves of pTOC-350-I₂ which is either evacuated under dynamic vacuum for 3 days (blue circles) or washed with acetone and dried (green squares), showing decreased conductivity of $1.6 \times 10^{-5}$ S/cm and $6.9 \times 10^{-6}$ S/cm, respectively. However, these values are still obviously higher than the pristine pTOC-350, suggesting the increased conductivity is robust in pTOC-350-I₂.
Figure S25 (A) The comparison of DRIFTS of pristine pTOC-350 and pTOC-350 (I	extsubscript{2}). The peak profiles did not change, however, the Drude-type absorption became significant after I	extsubscript{2} doping, suggesting the substantial increase of free carrier concentration. This is likely the result of redox doping that generated a lot of carriers.

(B) The comparison of DRUV (plotted in the wavelength scale) of pristine pTOC-350 and pTOC-350 (I	extsubscript{2}). The absorption maximum red shifted almost 100 nm to ~436 nm, suggesting a smaller band gap. The growth of a broad NIR band was also observed, which we attribute to the polaronic transition that caused by I	extsubscript{2} doping. The intense background absorption matches well with DRIFTS.
**Figure S26.** I–V curves for a two-probe pressed pellet of (A, B) pTOC-350 and (C, D) pTOC-350-I₂ taken at different temperatures.

**Figure S27.** Multiple cycles of VT electrical conductivity data of pTOC-350 plotted for thermally activated hopping transport (A) and pTOC-350-I₂ plotted for 3D VRH mechanism (B). The conductivity of pTOC-350-I₂ only decreased very slightly after the first heating measurement that went to 375 K under high vacuum, confirming that the I₂ doping of pTOC-350 is robust.
Figure S28 The VT electrical conductivity data of pTOC-350-I₂ plotted for thermally activated hopping transport (ln(σ) versus T⁻¹) from 294 K to 100 K. The linear fittings of low temperatures (210 K to 100 K) or high temperatures (294 K to 210 K) both revealed deviation of the experimental data from linear behaviour, although with R² ~ 0.99. The linear fitting of the full temperature range (100 K to 294 K, not shown for clarity) gave a R² of 0.97, indicating poor correlation.

Figure S29 The comparison of DRUV (plotted in the wavelength scale) of pristine pTOCs and pTOCs (LR). The absorption maximum of pTOC-250 significantly blue shifted to ~385 nm upon LR treatment, indicating that the extended conjugation might be interrupted by defect engineering. However, slight increase of the background absorption was observed, implying the small increase of free carrier concentration. On the other hand, the DRUV spectrum of pTOC-350 changed substantially upon LR treatment. Although the main absorption changed little, which in fact is in great agreement with the defect engineer strategy rather than global doping, the NIR band centered close to 800 nm significantly gained intensity, indicating that the incorporation of heavier atoms (S in this case) can assist intermolecular interactions. The background absorption also increased a lot for pTOC-350. The changes of electronic structure reflected well on the electrical conductivity changes.
Figure S30: Valence-band (VB) XPS of pristine pTOC-350 (blue), pTOC-350 (LR) (orange), and pTOC-350 (I$_2$) (red). Significant increase of DOS near Fermi level was observed for both pTOC-350 (I$_2$), suggesting the increase of carrier concentration.
Table S13. Conductivity and surface area data for POPs and COFs.

| Material description | Cryst. | Conductivity (S cm$^{-1}$) | BET SA (m$^2$ g$^{-1}$) | Ref |
|----------------------|--------|----------------------------|--------------------------|-----|
| pTOC-250             | -      | $1.7 \times 10^5$          | 411                      | this work |
| pTOC-300             | -      | $1.2 \times 10^5$          | 1075                     | this work |
| pTOC-350             | -      | $1.0 \times 10^6$          | 1856                     | this work |
| pTOC-350 ox (I2)     | -      | $4.1 \times 10^4$          | n.a.                     | this work |
| pTOC-350 LR$^*$      | -      | $1.2 \times 10^5$          | n.a.                     | this work |
| 3D ep-POP            | -      | $8 \times 10^{10}$         | 779                      | [6] |
| 3D p-POP             | -      | $5 \times 10^8$            | 801                      | [6] |
| 3D p-POP ox (I2)     | -      | $6 \times 10^4$            | n.a.                     | [6] |
| SP-BTT               | -      | $4.2 \times 10^6$          | 356                      | [7] |
| SP-BTT-HCl           | H$^+$  | $1 \times 10^4$            | n.a.                     | [7] |
| 1-S                  | x      | $3.7 \times 10^{10}$       | 1424                     | [8] |
| 1-Se                 | x      | $8.4 \times 10^9$          | 1634                     | [8] |
| 1-Te                 | x      | $1.3 \times 10^7$          | 352                      | [8] |
| sp$^2$c-COF          | -      | $6.1 \times 10^{16}$       | 692                      | [9] |
| sp$^2$c-COF ox (I2)  | x      | $7.1 \times 10^4$          | n.a.                     | [9] |
| BUCT-COF-1           | -      | $1.6 \times 10^7$          | 976                      | [10] |
| BUCT-COF-4           | -      | $5.8 \times 10^8$          | 477                      | [11] |
| BUCT-COF-4 ox (I2)   | x      | $2.8 \times 10^6$          | n.a.                     | [11] |
| ZnPc-pz-I2           | ox (I2)| $3.1 \times 10^4$          | 225                      | [12] |
| CuPc-pz              | x      | $3.3 \times 10^7$          | 485                      | [13] |
| ZnPc-pz              | x      | $7 \times 10^7$            | 487                      | [13] |
| P2PV                 | x      | $1 \times 10^9$            | 880                      | [14] |
| P3PcB                | x      | $1 \times 10^9$            | 1073                     | [14] |

$^*$ LR = Lawesson Reagent
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Author Contributions

AC, MD, PWF, TC and TA have conceived, designed, and conducted the experiments. PWF, TA and NAD performed the material synthesis. TC conducted doping and post-synthetic modification experiments. PWF, TA and TC conducted the characterization and data analysis of the materials at different stages. AC and MD acquired funding for the project. PWF and TC co-wrote the manuscript.