Supporting Information

Highly Conducting Wurster-Type Twisted Covalent Organic Frameworks

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Chemicals

All materials were purchased from Aldrich, Fluka, Acros or TCI Europe in the common purities purum, puriss or reagent grade. Materials were used as received without additional purification and handled under air unless noted. All solvents used were anhydrous and purged with inert gas.

Methods and Instruments

Nuclear magnetic resonance spectra were recorded on Bruker AV 400 and AV 400 TR spectrometers. Proton chemical shifts are expressed in parts per million (δ scale) and are calibrated using residual non-deuterated solvent peaks as an internal reference (e.g., DMSO-d6: 2.50).

Powder X-ray diffraction measurements were performed on a Bruker D8 Discover diffractometer using Ni-filtered Cu Kα radiation and a position sensitive LynxEye detector in Bragg-Brentano geometry.

Nitrogen sorption isotherms were recorded on a Quantachrome Autosorb 1 instrument at 77 K within pressure ranges of \( p/p_0 = 0.001 \) to 0.98. Samples for physisorption were directly taken from supercritical CO2 activation. Prior to the measurements, the samples were heated for 12 h at 100 °C under high vacuum. For the evaluation of the surface area the BET method was applied within a \( p/p_0 \) range of 0.05 to 0.3. Pore size distributions
were calculated using the QSDFT absorption model with a carbon kernel for cylindrical pores.

**Ultraviolet–Vis–infrared absorption** spectra were recorded on a Perkin-Elmer Lambda 1050 spectrometer equipped with a 150 mm integration sphere.

**Photoluminescence and time-correlated single photon counting measurements** were carried out using a FluoTime 300 from PicoQuant GmbH. Samples were excited using a 378 nm laser source pulsed at 40 MHz and a fluence of 300 nJ cm$^{-2}$/pulse.

**Scanning electron microscopy** images were recorded with an FEI Helios NanoLab G3 UC scanning electron microscope equipped with a field emission gun operated at 3 kV. Prior to the measurements, the samples were sputtered with carbon.

**Transmission electron microscopy** images were recorded with an FEI Titan Themis 60 - 300 equipped with a field emission gun operated at 300 kV.

**Electrochemical measurements** were performed on a Metrohm µAutolabIII/FRA2 instrument using a three-electrode setup with a Pt-wire counter-electrode and a silver wire as a pseudo reference electrode under argon atmosphere. Measurements were carried out in dry acetonitrile with tetrabutyl ammonium tetrafluoro borate (1 M) as the electrolyte. After recording CV data, the measurement was repeated after a small amount of ferrocene was added to the sample. The position of the redox couple from Fc/Fc$^+$ was then used as the reference system.

**Van-der-Pauw** measurements were carried out using an ECOPIA Model HMS 3000 setup. The samples were contacted with gold plated spring electrodes with an electrode separation of 5 mm. Powder pellets were pressed by using 20 mg of COF material and pressing into a cylindrical pellet with a circle diameter of 1 cm under a pressure of 8000 kPa.

**Electron paramagnetic resonance (EPR)**

EPR was measured with a modified Bruker X-Band spectrometer (E300) in the dark at room temperature with a magnetic field modulation of 1 Gauss and microwave power set to 100 µW (33 dB).

**Theoretical Calculations**

The initial structures of the COFs were built using the Forcite module of Accelrys Materials Studio 6.0 using the Universal Force Field as implemented. Pawley refinements were
carried out using the Reflex module of PXRD with the Howard-profile fitting function. DFTB+ calculations were carried out using the DFTB+ code with the 3ob parameter set.\textsuperscript{1} DFT calculations on the model pore systems were carried out using Gaussian 16 with the PBE0 functional and the def2SVP basis set with standard convergence criteria.

**Synthesis of WTA**

![Diagram of WTA-3D framework](image_url)

In a 5 mL culture tube, a solid mixture of terephthalaldehyde (\textbf{TA}, 0.025 mmol, 3.4 mg) and \textit{N,N,N',N'}-tetrakis(4-aminophenyl)-1,4-phenylenediamine (\textbf{W}, 0.013 mmol, 6.0 mg) was suspended in 1 mL mesitylene and benzyl alcohol (1:1 V:V). The loading of the culture tube was carried out in an argon filled glovebox. Subsequently, 50 µL of acetic acid (6 M) was added. Then, the culture tube was tightly sealed and heated at 100 °C for 72 h in an oven. The resulting dark red suspension was filtrated hot and the isolated powder was washed with 10 mL tetrahydrofuran (THF). The obtained red microcrystalline product was dried under vacuum and subsequently activated with supercritical CO\textsubscript{2} at 110 bar and 40 °C for 1 hour.
Synthesis of WBDT

In a 5 mL culture tube, a solid mixture of benzodithiophene-2,6-dicarboxaldehyde (BDT, 0.025 mmol, 6.26 mg) and N,N,N',N'-tetrakis(4-aminophenyl)-1,4-phenylenediamine (W, 0.013 mmol, 6.0 mg) was suspended in 1 mL mesitylene and benzyl alcohol (1:1 V:V). The loading of the culture tube was carried out in an argon filled glovebox. Subsequently, 50 µL of acetic acid (6M) was added. Then, the culture tube was tightly sealed and heated at 100 °C for 72 h in an oven. The resulting dark red suspension was filtrated hot and the isolated powder was washed with 10 mL tetrahydrofuran (THF). The obtained red microcrystalline product was dried under vacuum and subsequently activated with supercritical CO₂ at 110 bar and 40 °C for 1 hour.

Synthesis of WTA thin films

In a 25 mL Schott duran glass bottle, a solid mixture of terephthalaldehyde (TA, 0.1 mmol, 13.6 mg) and N,N,N',N'-tetrakis(4-aminophenyl)-1,4-phenylenediamine (W, 0.052 mmol, 24.0 mg) was suspended in 4 mL mesitylene and benzyl alcohol (1:1 V:V). The loading of the reaction vessel was carried out in an argon filled glovebox. 200 µL of acetic acid (6 M) was added. A substrate holder with two horizontally oriented substrates (1.5 cm × 1.5 cm) was placed into the suspension. The reaction vessel was tightly sealed and heated at 100 °C for 12 h in an oven. Then the substrate holder was taken from the vessel and the substrates from the holder. The upper sides of the substrates were cleaned from COF precipitates by wiping the surface with an aceton wetted cotton tip. Subsequently, the bottom sides of the substrates were washed with THF and dried under vacuum.
**Synthesis of WBDT thin films**

In a 25 mL Schott duran glass bottle, a solid mixture of benzodithiophene-2,6-dicarboxaldehyde (BDT, 0.1 mmol, 25.04 mg) and \(N,N,N',N'\)-tetrakis(4-aminophenyl)-1,4-phenylenediamine (W, 0.052 mmol, 24.0 mg) was suspended in 4 mL mesitylene and benzyl alcohol (1:1 V:V). The loading of the reaction vessel was carried out in an argon filled glovebox. 200 µL of acetic acid (6M) was added. A substrate holder with two horizontally oriented substrates (1.5 cm × 1.5 cm) was placed into the suspension. The reaction vessel was tightly sealed and heated at 100 °C for 12 h in an oven. Then the substrate holder was taken from the vessel and the substrates from the holder. The upper sides of the substrates were cleaned from COF precipitates by wiping the surface with an aceton wetted cotton tip. Subsequently, the bottom sides of the substrates were washed with THF and dried under vacuum.

**Synthesis of the WBDT molecular fragment and single crystal growth**

In a 5 mL culture tube, a solid mixture of benzothiophene-2-carboxaldehyde (0.25 mmol, 62.6 mg) and \(N,N,N',N'\)-tetrakis(4-aminophenyl)-1,4-phenylenediamine (W, 0.05 mmol, 23.0 mg) was suspended in 4 mL of CHCl₃. The culture tube was sealed and heated for 24 h at 60 °C. Subsequently, the reaction was cooled to room temperature and the resulting precipitate was collected by filtration and washed with methanol (20 mL). The dark red material was dried under vacuum.

\[1^1\text{H} \text{NMR (400 MHz, DMSO-}d_6\text{)} \delta (\text{ppm}): 8.50 (4\text{H}), 7.79 (8\text{H}), 7.45 (8\text{H}), 7.32 (8\text{H}), 7.30 (4\text{H}), 7.18 (8\text{H}), 7.14 (4\text{H}).\]

\text{MS-EI: calculated (m/z): C}_{66}\text{H}_{44}\text{N}_6\text{S}_4 1048.2510, found 1048.2478.\]
Single crystals were grown by dissolving 5 mg of the WBDT molecular fragment in dichloromethane (10 mL) in a 25 mL screw-capped vial equipped with a septum. A needle was pierced through the septum to allow for slow evaporation of the solvent at room temperature. After 5 days, red platelet-like crystals were obtained, which were removed from solution directly prior to single-crystal analysis.
Figure S1: The molecular arrangement of the WBDT molecular fragment, obtained from single crystal data in ORTEP and stick-ball representation.

Table S1: Summary of the single crystal data of the WBDT molecular fragment.

| Description                  | Value                          |
|------------------------------|-------------------------------|
| net formula                  | $C_{67.53}H_{47.10}Cl_{3.09}N_6S_4$ |
| $M_r$/g mol$^{-1}$           | 1180.73                       |
| crystal size/mm              | $0.090 \times 0.070 \times 0.020$ |
| $T$/K                        | 106.(2)                       |
| radiation                    | Mo K$_\alpha$                 |
| diffractometer               | 'Bruker D8 Venture TXS'        |
| crystal system               | triclinic                     |
| space group                  | 'P -1'                        |
| $a$/Å                        | 13.8855(6)                    |
| $b$/Å                        | 17.9904(7)                    |
| $c$/Å                        | 19.1860(7)                    |
$\alpha/^{\circ}$ 77.1720(10)
$\beta/^{\circ}$ 78.2210(10)
$\gamma/^{\circ}$ 69.1000(10)
$V/\text{Å}^3$ 4324.4(3)
$Z$ 3
calc. density/g cm$^{-3}$ 1.360
$\mu$/mm$^{-1}$ 0.357
absorption correction Multi-Scan
transmission factor range 0.96–0.99
refls. measured 58603
$R_{int}$ 0.0538
mean $\sigma(I)/I$ 0.0600
$\theta$ range 2.337–25.350
observed refls. 10556
$x$, $y$ (weighting scheme) 0.1012, 10.3561
hydrogen refinement Constr.
Refls. in refinement 15789
parameters 1321
restraints 406
$R(F_{\text{obs}})$ 0.0811
$R_w(F^2)$ 0.2308
$S$ 1.023
shift/error$_{\text{max}}$ 0.001
max electron density/e Å$^{-3}$ 1.274
There are several disordered parts in this structure. All methylene chloride molecules are disordered. Split models have been applied. SADI instructions have been used to restrain all C-Cl and all Cl-Cl distances to similar values. All but one of the CH₂Cl₂ moieties have been refined isotropically. The SIMU restraint has been used to refine the $U_{ij}$ of adjacent atoms (to a distance of 0.8 Å) similarly. The SAME instruction has been applied to obtain good bond geometries in two disordered branches of the macromolecules using well-refined branches as model. ISOR and FLAT restraints have been used to improve vibration ellipsoids and geometry, respectively.

The figure above does not show the methylene chloride molecules and the minor parts of disordered sections.

Symmetry code $i = 2-x, 1-y, 1-z$. 

min electron density/e Å⁻³

−1.050
Simulated tetragonal structure of WTA

Figure S2: Simulated tetragonal structure of WTA and the corresponding calculated PXRD pattern vs. the experimental pattern.

Simulated tetragonal structure of WBDT

Figure S3: Simulated tetragonal structure of WBDT and the corresponding calculated PXRD pattern vs. the experimental pattern.
Hexagonal kagome vs. kagome-like arrangement of WTA

Figure S4: Representation of the geometric arrangement of the central W unit in WTA in a hexagonal $P6$ symmetry and in $P-1$ symmetry.

Hexagonal kagome vs. kagome-like arrangement of WBDT

Figure S5: Representation of the geometric arrangement of the central W unit in WBDT in a hexagonal $P6$ symmetry and in $P-1$ symmetry.
Figure S6: Pore size distribution and cumulative pore volume profiles of WTA obtained by QSDFT calculations on the N$_2$ adsorption curve.
Pore size distribution of WBDT

Figure S7: Pore size distribution and cumulative pore volume profiles of WBDT obtained by QSDFT calculations on the N₂ adsorption curve.
Figure S8: Tauc plot of the UV-vis absorption data of WTA.
Figure S9: Tauc plot of the UV-vis absorption data of WBDT.
TCSPC decay data for WTA

Figure S10: PL decay of WTA COF excited at 378 nm and measured at the maximum of the PL emission at 640 nm. Experimental decay: blue dots, biexponential fit of the decay: cyan line.

Table S2: PL decay times of WTA COF shown above. 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 / % |
|------------|------------|--------------------------|
| $\tau_1$   | 0.726      | ±0.04                    | 17.3                     |
| $\tau_2$   | 0.100      | ±0.003                   | 82.7                     |
Figure S11: PL decay of WBDT COF excited at 378 nm and measured at the maximum of the PL emission at 675 nm. Experimental decay: red dots, biexponential fit of the decay: cyan line.

Table S3: PL decay times of WBDT COF shown above. 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 / % |
|-----------------|------------|--------------------------|
| \( \tau_1 \)    | 0.720      | ±0.04                    | 13.6                     |
| \( \tau_2 \)    | 0.127      | ±0.002                   | 86.4                     |
Figure S12: $F_4$TCNQ concentration-dependent electrical conductivities of WBDT.
PXRD of pristine WBDT vs. F$_4$TCNQ-doped WBDT

Figure S13: PXRD of pristine WBDT in comparison to F$_4$TCNQ-doped WBDT.
### Electrical Conductivity

Table S4: Summary of electrical conductivity data of reported examples of doped Covalent Organic Frameworks.

| Entry | Doped COF system (COF/dopant) | Room temperature conductivity (S/m) | Reference |
|-------|-------------------------------|-------------------------------------|------------|
| 1     | WBDT / F₄TCNQ                 | 3.67                                | Present work |
| 2     | TANG-COF / iodine             | 0.2 (air)                           | ref.²      |
|       |                               | 1 (vacuum)                          |            |
| 3     | COF-DL229 / iodine            | 1.5                                 | ref.³      |
| 4     | JUC-518 / iodine              | 2.7 × 10⁻²                          | ref.⁴      |
|       |                               | 1.4 (at 120 °C)                     |            |
| 5     | COF-DC-8 / iodine             | around 2.5                          | ref.⁵      |
| 6     | TTF-COF / iodine              | 0.28                                | ref.⁶      |
**EPR quantification**

To quantify the signal intensity of the EPR data, an \( \alpha,\gamma\)-bis-diphenylene-\( \beta \)-phenyl allyl (BDPA) specimen was used as reference. The quantified data in Table S4 were obtained using Equation S1:

\[
N = \frac{\text{[total spin number]}}{(N_A m) / M_{\text{u.c.}}}
\]

\( N \) is the number of radicals per unit cell, \( N_A \) the Avogadro constant, \( m \) the mass of investigated sample and \( M_{\text{u.c.}} \) molar mass of WBDT (2679.39 g/mol) or WTA (2006.36 g/mol) unit cell.

Table S5: Overview of the total spin number and the calculated quantity of radicals for WTA and WBDT COF.

| COF SYSTEM          | TOTAL SPIN NUMBER | NUMBER OF RADICALS PER UNIT CELL |
|---------------------|-------------------|----------------------------------|
| WTA, PRISTINE       | \( 3.80 \cdot 10^{15} \) | \( 2.53 \cdot 10^{-3} \)         |
| WTA / \( F_4 \)TCNQ | \( 3.31 \cdot 10^{17} \) | \( 2.21 \cdot 10^{-1} \)         |
| WBDT, PRISTINE      | \( 2.72 \cdot 10^{15} \) | \( 2.42 \cdot 10^{-3} \)         |
| WBDT / \( F_4 \)TCNQ| \( 3.83 \cdot 10^{17} \) | \( 3.40 \cdot 10^{-1} \)         |
| WBDT / SbCl\(_5\)   | \( 5.82 \cdot 10^{17} \) | \( 5.18 \cdot 10^{-1} \)         |
| WBDT / IODINE       | \( 3.70 \cdot 10^{17} \) | \( 3.29 \cdot 10^{-1} \)         |
Structural parameters of WTA

Unit Cell Parameters (P-1)

\[ a = 42.12, b = 42.82, c = 4.00 \text{ Å} \]
\[ \alpha = 91.3^\circ, \beta = 86.7^\circ, \gamma = 118.8^\circ \]

Table S6: Fractional coordinates for WTA.

|   |   |   |   |   |
|---|---|---|---|---|
| N1 | N | 0.56807 | 100.117 | 0.47259 |
| C2 | C | 0.53414 | 100.065 | 0.48675 |
| C3 | C | 0.50375 | 0.97391 | 0.66456 |
| H4 | H | 0.50603 | 0.95338 | 0.80155 |
| C5 | C | 0.47045 | 0.97327 | 0.67718 |
| H6 | H | 0.44783 | 0.95221 | 0.82277 |
| N7 | N | 0.57398 | 0.87287 | 0.50853 |
| C8 | C | 0.56912 | 0.96878 | 0.47503 |
| C9 | C | 0.54211 | 0.93803 | 0.32626 |
| H10 | H | 0.52029 | 0.93912 | 0.19965 |
| C11 | C | 0.54268 | 0.90605 | 0.33261 |
| H12 | H | 0.52125 | 0.88312 | 0.20962 |
| C13 | C | 0.57069 | 0.90348 | 0.48614 |
| C14 | C | 0.5979 | 0.93435 | 0.63096 |
| H15 | H | 0.61969 | 0.9329 | 0.75493 |
| C16 | C | 0.59712 | 0.9662 | 0.62746 |
| H17 | H | 0.61844 | 0.98932 | 0.74836 |
| C18 | C | 0.55091 | 0.84221 | 0.39954 |
| H19 | H | 0.52575 | 0.83712 | 0.27411 |
| C20 | C | 0.39932 | 0.96613 | 0.53681 |
| C21 | C | 0.36758 | 0.96295 | 0.70525 |
| H22 | H | 0.36795 | 0.98565 | 0.83773 |
| C23 | C | 0.33546 | 0.93107 | 0.70855 |
| H24 | H | 0.31119 | 0.92925 | 0.84221 |
| C25 | C | 0.33339 | 0.90089 | 0.54395 |
| C26 | C | 0.36533 | 0.90376 | 0.38211 |
| H27 | H | 0.3654 | 0.88103 | 0.2532 |
| C28 | C | 0.39746 | 0.9357 | 0.37839 |
| H29 | H | 0.42153 | 0.93696 | 0.24628 |
| N30 | N | 0.29973 | 0.87024 | 0.56212 |
| C31 | C | 0.29195 | 0.84209 | 0.38907 |
| H32 | H | 0.31153 | 0.83958 | 0.20396 |
| N33 | N | 0.56395 | 0.567 | 0.48736 |
| C34 | C | 0.53201 | 0.53359 | 0.49375 |
|    |    |    |    |    |
|----|----|----|----|----|
| C35 | C  | 0.46968 | 0.49584 | 0.34229 |
| H36 | H  | 0.44645 | 0.49326 | 0.21118 |
| C37 | C  | 0.50088 | 0.5286 | 0.33649 |
| H38 | H  | 0.50093 | 0.55047 | 0.20148 |
| N39 | N  | 0.30219 | 0.43331 | 0.55131 |
| C40 | C  | 0.40189 | 0.43175 | 0.33649 |
| C41 | C  | 0.44645 | 0.49326 | 0.21118 |
| H42 | H  | 0.41926 | 0.48021 | 0.81528 |
| C43 | C  | 0.36381 | 0.45817 | 0.69159 |
| H44 | H  | 0.3606 | 0.47931 | 0.82062 |
| C45 | C  | 0.33404 | 0.4309 | 0.53396 |
| C46 | C  | 0.33865 | 0.40346 | 0.37841 |
| H47 | H  | 0.31631 | 0.38147 | 0.55131 |
| C48 | C  | 0.27393 | 0.41352 | 0.38746 |
| H49 | H  | 0.2721 | 0.3922 | 0.21113 |
| C50 | C  | 0.24218 | 0.41882 | 0.42695 |
| C51 | C  | 0.2441 | 0.44806 | 0.60843 |
| C52 | C  | 0.21416 | 0.45334 | 0.64861 |
| H55 | H  | 0.21614 | 0.47615 | 0.79332 |
| C56 | C  | 0.1812 | 0.42968 | 0.50774 |
| C57 | C  | 0.17929 | 0.40049 | 0.32536 |
| C58 | C  | 0.20925 | 0.39517 | 0.28567 |
| H59 | H  | 0.20728 | 0.37236 | 0.141 |
| C60 | C  | 0.56117 | 0.59855 | 0.49227 |
| C61 | C  | 0.58769 | 0.62956 | 0.32652 |
| H62 | H  | 0.6109 | 0.62966 | 0.18808 |
| C63 | C  | 0.58488 | 0.66048 | 0.33234 |
| H64 | H  | 0.60561 | 0.68398 | 0.1957 |
| C65 | C  | 0.55477 | 0.66114 | 0.49619 |
| C66 | C  | 0.52771 | 0.63 | 0.65446 |
| H67 | H  | 0.50436 | 0.6302 | 0.78744 |
| C68 | C  | 0.53133 | 0.59961 | 0.65921 |
| H69 | H  | 0.51028 | 0.57618 | 0.79328 |
| N70 | N  | 0.54956 | 0.69079 | 0.48322 |
| C71 | C  | 0.57435 | 0.72227 | 0.54939 |
| H72 | H  | 0.60122 | 0.72778 | 0.6412 |
| C73 | C  | 0.56827 | 0.75276 | 0.51297 |
| C74 | C  | 0.53712 | 0.74889 | 0.3638 |
| C75 | C  | 0.53154 | 0.77787 | 0.32634 |
| H76 | H  | 0.50726 | 0.77438 | 0.2061 |
| C77 | C  | 0.55682 | 0.81171 | 0.43806 |
| C78 | C  | 0.58791 | 0.81552 | 0.58827 |
| C79 | C  | 0.59361 | 0.7866 | 0.62375 |
| H80 | H  | 0.61792 | 0.79007 | 0.74324 |
|   |   |   |   |   |
|---|---|---|---|---|
|N81 | N | 0.00549 | 0.56852 | 0.52085 |
|C82 | C | 0.00281 | 0.53436 | 0.51062 |
|C83 | C | 0.02825 | 0.52794 | 0.32203 |
|H84 | H | 0.05046 | 0.54926 | 0.17518 |
|C85 | C | 0.02549 | 0.49443 | 0.31146 |
|H86 | H | 0.04564 | 0.49075 | 0.15642 |
|N87 | N | 0.14367 | 0.69002 | 0.45561 |
|C88 | C | 0.04004 | 0.59919 | 0.50487 |
|C89 | C | 0.07015 | 0.59901 | 0.6395 |
|H90 | H | 0.06712 | 0.57512 | 0.76159 |
|C91 | C | 0.10417 | 0.62885 | 0.61926 |
|H92 | H | 0.12706 | 0.62815 | 0.72885 |
|C93 | C | 0.10898 | 0.6606 | 0.47822 |
|C94 | C | 0.0791 | 0.66103 | 0.3429 |
|H95 | H | 0.08254 | 0.68501 | 0.21822 |
|C96 | C | 0.04542 | 0.63068 | 0.3514 |
|H97 | H | 0.023 | 0.63165 | 0.2354 |
|C98 | C | 0.14971 | 0.72113 | 0.54655 |
|H99 | H | 0.12786 | 0.72613 | 0.66572 |
|C100 | C | 0.19336 | 0.78465 | 0.64917 |
|C101 | C | 0.18599 | 0.75181 | 0.50591 |
|C102 | C | 0.21408 | 0.74922 | 0.32187 |
|H103 | H | 0.20856 | 0.72385 | 0.20647 |
|C104 | C | 0.24832 | 0.77851 | 0.28171 |
|C105 | C | 0.25583 | 0.81126 | 0.42841 |
|C106 | C | 0.22774 | 0.81378 | 0.61346 |
|H107 | H | 0.23332 | 0.83913 | 0.72998 |
|C108 | C | 0.02644 | 0.42832 | 0.45812 |
|C109 | C | 0.02764 | 0.3996 | 0.2922 |
|H110 | H | 0.00379 | 0.37937 | 0.17051 |
|C111 | C | 0.05909 | 0.39671 | 0.276 |
|H112 | H | 0.0594 | 0.37425 | 0.14391 |
|C113 | C | 0.09077 | 0.42226 | 0.42357 |
|C114 | C | 0.08981 | 0.45138 | 0.58384 |
|H115 | H | 0.1137 | 0.47222 | 0.70061 |
|C116 | C | 0.0583 | 0.45413 | 0.60195 |
|H117 | H | 0.05851 | 0.47682 | 0.73349 |
|N118 | N | 0.12111 | 0.41718 | 0.39226 |
|C119 | C | 0.14995 | 0.43565 | 0.55347 |
|H120 | H | 0.15284 | 0.45693 | 0.73506 |
|H121 | H | 0.26959 | 0.46655 | 0.72058 |
|H122 | H | 0.15385 | 0.38198 | 0.21265 |
|H123 | H | 0.51734 | 0.72269 | 0.27437 |
|H124 | H | 0.60763 | 0.84171 | 0.67857 |
|H125 | H | 0.17183 | 0.78714 | 0.79505 |
|H126 | H | 0.26976 | 0.77609 | 0.13374 |
**Structural parameters of WBDT**

Unit Cell Parameters ($P-1$)

$a = 50.55$, $b = 49.64$, $c = 3.93$ Å  
$\alpha = 102.3^\circ$, $\beta = 82.2^\circ$, $\gamma = 120.8^\circ$

Table S7: Fractional coordinates for WBDT.

|   |   |   |   |
|---|---|---|---|
| N1 | N | 0.55374 | 0.99687 |
| C2 | C | 0.52694 | 0.99856 |
| C3 | C | 0.50431 | 0.9766 |
| H4 | H | 0.50775 | 0.95834 |
| C5 | C | 0.47802 | 0.97806 |
| H6 | H | 0.4611 | 0.96102 |
| S7 | S | 0.56531 | 0.84115 |
| N8 | N | 0.55291 | 0.88478 |
| C9 | C | 0.55336 | 0.96869 |
| C10 | C | 0.52759 | 0.94343 |
| H11 | H | 0.50758 | 0.94559 |
| C12 | C | 0.5273 | 0.91583 |
| H13 | H | 0.50692 | 0.89656 |
| C14 | C | 0.55252 | 0.91227 |
| C15 | C | 0.57803 | 0.93733 |
| H16 | H | 0.59771 | 0.93479 |
| C17 | C | 0.57861 | 0.96509 |
| H18 | H | 0.59869 | 0.98428 |
|   |   |     |     |     |
|---|---|-----|-----|-----|
| C19 | C | 0.53669 | 0.86342 | - | 0.82589 |
| H20 | H | 0.52182 | 0.86542 | - | 1.00479 |
| C21 | C | 0.53994 | 0.83649 | - | 0.77446 |
| C22 | C | 0.52782 | 0.80856 | - | 0.89572 |
| H23 | H | 0.51147 | 0.80152 | - | 1.07651 |
| C24 | C | 0.41887 | 0.97625 | - | 0.34965 |
| C25 | C | 0.39763 | 0.97539 | - | 0.15227 |
| H26 | H | 0.40252 | 0.99595 | - | 0.03827 |
| C27 | C | 0.3711 | 0.94893 | - | 0.09736 |
| H28 | H | 0.35549 | 0.94916 | - | 0.05724 |
| C29 | C | 0.36489 | 0.92251 | - | 0.23177 |
| C30 | C | 0.38506 | 0.92317 | - | 0.43853 |
| H31 | H | 0.38111 | 0.90359 | - | 0.56207 |
| C32 | C | 0.41181 | 0.9496 | - | 0.49561 |
| H33 | H | 0.42776 | 0.95014 | - | 0.65923 |
| S34 | S | 0.2414 | 0.8349 | - | 0.32396 |
| N35 | N | 0.31609 | 0.88778 | - | 0.0643 |
| C36 | C | 0.2983 | 0.86168 | - | -0.0272 |
| H37 | H | 0.30467 | 0.85348 | - | 0.23181 |
| C38 | C | 0.2683 | 0.83701 | - | 0.06684 |
| C39 | C | 0.25625 | 0.81046 | - | 0.08154 |
| H40 | H | 0.26749 | 0.80476 | - | 0.24972 |
| N41 | N | 0.55388 | 0.55424 | - | 0.49343 |
| C42 | C | 0.52687 | 0.52702 | - | 0.49671 |
| C43 | C | 0.47469 | 0.49789 | - | 0.36069 |
| H44 | H | 0.45507 | 0.49603 | - | 0.24683 |
| C45 | C | 0.5014 | 0.52471 | - | -0.3578 |
| H46 | H | 0.50272 | 0.54391 | - | - |
|   |   |   |   |
|---|---|---|---|
| S47 | S | 0.28988 | 0.45744 | 0.32772 |
| N48 | N | 0.33435 | 0.44555 | 0.49764 |
| C49 | C | 0.41826 | 0.44603 | 0.49583 |
| C50 | C | 0.41405 | 0.4695  | 0.35706 |
| H51 | H | 0.4328  | 0.48814 | 0.24117 |
| C52 | C | 0.38624 | 0.46891 | 0.36173 |
| H53 | H | 0.38306 | 0.48715 | 0.25415 |
| C54 | C | 0.36183 | 0.44526 | 0.50778 |
| C55 | C | 0.3661  | 0.42192 | 0.64671 |
| H56 | H | 0.34755 | 0.40313 | 0.75992 |
| C57 | C | 0.39377 | 0.42232 | 0.64061 |
| H58 | H | 0.39708 | 0.40427 | 0.75278 |
| C59 | C | 0.31278 | 0.42949 | 0.74669 |
| H60 | H | 0.31472 | 0.41507 | 0.86249 |
| C61 | C | 0.28571 | 0.43224 | 0.62199 |
| C62 | C | 0.25781 | 0.41973 | 0.74669 |
| H63 | H | 0.25118 | 0.40335 | 0.92866 |
| C64 | C | 0.23872 | 0.43064 | 0.60577 |
| C65 | C | 0.25341 | 0.45192 | 0.36921 |
| C66 | C | 0.2386  | 0.46534 | 0.20682 |
| H67 | H | 0.24976 | 0.48158 | 0.02454 |
| C68 | C | 0.20907 | 0.45786 | 0.27955 |
| C69 | C | 0.19442 | 0.43661 | 0.51632 |
| C70 | C | 0.20916 | 0.42306 | 0.67776 |
| H71 | H | 0.198  | 0.40686 | 0.86042 |
| C72 | C | 0.55294 | 0.58182 | -       | 0.49046 |
| C73 | C | 0.57562 | 0.60613 | -       | 0.33761 |
| H74 | H | 0.59343 | 0.60302 | -       | 0.21865 |
| C75 | C | 0.57538 | 0.63351 | -       | 0.33323 |
| H76 | H | 0.59341 | 0.65192 | -       | 0.21386 |
| C77 | C | 0.55242 | 0.63763 | -       | 0.48156 |
| C78 | C | 0.52974 | 0.61335 | -       | 0.63476 |
| H79 | H | 0.51176 | 0.61633 | -       | 0.7501 |
| C80 | C | 0.52982 | 0.58584 | -       | 0.63782 |
| H81 | H | 0.51199 | 0.56724 | -       | 0.76009 |
| S82 | S | 0.53925 | 0.70892 | -       | 0.67797 |
|    |    |     |     |     |
|----|----|-----|-----|-----|
| N83 | N  | 0.55166 | 0.66488 | -0.49642 |
| C84 | C  | 0.56703 | 0.68657 | -0.31776 |
| H85 | H  | 0.58113 | 0.68494 | 0.12895  |
| C86 | C  | 0.5641  | 0.71344 | 0.38114  |
| C87 | C  | 0.57644 | 0.74152 | -0.2628  |
| H88 | H  | 0.59258 | 0.74843 | 0.08024  |
| C89 | C  | 0.56572 | 0.76043 | 0.41147  |
| C90 | C  | 0.5447  | 0.74543 | 0.64619  |
| C91 | C  | 0.53144 | 0.76003 | 0.81534  |
| H92 | H  | 0.5154  | 0.74858 | -0.9964  |
| C93 | C  | 0.53896 | 0.78974 | -0.7516  |
| C94 | C  | 0.56007 | 0.80474 | 0.51755  |
| C95 | C  | 0.57336 | 0.79018 | 0.34886  |
| H96 | H  | 0.58939 | 0.80158 | 0.16763  |
| C97 | C  | 0.02094 | 0.52108 | 0.69036  |
| H98 | H  | 0.0371  | 0.53714 | 0.84593  |
| C99 | C  | 0.02231 | 0.49469 | 0.64116  |
| H100| H  | 0.03943 | 0.4902  | 0.75515  |
| S101| S  | 0.15423 | 0.70685 | -0.125   |
| N102| N  | 0.09957 | 0.66077 | 0.10778  |
| C103| C  | 0.02281 | 0.58013 | 0.32738  |
| C104| C  | 0.05129 | 0.5873  | 0.43623  |
| H105| H  | 0.05352 | 0.57185 | 0.58489  |
| C106| C  | 0.07644 | 0.6139  | 0.36165  |
| H107| H  | 0.09834 | 0.61897 | 0.44748  |
| C108| C  | 0.07402 | 0.63416 | 0.17333  |
| C109| C  | 0.04549 | 0.62711 | 0.06862  |
| H110| H  | 0.04269 | 0.64247 | 0.07407  |
| C111| C  | 0.02038 | 0.60069 | 0.14267  |
|   |   |   |   |   |
|---|---|---|---|---|
| C112 | C | 0.10041 | 0.67784 | 0.10428 |
| H113 | H | 0.08156 | 0.6719 | 0.25709 |
| C114 | C | 0.12833 | 0.70534 | 0.12721 |
| C115 | C | 0.13851 | 0.73048 | 0.2955 |
| H116 | H | 0.12464 | 0.73349 | 0.45343 |
| C117 | C | 0.16848 | 0.75241 | 0.22041 |
| C118 | C | 0.18027 | 0.74227 | 0.00739 |
| C119 | C | 0.20902 | 0.76011 | 0.11437 |
| H120 | H | 0.21769 | 0.75207 | 0.29008 |
| C121 | C | 0.22653 | 0.78857 | 0.00259 |
| C122 | C | 0.21478 | 0.79878 | 0.2277 |
| C123 | C | 0.1859 | 0.78078 | 0.33872 |
| H124 | H | 0.17683 | 0.78853 | 0.51371 |
| C125 | C | 0.03143 | 0.44681 | 0.4072 |
| C126 | C | 0.03419 | 0.42138 | 0.51286 |
| H127 | H | 0.01429 | 0.40148 | 0.59831 |
| C128 | C | 0.0618 | 0.42149 | 0.51472 |
| H129 | H | 0.06382 | 0.40174 | 0.5978 |
| C130 | C | 0.08748 | 0.44668 | 0.40428 |
| C131 | C | 0.08487 | 0.47222 | 0.30341 |
| H132 | H | 0.10473 | 0.49238 | 0.22577 |
| C133 | C | 0.05736 | 0.47233 | 0.30539 |
| H134 | H | 0.05555 | 0.49236 | 0.2245 |
| S135 | S | 0.15826 | 0.43169 | 0.56375 |
| N136 | N | 0.11454 | 0.44552 | 0.41008 |
| C137 | C | 0.13589 | 0.46102 | 0.22625 |
| H138 | H | 0.13391 | 0.4757 | 0.04395 |
| C139 | C | 0.16253 | 0.45727 | 0.27273 |
| C140 | C | 0.19018 | 0.46922 | 0.14302 |
| H141 | H | 0.19686 | 0.48574 | - |
| N142 | N | 0.99684 | 1.55341 | 0.59983 |
| C143 | C | 0.99869 | 1.52683 | 0.55075 |
| H144 | H | 0.99841 | 1.59543 | 0.9461 |
References

(1) Aradi, B.; Hourahine, B.; Frauenheim, T. DFTB+, a sparse matrix-based implementation of the DFTB method. *J. Phys. Chem. A* 2007, 111, 5678–5684.

(2) Lakshmi, V.; Liu, C.; Rao, M.R.; Chen, Y.; Fang, Y.; Dadvand, A.; Hamzehpoor, E.; Sakai-Otsuka, Y.; Stein, R.S.; Perepichka, D.F. A Two-Dimensional Poly(azatriangulene) Covalent Organic Framework with Semiconducting and Paramagnetic States. *J. Am. Chem. Soc.* 2020, 142, 2155-2160.

(3) Wang, C.; Wang, Y.; Ge, R.; Song, X.; Xing, X.; Jiang, Q.; Lu, H.; Hao, C.; Guo, X.; Gao, Y.; Jiang, D., A 3D Covalent Organic Framework with Exceptionally High Iodine Capture Capability. *Chem. Eur. J.* 2018, 24, 585-589.

(4) Li, H.; Chang, J.; Li, S.; Guan, X.; Li, D.; Li, C.; Tang, L.; Xue, M.; Yan, Y.; Valtchev, V.; Qiu, S.; Fang, Q., Three-Dimensional Tetrathiafulvalene-Based Covalent Organic Frameworks for Tunable Electrical Conductivity. *J. Am. Chem. Soc.* 2019, 141, 13324-13329.

(5) Meng, Z.; Stolz, R. M.; Mirica, K. A., Two-Dimensional Chemiresistive Covalent Organic Framework with High Intrinsic Conductivity. *J. Am. Chem. Soc.* 2019, 141, 11929-11937.

(6) Cai, S.-L.; Zhang, Y.-B.; Pun, A. B.; He, B.; Yang, J.; Toma, F. M.; Sharp, I. D.; Yaghi, O. M.; Fan, J.; Zheng, S.-R.; et al. Tunable electrical conductivity in oriented thin films of tetrathiafulvalene-based covalent organic framework. *Chem. Sci.* 2014, 5, 4693–4700.