Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Interdigitated conducting tetrathiafulvalene-based coordination networks

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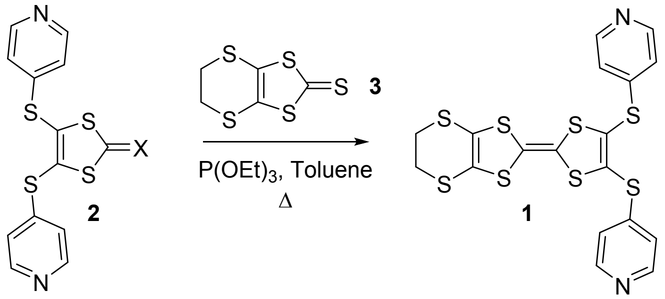
Synthesis

^{1}H- and ^{13}C-NMR spectra were recorded at 25 °C on a Bruker AV500 (500 MHz) spectrometer with the deuterated solvent as the internal reference. NMR chemical shifts and *J* values are given in parts per million (ppm) and in Hertz, respectively. Dithiolone **2** and dithiolthione **3** were prepared as described.[1,2] All other reagents were obtained from commercial sources and used as received.



EDT-TTF **1**:

Dithiolone **2** (500 mg; 1.4 mmol; 1eq) and dithiolthione **3** (333 mg; 1.4 mmol; 1eq) were finely ground together and dissolved in dry toluene (12 mL). Then dry triethylphosphite (4 mL) was added and the mixture was heated at 110°C overnight. It was then cooled to room temperature and the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 95/5) to afford **1** as a red solid. (210 mg; 29 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm) = 8.51 (dd, J = 6.1, 1.6 Hz, 4H), 7.18 (dd, J = 6.1, 1.6 Hz, 4H), 3.31 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ(ppm) = 150.10, 145.47, 129.82, 121.93, 114.05, 30.29. HR-MS (ESI): m/z $(M+H)^+$ calcd. for $C_{18}H_{13}N_2S_8$: 512.8839; found 512.8834. UV-vis(CH_2Cl_2), λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), 309 (18200), 341 (13400), 418 (2800).

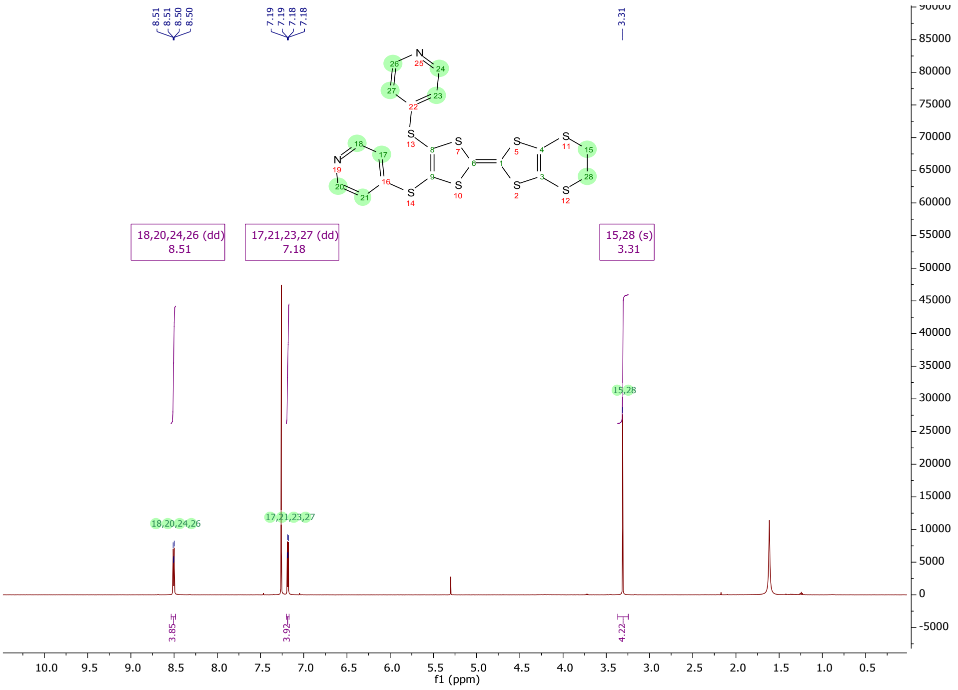


Figure ESI1. ^{1}H NMR of **1** in $CDCl_3$ at room temperature.

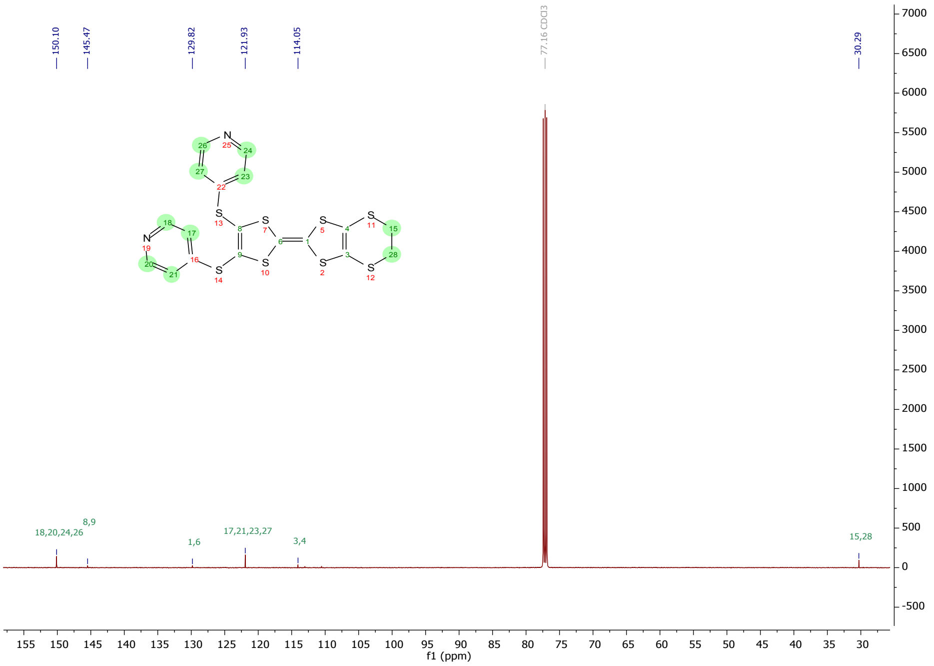


Figure ESI2. ^{13}C NMR of **1** in $CDCl_3$ at room temperature.

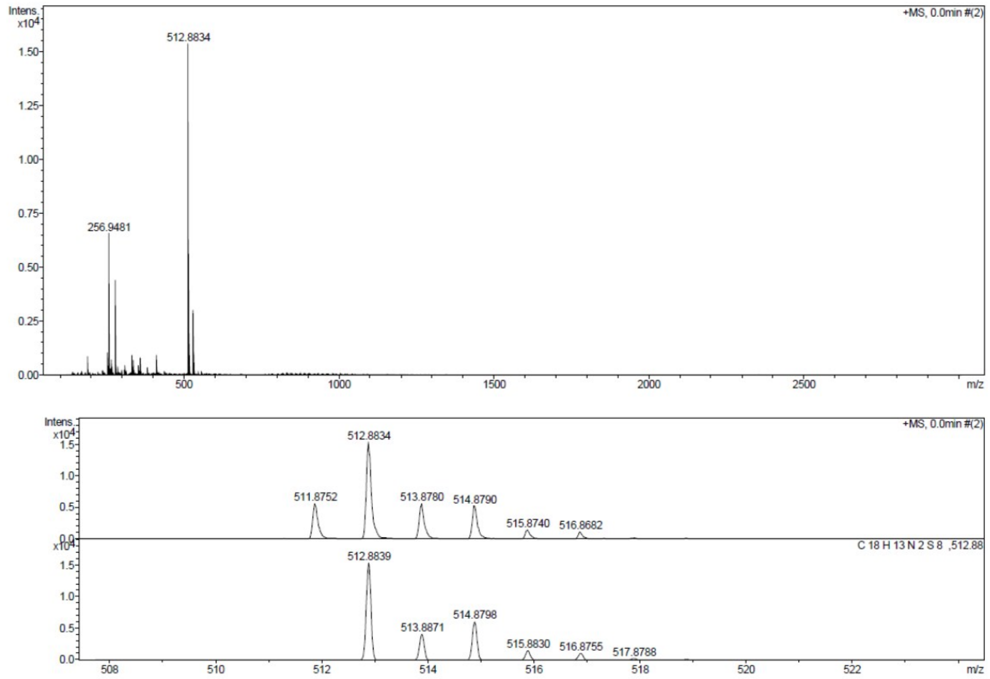


Figure ESI3. High-resolution mass spectrum of **1**.

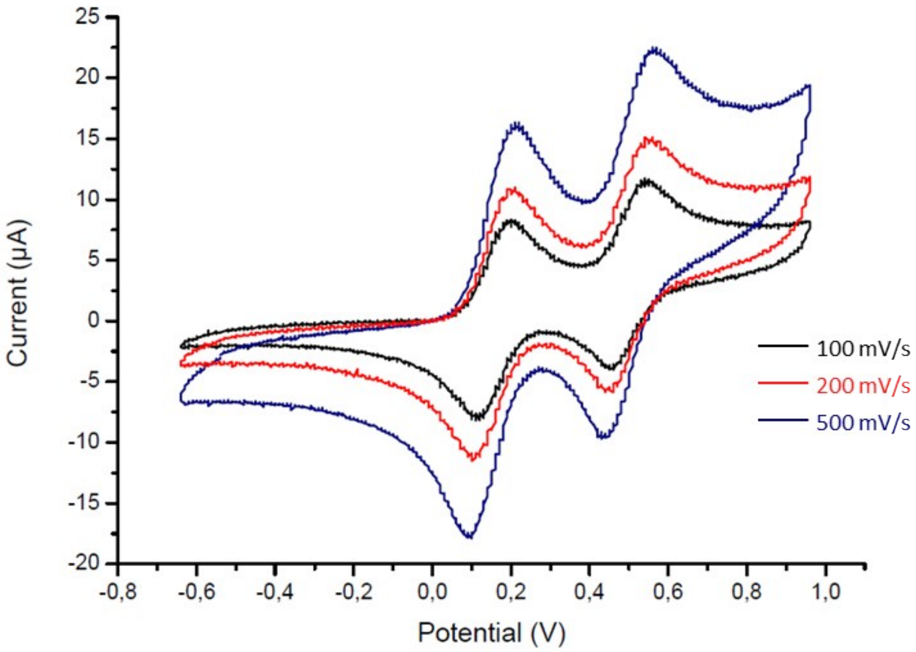


Figure ESI4. Cyclic voltammetry of **1** in CH_2Cl_2 [5.10^{-4} mol.L^{-1}], 0.1M *n*Bu_4NPF_6 *vs*. Fc/Fc^+.

Network **4** :

In a crystallization tube, a $CHCl_3$ solution (8 mL, 2.9 mM) of **1** was layered with an EtOH/ $CHCl_3$ (2 mL, 1/1) buffer and then an EtOH solution (8 mL, 4 mM) of $Co(NCS)_2$●$(4Py)_4$. Orange crystals were obtained after few days (11.8 mg; 33%). Elemental analysis calculated for $C_{41}H_{27}Cl_9CoN_6S_{18}$: C, 31.59; H, 1.75; N, 5.39. Found: C, 31.94; H, 1.82; N, 5.49. IR(ATR)

ν(cm^{-1})/strength: 2921(w); 2049(s); 1585(s); 1539; 1482(s); 1410(s); 1321(w); 1284(w); 1217(m); 1104(w); 1052(m); 1009(m); 898(w); 854(w); 812(m); 749(s); 712(s); 665(m); 491(s); 436(w).

Network **5 :**

Under an argon atmosphere, in a crystallization tube a $CHCl_3$ solution (8 mL, 2.9 mM) of **1** was layered with an EtOH/ $CHCl_3$ (2 mL, 1/1) buffer and then with an EtOH solution (8 mL, 4 mM) of $Fe(NCS)_2\bullet(4Py)_4$. Orange crystals were obtained after few days (10 mg; 28%). Elemental analysis calculated for $C_{41}H_{27}Cl_9FeN_6S_{18}$: C, 31.65; H, 1.75; N, 5.40. Found: C, 32.39; H, 1.88; N, 5.63.

Oxidation method :

The crystals were filtered and washed with 5 mL of $CHCl_3$ and 5 mL of EtOH. The materials were soaked 5 mL in a 0.05 M of I_2 of $CHCl_3$ for 3 hours and then, the crystals were washed several times with a $CHCl_3$/EtOH (1/1) solution.

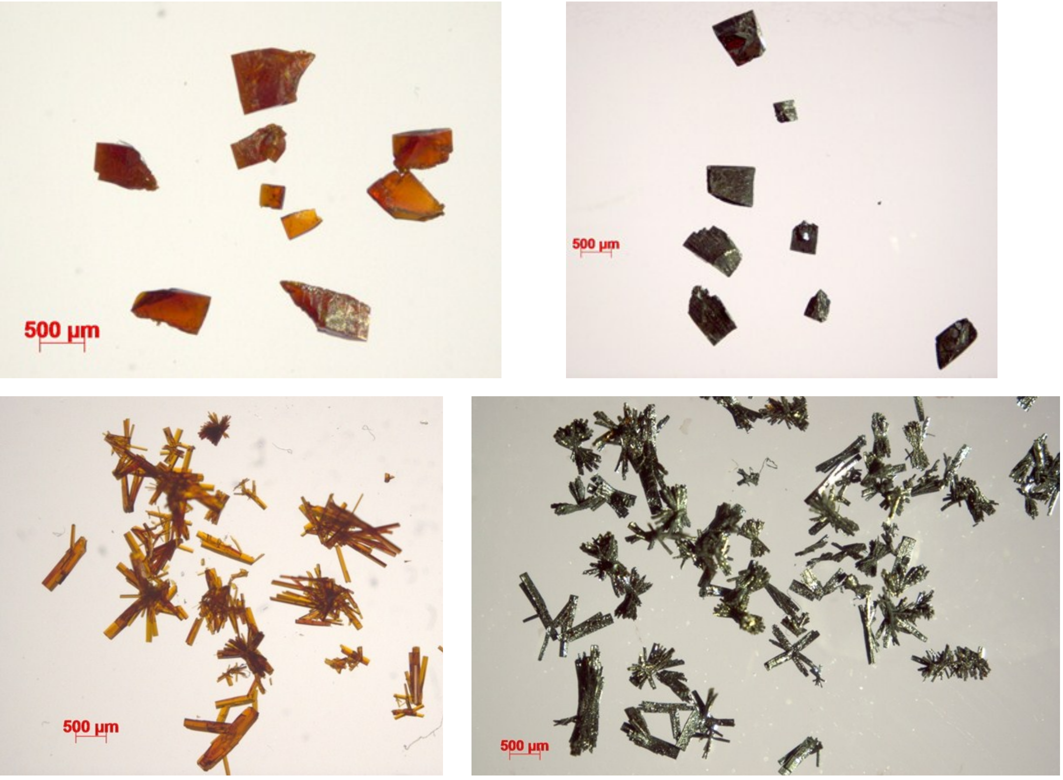


Figure ESI 5. Photographs of the crystals of compounds **4** (top) and **5** (bottom) before (left) and after (right) standing in a [0.05 M] I_2 solution in $CHCl_3$ for 3 hours.

X-ray crystallography

Data (Table 1) were collected on a Bruker SMART CCD diffractometer with Mo-Kα radiation at 173 K. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-2014 with anisotropic thermal parameters for all non-hydrogen atoms.[4] In the structure of **4** and **5**, the carbon atoms of the ethylenedithio groups show disorder that has been refined over two position using the PART command. CCDC 1973791-1973793.

Table 1. Crystallographic data for EDT-TTF **1** and networks **4** and **5**.

	1	**4**	**5**
Formula	$C_{18}H_{12}N_2S_8$	$C_{41}H_{27}Cl_9CoN_6S_{18}$	$C_{41}H_{27}Cl_9FeN_6S_{18}$
FW	512.84	1558.74	1555.66
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$C2/c$
a / Å	13.6086(6)	36.6636(17)	36.701(4)
b / Å	12.8562(6)	9.5680(5)	9.6026(9)
c / Å	11.7791(6)	20.1665(13)	20.2170(19)
β / °	97.382(2)	121.372(4)	121.187(2)
V /Å^3	2043.73(17)	6040.1(6)	6095.3(10)
Z	4	4	4
T / K	173 (2)	173 (2)	173 (2)
μ / mm^{-1}	0.883	1.344	1.298
Refls. coll.	23088	215279	33714
Ind. refls. (R_{int})	6025 (0.0480)	8812 (0.0440)	8904 (0.0634)
R_1 ($I>2\sigma(I)$)^a	0.0309	0.0604	0.0605
wR_2 ($I>2\sigma(I)$)^a	0.0720	0.1663	0.1391
R_1 (all data)^a	0.0424	0.0698	0.1056
wR_2 (all data)^a	0.0790	0.1792	0.1610
GOF	1.020	1.064	1.032

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum wF_o^4]^{1/2}$.

EPR spectroscopy

EPR spectra were recorded on an EMXplus spectrometer (Bruker Biospin GmbH), equipped with a high sensitivity resonator (4119HS-W1, Bruker) operating at X-band (*ca.* 9.4 GHz). An ESR900 cryostat (Oxford Instruments) was used for the low temperature measurements.

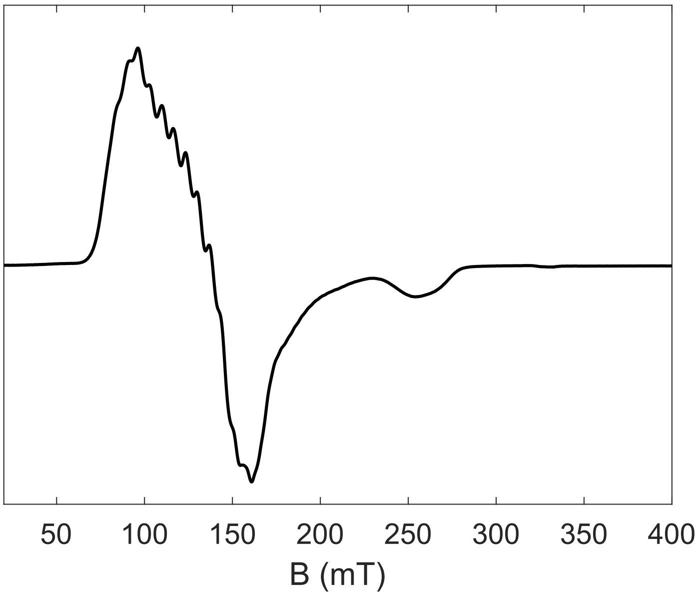


Figure ESI. 6. EPR spectrum of the Co material **4** in the as synthesized form recorded at 20K at a frequency of 9.3179 GHz with a power of 0.2 mW, a modulation amplitude of 0.4 mT showing the signal associated with the metal center and the absence of organic radical.

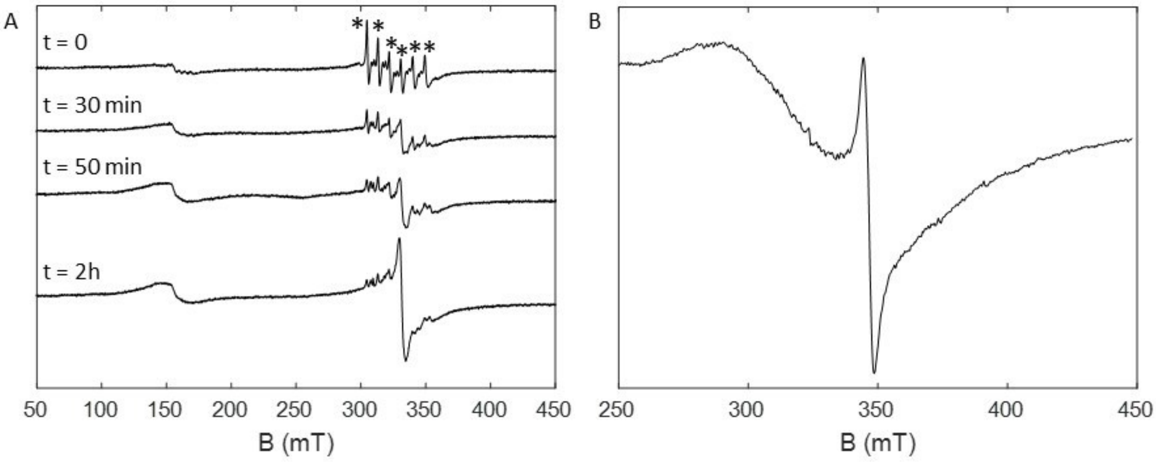


Figure ESI. 7. A) X-band EPR spectra recorded at 20 K of polycrystalline powder of **5** upon exposure to I_2 vapor showing the **1**$^{+\bullet}$ signature and the Fe(III) signatures. Spectra were recorded with a microwave power of 2 mW and a modulation amplitude of 0.2 mT. B) signal associated to **1**$^{+\bullet}$ observed at room temperature, upon leaving polycrystalline powder of **5** in a $CHCl_3$ solution of I_2 (0.05 M) for 3 hours. The spectrum was recorded with a microwave power of 4 mW and a modulation amplitude of 0.5 mT. The asterisks are associated with trace impurity of Mn(II) cations coming from the starting thiocyanate salts.

EDX analysis

EDX analysis were performed on a Quanta FEG 250 SEM from FEI equipped with an EDAX detector.

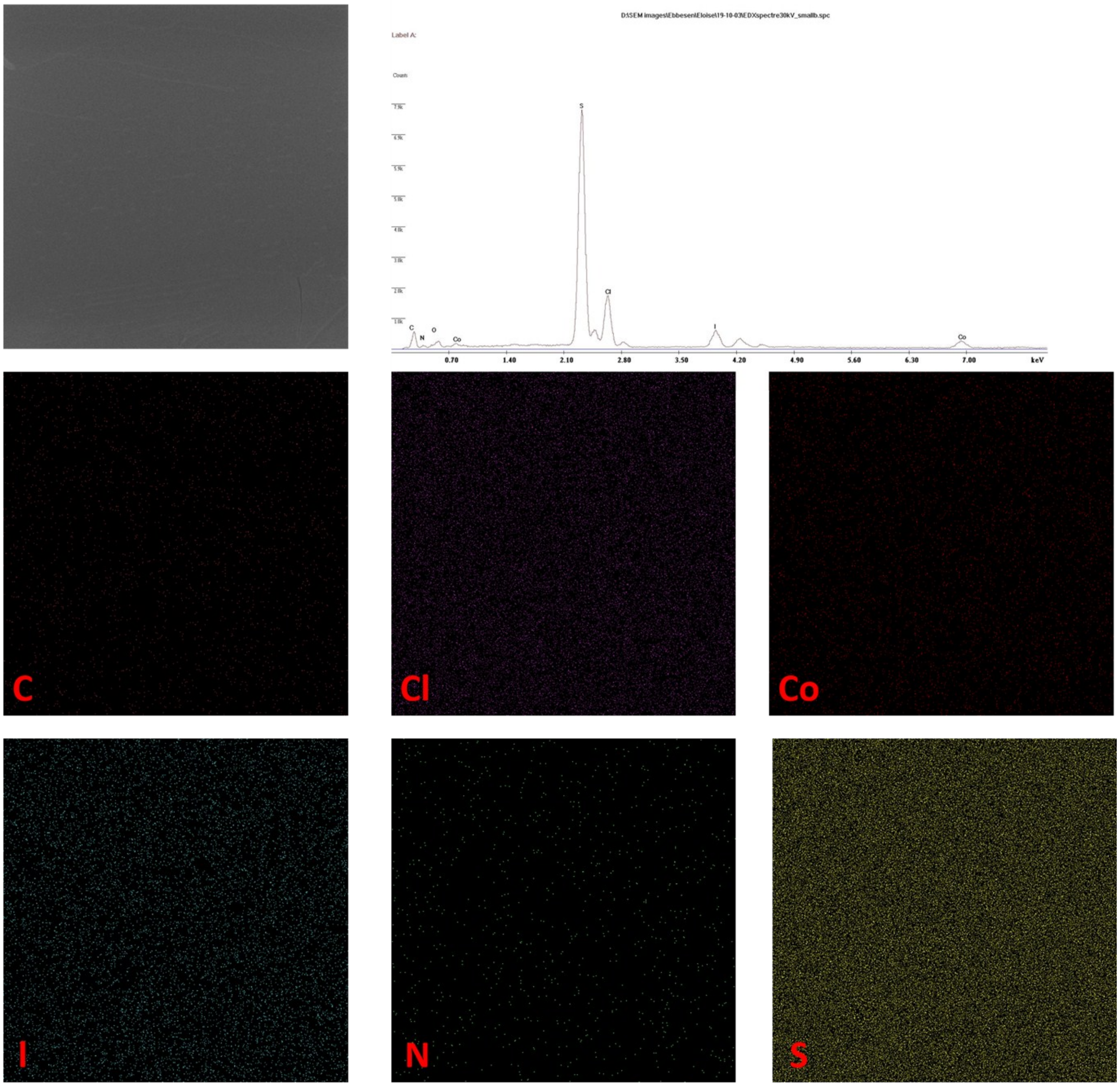


Figure ESI. 8. EDX analysis of the Co material **4** in the oxidized form showing the presence and homogeneous distribution of iodine on the crystal surface.

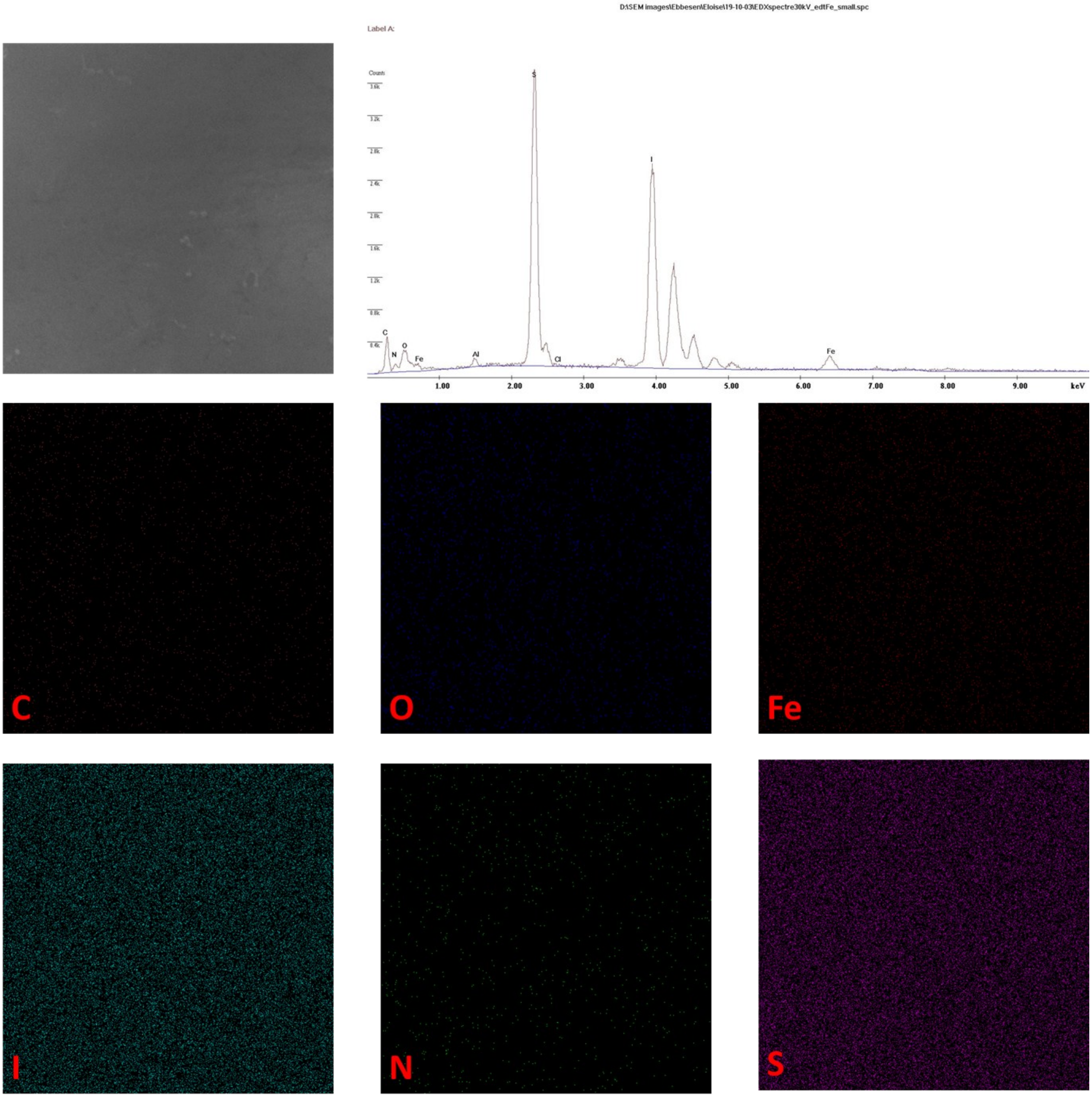
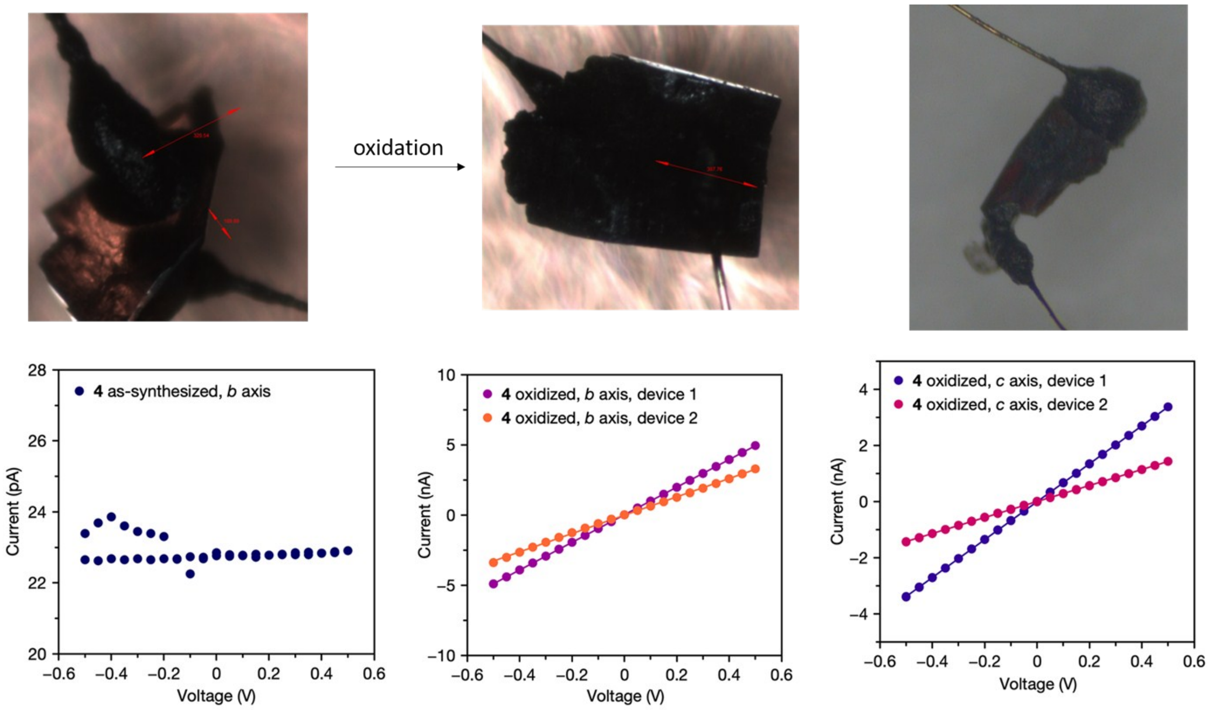


Figure ESI. 9. EDX analysis of the Fe material **5** in the oxidized form showing the presence and homogeneous distribution of iodine on the crystal surface.

Conductivity measurements

For single crystal conductivity measurements, two-probe single crystal devices of **4** and **5** (as-synthesized and oxidized) were fabricated by contacting single crystals with gold wires dipped in carbon paste (Electron Microscopy Sciences Graphite Conductive Adhesive 112) either along the *b* or *c* crystallographic axes (the shortest and longest crystal dimensions, respectively). The free ends of the wires were anchored to the surface of a glass slide using more carbon paste. After drying for at least one hour, the devices were contacted with gold-plated tungsten probes in a Janis Cryogenics probe station, and measurements were carried out using a Keithley 2450 sourcemeter under ambient conditions (296 K) by sweeping the voltage from –0.5 V to +0.5 V and measuring the current. Device dimensions were measured using a calibrated microscope.

For pellet measurements, two-probe pressed pellet devices were made using a home-built in situ press set-up described previously.[4] Samples were loaded into glass tubes and pressed between stainless steel rods under approximately 200 MPa. Measurements were carried out using a Keithley 2450 sourcemeter under ambient conditions (296 K) by sweeping the voltage from –0.5 V to +0.5 V and measuring the current. Pellet thicknesses were measured using a micrometer (Mitutoyo).

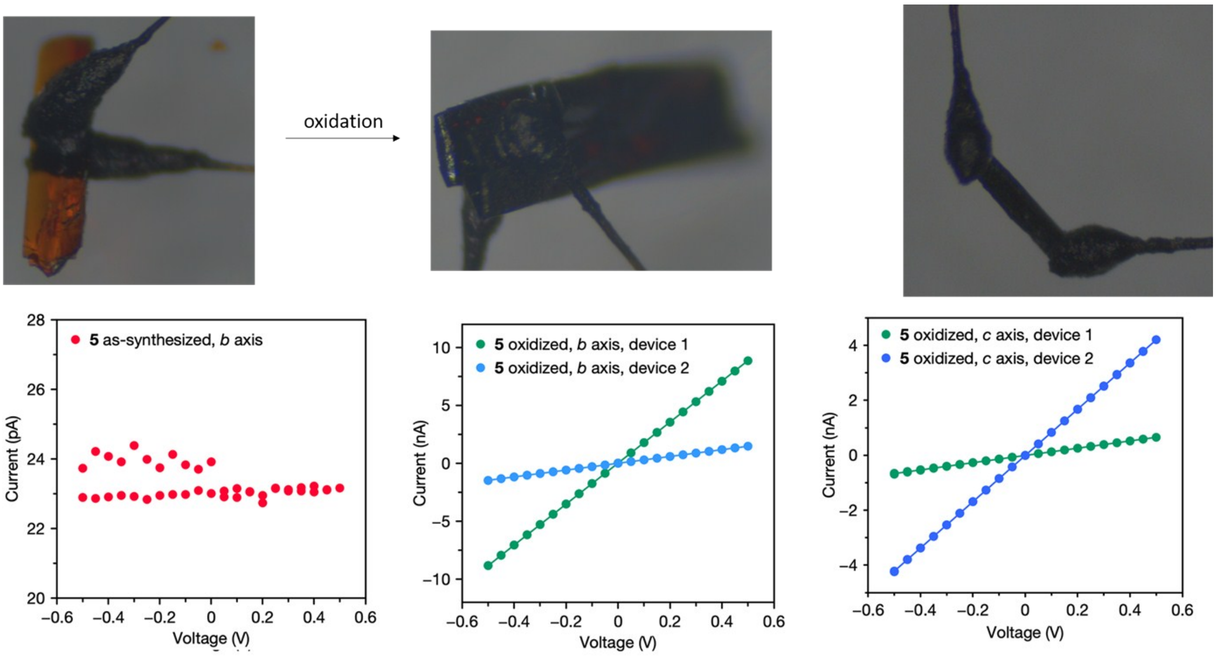


Too low for detection

Device 1: 1 × 10^{-7} S/cm
Device 2: 2 × 10^{-7} S/cm

Device 1: 1 × 10^{-6} S/cm
Device 2: 7 × 10^{-7} S/cm

Figure ESI 10. Conductivity measurements on single crystals of **4** in the as-synthesized form and oxidized along the *b* and *c* axes. Solid lines represent linear fits to the data.

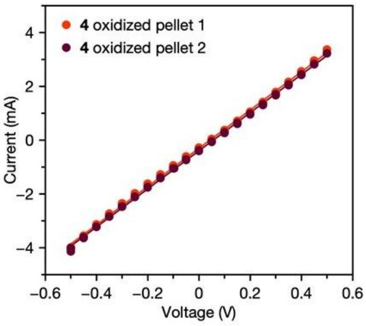


Too low for detection

Device 1: 3 × 10^{-7} S/cm
Device 2: 8 × 10^{-8} S/cm

Device 1: 2 × 10^{-7} S/cm
Device 2: 1 × 10^{-6} S/cm

Figure ESI 11. Conductivity measurements on single crystals of **5** in the as-synthesized form and oxidized along the *b* and *c* axes. Solid lines represent linear fits to the data.



Average = 1.1 x 10^{-5} S/cm

Figure ESI 12. Conductivity measurements on pellets of **4** after treatment with iodine.

References

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2. K. B. Simonsen, N. Svenstrup, J. Lau, O. Simonsen, P. Mørk, G. J. Kristensen and J. Becher, *Synthesis*, 1996, **3**, 407.

3. G. M. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3.

4. L. Sun, S. S. Park, D. Sheberla and M. Dincă, *J. Am. Chem. Soc.*, 2016, **138**, 14772.