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SUPPLEMENTARY INFORMATION

Probing charge transfer characteristics in a donor–acceptor metal-organic framework by Raman spectroelectrochemistry and pressure-dependence studies

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Additional Experimental Details

Materials. All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise stated. $LiClO_4$ and CH_2Cl_2 (anhydrous, Sure/Seal™) were purchased from Sigma Aldrich. Ethylene glycol was obtained from BDH Chemicals Ltd. DPNI, H_4TTFTC and $[(Zn(DMF))_2(TTFTC)(DPNI)]$ were synthesised according to literature methods.[1]

Powder X-ray Diffraction. The measurements were performed on a PANalytical X'Pert Pro diffractometer fitted with a solid-state PIXcel detector (40 kV, 30 mA, 1° divergence and anti-scatter slits, and 0.3 mm receiver and detector slits) using Cu-Kα (λ = 1.5406 Å) radiation. The powdered samples were placed on the Si reflective discs. For the stability testing screen-printed electrodes were mounted onto the PXRD sample holders.

Electron Paramagnetic Resonance Spectroscopy. Continuous wave solid-state EPR spectra were collected at room temperature using a Bruker Elexsys 500 spectrometer equipped with an X-band microwave bridge. The spectra were referenced against strong pitch.

Cyclic Voltammetry. Voltammetry experiments were performed on a BASi Epsilon Electrochemical

Analyser using an electrochemical cell with a standard three-electrode configuration. 0.2 M $LiClO_4$/Ethylene glycol was used as a supporting electrolyte after degassing with high purity Ar.

For voltammetric studies in solution, a glassy carbon disc electrode (GC; nominal diameter 1 mm) embedded in an isolating inert sheath (BASi) was employed as a working electrode. Prior to use, the surface of the working electrode was thoroughly polished with alumina powder (0.3 µm) on a wet polishing cloth (BASi), and washed repeatedly with water. Finally, the working electrode surface was flushed with acetone and dried under an Ar stream.

For measurements with surface confined solids, powdered samples were mounted onto a glassy carbon disc electrode using mechanical immobilisation: the electrode was pressed against the powder forming a weakly bound layer on its surface. When this method was insufficient to maintain the contact, working electrodes were prepared by drop-casting and drying of an CH_2Cl_2 suspension of the powdered material onto a graphite paper strip (20 mm^2) with a Pt wire current collector (0.075 mm diameter; connected using silver paint).

High surface area Pt wire in contact with solvent (electrolyte) was used as a counter electrode and Ag wire as quasi-reference electrode The potential of the quasi-reference electrode was calibrated *vs.* the reversible potential of the $Fc^{0/+}$ couple measured in the same solution before or after the experiment.

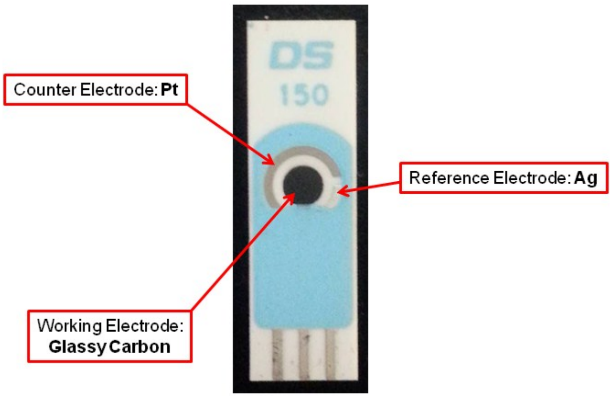


Figure S1. The screen-printed electrode (DS-150) utilised in Raman spectroelectrochemical experiments. Photograph is authors own image.

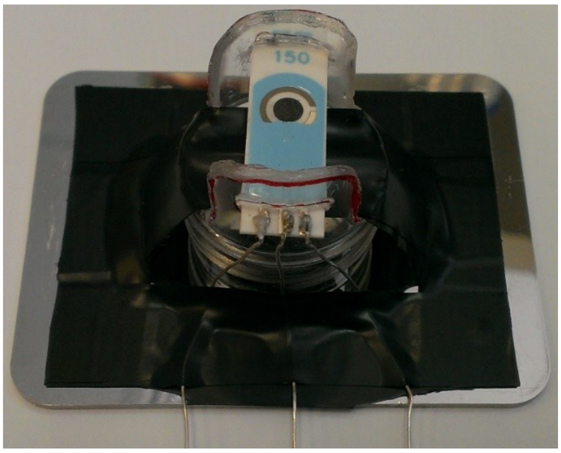


Figure S2. Photograph of custom-made Raman spectroelectrochemical cell. Photograph is authors own image.

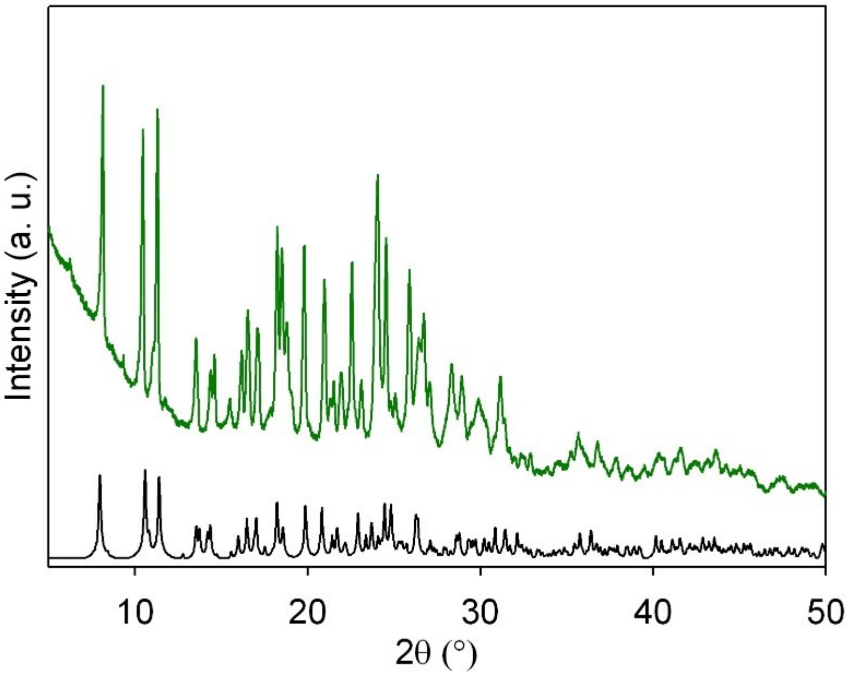
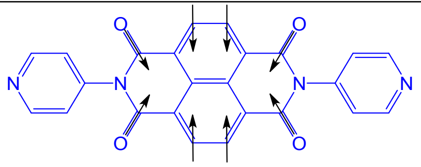
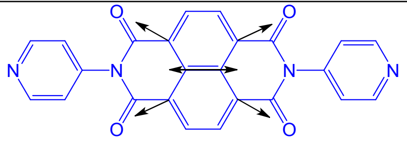
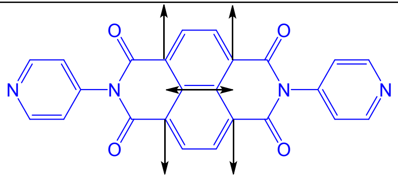
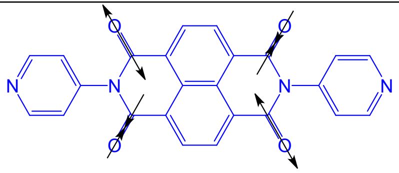
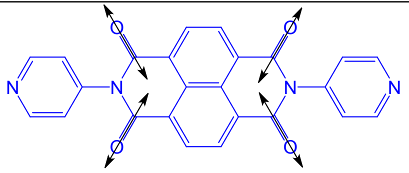
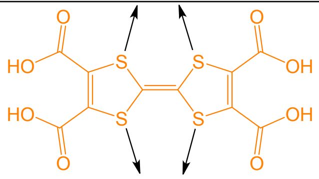
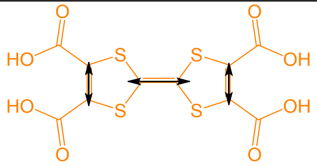
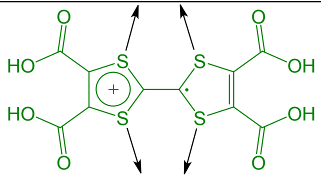
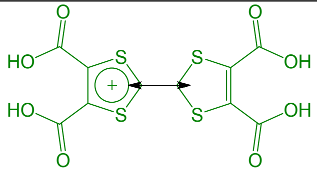


Figure S3. PXRD pattern of [(Zn(DMF))$_2$(TTFTC)(DPNI)] (*green*) compared to the predicted pattern (*black*).

Table S1. Assignment of vibrational modes of $DPNI^0$ (blue), $TTFTC^0$ (orange) and $TTFTC^{\bullet+}$ (green) to the Raman data of DPNI, H_4TTFTC and $[(Zn(DMF))_2(TTFTC)(DPNI)]$ predicted from DFT modelling.

Vibrational Modes	DPNI (cm^{-1})	H_4TTFTC (cm^{-1})	CT-MOF (cm^{-1})
	545	-	543
	1036	-	1039
	1413	-	1410
	1603	-	1605
	1722	-	1724
	-	-	474
	-	1524	1518
	-	499	-
	-	1404	-

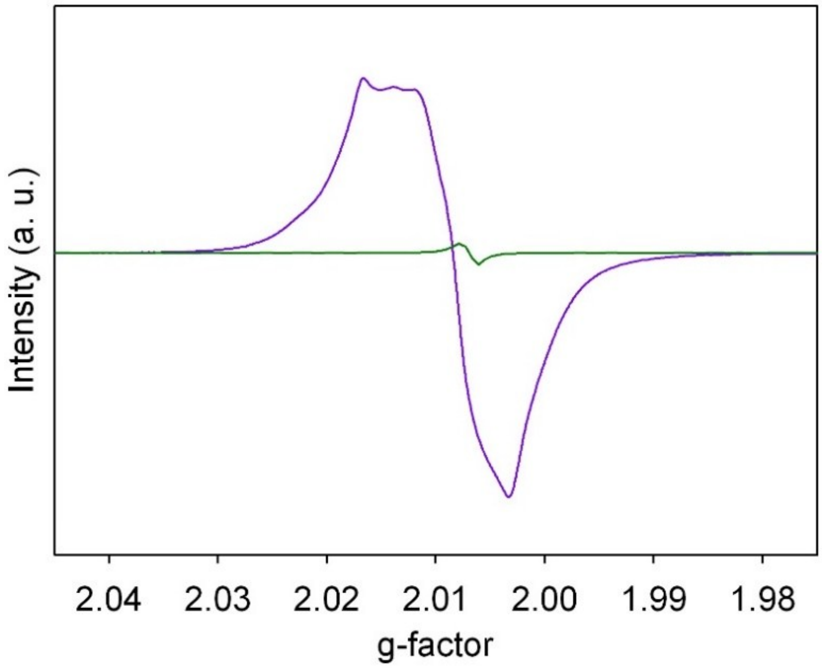


Figure S4. Solid-state EPR spectrum of TTFTC (purple) and DPNI (green).

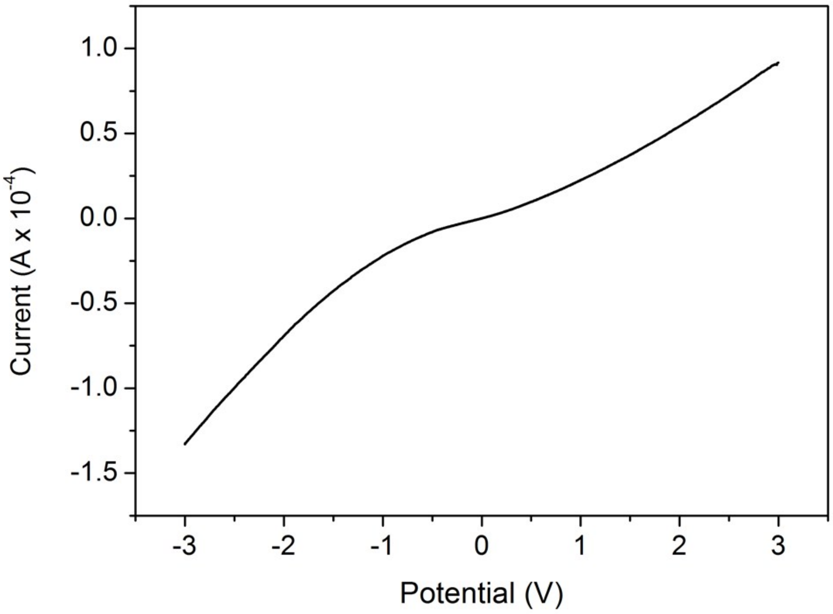


Figure S5. I–V curve of a pressed pellet of $[(Zn(DMF))_2(TTFTC)(DPNI)]$ at room temperature.

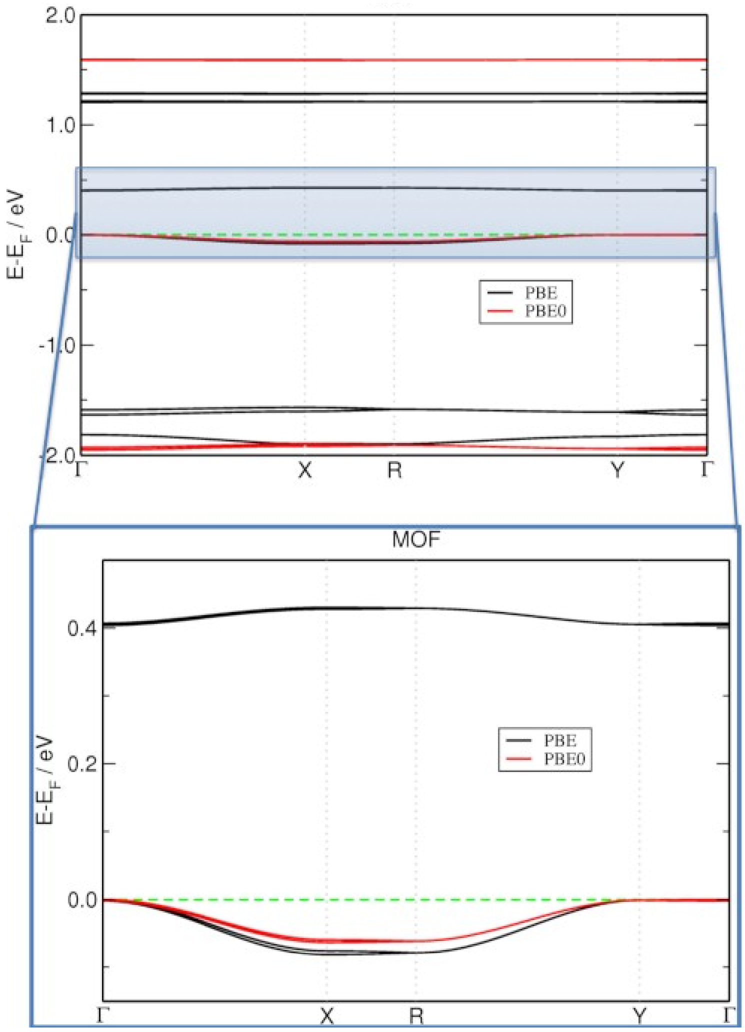


Figure S6. Calculated band structure of [(Zn(DMF))$_2$(TTFTC)(DPNI)] using PBE and PBE0 functionals. Inset: Close-up of the valence and conduction bands.

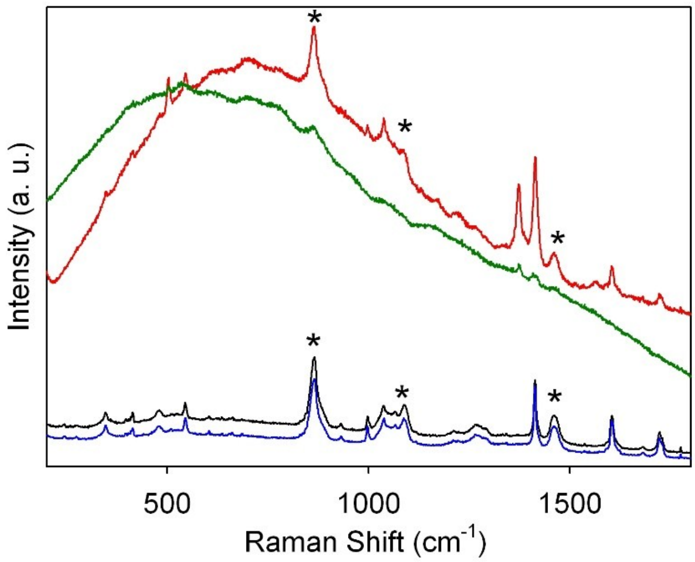


Figure S7. Raman spectra of DPNI collected on the screen-printed electrode (0.2 M LiClO$_4$/ethylene glycol) at 0 V (black), −0.3 V (blue), −0.7 V (red) and −0.8 V (green). Asterisks denote the peaks corresponding to the electrolyte. Spectra were collected under 785 nm laser excitation.

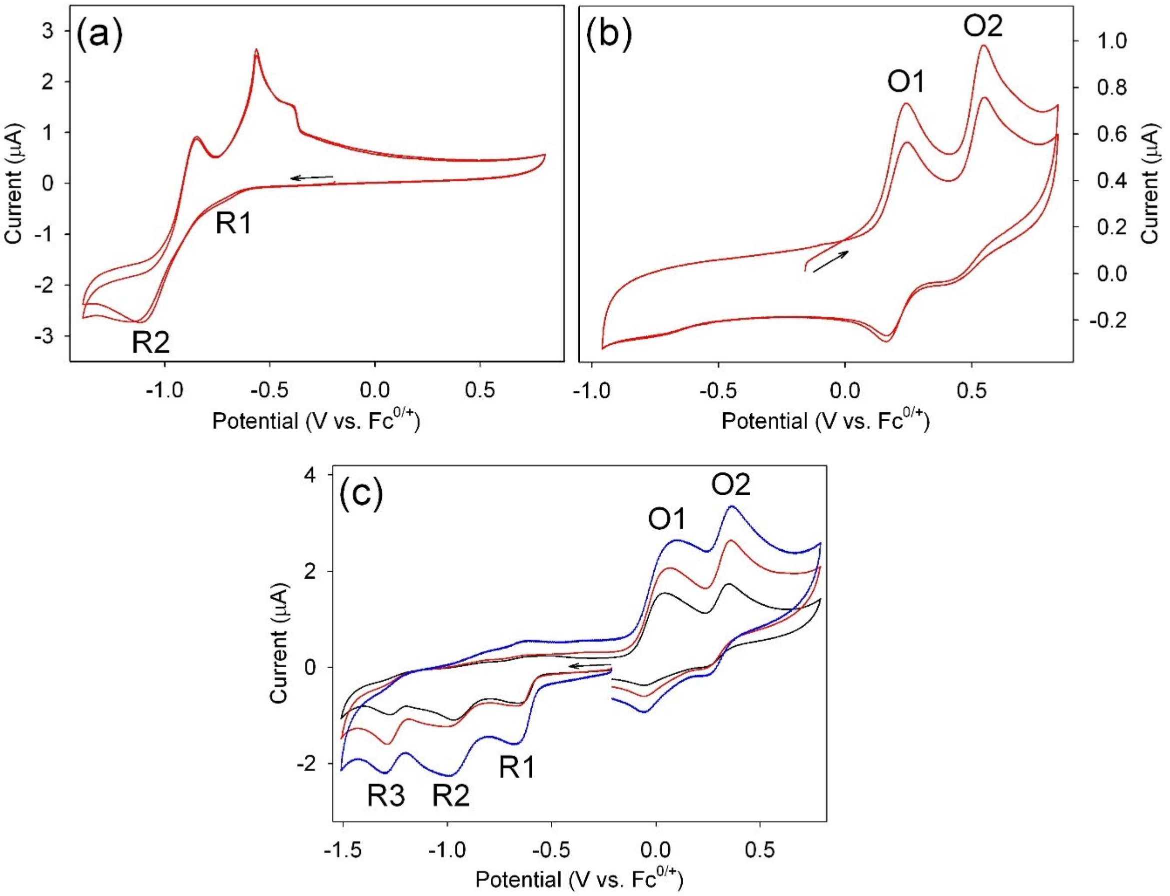


Figure S8. Cyclic voltammograms of (a) DPNI (solid-state), (b) H_4TTFTC (solution-state, 0.03 mM) and (c) [(Zn(DMF))$_2$(TTFTC)(DPNI)] (solid-state) measured in 0.2 M $LiClO_4$/ethylene glycol (ν = 50 (*black*), 100 (*red*) and 200 mVs^{-1} (*black*)). The arrows denote the direction of scan. R1, R2, R3 denote reduction processes 1, 2 and 3, respectively, whilst O1 and O2 indicate oxidation processes 1 and 2, respectively.

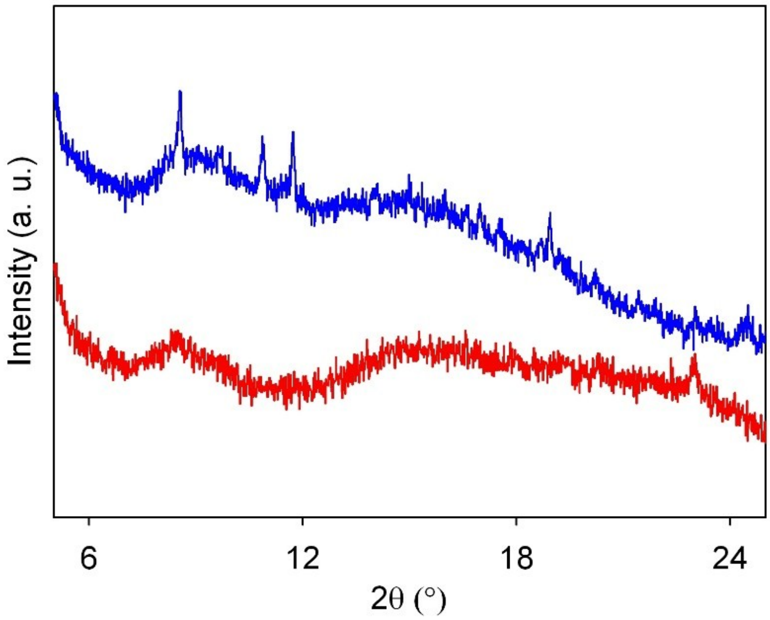


Figure S9. PXRD patterns of [(Zn(DMF))$_2$(TTFTC)(DPNI)] before the electrolysis (blue) and after (red).

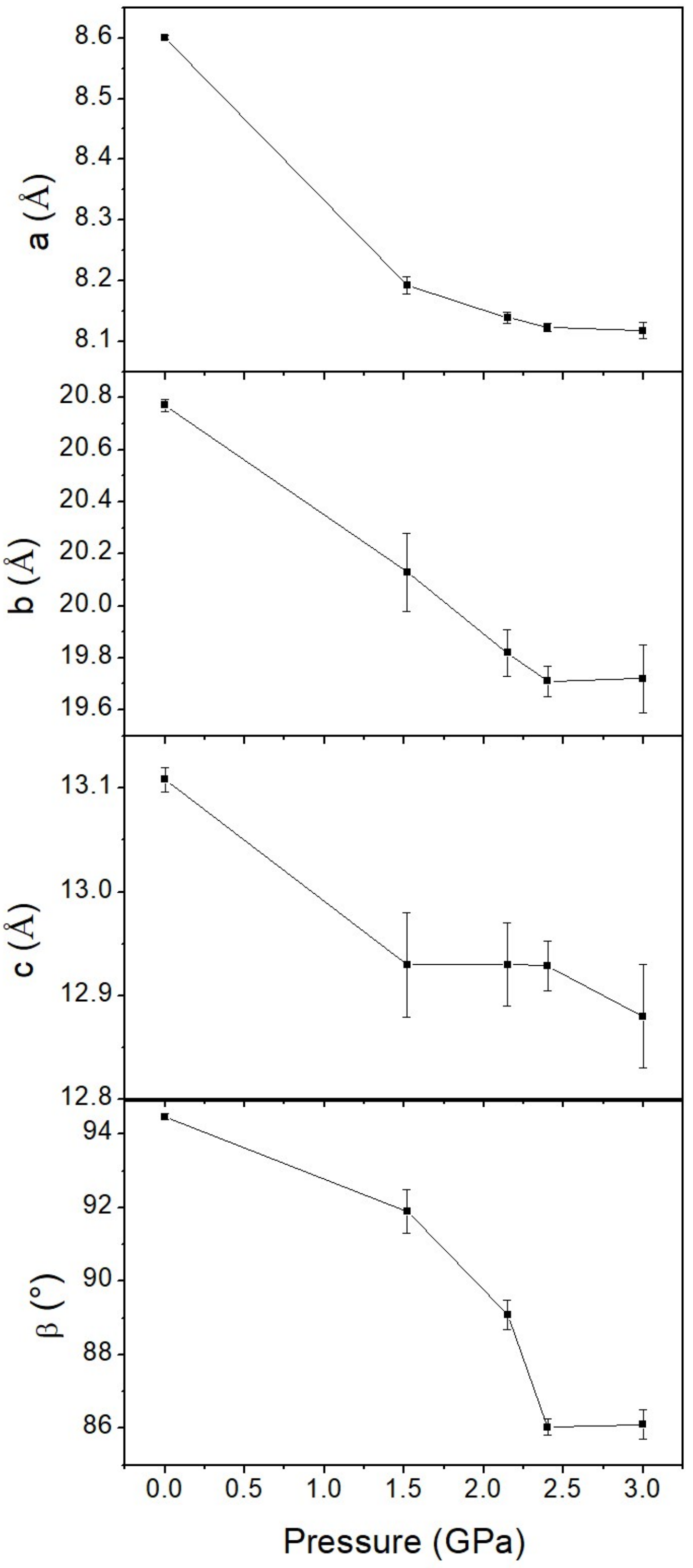


Figure S10. Change in unit cell parameters of [(Zn(DMF))$_2$(TTFTC)(DPNI)] as a function of applied pressure. 0 GPa data was extracted from the PXRD collected at the completion of the experiment.

References

1. Leong, C. F.; Chan, B.; Faust, T. B.; D'Alessandro, D. M. *Chem. Sci.* **2014,** *5*, 4724-4728.