

Supplementary Information

S1 Microscopic images

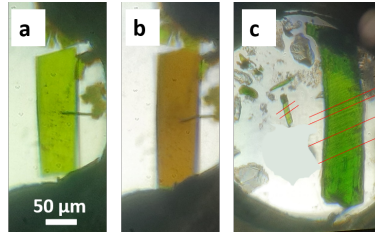


Figure S1: *TTF-FA* crystal inside the DAC, at a) 0.2 and b) 0.8 GPa. c) Crystal cracking after cycling the transition.

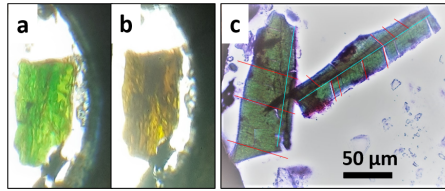


Figure S2: A *DMTTF-FA* crystal observed with polarized transmitted light, at a) 0.2 and b) 0.6 GPa. c) Crystal cracking after the transition (red lines). The blue lines indicate the stack direction. The crystal on the right is twinned.

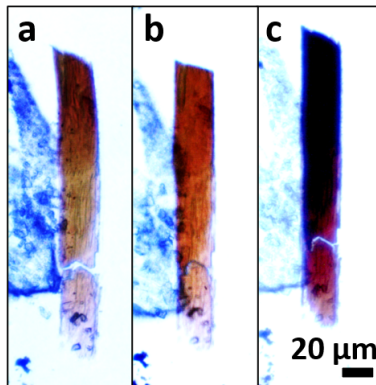


Figure S3: A *DMTTF-CA* crystal, at a) 0.5, b) 0.7 and c) 1.9 GPa. The elongation direction is the stack axis *c*.

S2 IR spectra

The IR spectra were recorded with a Bruker IFS-66 FT-IR spectrometer coupled to a Hyperion 1000 IR microscope, with the electric field vector polarized parallel or perpendicular to the stack direction, that coincided with the elongation axis of the crystals. The DAC was fitted under the microscope.

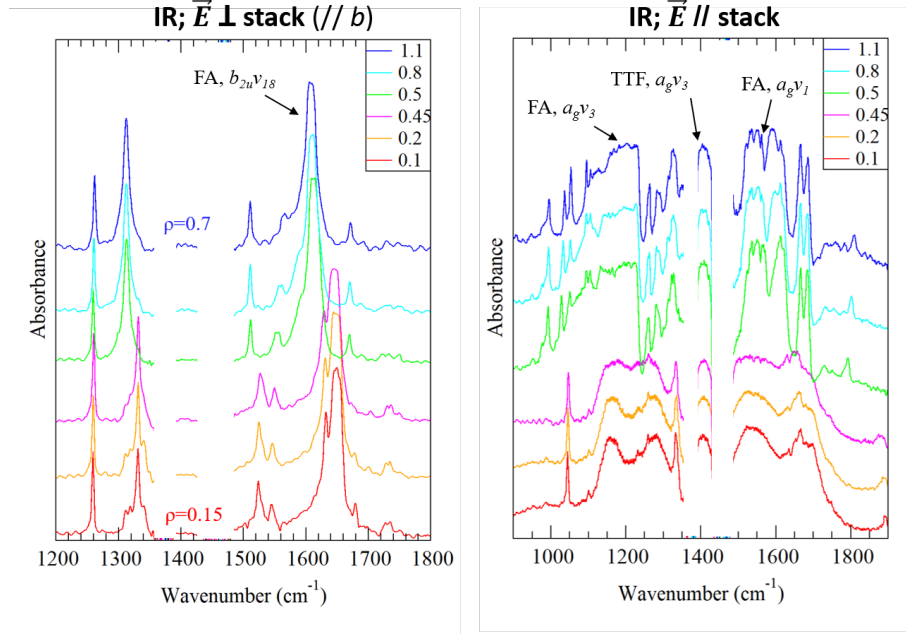


Figure S4: Pressure dependent IR spectra of TTF-FA, measured on the *ab* plane with the light polarized perpendicular (left panel) or parallel to the stack (right panel). The ionicity ρ was estimated from the frequency shift of the FA charge sensitive modes [1].

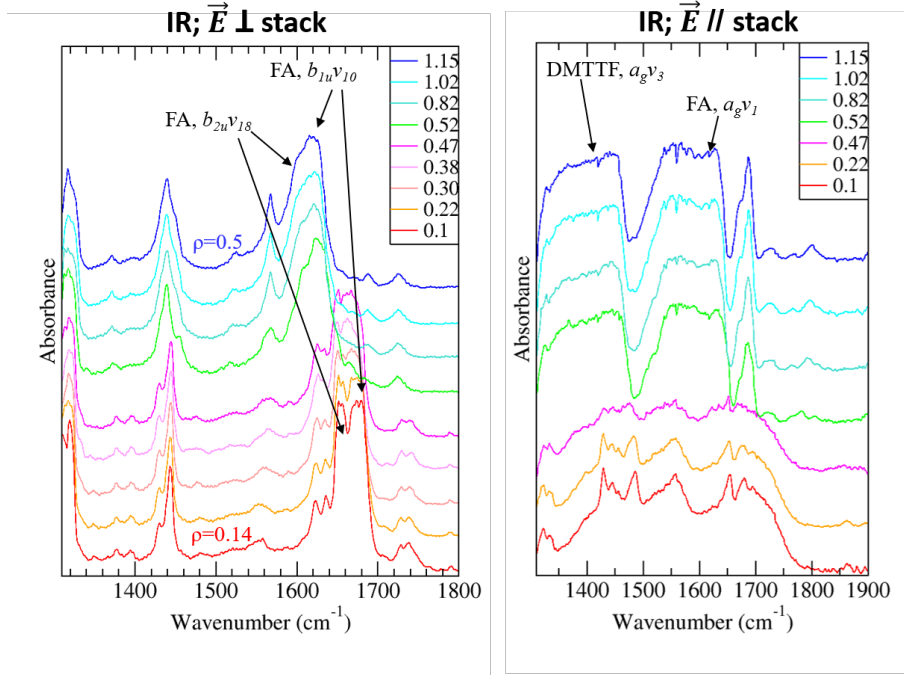


Figure S5: Pressure dependent IR spectra of DMTTF-FA, measured with the light polarized perpendicular (left panel) or parallel to the stack (right panel). The ionicity ρ was estimated from the frequency shift of the FA charge sensitive modes [1].

S3 Raman spectra

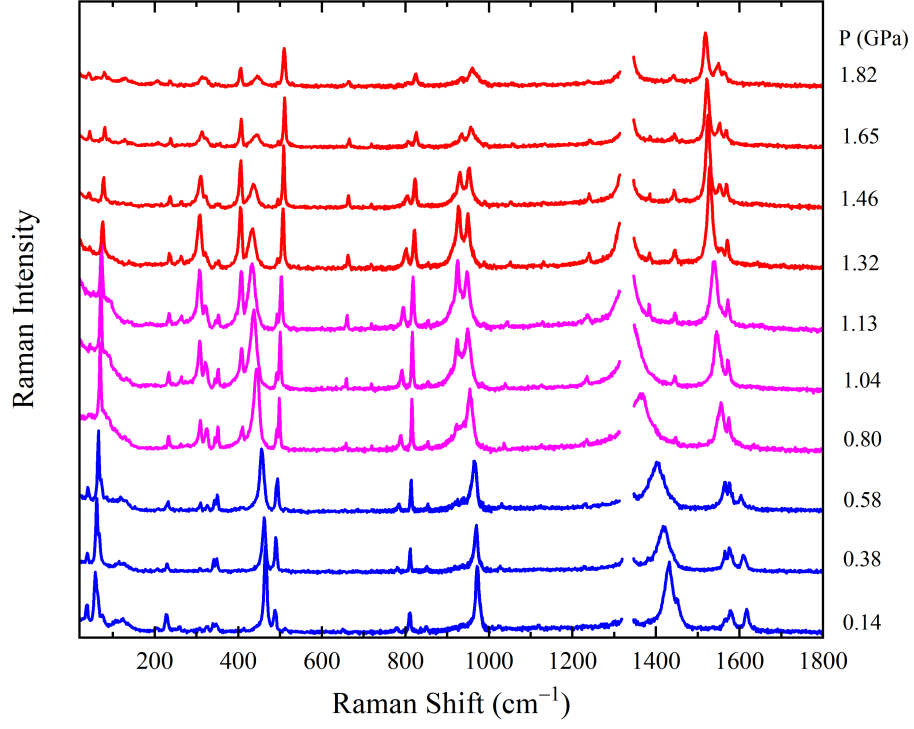


Figure S6: *Pressure dependent extended Raman spectra of DMTTF-CA, measured with both the exciting and scattered light polarized perpendicular to the stack. $\lambda_{exc} = 633 \text{ nm}$*

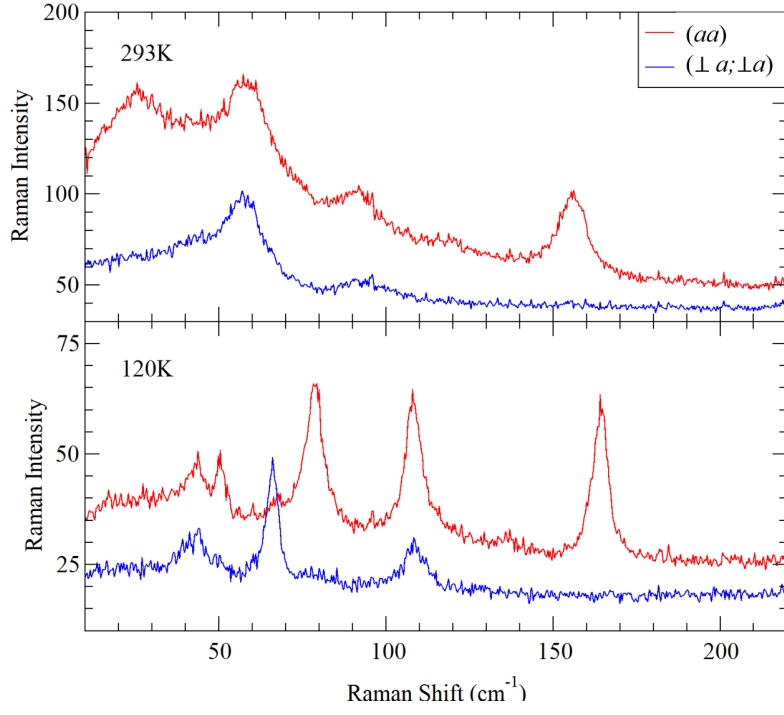


Figure S7: Polarized low frequency Raman spectra of DMTTF-FA at 293 (upper panel) and 120 K (lower panel).

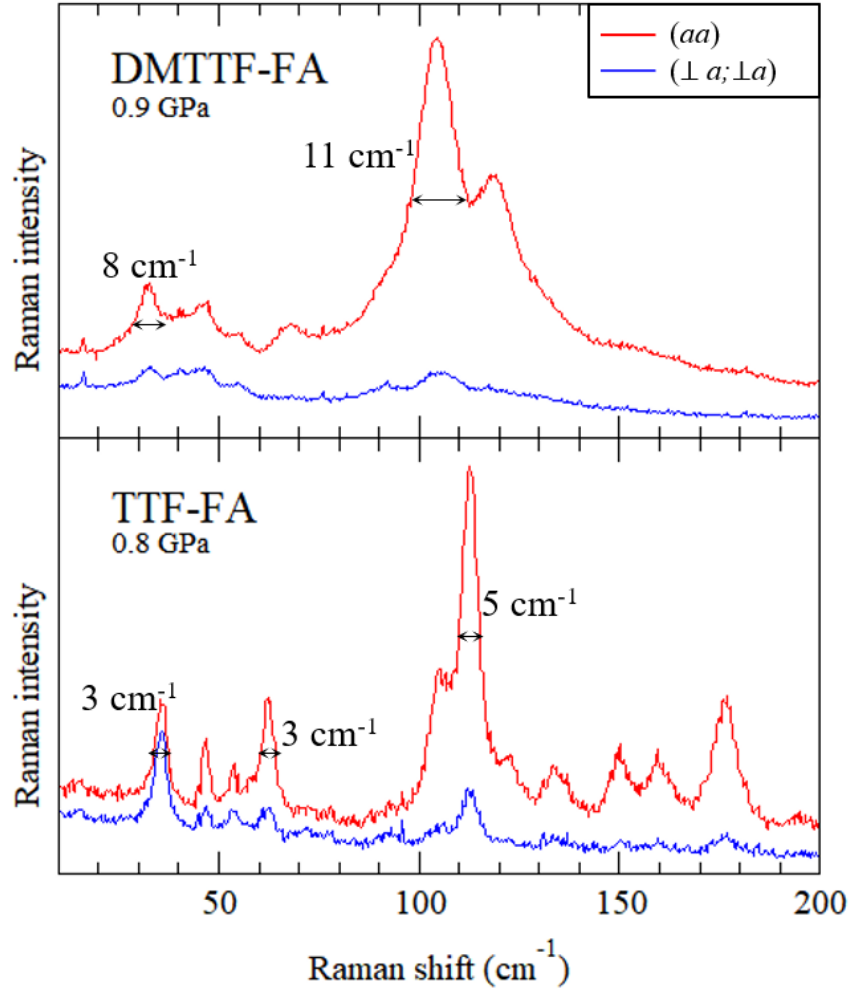


Figure S8: Comparison between the low frequency Raman spectra of the high pressure phases of DMTTF-FA (upper panel) and TTF-FA (lower panel). The phonon bands are much broader in DMTTF-FA due to disorder.

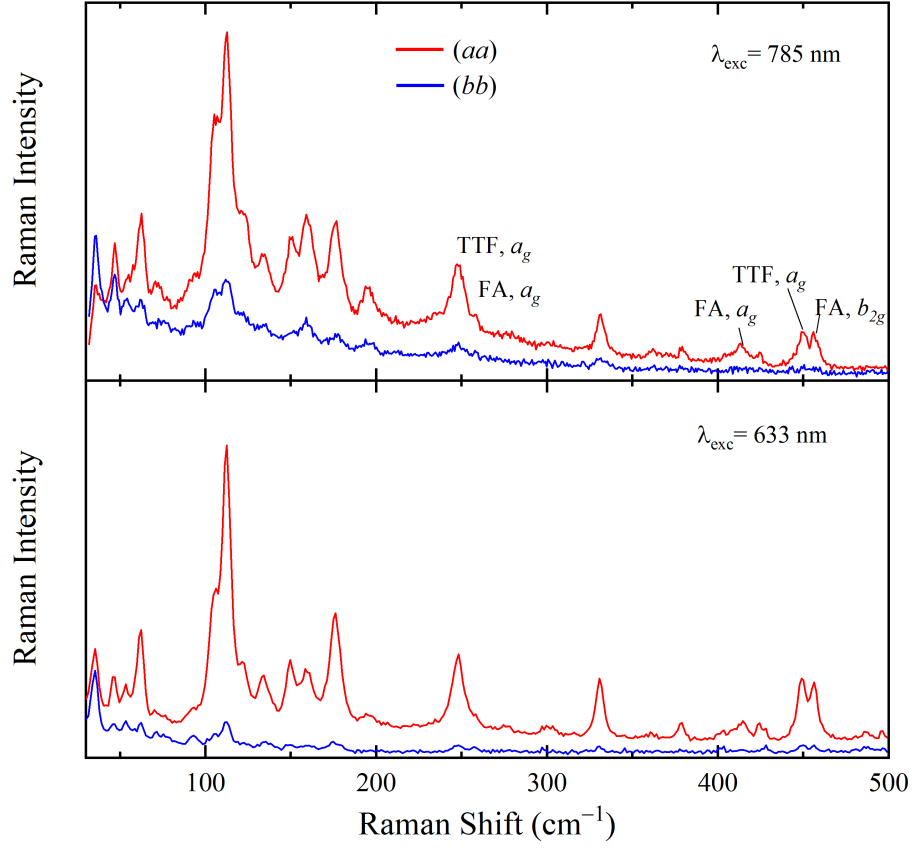


Figure S9: Raman spectra of TTF-FA at 0.9 GPa, measured with both the exciting and scattered light polarized parallel or perpendicular to the stack direction *a*. $\lambda_{exc}=785$ nm (upper panel) and 633 nm (lower panel). The band assignment is based on the spectra of pure TTF and FA, reported in Refs [2, 3].

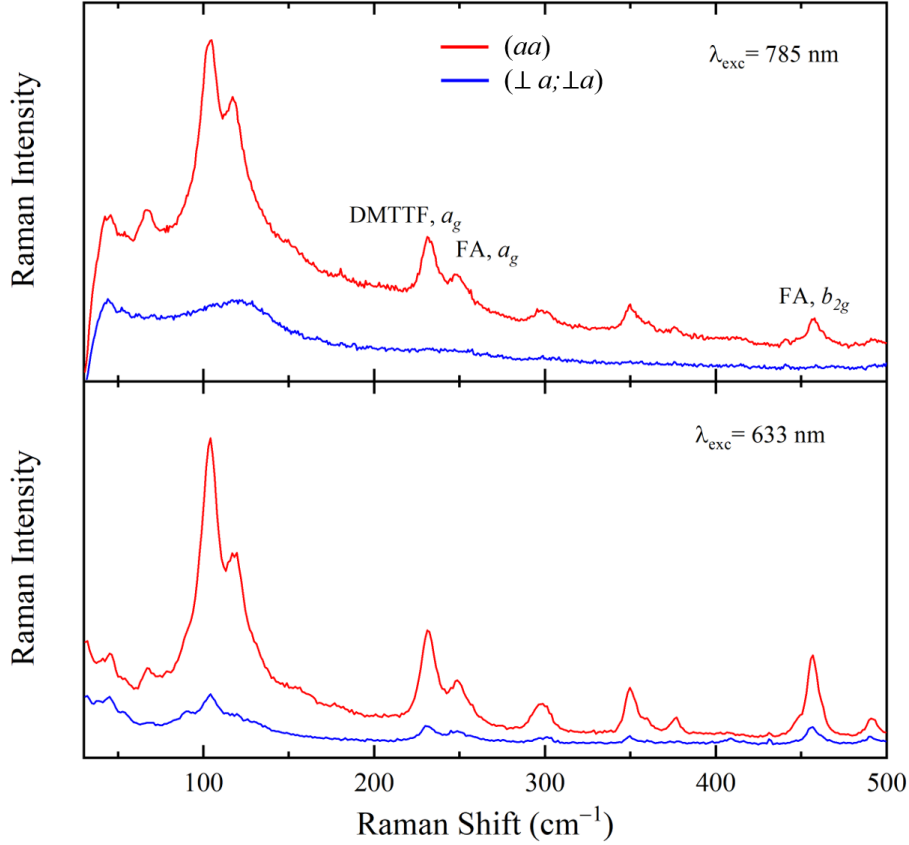


Figure S10: Raman spectra of DMTTF-FA at 0.9 GPa, measured with both the exciting and scattered light polarized parallel or perpendicular to the stack. $\lambda_{exc} = 785$ nm (upper panel) and 633 nm (lower panel). The band assignment is based on the comparison with the TTF-FA spectra shown in Figure S9.

References

- [1] E. Ferrari, F. Mezzadri, and M. Masino, “Temperature-induced neutral-to-ionic phase transition of the charge-transfer crystal tetrathiafulvalene-fluoranil,” *Physical Review B*, vol. 105, no. 5, p. 054106, 2022.
- [2] A. Girlando and C. Pecile, “Vibrational spectra of fluoranil. (2, 3, 5, 6-Tetrafluoro-p-benzoquinone),” *J. Chem. Soc., Faraday Trans. 2*, vol. 71, pp. 689–698, 1975.
- [3] R. Bozio, I. Zanon, A. Girlando, and C. Pecile, “Vibrational spectroscopy of molecular constituents of one-dimensional organic conductors. Tetrathiofulvalene (TTF), TTF+, and (TTF+)2 dimer,” *The Journal of Chemical Physics*, vol. 71, no. 5, pp. 2282–2293, 1979.