

## Inter-Layer Charge Disproportionation in the Dual-Layer Organic Metal (tTTF-I)<sub>2</sub>ClO<sub>4</sub> with Unsymmetrical I•••O Halogen Bond Interactions

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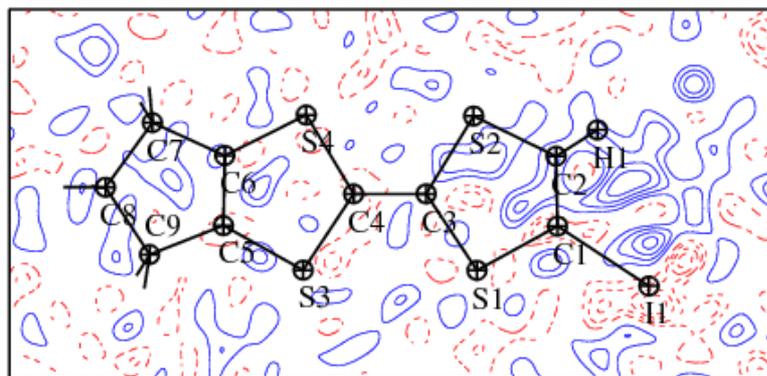
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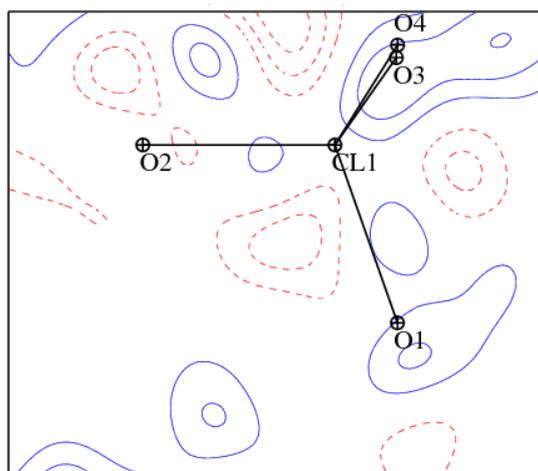
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### SUPPORTING INFORMATION

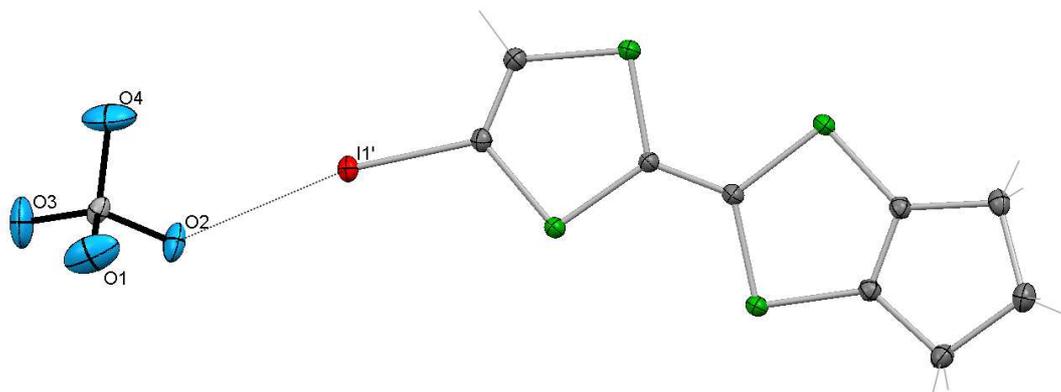


(a)

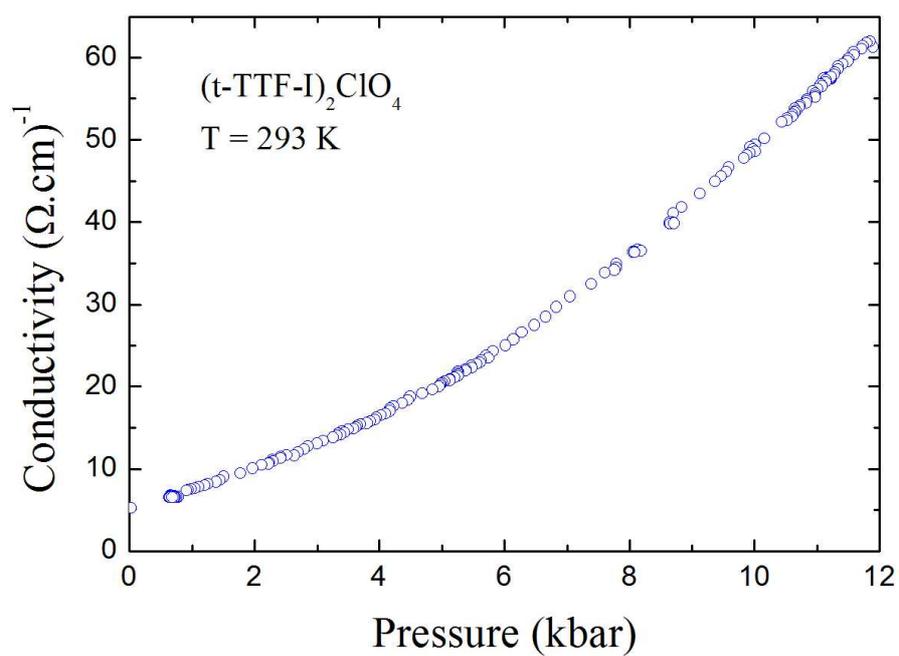


b)

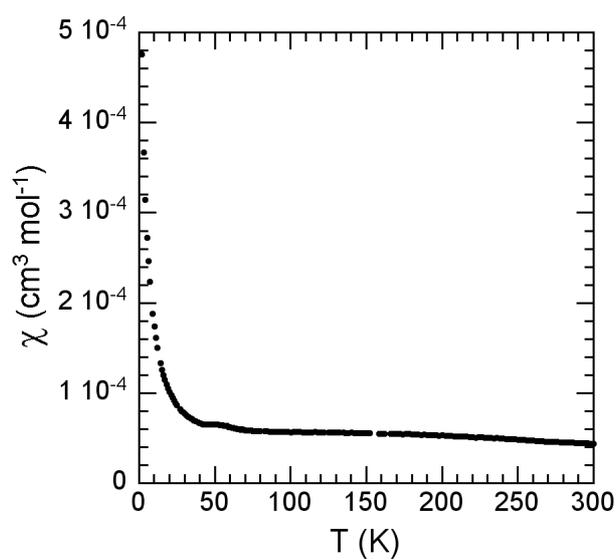
**Figure S1.** Residual electron density maps performed at 100 K, (a) for one of the two cations of the (tTTF-I)<sub>2</sub>ClO<sub>4</sub> asymmetric unit, calculated in the plane C4–C3–S1; (b) for the anion ClO<sub>4</sub><sup>-</sup>, calculated in the plane O1–CL1–O2. Contours at 0.05 e Å<sup>-3</sup> level: full lines in blue are positive, dotted lines in red are negative. Resolution range is  $0 \leq (\sin\theta/\lambda) \leq 0.8 \text{ \AA}^{-1}$ .



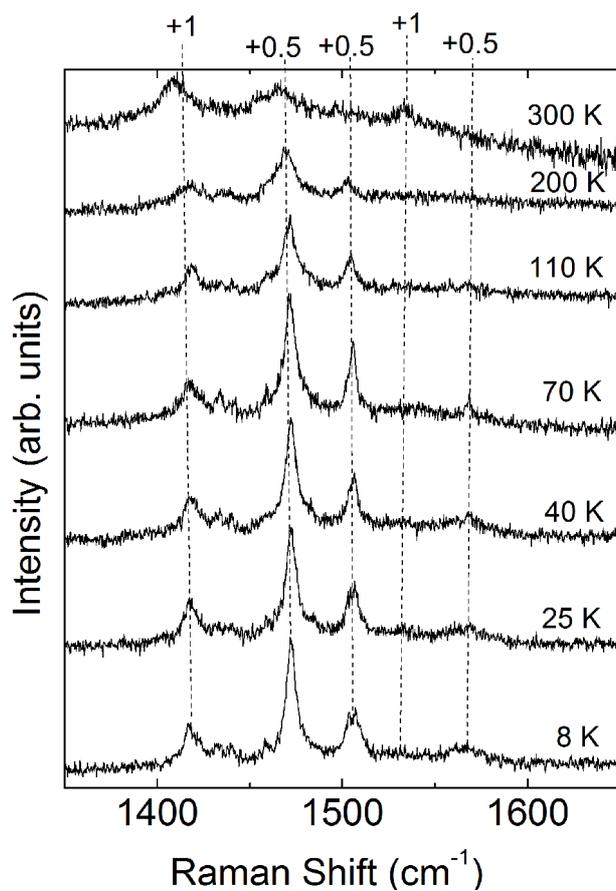
**Figure S2.** ORTEP view of the intermolecular interaction O(2)⋯I(1') in the (tTTF-I)<sub>2</sub>ClO<sub>4</sub> crystal structure at 100 K. ellipsoids are at the 50% probability level.



**Figure S3.** Pressure dependence of the room temperature conductivity of (tTTF-I)<sub>2</sub>ClO<sub>4</sub>.



**Figure S4.** Temperature dependence of the magnetic susceptibility of (tTTF-I)<sub>2</sub>ClO<sub>4</sub>.



**Figure S5.** Temperature dependence of the Raman spectra of the 2:1 salt (tTTF-I)<sub>2</sub>ClO<sub>4</sub>.