

Electrical conductivity and DFT investigations of a 2D Cu^I-TCNQ^{II-} framework

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Electronic Supplementary Information

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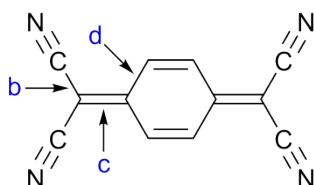
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S1 Kistenmacher relationship calculations

The Kistenmacher relationship may be used to estimate the charge on a TCNQ based on certain bond lengths determined by X-ray crystallography.¹

The Kistenmacher relationship is given by the expression:

$$q = -A[c/(b + d)] + B$$



Work with the dianionic (aromatic) form of TCNQ has led to the use of revised values for A and B ($A = -41.667$, $B = 19.818$).²

Table S1.1 Average bond lengths within the TCNQ species of the $[\text{Cu}_2(\text{TCNQ})(\text{Me}_2\text{pz})]$ framework and the estimated charge.

CT complex	b (Å)	c (Å)	d (Å)	$c/(b+d)$	Charge (q)
$[\text{Cu}_2(\text{TCNQ})(\text{Me}_2\text{pz})]$	1.395(7)	1.465(3)	1.401(5)	0.5240	-2.01(14)

S2 Electrical conductivity measurements

Electrical conductivity measurements were performed using a custom-built two-point conductivity apparatus. The apparatus consisted of a 2-electrode screw cell design adapted from a design described by Long and co-workers.³ The compound, in pellet form was pressed between two copper dies (contact area 7.069 mm²) using two brass screws. The pellets were formed by compression of microcrystalline powder. Callipers were used to measure the pellet thickness was measured with callipers and was in the range of 0.1 mm. The assembled cell was placed in a custom-built cryostat which allowed the temperature to be controlled. I-V profiles were recorded using an Ossila X100 Source Measure Unit.

Using the I-V profiles, the conductivity was calculated by modelling with Ohm's law, $R = \frac{V}{I}$, where R is resistance, V is voltage and I is current.

The temperature dependence of the conductivity was fitted to the Arrhenius equation,

$\sigma = \sigma_o e^{\frac{-E_a}{k_B T}}$, where σ is the conductivity, σ_o is the pre-exponential factor, E_a is the activation energy, k_B is the Boltzmann constant and T is the temperature.

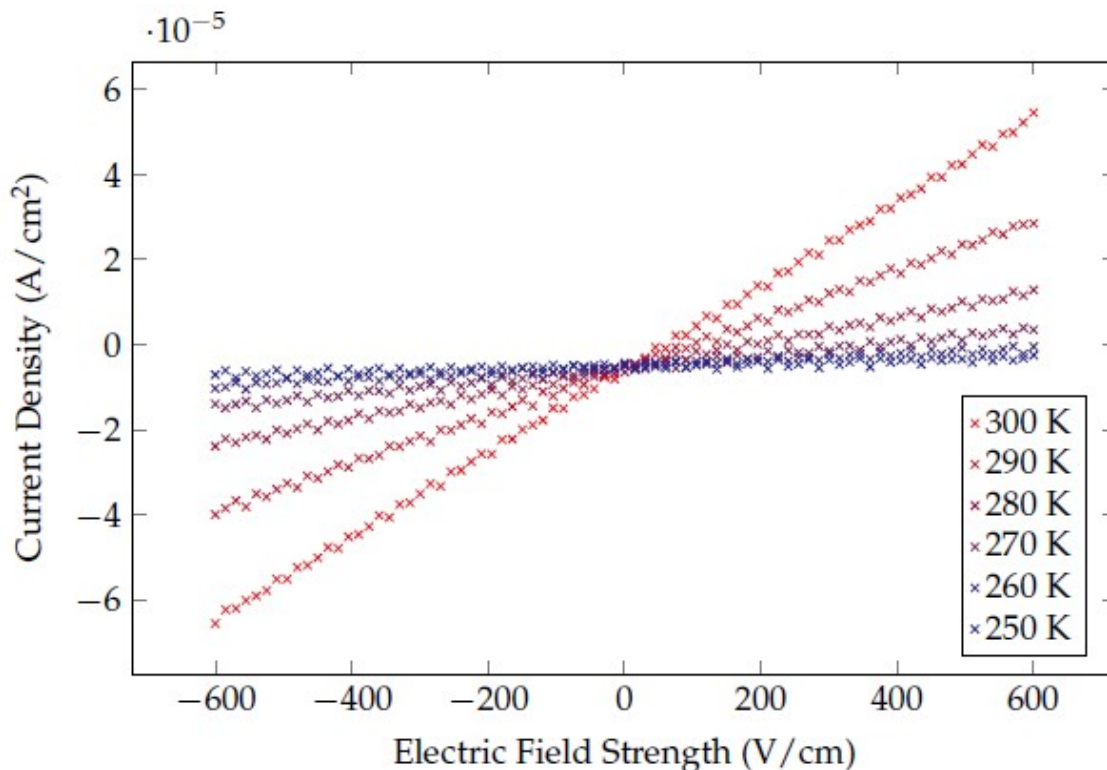


Fig. S2.1 Current Density-Electric Field Strength plots for $[\text{Cu}_2(\text{TCNQ})(\text{Me}_2\text{pz})]$

S3 Computational details

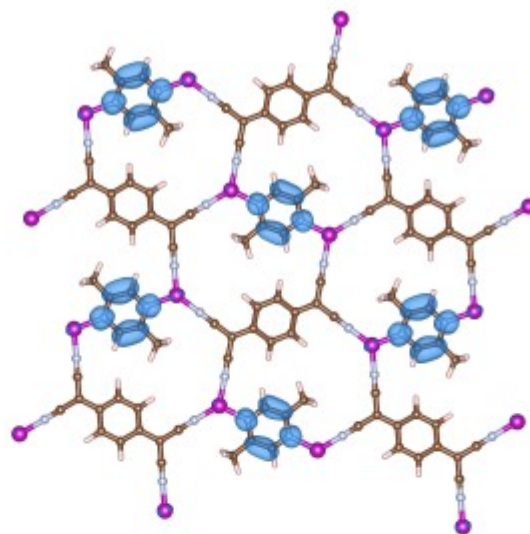
Electronic-structure calculations have been undertaken with the projected augmented wave (PAW) formalism combined with plane-wave based, periodic Density Functional Theory (DFT), as implemented within the Vienna Ab-initio Simulation Package (VASP).⁴⁻⁶

The single crystal structure of [Cu₂(TCNQ)(Me₂pz)] has been previously reported and the associated CIF is available from the CCDC.⁷ An input file was prepared from crystallographic data with the aid of the Bilbao Crystallographic Server resources. The atomic positions of the [Cu₂(TCNQ)(Me₂pz)] were allowed to relax using the Perdew-Burke-Ernzerhof functional (PBE).⁸ As van der Waals effects are expected to influence the structure, Grimme's DFT-D3 dispersion correction with Becke-Johnson damping in its periodic implementation has been applied.^{9,10} After preliminary tests – as is common for such cases – a plane-wave cut-off energy of 500 eV was found suitable for convergence of the electronic wave functions to give total energies within an accuracy of 0.01 eV/atom and was used for all calculations. A gamma centred *k*-mesh (3 x 2 x 2) was employed for the structure optimisation.

Key electronic properties (band structures and density of states) were calculated with single-point calculations with the HSE06¹¹ functional based on the PBE-D3(BJ) optimised structures. Electronic band-structures were calculated along high symmetry points according to the Bilbao Crystallographic Server.¹²⁻¹⁴ The density of states was calculated with a gamma centered *k*-mesh (3 x 2 x 2). The separation into partial density of states (PDOS) was carried out with a group-own code.

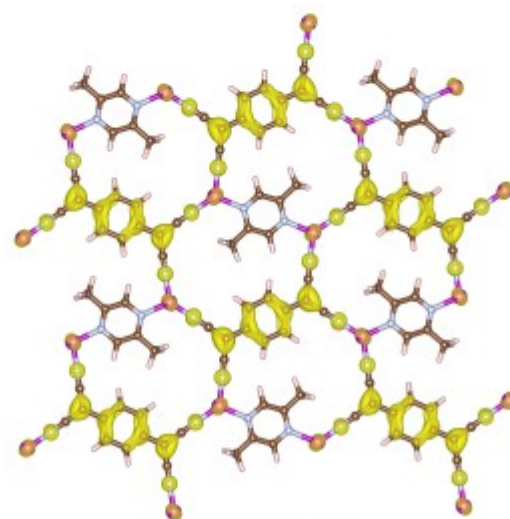
Band decomposed charge density plots were generated in Visualization for Electronic and Structural Analysis (VESTA, available from <http://jp-minerals.org/vesta/en/>).

(a)



Conduction Band

(b)



Valence Band

Fig S3.1 Band decomposed charge densities of the $[\text{Cu}_2(\text{TCNQ})(\text{Me}_2\text{pz})]$ framework. The a) conduction band and b) valence band charge densities.

S4 References

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