Supplementary Information (SI) for CrystEngComm.

Supplemental Information

Crystallography

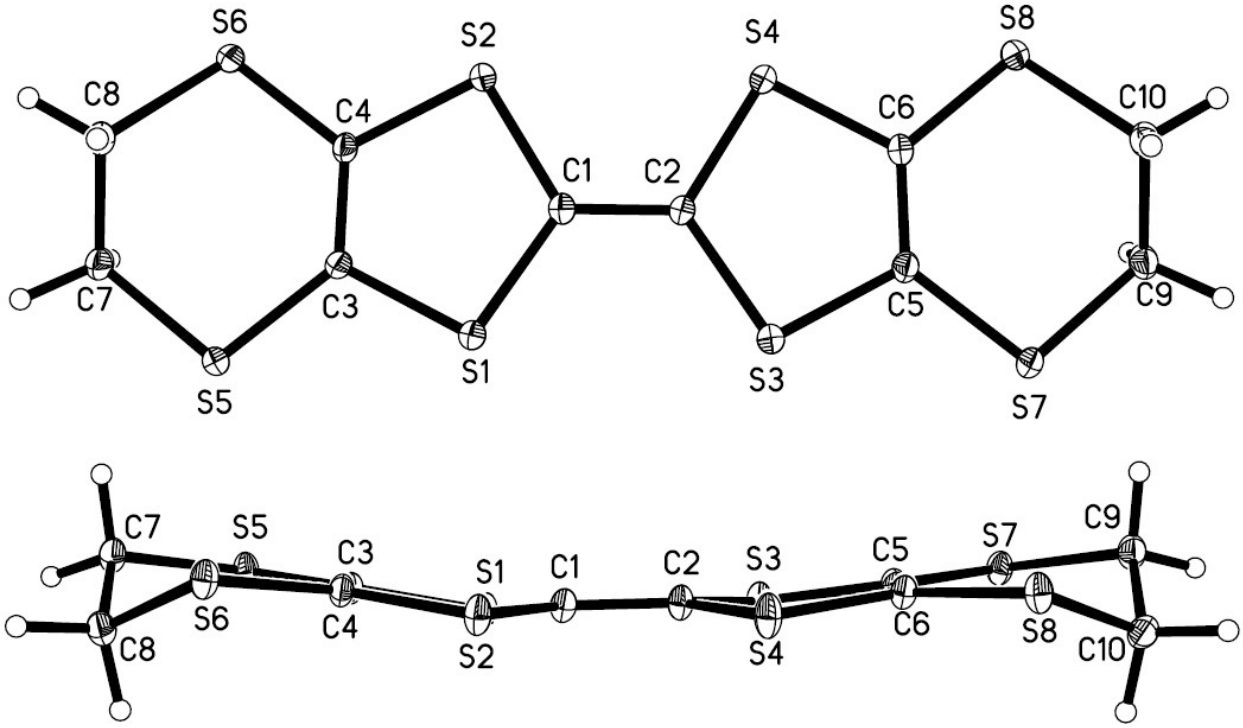

Figure S1. Thermal ellipsoid plot (50% probability level) with atom labeling scheme for the BEDT-TTF molecule (A) in the α-$(BEDT\text{-}TTF)_2Hg(SeCN)_2Cl$ structure at 100 K. Hydrogen atoms are drawn as spheres with arbitrary radius. Analysis of the bond lengths yields an oxidation state of +0.13. The molecule is puckered: the ten atoms of the TTF core have a RMS deviation of 0.1154 with 'outer' sulfur atoms out of the best TTF plane by 0.327(2) Å (S5), 0.311(2) Å (S6), 0.309(2) Å (S7), and 0.119(2) Å (S8).

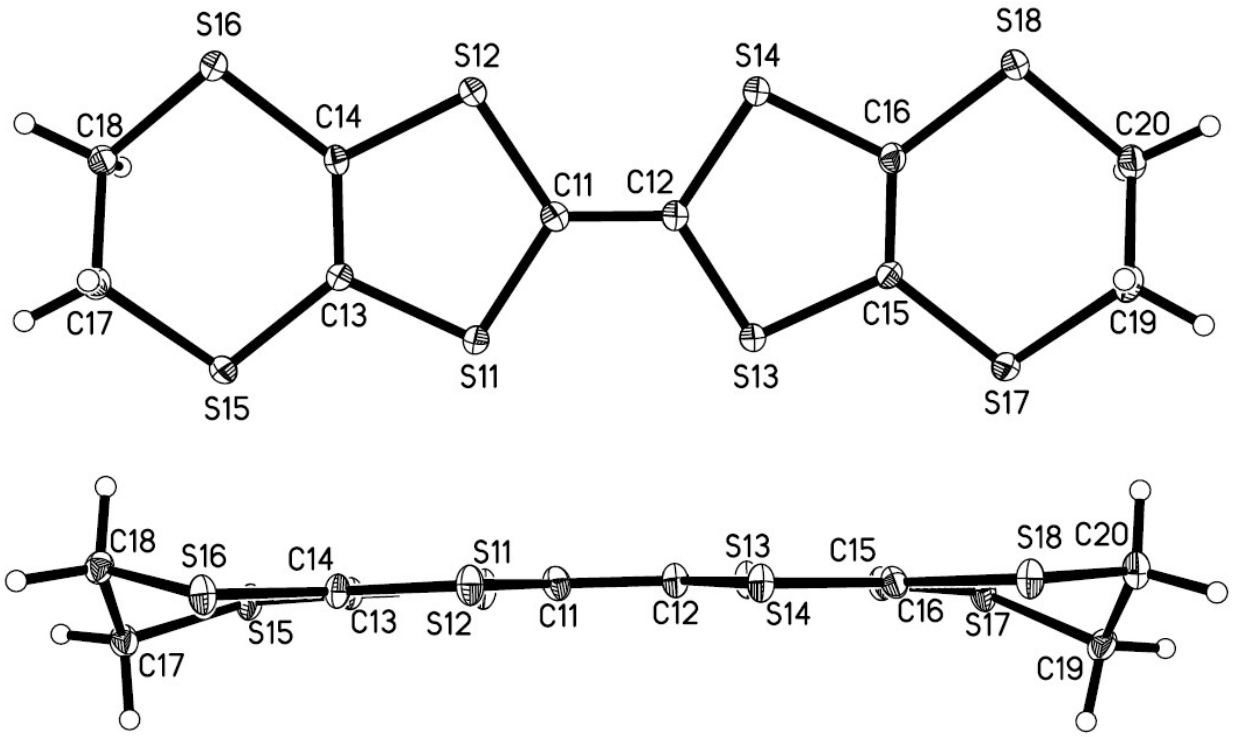

Figure S2. Thermal ellipsoid plot (50% probability level) with atom labeling scheme for the BEDT-TTF molecule (B) in the α-$(BEDT\text{-}TTF)_2Hg(SeCN)_2Cl$ structure at 100 K. Hydrogen atoms are drawn as spheres with arbitrary radius. Analysis of the bond lengths yields an oxidation state of +0.87. The molecule is relatively planar: the ten atoms of the TTF core have a RMS deviation of 0.0305 with 'outer' sulfur atoms out of the best TTF plane by 0.119(2) Å (S15), 0.029(2) Å (S16), 0.168(2) Å (S17), and 0.019(2) Å (S18).

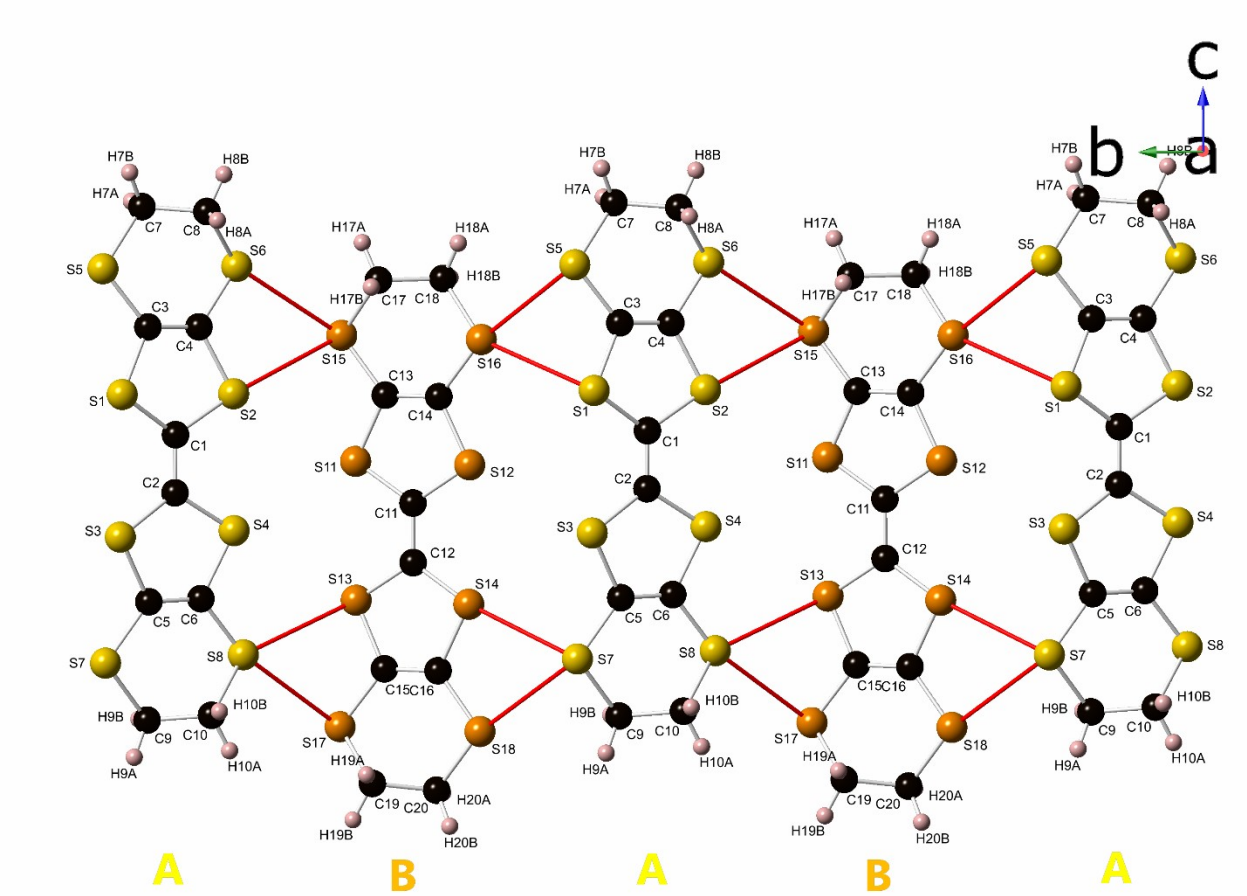

Figure S3. Intermolecular S···S interactions of less than 3.6 A BEDT-TTF molecule **A**. S1-S16 (3.504 A), S2-S15 (3.556 A), S5-S16 (3.336 A), S6-S15 (3.408 A), S7-S14 (3.402 A), S7-S18 (3.428 A), S8-S13 (3.442 A), and S8-S17 (3.421 A).

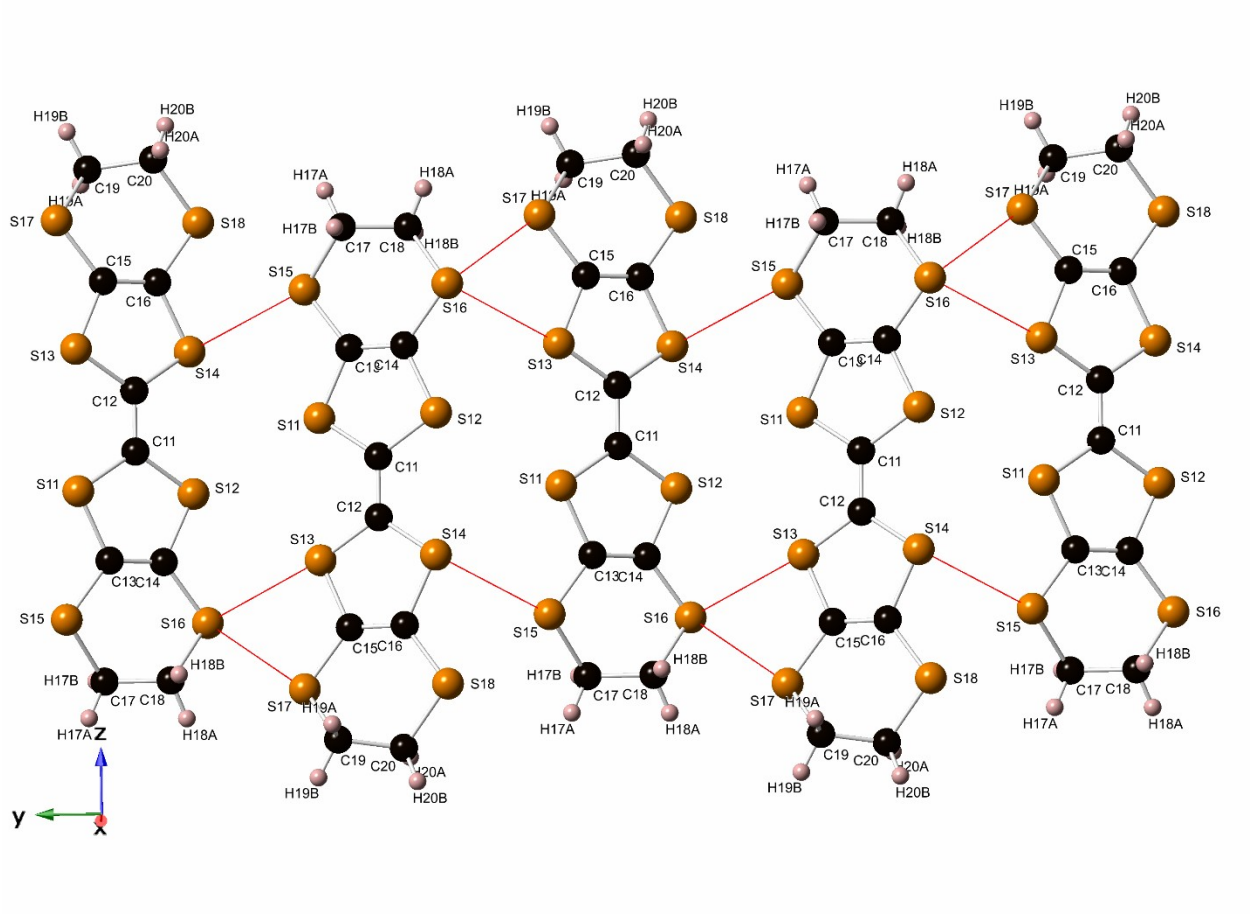

Figure S4. Intermolecular S···S interactions of less than 3.6 A for chains of **B** molecules along the b-axis. S13-S16 (3.546 A), S14-S15 (3.493 A), and S16-S17 (3.543 A).

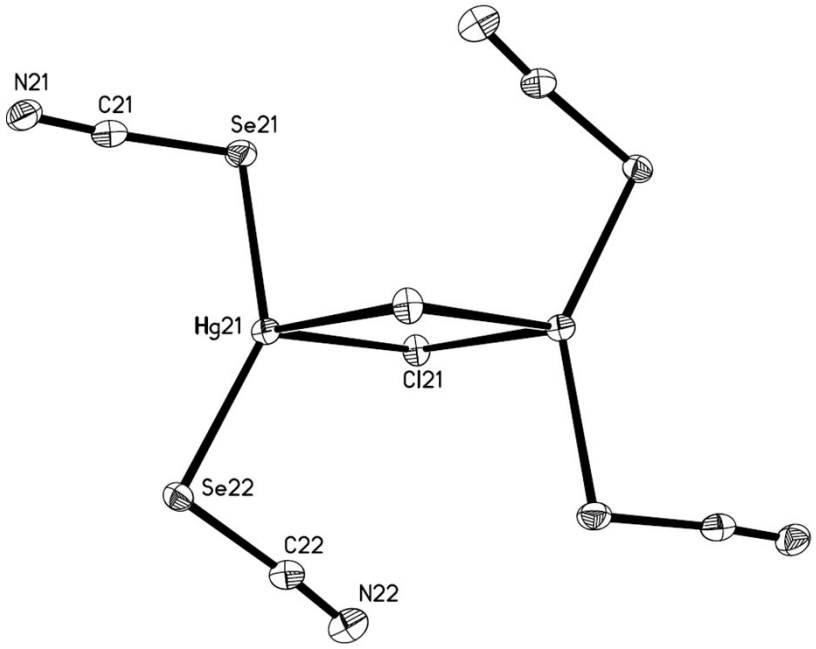

Figure S5. Thermal ellipsoid plot (50% probability level) with atom labeling scheme for the $Hg(SeCN)_2Cl^-$ anion in the α-$(BEDT\text{-}TTF)_2Hg(SeCN)_2Cl$ structure at 100 K. Hydrogen atoms are drawn as spheres with arbitrary radius.

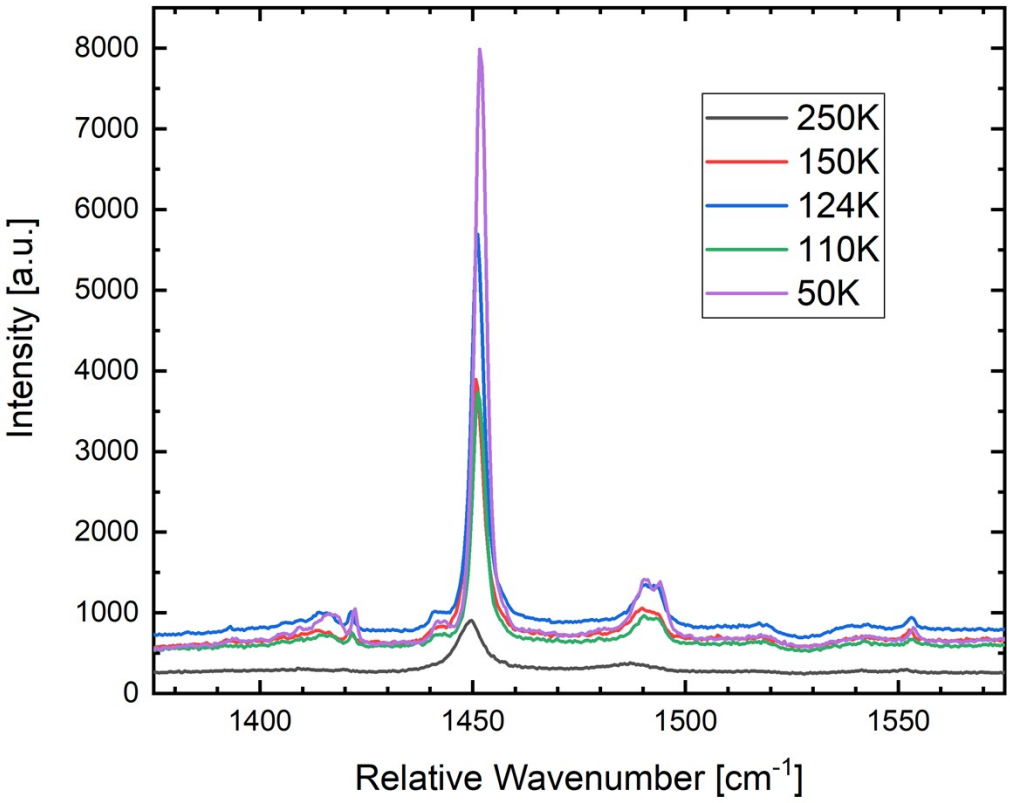

Figure S6. Raman spectra as a function of temperature is consistent with ν_3 and ν_4 symmetric C=C vibration frequencies of BEDT-TTF^0 and BEDT-TTF^{+1}.

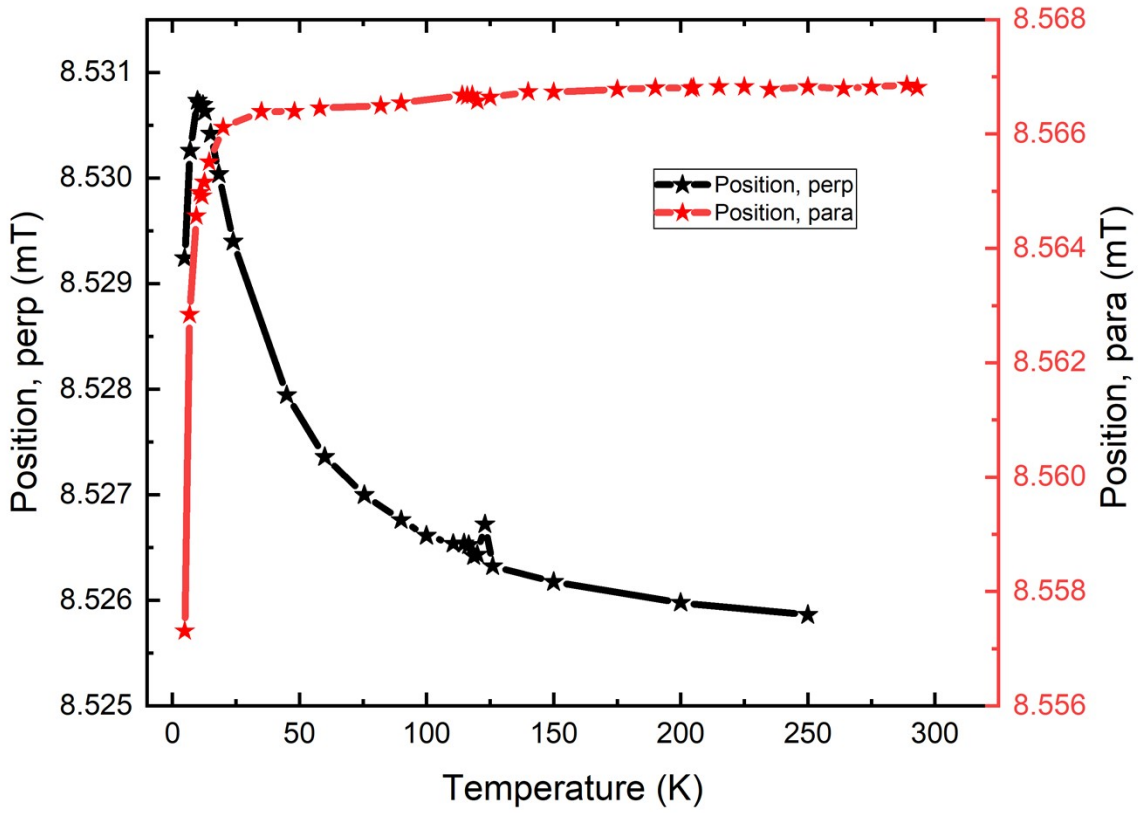

Figure S7. Electron paramagnetic resonance position at 120 GHz as a function of temperature with field perpendicular and parallel to the 2D layers.

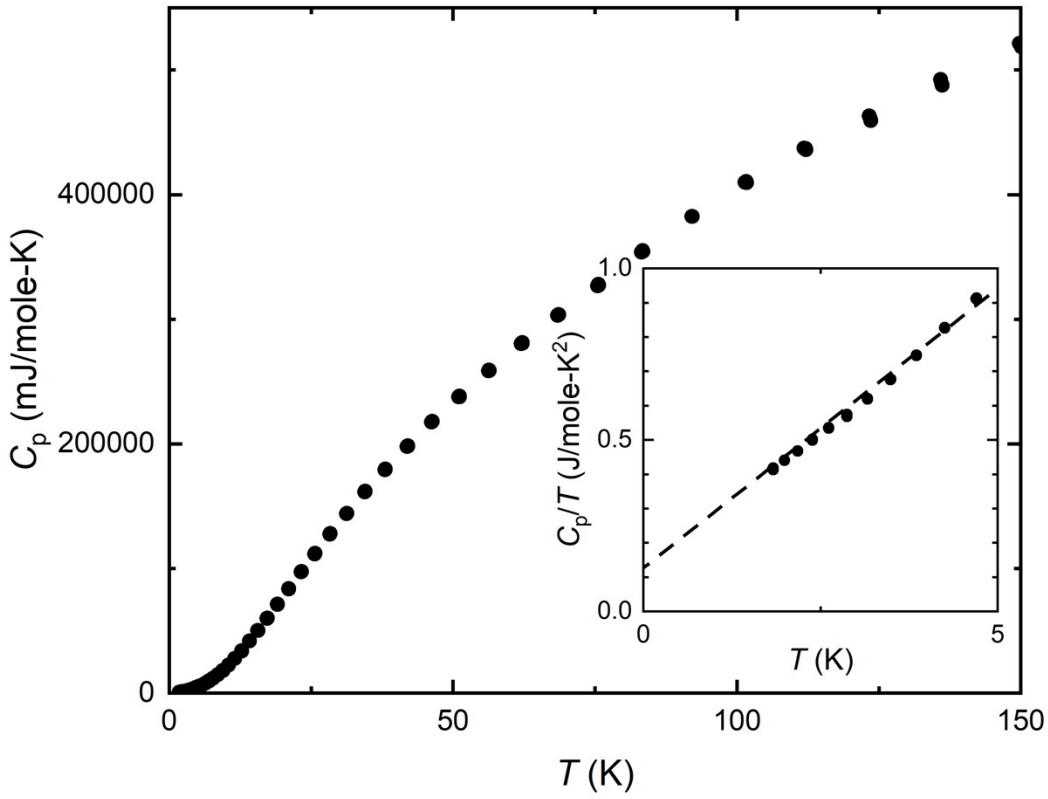

Figure S8. Specific heat as a function of temperature.

Theory

Methods:

As a starting point for the *ab initio* calculations, we used the experimental structure of α-$(ET)_2Hg(SeCN)_2Cl$, with the lattice constants a = 8.3995 Å, b = 10.9240 Å, c = 38.1055 Å and angles α = γ= 90°, β = 96.154° in the symmetry space group $P2_1/n$ obtained by experiments, as shown in the left panel of Fig. 1. The electronic properties are calculated using density functional theory (DFT) via the full potential local orbital package (FPLO) version 18.00-57.[1] As exchange-correlation functional, we used the generalized gradient approximation (GGA).[2] We performed non-spin polarized calculations on a 5×5×5 $\vec{k}$-grid in the primitive unit cell with convergence criterion for charge density to be 1×10^{-6} and for the energy to be 1×10^{-8} Ha. These results have been confirmed with more densed $\vec{k}$-grid of 7×7×7.

In the next step, we construct an effective Hamiltonian $H_{eff}=\sum_{i,j,\sigma}\left(t_{ij}\hat{c}^{\dagger}_{i\sigma}\hat{c}_{j\sigma}+h.c\right)+U\sum_{i}\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}=H_{kin}+H_U$,

where σ is the spin index and the first term, H_{kin}, contains the hopping parameters t_{ij} calculated from the first principles Wannier projection of the previously obtained electronic bands within FPLO. Each Wannier orbital centered at a BEDT-TTF-molecule. The second term H_U contains the two particle Coulomb interaction. We solve this problem numerically using a mean-field approximation. We rewrite the number operator $n_{i\sigma}$ as follows, $\hat{n}_{i\sigma}=\langle\hat{n}_{i\sigma}\rangle+\delta\hat{n}_{i\sigma}$,

where $\langle\hat{n}_{i\sigma}\rangle$ is the expectation value of the particle number operator and $\delta\hat{n}_{i\sigma}$ is the fluctuation. At this point, we neglect the fluctuation terms, $\delta\hat{n}_{i\sigma}$ and the resulting Hamiltonian is thus given by

$$H^{MF}_{eff}=\sum_{i,j,\sigma}\left(t_{ij}\hat{c}^{\dagger}_{i\sigma}\hat{c}_{j\sigma}+h.c\right)+U\sum_{i,\sigma}\hat{n}_{i\sigma}\langle\hat{n}_{i\bar{\sigma}}\rangle,$$

where to notation $\bar{\sigma}$ refers to the opposite spin. This Hamiltonian, H^{MF}_{eff}, is then diagonalized in k-space on a $43\times43\times5$ $\vec{k}$-grid and solved self-consistently until the expectation $\langle\hat{n}_{i\sigma}\rangle$ converges for each site i and spin σ. To fix the particle number as obtained from the *ab initio* results, we include the chemical potential term $\mu\sum_{i,\sigma}\hat{n}_{i\sigma}$, where μ is calculated at each iteration. Furthermore, we analyze the states by the magnetization value m_s given by

$$m_s=\langle\hat{n}_{i\uparrow}\rangle-\langle\hat{n}_{i\downarrow}\rangle.$$

1. K. Koepernik and H. Eschrig, *Phys. Rev. B*, 1999, **59**, 1743.
2. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.

DFT Results:

Each unit cell consists of an inorganic $Hg(SeCN)_2Cl$-layer separating the unit cell in two regions each containing four BEDT-TTF molecules along the c-axis.

Within DFT and considering PBE functional we calculated the electronic bands and density of states as shown in Figure S4. We obtain a metallic state since correlations beyond the GGA approximation are not included. Corrections within GGA+U are not possible to perform since the central objects are molecules and not atoms, and GGA+U is a functional developed to introduce directly the effect of correlations with atomic U's.

This is why we introduce correlations in the DFT-derived model through construction of Wannier molecular orbitals, where we can assign a 'U' to the molecule.

Two important things to notice here are the following:

First, when comparing these states with the atom-resolved density of state, we note that the main contributions come from C and S. The states originating from the inorganic atoms are not present around the Fermi energy, as it is known from all these charge-transfer salts where the inorganic anion complexes are only responsible for the charge transfer and the corresponding bands are deep into higher binding states. The Fermi surface is therefore well described by the organic BEDT-TTF molecules, which consists of only the C and S atoms.

Second, the electronic bands along the $\vec{k}$-path from Γ to Z (which is along k_z) are dispersionless. From these two facts we conclude that the physics of the systems is dominated by the BEDT-TTF molecules in each region

BEDT-TTF molecules along the c-axis and the interactions between the two regions is negligible due to the inorganic $Hg(SeCN)_2Cl$-layer. Therefore, we can model the system as a two-dimensional lattice.

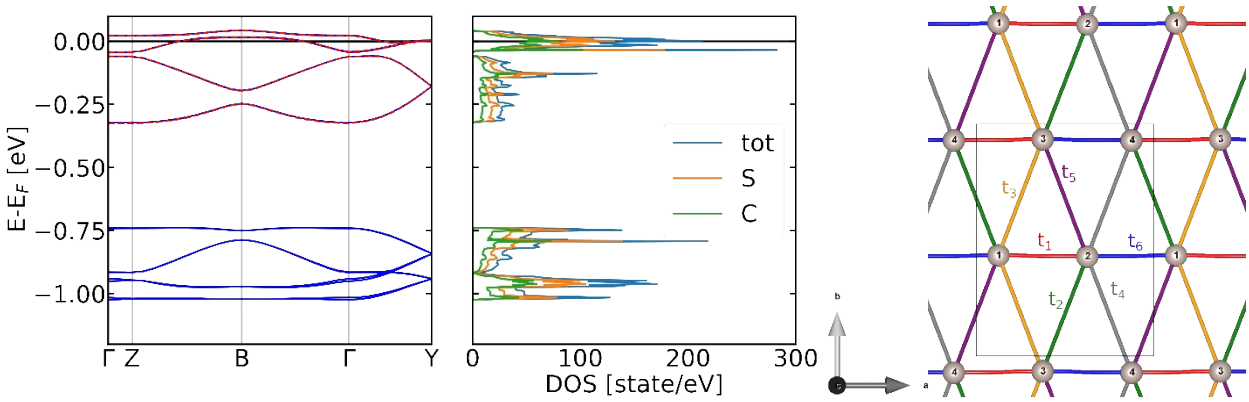

Figure S9: Electronic properties obtained by GGA. Left panel shows the DFT bands (blue) lines and the Wannier fit bands for the effective Hamiltonian (dashed red lines). The good overlap shows the quality of the fit. Middle panel displays the orbital resolved density of states in the GGA solution. The DOS is dominated by the atoms of the BEDT-TTF-molecules. The right panel shows the effective two-dimensional lattice used for the Wannierization and the dominated first neighbors hoppings t_{ij}.

We performed Wannier projections, where each site is centered at a BEDT-TTF molecule; the Wannier fit is shown by the red dashed lines in Figure S9 left panel and in Figure S10 we visualize a Wannier orbital obtained by FPLO along one BEDT-TTF molecule. This results to an effective lattice of two non-interacting two dimensional sub-lattices of four sites which are related by inversion symmetry, this leads to the same effective Hamiltonian for each organic layer. The effective lattice is shown in Figure S9 right panel.

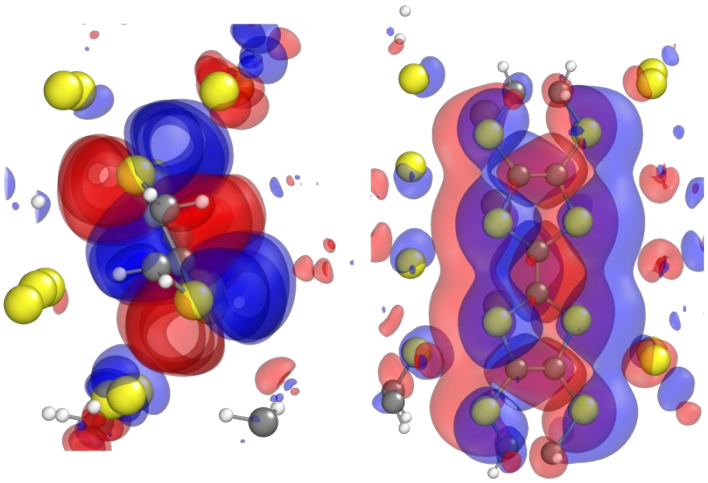

Figure S10 Top (left) and side (right) view Wannier orbitals along one BEDT-TTF molecule.

The kinetic contributions in H_{kin} are highly non-trivial, leading to a complex effective model, see Table S1. Due to space group symmetry relations we obtain two different on-site terms for the pair of sites 1,3 and 2,4, The first nearest-neighbors hoppings t_{ij} vary in the range of a factor 4; this does not depend on the distance between the sites but on the environment of the BEDT-TTF molecules.

site	ϵ_i [eV]	label	t_{ij} [eV]	distance [Å]
1	-0.069	t_1	-0.0559	4.186
2	-0.118	t_2	0.0526	6.106
3	-0.069	t_3	0.0417	6.064
4	-0.118	t_4	0.0366	5.991
		t_5	0.0359	6.206
		t_6	-0.0151	4.219

Table S1. Hamiltonian parameters obtained via the Wannierization on-site term ε_i and nearest neighbors hopping constants. t_{ij} are sorted by relative strengths and the corresponding distances.