## Supplementary material

The supplementary material is divided into sections corresponding to the results section of the main article and contain technical details and technical discussions of the results.

## Dispersion along the main translational directions

- 5 To enable the analysis of the band dispersion along the three main translational directions, the original lattice was transformed to a basis (**a**,**b**,**c**) in which **b** is the 1D stacking vector, (**a**,**b**) defines the 2D sheet and **c** is the intra-sheet translational vector. In the LT crystal the transformation is: (**a**,**b**,**c**)=(**c'-a'**, **b'-a'**,-**a'**) and for the HT crystal it is: (**a**,**b**,**c**)=(**a'+c'**,**b'**,**a'**), where the original basis vectors are accentuated.
- 10 The transformation of the unit cells enables the comparison of the band dispersion in the directions of translational symmetry in both crystals (see Fig. 5 in the article). There is no dispersion in the k-domains  $\Gamma$ -X and Z-U: there is no dispersion in the **a**\* direction. The dispersion in the **c**\* direction is opposite for  $\varphi_2$  and  $\varphi_3$ . From  $\Gamma$  to Z the dispersion in the LT (HT) crystal is towards higher (lower) energy. The strongest band dispersion is found in the **b**\* direction, as shown in the k-domains X-V, V- $\Gamma$ , U-R and R- $\Gamma$ . The LT band structure shows that the dispersion in the **b**\* direction of  $\varphi_1$  is toward lower energy and that of  $\varphi_2$  toward higher energy. In the HT crystal
- 15 the dispersion is larger and the two bands become degenerate at V and R. At V (R) the  $\varphi_2(\varphi_1)$  band is located above (below) the Fermi level. The valence (conduction) band becomes partly unoccupied (occupied) and the bands are overlapping in energy. This is reflected in the DOS. Similarly at lower energy the  $\varphi_3$  and  $\varphi_4$  bands become degenerate at V and R. The three separate energy ranges in the DOS at LT merge into one range at HT. The large peaks in the DOS occur at energies where the bands show a maximum or minimum; they are van Hove singularities.

## 20 Dispersion in molecular directions

For a better study of the inter-molecular interactions, the band dispersion was studied in the interesting molecular directions, i.e. along the three principal axes of inertia of the (planar) EDO-TTF molecules. We denoted these directions {u,v,w} (see Fig. 6 in the article and Table A.1). Direction **u** corresponds to 1D EDO-TTF stacking direction, **v** is the long molecular axis. Vectors **u** and **v** define the 2D sheet. The third principal axis, vector **w**, points in the inter sheet direction. In these directions we scan from the  $\Gamma$  point to the BZ edge,

25 essentially scanning through low energy levels towards the energies around the Fermi level. Please note that these molecular directions {**u**,**v**,**w**} are not coinciding precisely with the translational vectors (**b**,**a**,**c**}. We used the crystallographic unit cells in this study.

The slight differences in the HT2 DOS and HT4 DOS (see Fig. 7 in the article ) need to be addressed. Our choice to consider a tetramer unit cell instead of a dimer unit cell should not change the DOS nor the physics. With no apparent change in band widths and atomic **30** Mulliken charges we attribute the difference to taking the same number of k-points, halving the k-point density in the HT2 crystal, when optimising the wave function and computing the DOS. The difference in total energy is also typical for the different k-point density and is of the order of 3 meV.

		direct	space		k-space								
		Cartesian			Fractional			Normalised			BZ edge		
		Х	у	Ζ	А	b	С	a*	b*	c*	a*	b*	c*
LT	u	-0.51	0.85	-0.15	-0.58	0.80	-0.14	-0.46	0.85	-0.25	-0.25	0.50	-0.15
	v	0.65	0.26	-0.72	0.64	0.12	-0.76	0.53	0.24	-0.81	-0.30	-0.15	0.50
	w	0.57	0.46	0.68	0.64	0.51	0.57	0.60	0.55	0.59	0.50	0.45	0.50
RT	u	-0.13	0.98	-0.16	-0.19	1.00	-0.21	-0.13	0.97	-0.20	-0.05	0.50	-0.10
	v	0.59	0.21	0.78	0.81	0.31	1.00	0.34	0.26	0.90	0.20	0.15	0.50
	w	0.79	0.01	-0.61	1.00	0.05	-0.39	0.77	0.01	-0.63	0.50	0.00	-0.40

Tab.A1: Cartesian and fractional coordinates for the 3 principal axis of inertia {t,u,v}, see inset, of planar EDO-TTF molecules in the LT
35 and HT crystals and their corresponding direction in k-space both as a normalised vector and a vector intersecting the BZ edge. The latter was slightly rounded and used as program input.

	LT	HT
$\Delta_1$	0.19	0.11
$\Delta_2$	0.57	0.32
$\Delta_3$	0.71	0.36
$\Delta_4$	0.53	0.18
	TT 1/1 A (/ TD) C1	1

**Tab.A2**: Width  $\Delta_i$  (/eV) of bands  $\varphi_i$  in the LT and HT crystal.