Electronic Supplementary Information

for

Chalcogen bonding and variable charge transfer degree in

two polymorphs of 1:1 conducting salts with segregated stacks

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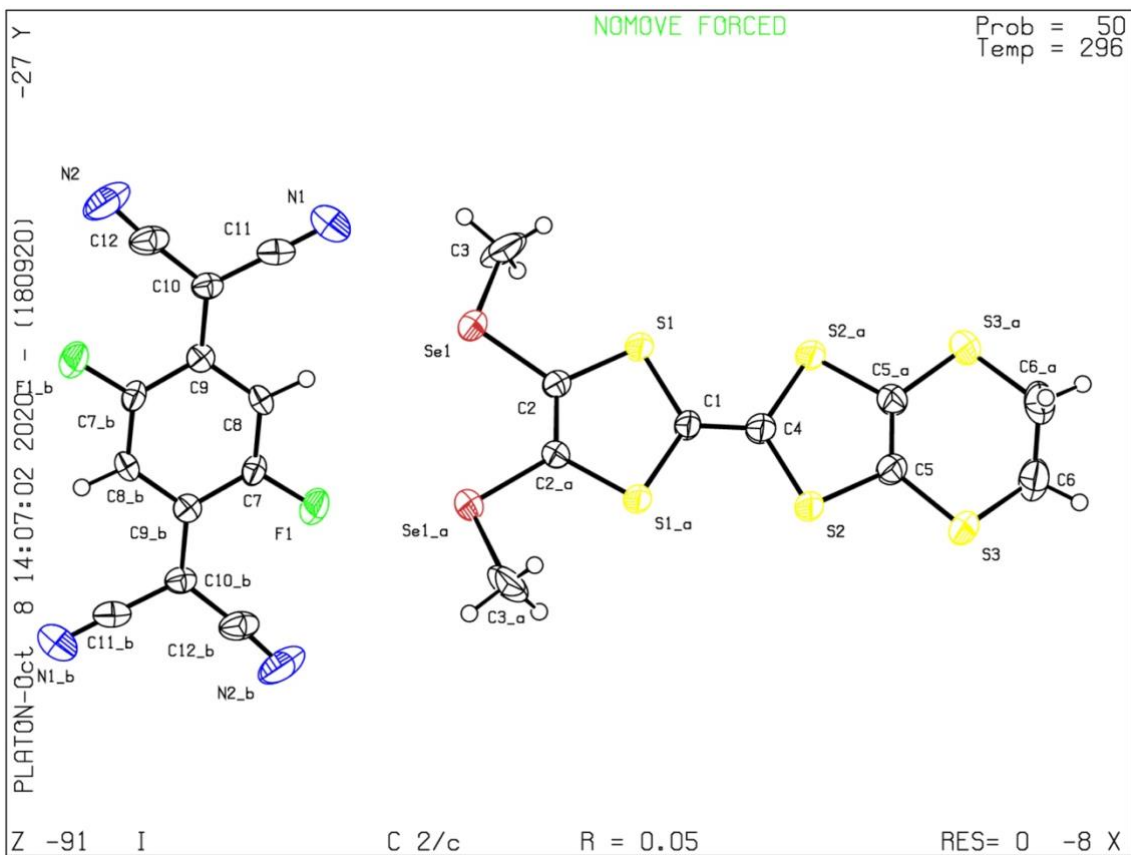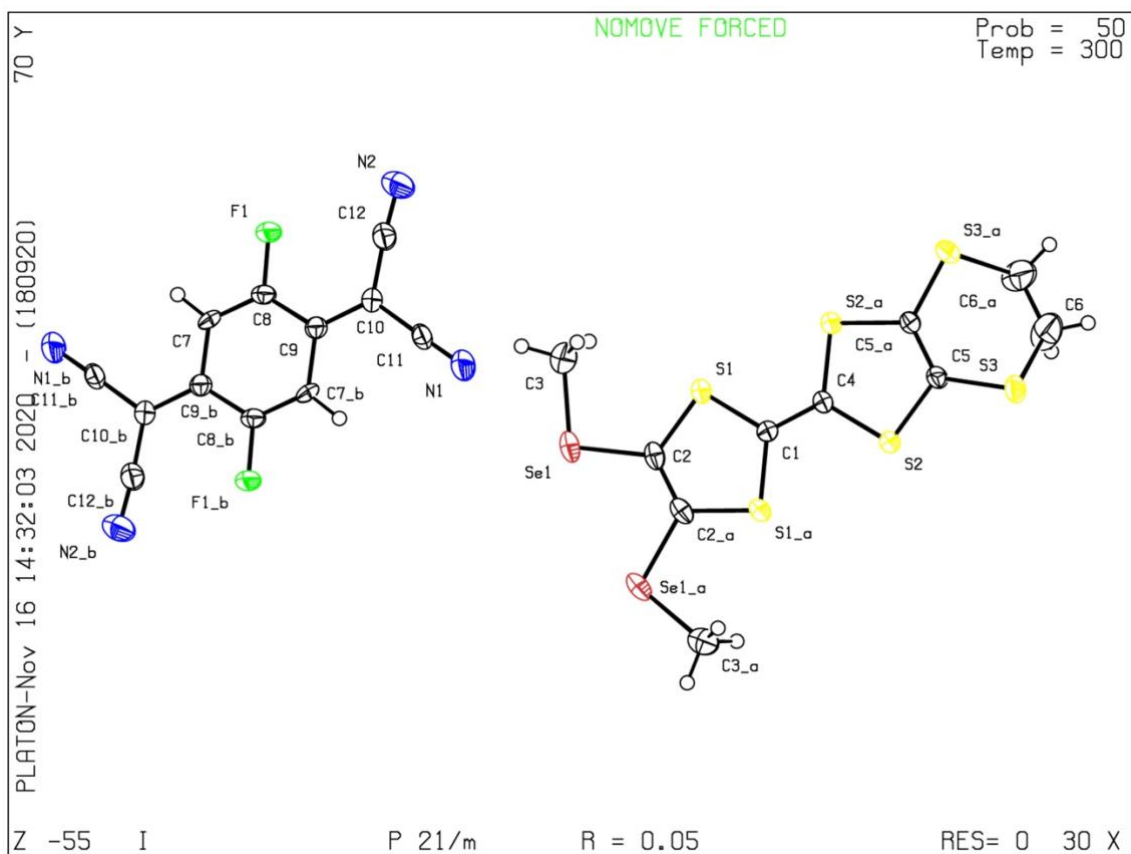
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Figure S1. Ellipsoid plots of α (top)– and β (bottom)–[EDT-TTF(SeMe)₂](F₂TCNQ)

Origin of the different charge transfer in the α- and β-(EDT-TTF(SeMe)₂](F₂TCNQ) salts.

What is the origin of the different amount of charge transfer in the α- and β-salts? The calculated band structures for both salts are shown in Figures S2a and S3a. These bands are mostly built from the HOMO of EDT-TTF-(SeMe)$_2$ and the LUMO of F$_2$TCNQ. Since the α-salt contains two sets of symmetry equivalent molecules along the *b* inter-chain direction, all bands in Figure S2a are actually the superposition of two almost identical bands except around the regions where the bands cross or intend to cross. In the β-salt, there are four symmetry equivalent molecules of each type, two along the inter-chain diagonal directions, *but also* two along the chain direction, *c*. This is why all bands in Figure S3a are folded along the Γ-Z direction (i.e. the chains direction). In order to facilitate the discussion, the different character of the bands undergoing a real/avoided crossing along the chain direction is indicated in the figures.
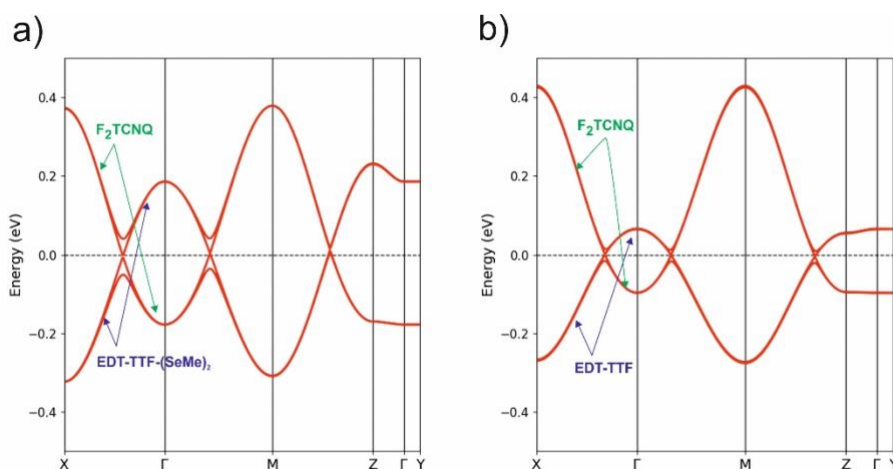

Figure S2. Comparison between the calculated band structures for: (a) α-[EDT-TTF-(SeMe)$_2$](F$_2$TCNQ), and (b) the same crystal structure where H atoms replace the -SeMe groups in the donors (i.e. using EDT-TTF donors). Γ, X, M, Z and Y refer to (0, 0, 0), *(a*/2, 0, 0)*, *(a*/2, 0, c*/2)*, *(0, 0, c*/2)* and *(0, b*/2, 0)*, respectively.

In the case of the α-salt (Figure S2a) it is worth noticing that the EDT-TTF-(SeMe)$_2$ HOMO band (upper, empty band at Γ) exhibits a weak but noticeable dispersion along the Γ-Z line, whereas neither the F$_2$TCNQ LUMO nor the EDT-TTF-(SeMe)$_2$ HOMO bands exhibit any dispersion along the Γ-Y line. This indicates that in this case there is some communication between the donor stacks along the c-direction, whereas both donor and acceptor stacks are practically independent along the b-direction. The interaction of donor stacks along c occurs through the Se•••H contacts (2.856 Å), shorter than the sum of the van der Waals radii between adjacent donors along this direction. In order to test this idea, we have repeated the calculation using exactly the same crystal structure where H atoms replace the whole –SeMe groups. The calculated band structure is shown in Figure S2b where two effects are clear. First, there is a practically nil dispersion along the b- (i.e. Γ-Y) and c- (i.e. Γ-Z) directions so that the weak communication between donor HOMOs along c is broken. Second, there is a quite strong reduction of the EDT-TTF(SeMe)$_2$ HOMO bandwidth along the chain direction (Γ-X) whereas that of the F$_2$TCNQ LUMO band remains unaltered. This results in a ~24% decrease of the charge transfer. Replacing H atoms for F in F$_2$TCNQ has a smaller effect: the bandwidths practically do not change whereas the charge transfer decreases only by ~9.5%, reflecting the increase in the acceptor character of TCNQ upon introducing the two fluorine substituents, although without noticeably altering the intra-chain interactions. In summary, the –SeMe substituents provide a weak but not nil connection between donors along c and, more importantly, induce a very substantial electron transfer through the increase of HOMO•••HOMO interactions along the chains because the Se orbitals have a sizeable participation in the HOMO. However, note that even with the beneficial role the Se orbitals, the total width of the HOMO bands is weaker than in the unsubstituted TTF-TCNQ salt. The presence of the –SeMe substituent is not favourable to the electronic delocalization within the donor stacks because of its structural requirements.
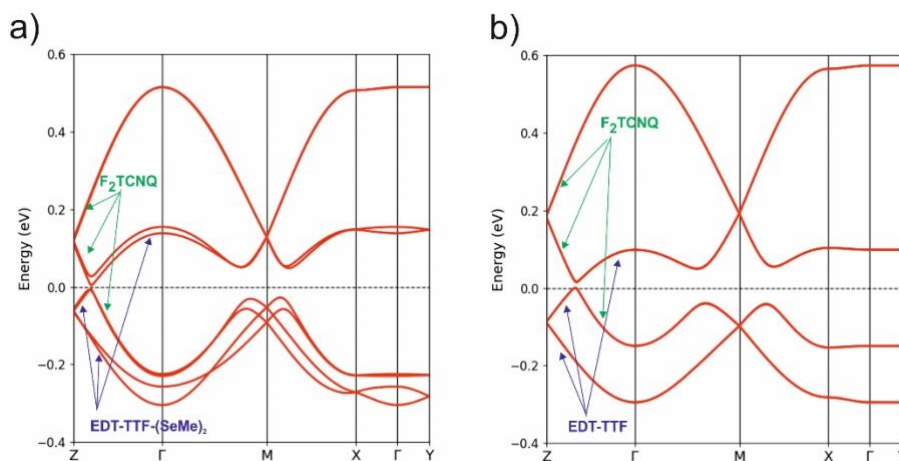
Figure S3. Comparison between the calculated band structures for: (a) β-[EDT-TTF-(SeMe)$_2$](F$_2$TCNQ), and (b) the same crystal structure where H atoms replace the -SeMe groups in the donors (i.e. using EDT-TTF donors). Γ, X, M, Z and Y refer to (0, 0, 0), (a*/2, 0, 0), (a*/2, 0, c*/2), (0, 0, c*/2) and (0, b*/2, 0), respectively.

The calculated total bandwidths for the β-salt of the F$_2$TCNQ LUMO band exhibit an increase of 35% and those of the EDT-TTF-(SeMe)$_2$ HOMO bands a decrease of 10% (Figure S3a) with respect to those of the α-salt. Consequently, although the different types of overlap in both the donor and acceptor stacks contribute to the electron transfer, the change in the acceptor stacks mostly controls the weaker transfer in the β-salt. The loss of direct Se•••Se interactions occurring in the donor stacks of the α-salt is partially compensated by the occurrence of Se•••S and additional S•••S ones. In contrast, the inter-planar separation in the acceptor stacks is clearly smaller (3.351 vs. 3.236 Å) and all C•••C contacts between adjacent acceptors are clearly shorter leading to the substantial increase of the F$_2$TCNQ LUMO bandwidth. The shorter inter-planar spacing in the acceptor stacks is imposed by the separation between the two –SeMe substituents of the donor because the Se atoms of one donor molecule make short contacts with the N atoms of two acceptor molecules *of the same stack*. This is possible because of the head-to-tail overlap mode of the donors. In contrast, the short Se•••N contacts of the α-salt are established with acceptor molecules *of different stacks* because of the

face-to-face overlap mode of the donors. It is also worth noticing in Figure S3 that when H atoms replace the –SeMe groups in the donors, all bands are effectively doubly degenerate (Figure S3b). This is not the case for most of the Brillouin zone in the full calculation (see Figure S3a, where the interaction is a bit stronger for the donor bands). This means that the different stacks are indeed weakly connected through the –SeMe substituents by van der Waals and hydrogen bond interactions. However, in the β-salt substitution of the –SeMe groups does not substantially decrease the bandwidth of the EDT-TTF(SeMe)$_2$ HOMO bands as found for the α salt. Thus, from the viewpoint of both the band dispersion along the stacks and the interconnection between stacks, the crystal structure of the β-salt is better prepared to sustain the electronic delocalization of a metallic state than that of the α-salt. Note that the larger tendency to delocalize is intimately related to the smaller charge transfer, both factors favouring a metallic state reminiscent of that in TTF-TCNQ. Ultimately, the activated or non-activated conductivity of the two [EDT-TTF(SeMe)$_2$](F$_2$TCNQ) salts is thus a consequence of the face-to-face or head-to-tail molecular overlap of the donors in the stacks.