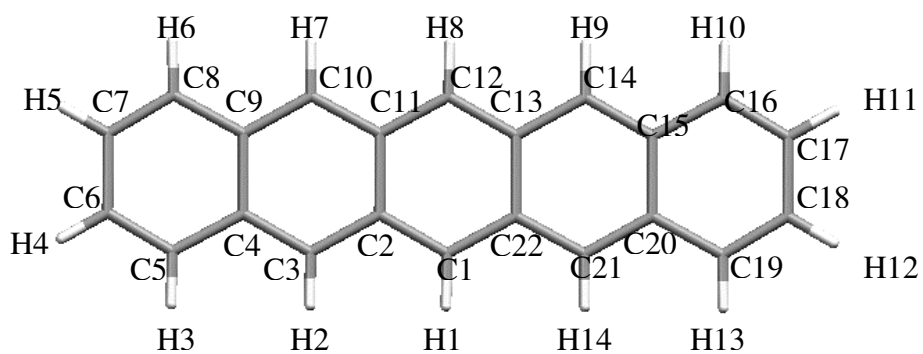


## SUPPORTING INFORMATION:

All DFT optimizations were performed 6-31G(d,p)/B3LYP level of theory until the largest component of the gradient was less than 0.0005 Hartree/Bohr. For the isolated planar DT-TTF molecule all atoms were initially placed in the x-y plane to assist obtaining the planar minimum during optimization. For all other isolated molecules no constraints were applied. For the embedded calculations molecules surrounding the central molecules were fixed at their crystallographic positions to represent the steric constraint of the full crystal packing, whilst the embedded molecule was allowed to relax with no symmetry constraints. The embedding molecules are fixed in the positions and geometries of the nearest neighboring molecules from the available X-ray crystal data with electronic properties of the environment i.e. polarization and charge transfer (delocalization) both fully incorporated. The molecules are fixed at the respective crystal positions in order to represent, as accurately as possible, the actual local embedding environment of the real crystal. If this constraint was not applied and the embedding environment allowed to fully relax, then the molecules would adopt the minimum energy configuration of a small cluster of molecules (e.g. molecules could freely reorientate and distort without the constraining effect of the long range crystal packing) which is very unlikely to accurately mirror the crystalline local environment we are trying to model. The method we use has the additional advantage that the effect of local intermolecular interactions on the reorganization energy of a single molecule can be discerned, rather than the reorganization energy of a sub-region of a crystal, thus enabling us to compare our embedded results with our single molecule calculations. Differences in bond lengths for isolated and embedded molecules when charged and neutral are reported below. The total charges per molecule quoted in table 1 in the text are estimated by summing over all Mulliken partitioned atomic charges within the embedded charged molecule. In order to check that the observed significant structural changes in the embedded charged DT-TTF molecule (with respect to the isolated +1-charged isolated DT-TTF molecule) are not caused by an effective improvement in the representation of the electronic environment of the embedded molecule due to basis set superposition effects, the isolated +1-charged DT-TTF molecule was also optimized at the 6-311++G(2d,2p)/B3LYP level resulting in maximal differences of only 0.003 Å with respect to the isolated 6-31G(d,p)/B3LYP calculation.

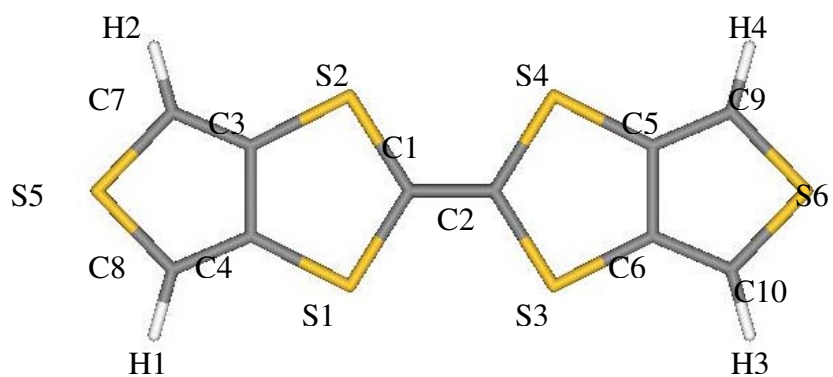
The electronic coupling between adjacent DT-TTF molecules in the crystal was estimated by the method described in reference 6 i.e. Two AM1-optimized DT-TTF molecules (in the planar conformation) were placed at the respective crystal positions as neighbours in a near cofacial stack along the conducting c-direction. The splitting of the HOMO levels due to this configuration were then calculated using the INDO/S Hamiltonian. Half of the calculated splitting gives an estimate of the transfer integral. For DT-TTF we found this value to be 34 meV. For pentacene the transfer integral has previously been calculated using this methodology in ref 5b giving values ranging from 47-80 meV depending on the direction taken through the crystal.

Pentacene:



Bond	$\Delta$ Length neutral / Å	$\Delta$ Length charged / Å
C1-C2	-0.002	0.000
C2-C3	0.000	-0.007
C3-C4	-0.003	0.007
C4-C5	0.002	-0.008
C5-C6	-0.001	0.006
C6-C7	0.003	-0.006
C7-C8	-0.001	0.006
C8-C9	0.000	-0.009
C9-C10	-0.002	0.007
C10-C11	-0.001	-0.006
C11-C12	-0.002	-0.001
C12-C13	-0.002	-0.002
C13-C14	-0.001	-0.007
C14-C15	-0.002	0.007
C15-C16	0.001	-0.009
C16-C17	-0.001	0.006
C17-C18	0.003	-0.006
C18-C19	-0.001	0.006
C19-C20	0.000	-0.008
C20-C21	-0.002	0.007
C21-C22	-0.002	-0.007
C22-C1	-0.002	0.001
C6-C7	0.003	-0.006
C4-C9	0.002	-0.002
C2-C11	0.001	0.000
C13-C22	0.001	-0.001
C15-C20	0.002	-0.003
C17-C18	0.003	-0.006
C1-H1	0.002	0.001
C3-H2	0.002	0.001
C5-H3	0.003	0.003
C6-H4	-0.001	-0.002
C7-H5	-0.002	-0.002
C8-H6	0.003	0.002
C10-H7	0.002	0.001
C12-H8	0.002	0.002
C14-H9	0.002	0.002
C16-H10	0.004	0.004
C17-H11	-0.001	0.00
C18-H12	0.000	-0.002
C19-H13	0.004	0.002
C21-H14	0.002	0.001

DT-TTF:



Bond	$\Delta$ Length neutral / Å	$\Delta$ Length charged / Å
C1-C2	0.000	0.039
C1-S1	0.003	-0.027
C1-S2	0.004	-0.028
C2-S3	0.003	-0.027
C2-S4	0.003	-0.028
S1-C4	0.002	-0.006
S2-C3	0.002	-0.006
S3-C6	0.002	-0.007
S4-C5	0.002	-0.006
C3-C4	-0.001	0.001
C5-C6	-0.002	0.001
C3-C7	0.000	0.003
C4-C8	-0.001	0.003
C5-C9	0.000	0.003
C6-C10	0.000	0.002
C7-S5	-0.001	-0.008
C8-S5	-0.001	-0.007
C9-S6	-0.001	-0.007
C10-S6	0.000	-0.007
C7-H2	0.000	0.002
C8-H1	0.000	0.001
C9-H4	0.000	0.000
C10-H3	0.000	0.002
S3-C6	0.000	0.039