Electronic Supplementary Material (ESI) for ChemComm.


# Correlating conducting properties with the molecular symmetry: segregation of *Z* and *E* isomers in the charge-assisted, halogen-bonded cocrystal [(*Z*,*E*)-$Me_2I_2TTF$)]$_2$Br

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## Supplementary material

**Table S1**. Structures of TTF derivatives with *Z*,*E* isomers, neutral or in cation radical salts.

| R1 | R2 | Refcode | Stereo | Counterion | Ref. |
|---|---|---|---|---|---|
| Me | H | UDEQUP | *E* | $QCl_4$ | 1 |
| Me | H | UDERAW | *E* | $QCl_2Br_2$ | 1 |
| Me | H | UDERIE | *E* | $QBr_4$ | 1 |
| tBu | H | – | *E* | neutral | 2 |
| tBu | H | – | *E* | TCNQ | 2 |
| $CF_3$ | H | CELPOZ | *E* | neutral | 3 |
| $CF_3$ | H | CEFXOB | *Z* | neutral | 3 |
| $CH_2OH$ | H | ZIYYOX | *E* | neutral | 4 |
| $CO_2Bu$ | H | DIHYIC | *E* | neutral | 5 |
| $CO_2Bu$ | H | DIHYIC01 | *Z* | neutral | 6 |
| I | H | PIRGOM | *E* | neutral | 7 |
| I | H | LELBIO | *E* | $[Re_6Se_8(CN)_6]^{4-}$ | 8 |
| Ph | H | CAKTAJ | *E* | $[Au(C_6F_5)_2]^-$ | 9 |
| Ph | H | DPTFUL | *E* | neutral | 10 |
| Ph | H | DPTFUL01 | *E* | neutral | 11 |
| $C_6H_4$-*p*-Me | H | MOPJOR | *E* | neutral | 11 |
| $C_6H_4$-*p*-Et | H | MOPJUX | *E* | neutral | 11 |
| $C_6H_4$-*p*-Cl | H | GOBVUP | *E* | neutral | 12 |
| $C_6H_4$-*p*-$CF_3$ | H | MOPKEI | *E* | neutral | 11 |
| 3-Py | H | YOLJUG | *E* | neutral | 13 |
| 4-Py | H | LILFIW | *E* | neutral | 14 |
| 2-thienyl | H | BENLOX | *Z* | neutral | 15 |
| 5-t-butyl-2-Th | H | SEZZEE | *E* | neutral | 15 |
| Ph | Me | JIYTAM | *E* | neutral | 16 |
| C≡C-$SiMe_3$ | Me | JOHDOB | *E* | neutral | 17 |
| C≡C-$SiMe_3$ | Me | JOHDUH | *Z* | neutral | 17 |
| $PPh_2$ | Me | NASNUQ | *Z* | neutral | 18 |
| C≡C–$SiMe_3$ | Ph | NOCSAZ | *E* | neutral | 19 |
| I | Ph | NOCRUS | *E* | neutral | 19 |
| $SiHPh_2$ | Ph | AGIYOF | *E* | neutral | 20 |
| $SiMe_2SiMe_3$ | Ph | AGIZAS | *E* | neutral | 20 |
| SMe | *p*-Cl-$C_6H_4$ | – | *E* | neutral | 21 |
| CHO | $CH(OEt)_2$ | SUDFUS | *E* | neutral | 22 |

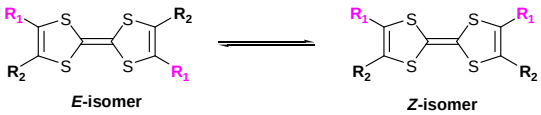
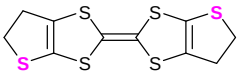


**Table S2**. Structures of bis(ethylenethio)tetrathiafulvalene (BET-TTF) derivatives

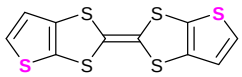


**BET-TTF**

| Refcode | Stereo | Counterion | Ref. |
|---|---|---|---|
| POKNUY | *E* | neutre | 23 |
| VILBAV | disordered | $[Cr(NCS)_6]^{3-}$ | 24 |
| DOGWAX | *E* | $Br^-$ | 25 |
| HIGMIT | *E* | $[Au(mnt)^2]$ | 26 |
| HULTUD | disordered | $ReO_4^-$ | 27 |
| KAZQEH | disordered | $ReO_4^-$ | 27 |
| KAZQIL | disordered | $ReO_4^-$ | 27 |
| KAZQOR | disordered | $ReO_4^-$ | 27 |
| MIWWIY | disordered | $[Fe(CN)_6]^{3-}$ | 28 |
| MIWWOE | disordered | $[Fe(CN)_5NO]^{3-}$ | 28 |
| PUQCIN | disordered | $[W_6O_{19}]^{2-}$ | 29 |
| PUQCOT | disordered | $[Mo_6O_{19}]^{2-}$ | 29 |
| ROQRAQ | *E* | $GaCl_4^-$ | 30 |
| ZEJVIT | disordered | $SbF_6^-$ | 31 |
| ZEJVOZ | disordered | $AsF_6^-$ | 31 |
| ZEJVUF | disordered | $PF_6^-$ | 31 |

**Table S3**. Structures of bis(α-thieno)tetrathiafulvalene (α-DT-TTF) derivatives

| Refcode | Stereo | Counterion | Ref. |
|---|---|---|---|
| DIHWIC | disordered | $[Pt(mnt)_2]$ | 32 |
| DIHWOI | disordered | $[Ni(mnt)_2]$ | 32 |
| DIHXAV | *E* | $[Ni(mnt)_2]$ | 32 |
| DIHWUO | disordered | $[Au(mnt)_2]$ | 32 |
| GEBTEO | *E* | neutre | 33 |
| GEBTEO01 | disordered | neutre | 34 |



α-DT-TTF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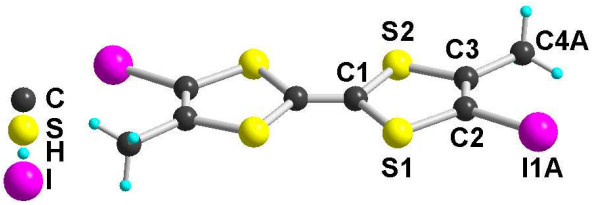


**Figure S1**. Molecular structure of neutral $Me_2I_2TTF$ deduced from its X-ray crystal structure

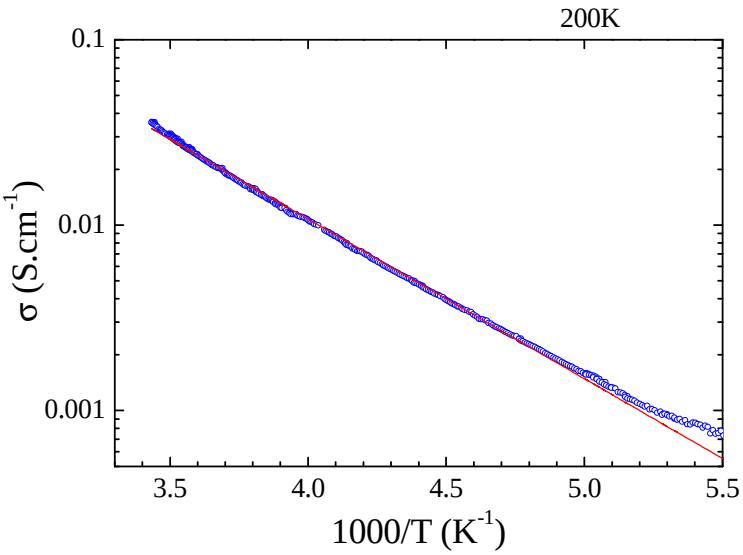


**Figure S2**. Temperature dependence of the conductivity, σ, of $[(Z,E)\text{-}Me_2I_2TTF]_2Br{\bullet}CH_3CN$ plotted as log σ versus the inverse temperature. The red line is the fit to the data with a law of the type $\sigma = \sigma_0 \exp(-E_a/T)$, giving the activation energy $E_a$ = 2000K (0.17eV).

Experimental: Electrical resistivity was measured in four points along the long axis of a needle-shaped single crystal. A DC current of 0.5μA was applied and the voltage was measured using a Keithley 2400 Source Meter. Variable temperature has been provided by a home-made cryostat equipped with a 4K pulse-tube, using a cernox thermometer in good thermal contact with the samples.

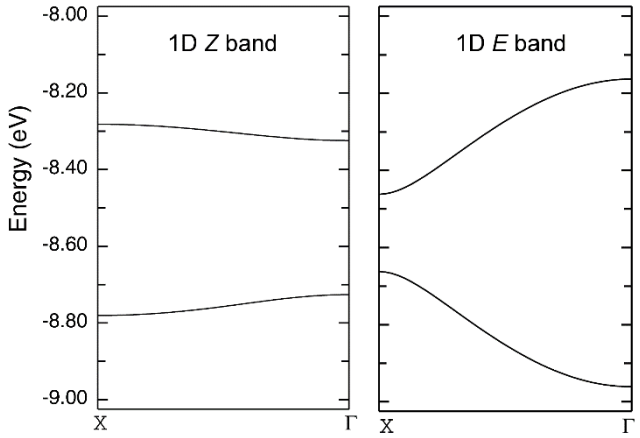


**Figure S3**. Calculated 1D band structure for each separated *Z* and *E* stacks.