

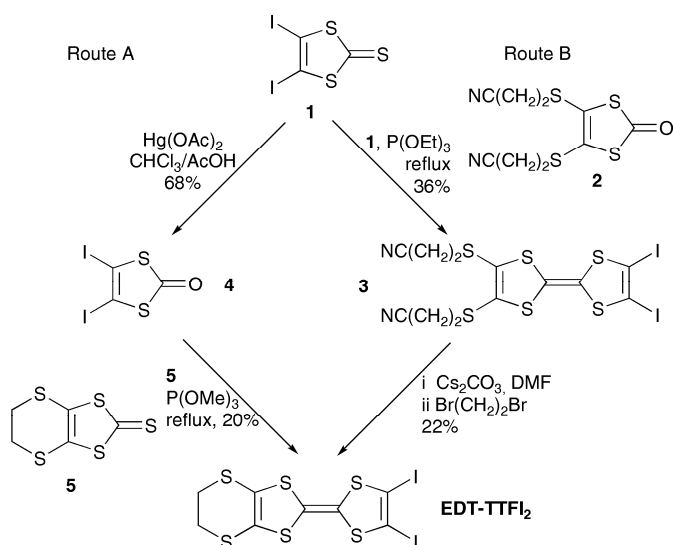
**C—I $\cdots$ NC Halogen bonding interactions in two polymorphs of the mixed-valence 2:1 charge-transfer salt (EDT-TTFI<sub>2</sub>)<sub>2</sub>(TCNQF<sub>4</sub>), with segregated vs. alternated stacks**

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**Supplementary material**

## Novel synthetic procedure for EDT-TTFI<sub>2</sub>.

The reported synthetic procedure (Domercq *et al.*, 2001) for EDT-TTFI<sub>2</sub> (route A in Scheme S1) involved the phosphite-assisted cross-coupling of the diiododithiocarbonate **4** with the trithiocarbonate **5**. Combined yield from the starting diiodotrithiocarbonate **1** does not exceed 14%. We have explored an alternative synthetic path (Route B in Scheme S1), which involves in a first step the phosphite cross-coupling of **1** with the dithiocarbonate **2**. A similar route has been indeed already described to provide the dibromo analogs in good yield (Batsanov *et al.*, 2001; Alberola *et al.*, 2006). The  $-(CH_2)_2CN$  substituents in **3** act as thiolate's protective groups. They therefore provide an attractive way to substitute diiodo tetrathiafulvalene derivatives with a variety of thioalkyl substituents. Albeit **3** was obtained in a reasonable yield (36%), its deprotection with Cs<sub>2</sub>CO<sub>3</sub> for further reaction with dibromoethane afforded in our hands the expected EDT-TTFI<sub>2</sub> only in low yield (22%), at variance with the reported preparation of the EDT-TTFBr<sub>2</sub>. This route has not been further used but provided crystals of the intermediate derivative **3**.



**Scheme S1.** Synthetic procedures used for EDT-TTFI<sub>2</sub>

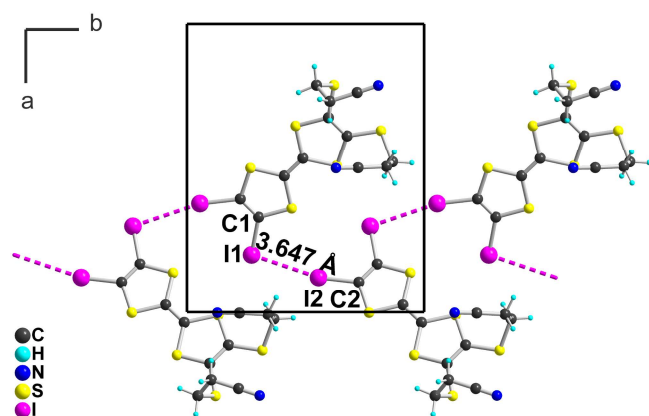
*Preparation of 3 (Route B).* A solution of **1** (1.04 mmol; 400 mg) and **2** (2.08 mmol ; 600 mg) in toluene (15 mL) was heated at reflux under Ar for 30 min. Freshly distilled P(OEt)<sub>3</sub> (1 mL) was then added dropwise and the solution was heated at reflux for 3h30. The solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>. The TTF **3** was isolated as light red powder in 36% yield (230 mg), and crystallized by concentration of a CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 3.09 (t, *J* = 7.0 Hz, 4H), 2.75 (t, *J* = 7.0 Hz, 4H). <sup>13</sup>C NMR (75 MHz, DMSO) δ 127.68 (TTF), 119.33

(TTF), 118.83 (CN), 107.95 (TTF), 80.04 (CI), 30.89 (CH<sub>2</sub>), 18.18 (CH<sub>2</sub>). HRMS (EI): *m/z* calc. for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>I<sub>2</sub>S<sub>6</sub> 625.7104; found 625.71013. Elem. Anal. Calc. for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>I<sub>2</sub>S<sub>6</sub>: C, 23.01%; H, 1.29%; N, 4.47%; S, 30.71%. Found: C, 23.11%; H, 1.25%; N, 4.54%; S, 30.75%. Cyclic voltammetry (CH<sub>2</sub>Cl<sub>2</sub>, 100mV.s<sup>-1</sup>, NBu<sub>4</sub>PF<sub>6</sub>, SCE, Pt, carbone) E<sub>1</sub><sup>1/2</sup> = 0.70 V, E<sub>2</sub><sup>1/2</sup> = 1.07 V vs. SCE.

*Preparation of EDT-TTFI<sub>2</sub> (Route B).* To a solution of TTF **3** (0.12 mmol; 77 mg) in DMF (5 mL) was slowly added a solution of Cs<sub>2</sub>CO<sub>3</sub> (0.369 mmol; 120 mg) in methanol (1 mL), and the solution was stirred at 50°C for 3h. Then, 1,2-dibromoethane (0.12 mmol; 11 µL) was slowly added and the solution was stirred at 50°C overnight. The solvent was evaporated under vacuum. CH<sub>2</sub>Cl<sub>2</sub> was added and the organic layer was washed with water, dried under MgSO<sub>4</sub> and the solvent was removed. The residue was purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (50:50). The product was isolated as an orange powder in 22% yield and exhibits analytic characteristics identical to those reported (Domercq *et al.*, 2001).

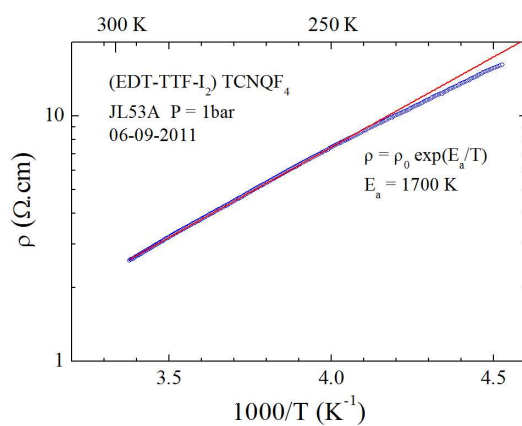
### Crystal structure of halogen bonded TTF **3**.

The structure of neutral **3** is indeed of interest as co-exist on the same molecule iodine atoms known to be able to act as halogen bond donor and nitrile substituents able to act as Lewis bases. It was found to crystallize in the orthorhombic system, space group Pbca. It is isostructural with the dibromo analog reported earlier (Batsanov *et al.* 2001). As shown in Figure S1, the molecules associated into chains running along the *b* axis, with a characteristic I...I halogen bond, where atom I(2) acts as halogen bond donor through its σ hole while iodine atom I(1) acts as Lewis base. The I...I distance, 3.6466(3) Å, amounts to 91% of twice the iodine van der Waals radius. Their relative orientation points for a strong, so-called type II interaction, as the angles C(2)–I(2)...I(1) and C(1)–I(1)...I(2) amount to 167.7(1)° and 93.8(1)° respectively, that is close to the optimal 180 and 90° values.

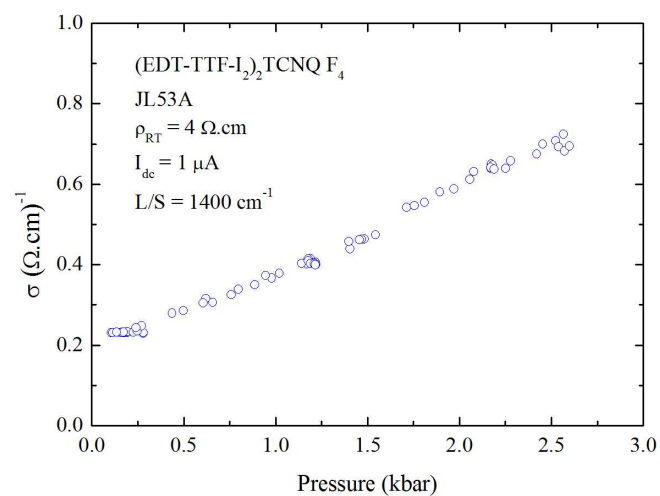


**Figure S1**

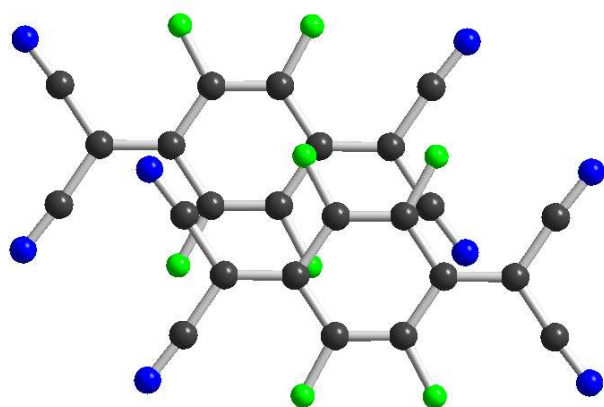
Projection view along  $c$  of one halogen bonded chain of molecules **3**.



**Figure S2.** Temperature dependence of the resistivity of phase I.



**Figure S3.** Pressure dependence of the room temperature conductivity of Phase I.



**Figure S4.** Overlap between TCNQF<sub>4</sub> molecules in Phase I.

## References

- Alberola, A., Collis, R. J., Garcia, F. & Howard, R. E. (2006). *Tetrahedron* **62**, 8152–8157.
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