-Supplementary Material-

Inter molecular interactions and Charge transfer of the 2:1 tetrathiafulvalene bromanil complex, $(TTF)_2$-BA.

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Figure S1: Temperature evolution of the cell parameters between 100 and 280K, cooling (circles) and warming (triangles). The standard error estimated on statistical grounds is 0.008Å and 0.06°.

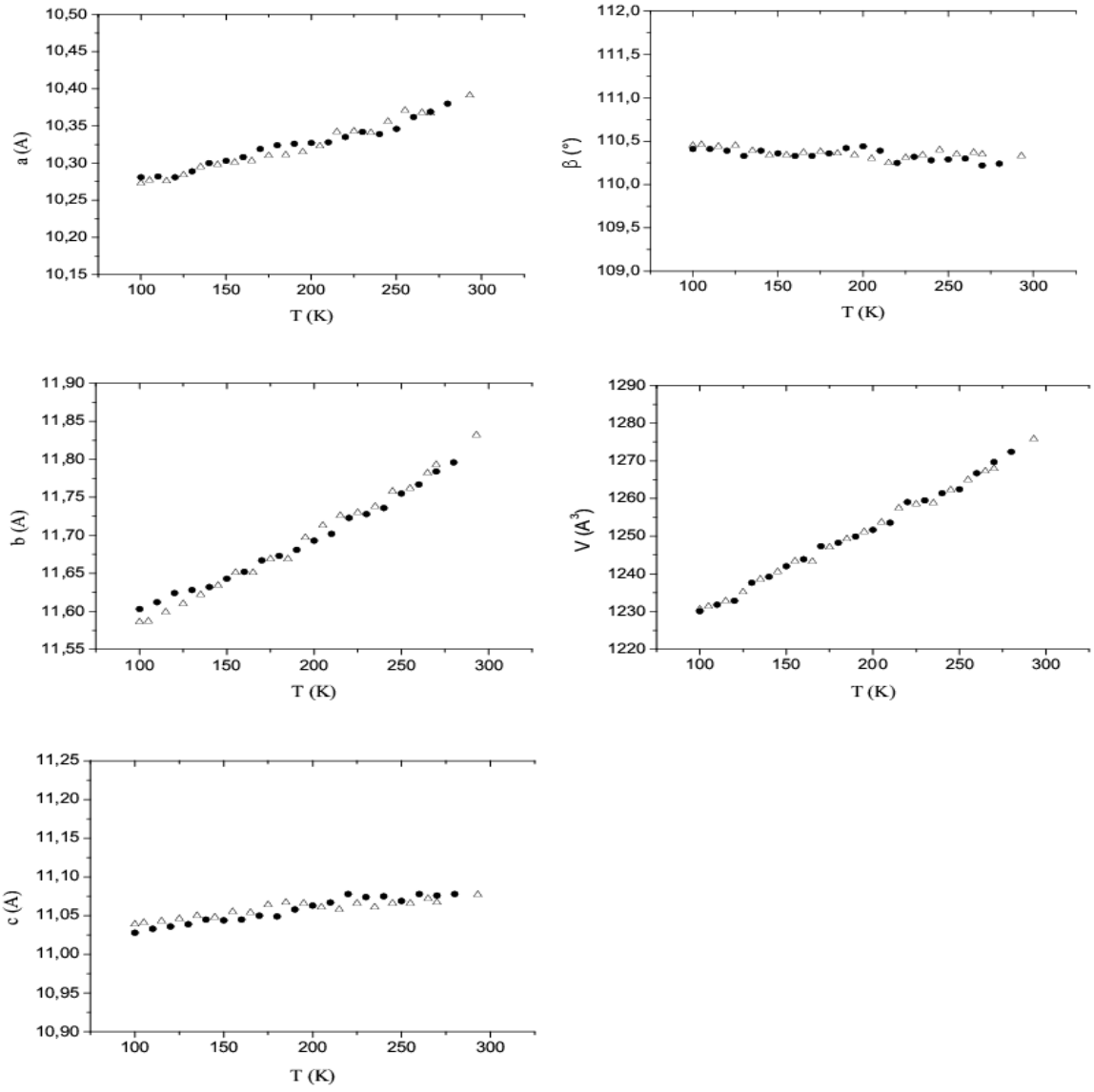

Table 1: TTF Bond lengths in TTF_2-BA at 293K, 100K and 25K, compared to those of TTF crystal at 100K. These TTF crystal bond lengths have been calculated as the mean bond lengths of the four independent molecules of the unit cell (CCDC reference number: 614385.)

	TTF-100K	293K	100K	25K
C8=C11	1.340(4)	1.354(4)	1.360(3)	1.360(3)
C8-S1	1.765(7)	1.755(3)	1.755(2)	1.750(2)
C11-S3		1.756(3)	1.761(2)	1.750(2)
C8-S2		1.754(3)	1.763(2)	1.762(2)
C11-S4		1.760(3)	1.761(2)	1.760(2)
S1-C7	1.752(5)	1.735(4)	1.750(2)	1.751(2)
S3-C10		1.733(4)	1.742(3)	1.750(2)
S2-C9		1.737(4)	1.746(2)	1.737(2)
S4-C12		1.735(4)	1.748(3)	1.744(2)
C7=C9	1.322(3)	1.321(5)	1.344(3)	1.343(3)
C10=C12		1.328(6)	1.348(4)	1.337(3)

Table 2: Geometrical parameters of the hydrogen bond between the layers. Symmetry codes: i)1-x, -y, -z ; iv) $\frac{3}{2}$-x, -½+y, ½-z ; v)1-x,-y,1-z

T	D-H···A	D-H (Å)	D···A (Å)	D···A (Å)	D-H···A (°)
293K	$C10^{v}$-$H10^{v}$ ···O1	0.930	2.738(4)	3.647(4)	166(1)
100K		0.950	2.630(4)	3.567(4)	169(1)
25K		0.950	2.592(4)	3.530(4)	169(1)
293K	$C9^{iv}$ -$H9^{iv}$ ···O1	0.930	2.704(4)	3.345(4)	127(1)
100K		0.950	2.661(4)	3.298(4)	125(1)
25K		0.950	2.649(4)	3.285(4)	125(1)

Table 3: Atomic deviation (Åx10^3) from the mean plane of TTF molecule at 293, 100 and 25K. Mean plane is defined as P.x+Q.y+R.z+S=0; with x;y;z fractional atomic coordinates.

		293 K	100 K	25 K
Equation	P	-5.684(4)	-5.619(3)	-5.595(2)
	Q	9.577(3)	9.461(2)	9.416(2)
	R	4.192(5)	4.065(3)	4.014(3)
	S	0.591(2)	0.546(2)	0.533(1)
Distances	S1	-41.5(9)	-56.1(1)	-57.7(5)
(10^{-3} Å)	S2	-4(1)	-8.5(6)	-10.1(5)
	S3	-31(1)	-42.9(6)	-47.6(5)
	S4	3(1)	-6(1)	-8.7(5)
	C7	46(4)	72(3)	75(2)
	C8	-60(3)	-85(2)	-91.5(2)
	C9	51(4)	67(3)	73(2)
	C10	40(3)	59(1)	66(2)
	C11	-49(3)	-68(2)	-70(1)
	C12	45(3)	67(2)	72(1)

Table 4: T, L and S tensors of TTF and BA molecules in TTF_2-BA, referred to their inertial axes.

	293 K	100 K	25 K
TTF	T ($x10^{-4}$ Å^2)	T ($x10^{-4}$ Å^2)	T ($x10^{-4}$ Å^2)
	$\begin{pmatrix} 456(8) & -10(8) & 9(8) \\ & 330(12) & -22(12) \\ & & 416(18) \end{pmatrix}$	$\begin{pmatrix} 179(3) & -12(3) & 4(3) \\ & 148(4) & 1(4) \\ & & 175(7) \end{pmatrix}$	$\begin{pmatrix} 117(3) & 3(2) & 1(1) \\ & 96(3) & -6(4) \\ & & 123(5) \end{pmatrix}$
	L (°^{2})	L (°^{2})	L (°^{2})
	$\begin{pmatrix} 20(3) & -1(1) & -1(1) \\ & 4.2(7) & 1(1) \\ & & 15(1) \end{pmatrix}$	$\begin{pmatrix} 5(1) & -0.5(2) & -0.1(4) \\ & 1.1(2) & 0.2(2) \\ & & 4.1(2) \end{pmatrix}$	$\begin{pmatrix} 1(1) & -0.1(2) & 0.4(4) \\ & 0.4(2) & -0.1(1) \\ & & 1.6(1) \end{pmatrix}$
	S ($x10^{-4}$ rad Å)	S ($x10^{-4}$ rad Å)	S ($x10^{-4}$ rad Å)
	$\begin{pmatrix} 7(5) & 9(8) & -11(4) \\ 11(2) & -12(3) & 1(2) \\ -25(2) & -26(2) & 4(6) \end{pmatrix}$	$\begin{pmatrix} 2(2) & 1(2) & -2(1) \\ 2(1) & -3(1) & 1(1) \\ -6(1) & -8(1) & 1(2) \end{pmatrix}$	$\begin{pmatrix} 0(1) & -1(2) & 0(1) \\ 1(1) & -1(1) & -1(1) \\ -2(1) & -1(1) & 1(2) \end{pmatrix}$
BA	T ($x10^{-4}$ Å^2)	T ($x10^{-4}$ Å^2)	T ($x10^{-4}$ Å^2)
	$\begin{pmatrix} 391(7) & 15(6) & -4(7) \\ & 354(7) & -13(7) \\ & & 347(11) \end{pmatrix}$	$\begin{pmatrix} 158(3) & 3(3) & -14(4) \\ & 153(2) & 3(3) \\ & & 166(5) \end{pmatrix}$	$\begin{pmatrix} 107(3) & 9(3) & -5(4) \\ & 117(4) & -8(5) \\ & & 110(6) \end{pmatrix}$
	L (°^{2})	L (°^{2})	L (°^{2})
	$\begin{pmatrix} 17(1) & 3.2(4) & -1.0(5) \\ & 6.6(6) & -0.5(5) \\ & & 8.5(4) \end{pmatrix}$	$\begin{pmatrix} 4.7(4) & 1.1(1) & -0.(3) \\ & 1.3(2) & -0.1(2) \\ & & 2.1(2) \end{pmatrix}$	$\begin{pmatrix} 1.2(5) & 0.2(2) & -0.1(3) \\ & 0.1(3) & 0.1(2) \\ & & 0.3(2) \end{pmatrix}$