Supplementary Information

For

The role of dispersion type metal···π interaction in the enantiotropic phase transition of two polymorphs of tris(thienyl)bismuthine

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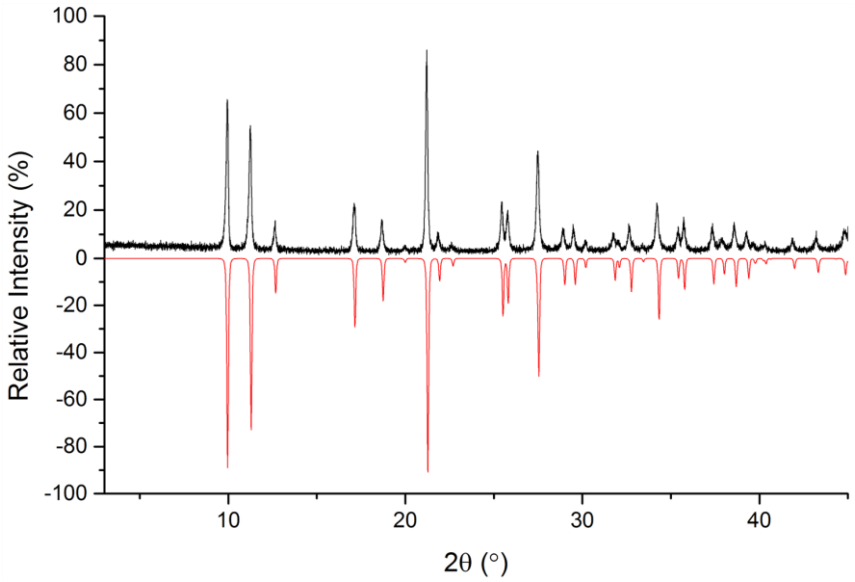

Figure S1. Powder X-ray diffraction pattern at 293 K of $Bi(2\text{-}C_4H_3S)_3$ (**1**-HT), measured for isolated material (black) and calculated from single crystal X-ray data measured at 293 K (red).

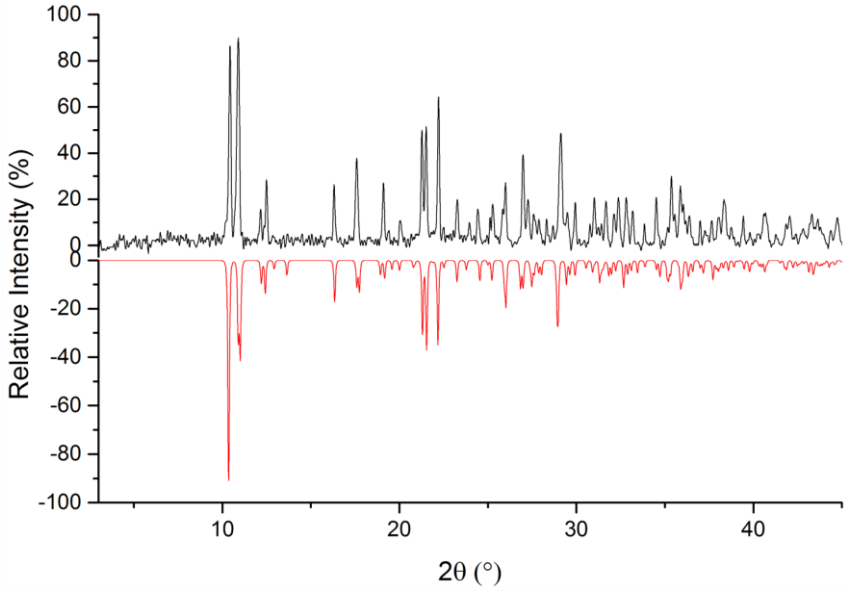

Figure S2. Powder X-ray diffraction pattern at 110 K of $Bi(2\text{-}C_4H_3S)_3$ (**1**-LT), measured for isolated material (black) and calculated from single crystal X-ray data measured at 100 K (red).[1]

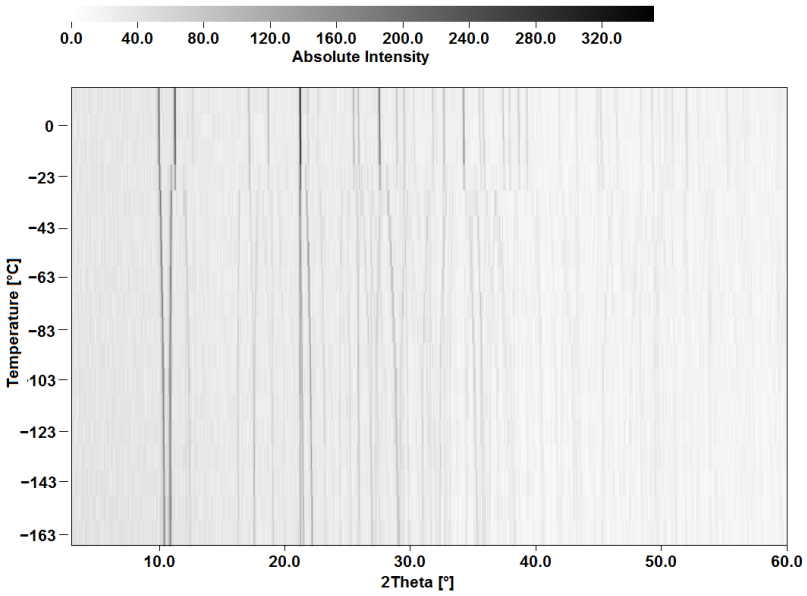

Figure S3. Temperature dependent PXRD of $Bi(C_4H_3S)_3$ (**1**) showing the phase transition at 250 K of the triclinic phase [polymorph I (**1**-HT)] into the trigonal phase [polymorph II (**1**-LT)].

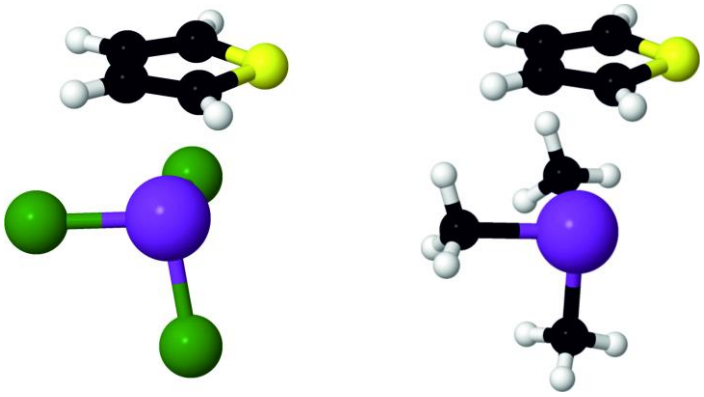

Figure S4. Optimized geometries of $BiCl_3 \cdot C_4H_4S$ (left) and $Bi(CH_3)_3 \cdot C_4H_4S$ (right) calculated at the D3-B3LYP/def2-TZVP level of theory.

References:

1. A. M. Preda, W. B. Schneider, M. Rainer, T. Rüffer, D. Schaarschmidt, H. Lang and M. Mehring, *Dalton Trans.*, 2017, **46**, 8269-8278.

Table S1. The unit cell parameters in dependence with the temperature [K] for polymorph **1**-LT.

$P\bar{1}$ **XRD** **100K (-173°C)**	$P\bar{1}$ **PXRD** **110K (-163°C)**	$P\bar{1}$ **PXRD** **120K (-153°C)**	$P\bar{1}$ **PXRD** **130K (-143°C)**	$P\bar{1}$ **PXRD** **140K (-133°C)**	$P\bar{1}$ **PXRD** **150K (-123°C)**	$P\bar{1}$ **PXRD** **160K (-113°C)**	$P\bar{1}$ **PXRD** **170K (-103°C)**
a = 8.9848(8)	a = 8.9807(28)	a = 8.9888(16)	a = 8.9909(19)	a = 9.0002(18)	a = 9.0095(15)	a = 9.0152(12)	a = 9.0208(16)
b = 9.3411(7)	b = 9.3957(20)	b = 9.3938(20)	b = 9.3932(17)	b = 9.401(3)	b = 9.4027(17)	b = 9.4076(14)	b = 9.4095(19)
c = 9.6115(11)	c = 9.532(3)	c = 9.5412(25)	c = 9.5625(25)	c = 9.5797(24)	c = 9.583(3)	c = 9.6048(14)	c = 9.6181(18)
a = 64.493(9)	a = 64.436(19)	a = 64.455(15)	a = 64.495(17)	a = 64.482(22)	a = 64.451(15)	a = 64.429(13)	a = 64.454(14)
b = 71.427(9)	b = 71.909(21)	b = 71.860(21)	b = 71.763(22)	b = 71.66(3)	b = 71.600(17)	b = 71.495(18)	b = 71.416(15)
γ = 66.556(8)	γ = 67.133(18)	γ = 67.067(18)	γ = 66.969(21)	γ = 66.89(3)	γ = 66.827(17)	γ = 66.791(17)	γ = 66.703(18)
V = 657.31(13)	**V = 658.59(20)**	**V = 659.40(16)**	**V = 660.57(18)**	**V = 662.35(23)**	**V = 662.83(17)**	**V = 664.60(14)**	**V = 665.63(15)**

$P\bar{1}$ **PXRD** **180K (-93°C)**	$P\bar{1}$ **PXRD** **190K (-83°C)**	$P\bar{1}$ **PXRD** **200K (-73°C)**	$P\bar{1}$ **PXRD** **210K (-63°C)**	$P\bar{1}$ **PXRD** **220K (-53°C)**	$P\bar{1}$ **PXRD** **230K (-43°C)**	$P\bar{1}$ **PXRD** **240K (-33°C)**	$P\bar{1}$ **PXRD** **250K (-23°C)**
a = 9.0258(14)	a = 9.0342(15)	a = 9.0459(10)	a = 9.0605(21)	a = 9.0739(25)	a = 9.0889(14)	a = 9.1094(16)	a = 9.107(4)
b = 9.4060(14)	b = 9.4074(14)	b = 9.4027(12)	b = 9.3966(19)	b = 9.3945(17)	b = 9.3943(16)	b = 9.3951(15)	b = 9.392(3)
c = 9.6369(15)	c = 9.6766(19)	c = 9.7134(14)	c = 9.7583(20)	c = 9.8020(22)	c = 9.8438(15)	c = 9.8987(17)	c = 9.975(3)
a = 64.485(11)	a = 64.467(15)	a = 64.492(12)	a = 64.472(17)	a = 64.499(18)	a = 64.459(13)	a = 64.423(13)	a = 64.58(3)
b = 71.280(13)	b = 71.039(16)	b = 70.815(11)	b = 70.508(20)	b = 70.194(21)	b = 69.861(23)	b = 69.409(13)	b = 69.12(4)
γ = 66.643(15)	γ = 66.432(17)	γ = 66.231(12)	γ = 65.984(17)	γ = 65.738(16)	γ = 65.469(14)	γ = 65.101(11)	γ = 64.76(4)
V = 666.62(12)	**V = 668.51(15)**	**V = 670.27(12)**	**V = 672.05(17)**	**V = 674.11(18)**	**V = 675.78(13)**	**V = 678.1(13)**	**V = 681.1(3)**