Tetrabromobenzene-based molecular alloys – a tool for tailoring the temperature of the thermosalient phase transition

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SUPPLEMENTARY INFORMATION

Table S1. Elemental analysis by EDS of TBB-TCB molecular alloys

Sample	Ratio $Br(wt\%)/Cl(wt\%)$ (nominal composition)	Ratio $Br(wt\%)/Cl(wt\%)$ (determined by EDS)
76%TBB-24%TCB	3.88	3.23
80%TBB-20%TCB	4.94	4.11
84%TBB-16%TCB	6.49	5.29
88%TBB-12%TCB	8.88	6.97
90%TBB-10%TCB	11.12	9.47
92%TBB-8%TCB	14.21	11.33
94%TBB-6%TCB	19.36	14.80
95%TBB-5%TCB	23.48	19.20
96%TBB-4%TCB	29.00	25.40
98%TBB-2%TCB	60.56	65.67

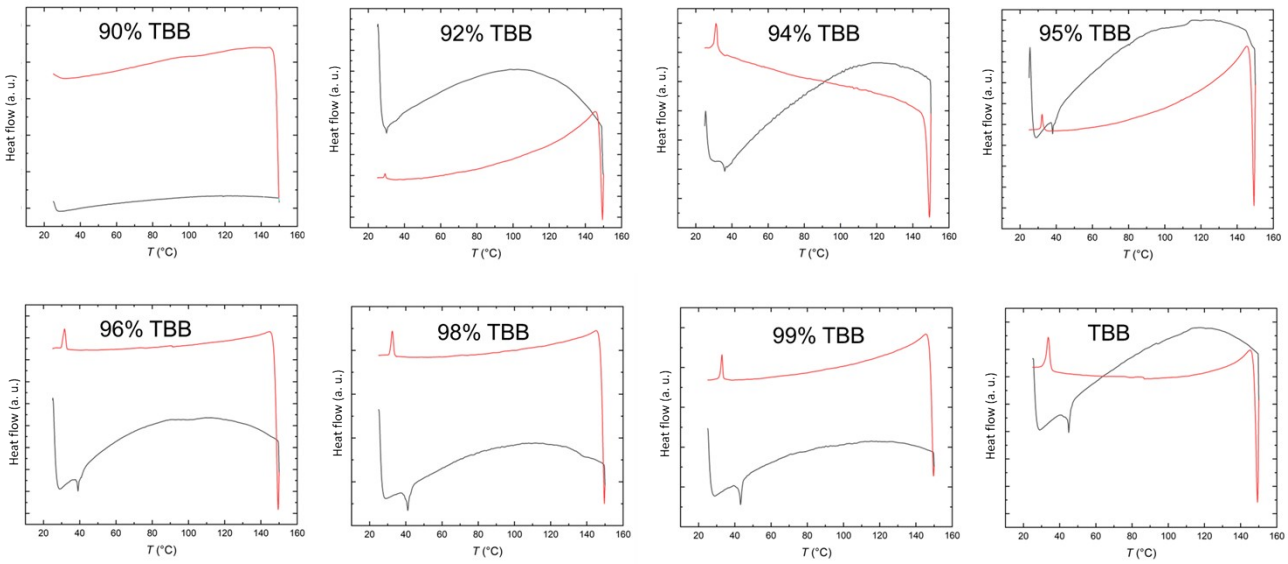

Fig S1 DSC curves of samples with 90% - 100% wt% TBB during the heating run and cooling runs.

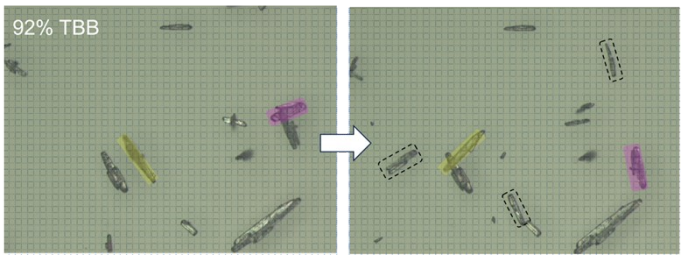

Fig S2 Hot-stage microscopy screenshots prior and after the thermosalient phase transition from RT β-phase to HT γ-phase for sample with 92% TBB. Dashed lines represent crystals that have jumped into the frame. Crystals that jumped and remained inside the frame are coloured in blue, yellow, pink, green, orange and purple.

Table S2. Crystal data and structure refinement for $C_6H_2Br_{3.86}Cl_{0.14}$.

Identification code	98 wt.% TBB – 2 wt.% TCB
CCDC Deposition Number	2393428
Empirical formula	$C_6H_2Br_{3.86}Cl_{0.14}$
Formula weight	387.27
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	4.0201(14)
b/Å	10.706(3)
c/Å	10.245(2)
α/°	90
β/°	100.13(3)
γ/°	90
Volume/Å^3	434.1(2)
Z	2
ρ_{calc}g/cm^3	2.963
μ/mm^{-1}	18.119
F(000)	351.0
Crystal size/mm^3	0.49 × 0.16 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	8.62 to 55.988
Index ranges	-3 ≤ h ≤ 5, -12 ≤ k ≤ 14, -13 ≤ l ≤ 13
Reflections collected	1922
Independent reflections	1030 [R_{int} = 0.0885, R_{sigma} = 0.1418]
Data/restraints/parameters	1030/20/64
Goodness-of-fit on F^2	0.952
Final R indexes [I>=2σ (I)]	R_1 = 0.0672, wR_2 = 0.0904
Final R indexes [all data]	R_1 = 0.1275, wR_2 = 0.1127
Largest diff. peak/hole / e Å^{-3}	0.80/-0.88

Table S3. Bond lengths for $C_6H_2Br_{3.86}Cl_{0.14}$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.390(14)	C2	C3	1.378(14)
C1	C3^1	1.399(13)	C2	Br2	1.868(10)
C1	Br1	1.897(11)	C2	Cl2	1.722(12)

C1	Cl1	1.722(12)

[1]-X,1-Y,2-Z

Table S4. Bond angles for $C_6H_2Br_{3.86}Cl_{0.14}$

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	C1	C3[1]	121.2(1)	C1	C2	Cl2	122.3(1)
C2	C1	Br1	120.4(8)	C3	C2	C1	118.5(9)
C2	C1	Cl1	120.8(1)	C3	C2	Br2	118.2(8)
C3[1]	C1	Br1	118.3(8)	C3	C2	Cl2	119.3(2)
C3[1]	C1	Cl1	118.0(2)	Cl2	C2	Br2	1.1(1)
Cl1	C1	Br1	1(2)	C2	C3	C1[1]	120.3(9)
C1	C2	Br2	123.3(9)				

[1]-X,1-Y,2-Z

Table S5. Torsion angles for $C_6H_2Br_{3.86}Cl_{0.14}$

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C1	C2	C3	C1[1]	0.7(1)	Br1	C1	C2	Cl2	1(3)
C3[1]	C1	C2	C3	-0.7(1)	Br2	C2	C3	C1[1]	-179.9(7)
C3[1]	C1	C2	Br2	179.9(7)	Cl2	C2	C3	C1[1]	-180(3)
C3[1]	C1	C2	Cl2	180(3)	Cl1	C1	C2	C3	180(2)
Br1	C1	C2	C3	-179.4(7)	Cl1	C1	C2	Br2	0(3)
Br1	C1	C2	Br2	0.9(1)	Cl1	C1	C2	Cl2	0(3)

[1]-X,1-Y,2-Z

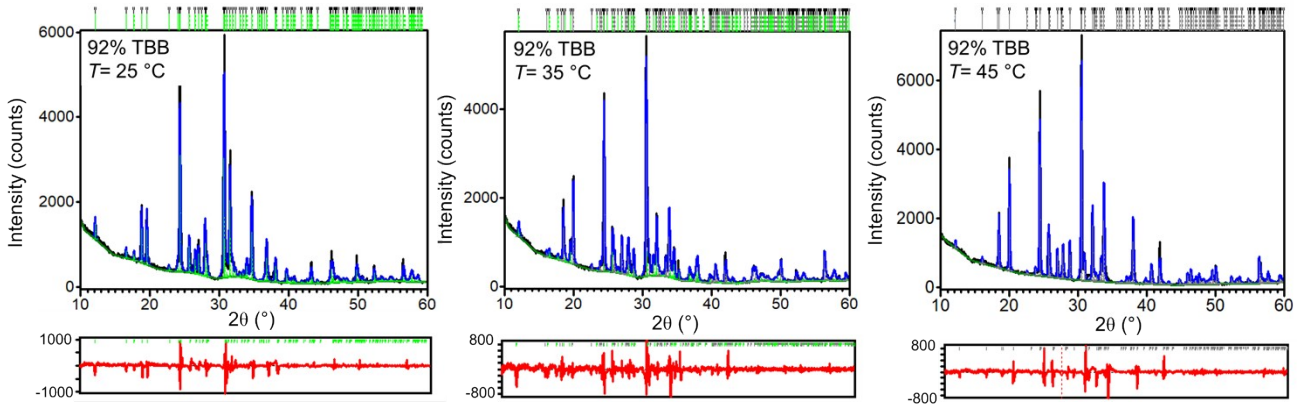

Fig S3 Refinement of the molecular alloy with 92 wt.% TBB at 25, 35 and 45 °C. Experimental *in-situ* XRPD data are given as black lines, calculated profile in blue while the difference in giving in red bellow. Green vertical lines mark the positions of reflections belonging to the RT β-phase while the positions of HT γ-phase reflections are shown in grey.

Table S6. Principal axes *X, Y, Z;* coefficients of linear thermal expansion along principal axes; normalised components of the principal axes

TTB 92%	LT form				HT form			
Axis	α (MK^{-1})	a	b	c	α (MK^{-1})	a	b	c
X	-311	0.522	0.0	0.853	-212	0.4387	0.0	0.8987
Y	190	1.0	0.0	0.0098	209	9.9999	0.0	0.0118
Z	243	0	1	0	323	0	1	0
Volume	121				317			
TTB 98%	LT form				HT form			
X	-374	0.5634	0.0	0.8262	-217	0.5067	0.0	0.8621
Y	175	0.9998	0.0	-0.0216	191	1.0	0.0	-0.006
Z	366	0.0	1.0	0.0	293	0.0	1.0	0.0
Volume	167				267			

TTB 100%	LT form				HT form			
X	-341	0.6759	0.0	0.737	-198	0.6522	0.0	0.7581
Y	203	0.9982	0.0	-0.606	213	0.9985	0.0	-0.0554
Z	388	0.0	1.0	0.0	311	0.0	1.0	0.0
Volume	250				326			

Video S1. Video of the sample 92%TBB-8%TCB during heating.
Video S2. Video of the sample 92%TBB-8%TCB during cooling.
Video S3. Video of the sample 98%TBB-2%TCB during heating.
Video S4. Video of the sample 98%TBB-2%TCB during cooling.