Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Synthesis of Bi_2Te_3 and $(Bi_xSb_{1-x})_2Te_3$ Nanoparticles using the novel IL $[C_4mim]_3[Bi_3I_{12}]$.

Manuel Loor, Georg Bendt, Ulrich Hagemann, Christoph Wölper, Wilfried Assenmacher, Stephan Schulz*

Content

Fig. S1. ^{1}H-NMR spectrum of **1** in DMSO-d6.

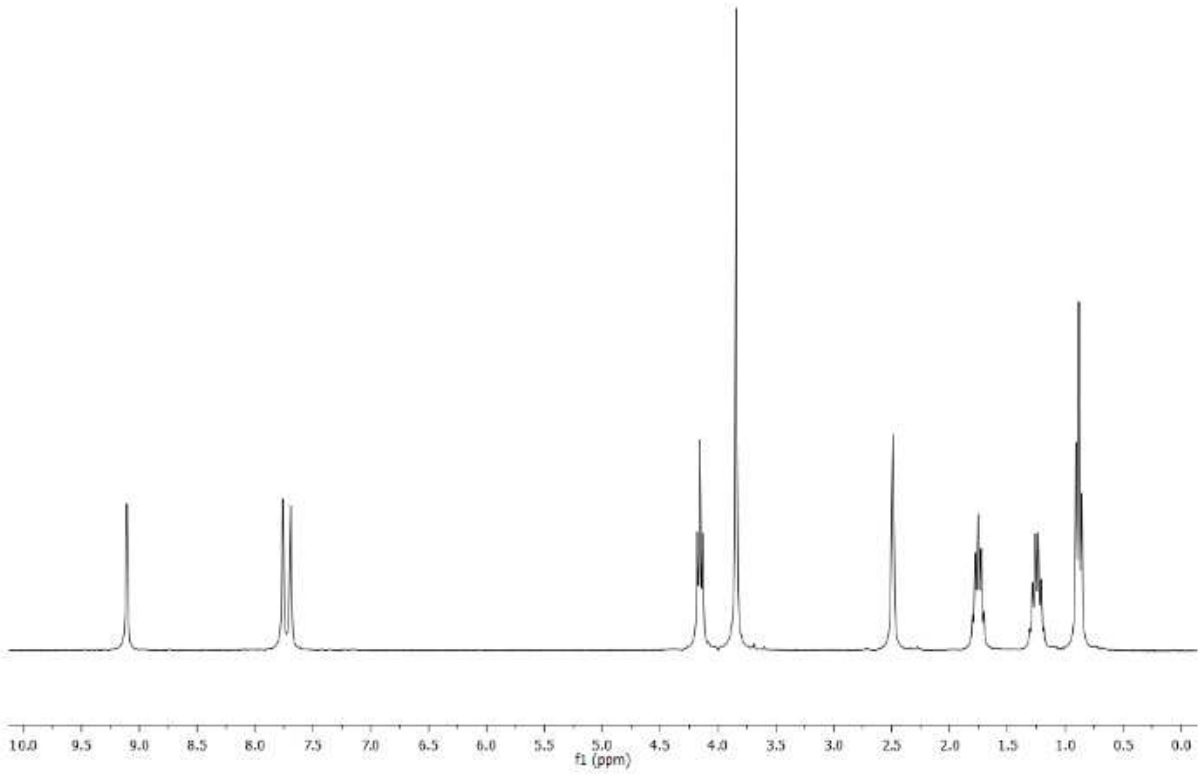

Fig. S2. ^{13}C-NMR spectrum of **1** in DMSO-d6.

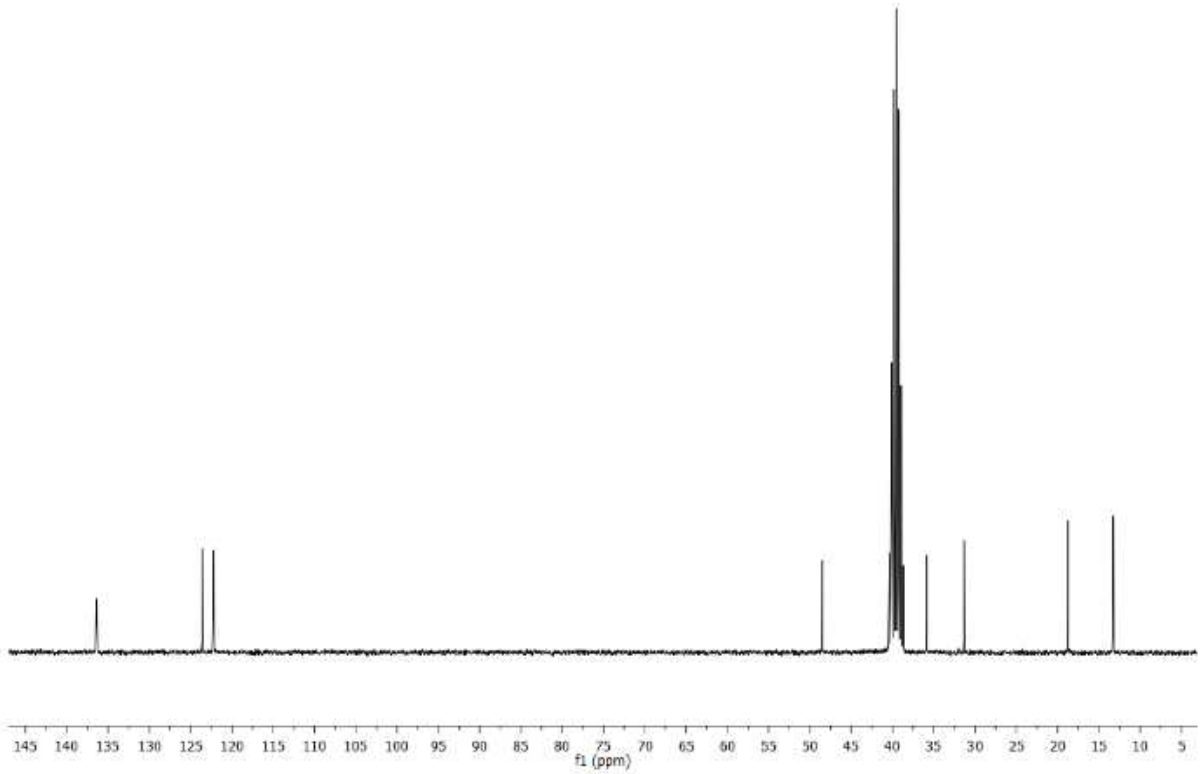

Fig. S3. IR absorption spectrum of **1**.

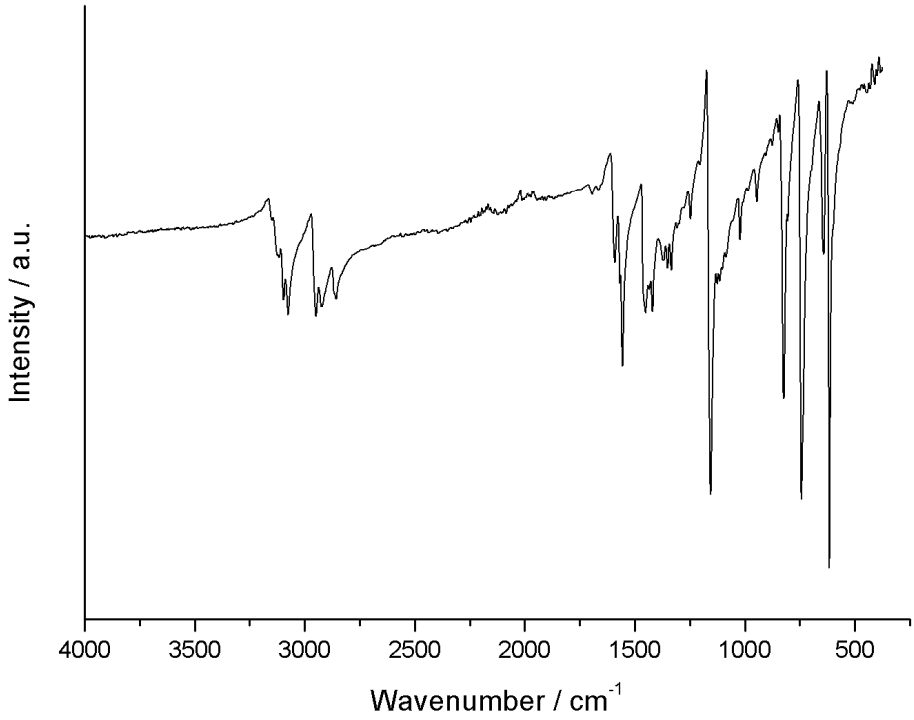

Fig. S4a. ^{1}H-NMR spectroscopic study in $CDCl_3$ of the byproducts of the reaction of $(Et_3Si)_2Te$ and $[C_4mim]_3[Bi_3I_{12}]$; peaks marked with * correspond to Et_3SiI and those with # to Si_2Et_6.

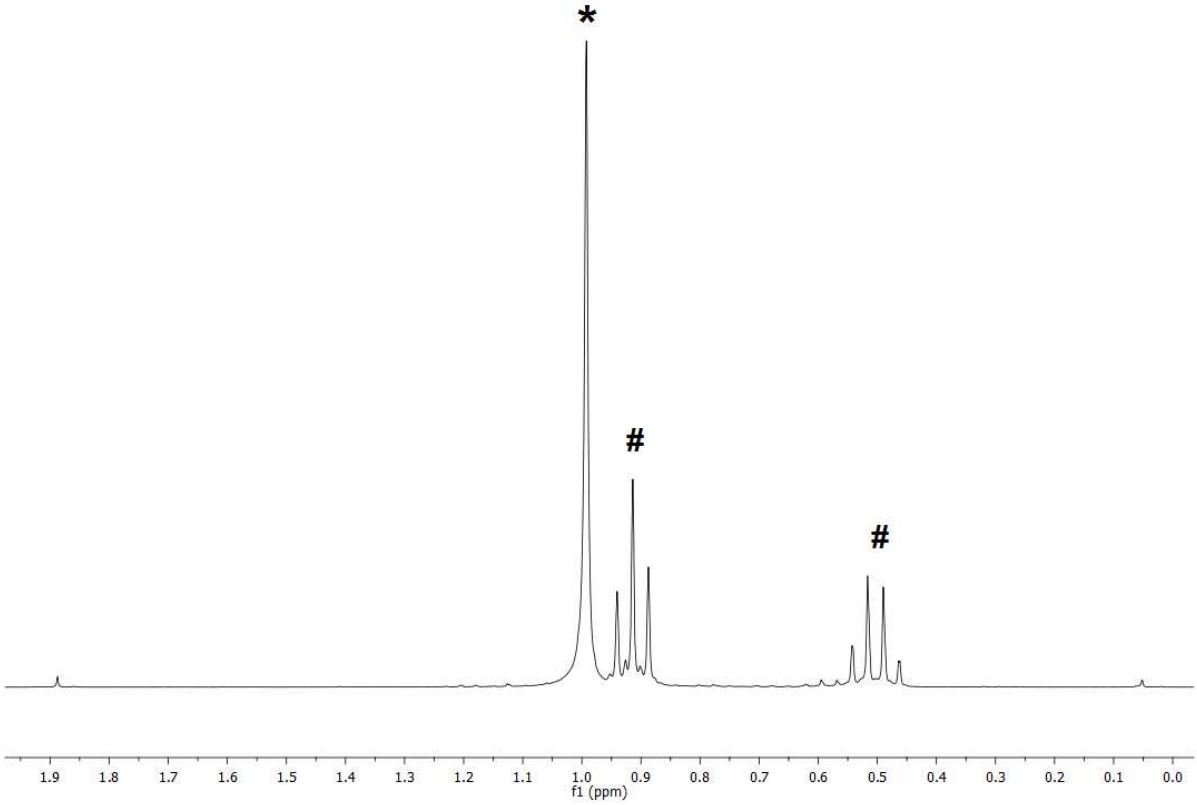

Fig. S4b. ^{13}C-NMR spectroscopic study in $CDCl_3$ of the byproducts of the reaction of $(Et_3Si)_2Te$ and $[C_4mim]_3[Bi_3I_{12}]$; peaks marked with * correspond to Et_3SiI and those with # to Si_2Et_6.

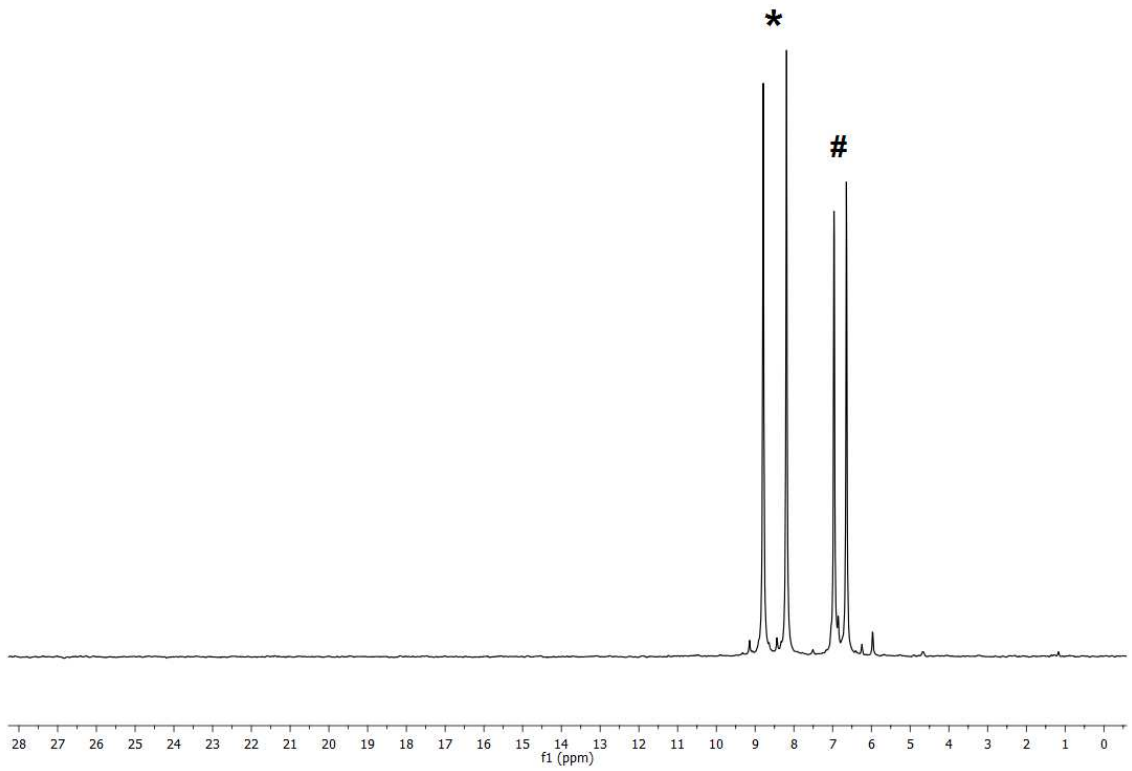

Fig. S4c. ^{29}Si-NMR spectroscopic study in $CDCl_3$ of the byproducts of the reaction of $(Et_3Si)_2Te$ and $[C_4mim]_3[Bi_3I_{12}]$; peaks marked with * correspond to Et_3SiI and those with # to Si_2Et_6.

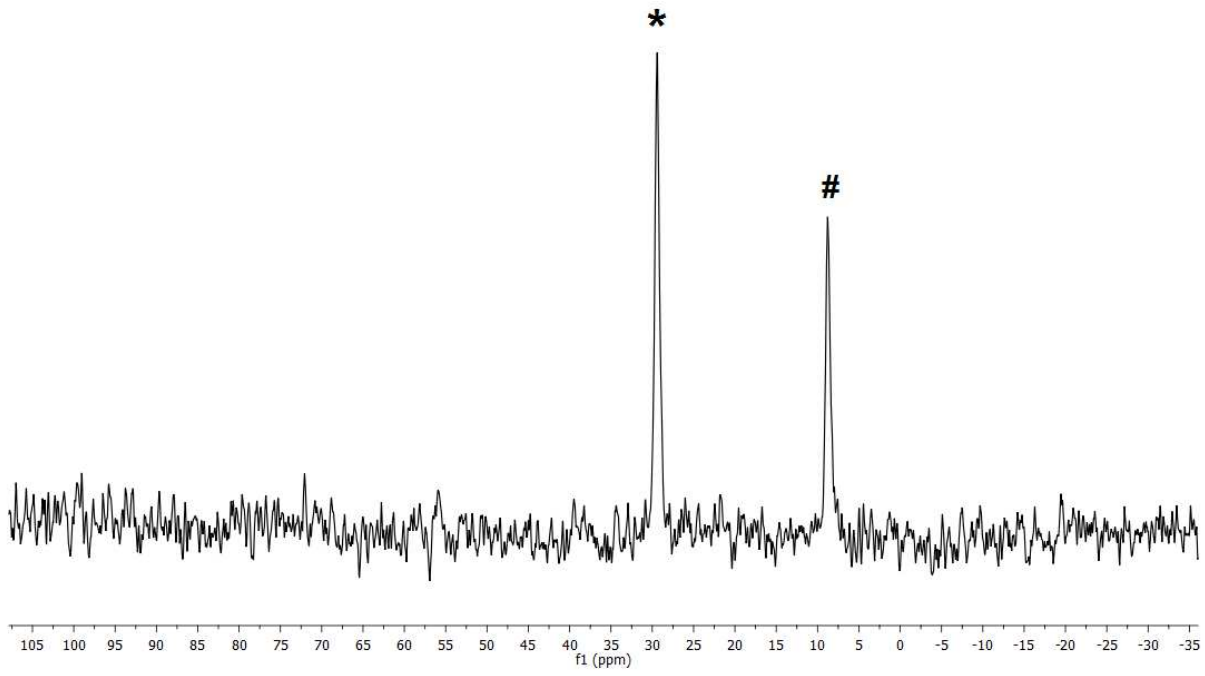

Fig. S5. ^{1}H-NMR spectrum of [C_4mim][I] in DMSO-d6.

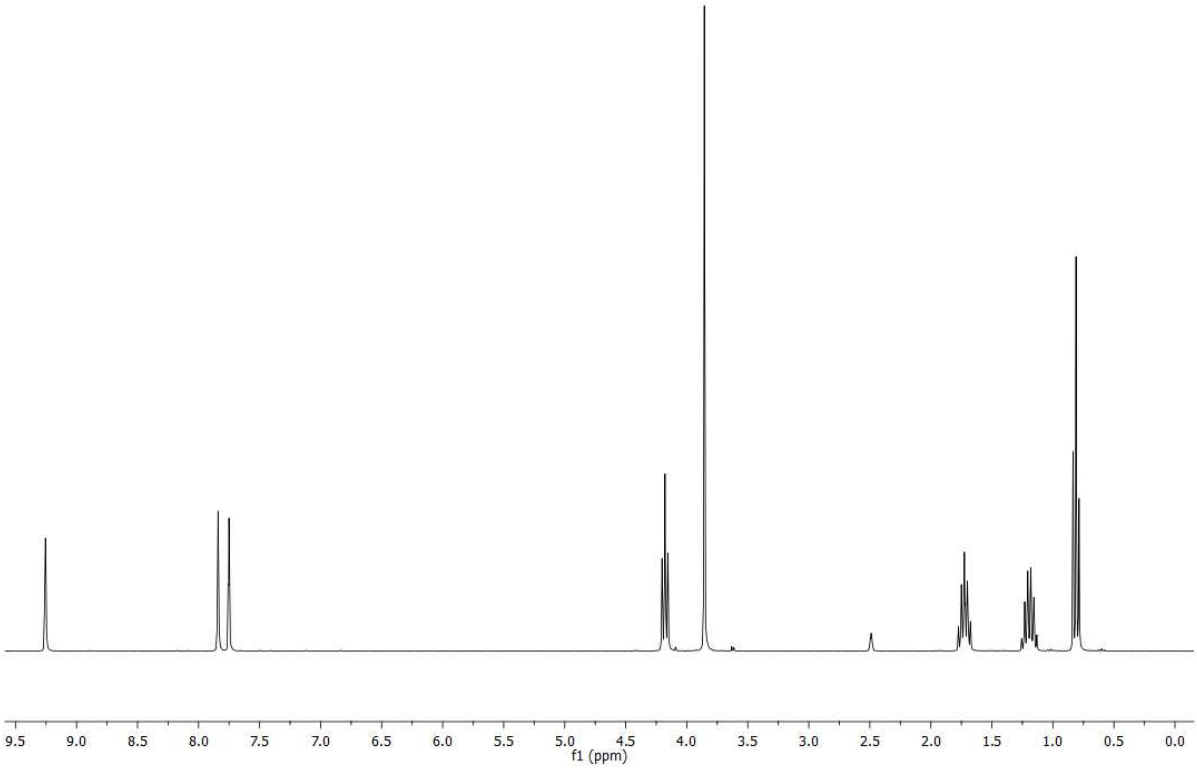

Fig. S6. ^{13}C-NMR spectrum of [C_4mim][I] in DMSO-d6.

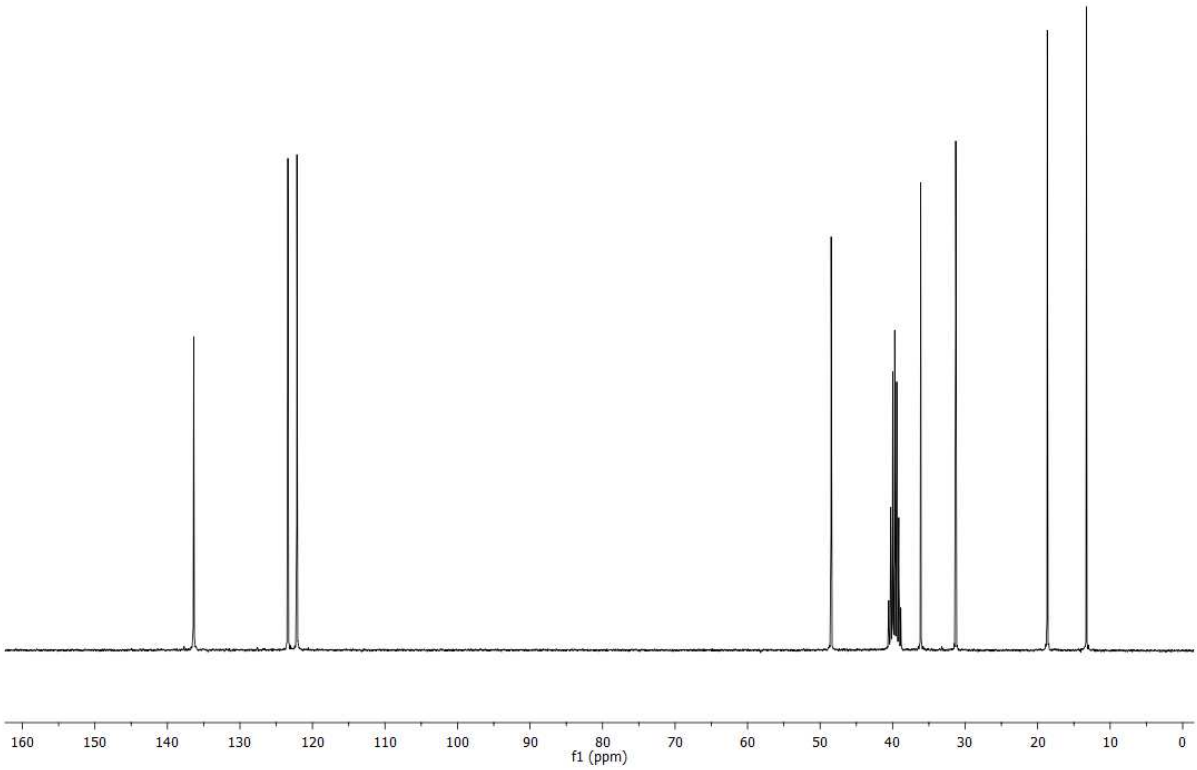

Fig. S7. IR-absorption spectrum of [C_4mim][I]

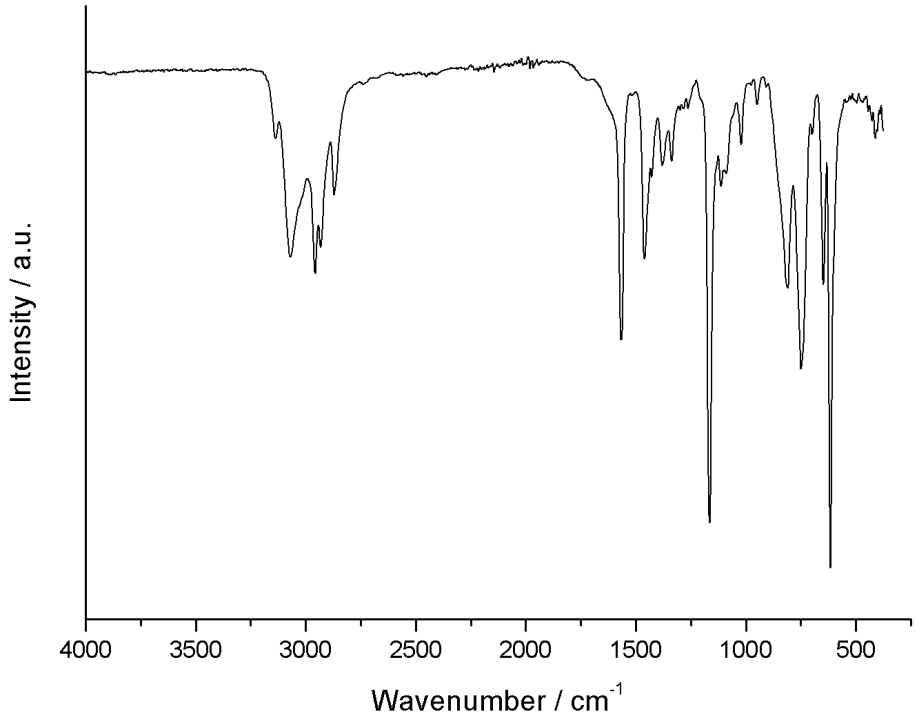

Fig. S8. Thermochromic behavior of **1.**

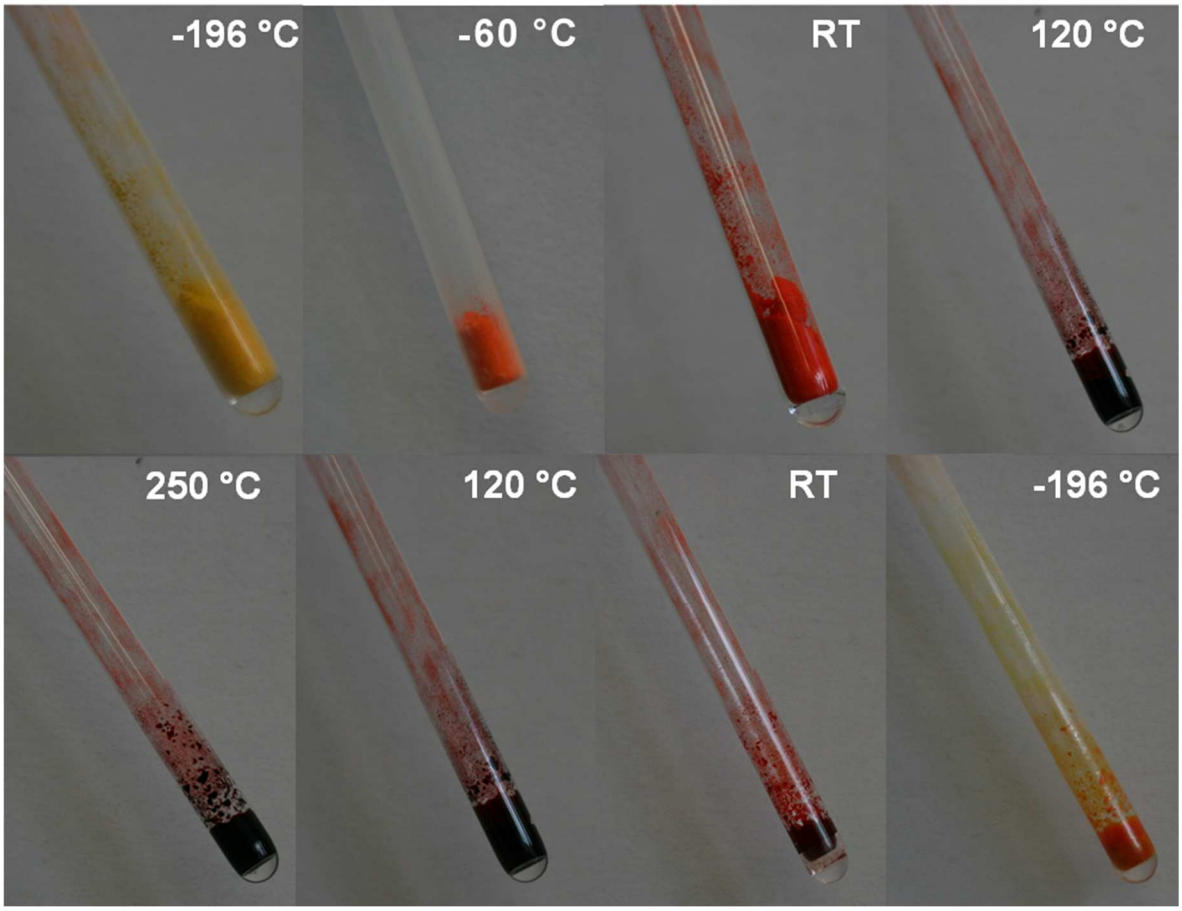

Fig. S9. Temperature-dependent DSC study of **1.**

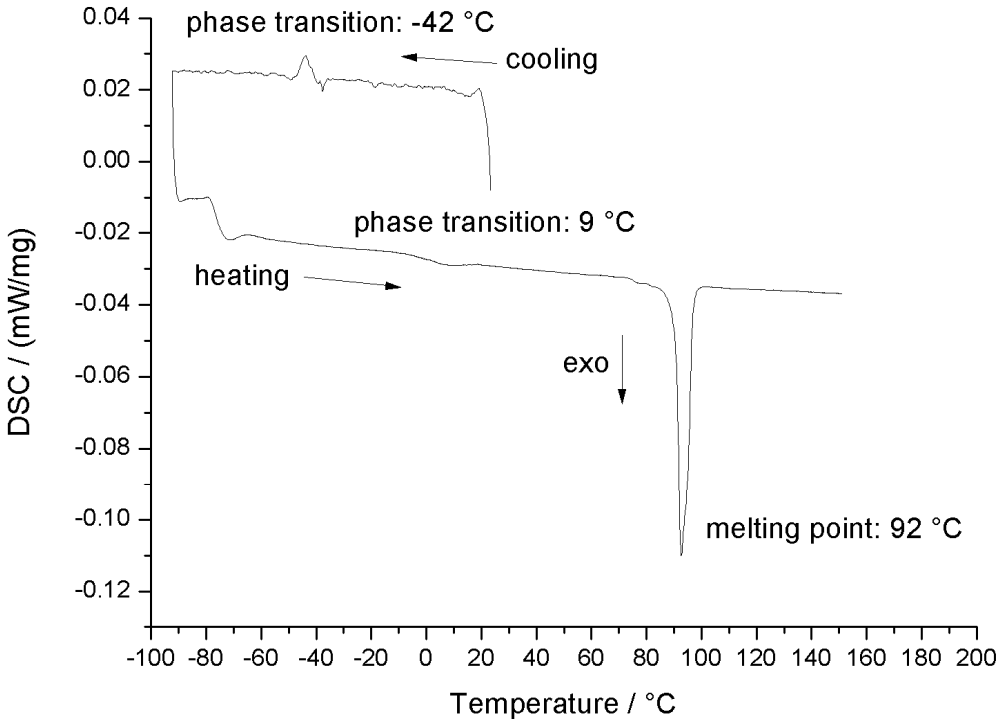

Table S1: Hydrogen bonds [Å] and °] for **1**.

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠(DHA)
C(11)-H(11C)···I(13)	0.98	3.07	3.813(13)	133.7
C(13)-H(13)···I(23)#3	0.95	3.18	3.851(12)	129.3
C(13)-H(13)···I(24)	0.95	3.21	4.014(14)	143.5
C(16)-H(16A)···I(14)	0.99	3.26	4.089(12)	142.9
C(16)-H(16A)···I(16)	0.99	3.27	3.932(12)	126.1
C(21)-H(21A)···I(26)#3	0.98	3.27	4.035(13)	135.9
C(22)-H(22)···I(26)#3	0.95	3.09	3.929(12)	148.0
C(23)-H(23)···I(14)#4	0.95	3.13	3.981(13)	150.3
C(26)-H(26B)···I(24)#4	0.99	3.32	4.235(11)	153.7
C(31)-H(31A)···I(26)	0.98	3.28	4.168(15)	152.4
C(31)-H(31B)···I(16)#5	0.98	3.28	3.780(12)	113.3
C(31)-H(31C)···I(14)#4	0.98	3.31	4.167(13)	147.4
C(32)-H(32)···I(21)	0.95	3.23	3.928(13)	131.8
C(32)-H(32)···I(26)	0.95	3.11	3.860(12)	137.5
C(34)-H(34)···I(15)#6	0.95	3.29	4.128(13)	148.1
C(36)-H(36B)···I(16)#6	0.99	3.31	4.230(15)	155.4

#3 x,-y+3/2,z+1/2 #4 -x+1,y-1/2,-z+1/2 #5 x+1,y,z #6 x+1,-y+3/2,z-1/2

Table S2: Inter-halide interactions [Å and °] for **1**.

Bi–I···I–Bi	d(I···I)	∠(Bi–I···I)	∠(I···I–Bi)
Bi(12)–I(16)···I(11)#7–Bi(11)#7	3.8510(10)	152.58(2)	150.33(3)
Bi(12)–I(16)···I(11)#7–Bi(12)#7			97.76(2)
Bi(22)–I(24)···I(23)#3–Bi(22)#3	3.8778(10)	175.95(3)	144.51(3)
Bi(22)–I(24)···I(23)#3–Bi(21)#3			137.01(2)

#3 x, -y+3/2, z+1/2 #7 -x, y-1/2, -z+1/2

Table S3: EDX results from STEM spot analyses on single crystals

a) $(Bi_xSb_{1-x})_2Te_3$ with x = 0.25

Philips/FEI CM300 UT FEG; 300 keV acc. Voltage; Thermo Noran NSS Ge-Detector

Atom%	*Sb-L*	*Te-L*	*Bi-L*
10(1)_pt1	26.11	60.68	13.22
10(1)_pt2	26.23	65.88	7.89
10(1)_pt3	24.6	62.19	13.21
10(2)_pt1	27.39	63.65	8.96
10(2)_pt2	25.16	60.9	13.94
10(2)_pt3	24.31	63.32	12.37
10(2)_pt4	28.05	59.06	12.89
10(2)_pt5	24.17	61.08	14.75
10(2)_pt6	29.04	59.3	11.67
10(2)_pt7	23.24	61.47	15.29
10(2)_pt8	24.21	59.62	16.17
10(3)_pt1	30.57	55.29	14.14
10(3)_pt2	23.55	66.51	9.94
10(3)_pt4	30.16	61.56	8.29
10(3)_pt5	28.27	61.6	10.14
10(3)_pt6	28.18	58.59	13.23
10(3)_pt7	26.43	59.15	14.41
10(3)_pt8	30.97	56.21	12.82
Average:	**26.70**	**60.89**	**12.41**

esd	*Sb-L*	*Te-L*	*Bi-L*
10(1)_pt1	1.6	1.75	0.77
10(1)_pt2	3.47	7.14	1.51
10(1)_pt3	2.22	2.39	1.05
10(2)_pt1	2.53	5.3	1.07
10(2)_pt2	2.29	2.49	1.14
10(2)_pt3	2.16	4.52	1.02
10(2)_pt4	1.85	1.98	1.29
10(2)_pt5	1.33	1.48	0.94
10(2)_pt6	1.97	2.14	0.93
10(2)_pt7	1.56	3.52	1.14
10(2)_pt8	2.25	2.23	1.16
10(3)_pt1	4.59	5.63	1.16
10(3)_pt2	3.84	7.95	1.94
10(3)_pt4	2.78	3.02	1.2
10(3)_pt5	1.82	2.2	0.57
10(3)_pt6	2.39	2.56	1.13
10(3)_pt7	1.44	1.57	0.69
10(3)_pt8	2.72	1.68	0.92
	2.38	**3.31**	**1.09**

b) $(Bi_xSb_{1-x})_2Te_3$ with x = 0.5

Philips/FEI CM300 UT FEG; 300 keV acc. Voltage; Thermo Noran NSS Ge-Detector (yellow cell color)

Philips/FEI CM30 T Lab_6; 300 keV acc. Voltage; Thermo Noran NSS Si(Li)-Detector (white cell color)

Atom%	*Sb-L*	*Te-L*	*Bi-L*
01(1)_pt1	16.73	56.46	26.81
01(1)_pt2	15.43	62.01	22.56
01(1)_pt3	15.25	61.13	23.63
01(1)_pt4	14.01	61.97	24.02
01(2)_pt1	16.03	58.31	25.66
01(2)_pt2	16.07	60.58	23.34
01(2)_pt3	16.6	59.8	23.6
01(2)_pt4	16.87	60.65	22.48
01(2)_pt6	16.81	60.2	22.99
01(3)_pt1	17.12	59.27	23.61
01(3)_pt2	16.28	58.65	25.07
01(3)_pt3	16.39	60.57	23.04
01(3)_pt4	17	59.51	23.5

esd	*Sb-L*	*Te-L*	*Bi-L*
01(1)_pt1	2	4.27	1.46
01(1)_pt2	0.92	1.02	0.84
01(1)_pt3	0.89	2.17	0.66
01(1)_pt4	2.28	2.27	2.23
01(2)_pt1	1.91	4	1.33
01(2)_pt2	1.33	1.31	1.01
01(2)_pt3	1.57	1.57	1.17
01(2)_pt4	1.83	1.82	1.28
01(2)_pt6	1.82	1.8	1.31
01(3)_pt1	1.14	1.15	0.88
01(3)_pt2	1.61	0.97	0.63
01(3)_pt3	1.38	1.71	0.63
01(3)_pt4	1.3	1.61	0.59

01(3)_pt5	15.53	57.48	26.98	*01(3)_pt5*	1.24	2.66	1.18
01(3)_pt6	16.34	59.6	24.06	*01(3)_pt6*	0.61	0.67	0.47
1(1)_pt1	14.78	61.97	23.25	*1(1)_pt1*	1.59	3.67	1.41
1(1)_pt2	15.76	59.92	24.32	*1(1)_pt2*	2.72	3.23	1.24
1(1)_pt3	14.05	63.11	22.84	*1(1)_pt3*	2.57	5.54	1.55
1(1)_pt4	34.87	47.39	17.75	*1(1)_pt4*	2.43	2.83	0.94
1(1)_pt5	16.75	61.4	21.85	*1(1)_pt5*	1.3	2.77	1.07
1(2)_pt1	20.08	62.13	17.8	*1(2)_pt1*	2.01	4.29	1.11
1(2)_pt3	18.5	58.65	22.86	*1(2)_pt3*	2.47	2.93	1.08
1(2)_pt4	16.18	64.99	18.82	*1(2)_pt4*	1.97	2.07	1.14
1(2)_pt5	17.71	60.25	22.03	*1(2)_pt5*	2.64	3.16	1.18
1(3)_pt1	14.55	63.74	21.71	*1(3)_pt1*	2.83	5.97	1.74
1(3)_pt2	14.34	64.87	20.79	*1(3)_pt2*	1.73	3.63	1.04
Average:	**16.92**	**60.18**	**22.90**		**1.77**	**2.66**	**1.12**

c) $(Bi_xSb_{1-x})_2Te_3$ with x = 0.75

Philips/FEI CM300 UT FEG; 300 keV acc. Voltage; Thermo Noran NSS Ge-Detector

Atom%	*Sb-L*	*Te-L*	*Bi-L*	*esd*	*Sb-L*	*Te-L*	*Bi-L*
11(1)_pt1	6.63	57.99	35.37	*11(1)_pt1*	1.34	2.92	1.48
11(1)_pt2	4.61	59.22	36.17	*11(1)_pt2*	1.35	2.92	1.47
11(1)_pt3	8.43	59.81	31.76	*11(1)_pt3*	1.22	2.63	1.26
11(1)_pt4	8.93	59.8	31.27	*11(1)_pt4*	2.6	2.66	2.74
11(3)_pt1	9.31	62.02	28.68	*11(3)_pt1*	2.28	4.88	2.3
11(3)_pt2	6.97	59.86	33.17	*11(3)_pt2*	1.57	3.4	1.64
11(3)_pt3	6.08	61.08	32.84	*11(3)_pt3*	1.46	3.18	1.62
11(4)_pt2	10.44	56.9	32.66	*11(4)_pt2*	1.47	1.56	1.62
11(4)_pt3	5.9	61.37	32.73	*11(4)_pt3*	1.89	4.03	2.01
Average:	**7.48**	**59.78**	**32.74**		**1.69**	**3.13**	**1.79**