Supporting Information

Thiophosphates Containing Ag^+ and Lone-pair Cations with Interchiral Double Helix Show Both Ionic Conductivity and Phase Transition

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Table S1. Atomic coordinates and equivalent isotropic displacement parameters for **1**–**3** at 25 °C.

Atom	*x*	*y*	*z*	U_{eq}	SOF
			1		
Bi(1)	-0.14752(11)	-0.07144(3)	0.15585(7)	0.0276(2)	1
Ag(1)	-0.8404(2)	-0.18344(7)	-0.01502(15)	0.0388(4)	1
Ag(2)	-0.6081(3)	-0.23364(8)	0.29094(16)	0.0513(4)	1
Ag(3A)	0.713(3)	-0.0869(8)	0.5790(17)	0.0771(10)	0.17
Ag(3B)	0.6078(6)	-0.09600(13)	0.5896(3)	0.0771(10)	0.83
P(1)	-0.5696(7)	-0.03247(19)	0.2237(4)	0.0220(9)	1
P(2)	-1.2088(7)	-0.26236(19)	-0.3466(4)	0.0229(9)	1
S(1)	-0.6182(7)	-0.07204(18)	0.0323(4)	0.0244(9)	1
S(2)	-0.1254(7)	-0.17265(18)	0.3183(4)	0.0243(9)	1
S(3)	-0.9778(7)	-0.18834(18)	-0.2923(4)	0.0279(9)	1
S(4)	-0.2262(7)	-0.18441(19)	-0.0168(4)	0.0273(9)	1
S(5)	-0.2376(7)	-0.0014(2)	0.3437(4)	0.0329(10)	1
S(6)	0.3497(7)	-0.1042(2)	0.3261(4)	0.0288(9)	1
S(7)	256(6)	421(2)	8236(4)	29(1)	1
S(8)	6155(6)	2765(2)	869(5)	31(1)	1
			2		
Ag(1)	-0.01540(11)	-0.61875(9)	-0.42603(6)	0.0452(3)	1
Ag(2)	-0.35941(11)	-1.40161(10)	-0.43486(7)	0.0472(3)	1
Ag(3)	-0.33816(13)	-0.62368(9)	-0.23799(6)	0.0471(3)	1
Ag(4A)	-0.350(2)	-1.320(3)	-0.5927(12)	0.145(8)	0.5
Ag(4B)	-0.329(2)	-1.258(3)	-0.5826(12)	0.145(8)	0.5
Ag(5)	-0.36707(12)	-1.11650(10)	-0.42250(7)	0.0567(3)	1
Ag(6)	0.00592(11)	-0.90407(9)	-0.43448(6)	0.0481(3)	1

Ag(7)	-0.37882(12)	-0.90955(9)	-0.90955(9)	0.0443(3)	1
Sn(1)	-0.00156(9)	-0.60488(7)	-0.24604(5)	0.0327(2)	1
P(1)	-0.6861(2)	-0.7635(2)	-0.26437(12)	0.0136(5)	1
P(2)	0.0286(2)	-0.7555(2)	-0.07870(13)	0.0139(5)	1
P(3)	-0.3439(2)	-0.7517(2)	-0.40739(12)	0.0130(5)	1
S(1)	-0.1549(3)	-1.0932(3)	-0.4446(2)	0.0372(7)	1
S(2)	-0.2494(3)	-1.0976(2)	-0.17364(14)	0.0277(6)	1
S(3)	-0.0888(3)	-0.7866(2)	-0.18959(13)	0.0203(5)	1
S(4)	-0.4719(2)	-0.7652(2)	-0.18970(13)	0.0206(5)	1
S(5)	-0.4442(3)	-0.9081(2)	-0.38982(14)	0.0251(6)	1
S(6)	0.2066(3)	-0.7814(3)	-0.20632(14)	0.0243(6)	1
S(7)	-0.1221(3)	-0.7776(3)	-0.35415(13)	0.0215(5)	1
S(8)	-0.2645(3)	-0.4167(2)	-0.16448(14)	0.0268(6)	1
S(9)	-0.1653(3)	-1.4129(2)	-0.46849(14)	0.0233(5)	1
S(10)	-0.5923(3)	-1.2679(3)	-0.48581(13)	0.0208(5)	1
S(11)	-0.1195(3)	-0.7595(3)	-0.54531(13)	0.0228(5)	1
S(12)	-0.3964(3)	-0.5907(2)	-0.36801(15)	0.0287(6)	1
			3		
Pb(1)	0.06617(4)	-0.54341(4)	-0.21912(2)	0.01591(15)	1
Ag(1)	0.01980(9)	-1.10537(8)	-0.07019(5)	0.0195(2)	1
Ag(2)	0.35807(9)	-0.85738(9)	-0.08126(5)	0.0183(2)	1
Ag(3)	-0.32154(10)	-0.60988(8)	-0.24143(5)	0.0182(2)	1
Ag(4)	-0.38860(10)	-0.89470(8)	0.25660(5)	0.0197(2)	1
Ag(5)	0.38244(9)	-0.50975(9)	-0.03070(5)	0.0215(2)	1
Ag(6)	-0.03210(10)	-1.39107(9)	-0.07118(5)	0.0278(3)	1
Ag(7)	0.33650(10)	-0.80469(13)	0.08585(5)	0.0313(3)	1
P(1)	0.6695(3)	-0.7514(2)	0.09479(15)	0.0096(5)	1

P(2)	0.0272(3)	-0.7434(2)	-0.08303(14)	0.0090(5)	1
P(3)	-0.3133(3)	-0.2507(2)	-0.23198(15)	0.0092(5)	1
S(1)	0.5979(3)	-0.7494(3)	-0.01365(15)	0.0137(5)	1
S(2)	-0.0863(3)	-0.7566(2)	-0.19349(14)	0.0110(5)	1
S(3)	0.1730(3)	-0.8969(2)	-0.04013(14)	0.0124(5)	1
S(4)	0.4211(3)	-1.0920(2)	-0.12287(14)	0.0120(5)	1
S(5)	0.1150(3)	-1.2376(2)	-0.14845(14)	0.0115(5)	1
S(6)	-0.2860(3)	-0.4053(2)	-0.15997(14)	0.0133(5)	1
S(7)	-0.3788(3)	-0.9307(3)	-0.37260(14)	0.0116(5)	1
S(8)	0.1973(3)	-0.7905(3)	-0.21625(14)	0.0122(5)	1
S(9)	-0.2389(3)	-1.0788(3)	-1.0788(3)	0.0143(5)	1
S(10)	0.1424(3)	-0.5670(3)	-0.06678(14)	0.0127(5)	1
S(11)	-0.4795(3)	-0.7376(3)	-0.19267(14)	0.0132(5)	1
S(12)	0.1126(3)	-1.2582(2)	0.04437(14)	0.0119(5)	1

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for **3** at 212 °C.[a]

Atom	*x*	*y*	*z*	U_{eq}	SOF
Pb(1)	0.9333(19)	0.940(2)	0.522(2)	0.078(5)	1
Pb(2)	1.0000	1.0000	0.5616(11)	0.102(8)	0.33
Ag(1)	0.6633(7)	0.6446(8)	0.6262(11)	0.0592(18)	0.17
Ag(2)	0.6667	0.3333	0.2500	0.079(4)	0.17
Ag(3)	0.3117(4)	0.3389 (3)	0.7500	0.0275(6)	0.5
Ag(4)	0.5252(3)	0.4079(3)	0.7500	0.0467(9)	0.5
Ag(5)	0.9156(3)	0.7966(3)	0.7500	0.0489(9)	0.5
Ag(6)	0.7496(3)	0.5892(4)	0.4126(3)	0.0694(10)	1
Ag(7)	0.6138(16)	0.6143(10)	0.5950(9)	0.121(5)	1

Ag(8)	0.6470(15)	0.6598(13)	0.6048(10)	0.098(4)	1
Ag(9)	0.6667	0.3333	0.352(3)	0.154(8)	0.33
Ag(10)	0.6667	0.3333	1.462(10)	0.58(10)	0.33

[a] The structure of **3** at high temperature is highly disordered, only heavy atoms Pb and Ag are assigned to the largest electron density peaks during the structure determination and refinement. The P and S atoms should mixed occupy the heavy atom positions and residual electron density peaks, so the occupancy (SOF) shown in the table is not exactly determined.

Table S3. Selected bond lengths[a] for **1** at 25 °C.

Polyhedron	Bond	Distance (Å)	Polyhedron	Bond	Distance (Å)
BiS_5	Bi(1)-S(2)	2.664(4)	$Ag(3A)S_3$	Ag(3A)-S(7)	2.556(16)
	Bi(1)-S(1)	2.747(4)		Ag(3A)-S(6)	2.608(17)
	Bi(1)-S(5)	2.780(4)		Ag(3A)-S(3)#5	2.764(19)
	Bi(1)-S(4)	2.841(4)	$Ag(3B)S_3$	Ag(3B)-S(7)	2.441(5)
	Bi(1)-S(6)	2.967(4)		Ag(3B)-S(6)	2.481(5)
				Ag(3B)-S(8)#4	2.755(5)
$Ag(1)S_4$	Ag(1)-S(4)#1	2.580(5)	$P(1)S_4$	P(1)-S(5)	2.037(6)
	Ag(1)-S(8)	2.627(4)		P(1)-S(7)#8	2.038(5)
	Ag(1)-S(1)	2.628(4)		P(1)-S(6)#1	2.066(5)
	Ag(1)-S(3)	2.648(4)		P(1)-S(1)	2.083(5)
			$P(2)S_4$	P(2)-S(3)	2.033(6)
$Ag(2)S_3$	Ag(2)-S(8)	2.657(5)		P(2)-S(8)#9	2.052(6)
	Ag(2)-S(3)#3	2.697(5)		P(2)-S(2)#9	2.056(5)
	Ag(2)-S(6)#1	2.706(5)		P(2)-S(4)#9	2.084(5)

[a]Symmetry transformations used to generate equivalent atoms. (#1) x-1,y,z; (#2) x,-y-1/2,z-1/2; (#3) x,-y-1/2,z+1/2; (#4) x+1,-y-1/2,z+1/2; (#5) x+2,y,z+1; (#6) x-2,y,z-1; (#7) x+1,y,z; (#8) -x,-y,-z+1; (#9) x-1,-y-1/2,z-1/2.

Table S4. Selected bond lengths[a] for **2** at 25 °C.

Polyhedron	Bond	Distance (Å)	Polyhedron	Bond	Distance (Å)
SnS_3	Sn(1)-S(3)	2.612(3)	$Ag(5)S_3$	Ag(5)-S(5)	2.514(3)
	Sn(1)-S(6)	2.639(3)		Ag(5)-S(1)	2.543(3)
	Sn(1)-S(7)	2.658(3)		Ag(5)-S(10)	2.623(3)
$Ag(1)S_4$	Ag(1)-S(9)#8	2.514(3)	$Ag(6)S_3$	Ag(6)-S(8)#5	2.488(3)
	Ag(1)-S(2)#9	2.543(3)		Ag(6)-S(1)	2.512(3)
	Ag(1)-S(11)	2.623(3)		Ag(6)-S(11)	2.518(3)
	Ag(1)-S(7)	2.816(3)	$Ag(7)S_4$	Ag(7)-S(5)	2.499(3)
$Ag(2)S_3$	Ag(2)-S(9)	2.491(3)		Ag(7)-S(2)	2.521(3)
	Ag(2)-S(12)#6	2.536(3)		Ag(7)-S(4)	2.593(3)
	Ag(2)-S(10)	2.542(3)	$P(1)S_4$	P(1)-S(2)#13	2.040(3)
$Ag(3)S_4$	Ag(3)-S(8)	2.507(3)		P(1)-S(4)	2.018(3)
	Ag(3)-S(12)	2.525(3)		P(1)-S(6)#15	2.055(3)
	Ag(3)-S(4)	2.565(3)		P(1)-S(8)#10	2.049(3)
	Ag(3)-S(4)	2.845(3)	$P(2)S_4$	P(2)-S(1)#9	2.030(4)
$Ag(4A)S_3$	Ag(4A)-S(12)#1	2.547(18)		P(2)-S(3)	2.061(3)
	Ag(4A)-S(9)	2.55(3)		P(2)-S(9)#9	2.057(3)
	Ag(4A)-S(2)#2	2.57(3)		P(2)-S(11)#14	2.022(3)
$Ag(4B)S_4$	Ag(4B)-S(9)	2.68(3)	$P(3)S_4$	P(3)-S(5)	2.051(3)
	Ag(4B)-S(5)#1	2.76(3)		P(3)-S(7)	2.055(4)
	Ag(4B)-S(8)#3	2.80(3)		P(3)-S(10)#1	2.021(3)
	Ag(4B)-S(2)#2	2.86(3)		P(3)-P(12)	2.042(3)

[a]Symmetry transformations used to generate equivalent atoms. (#1) -x-1,-y-2,-z-1; (#2) x,-y-5/2,z-1/2; (#3) x,-y-3/2,z-1/2; (#4) -x,-y-2,-z-1; (#5) -x,y-1/2,-z-1/2; (#6) x,y-1,z; (#7) -x-1,-y-3,-z-1; (#8) x,y+1,z; (#9) -x,y+1/2,-z-1/2; (#10) -x-1,y-1/2,-z-1/2; (#11) x,-y-5/2,z+1/2; (#12) x+1,y,z; (#13) -x-1,y+1/2,-z-1/2; (#14) x,-y-3/2,z+1/2; (#15) x-1,y,z.

Table S5. Selected bond lengths[a] for **3** at 25 °C.

Polyhedron	Bond	Distance (Å)	Polyhedron	Bond	Distance (Å)
PbS_3	Pb(1)-S(8)	2.809(3)	$Ag(6)S_3$	Ag(6)-S(6)#7	2.461(3)
	Pb(1)-S(2)	2.876(3)		Ag(6)-S(10)#7	2.527(3)
	Pb(1)-S(10)	2.918(3)		Ag(6)-S(12)	2.538(3)
$Ag(1)S_4$	Ag(1)-S(3)	2.524(3)	$Ag(7)S_4$	Ag(7)-S(4)#9	2.546(3)
	Ag(1)-S(9)	2.567(3)		Ag(7)-S(3)	2.548(3)
	Ag(1)-S(12)	2.608(3)		Ag(7)-S(9)#10	2.705(3)
	Ag(1)-S(5)	2.664(3)		Ag(7)-S(6)#11	2.805(3)
$Ag(2)S_4$	Ag(2)-S(1)	2.507(3)	$P(1)S_4$	P(1)-S(1)	2.032(4)
	Ag(2)-S(3)	2.551(3)		P(1)-S(5)#9	2.033(4)
	Ag(2)-S(8)	2.608(3)		P(1)-S(4)#9	2.063(4)
	Ag(2)-S(4)	2.682(3)		P(1)-S(7)#5	2.082(4)
$Ag(3)S_3$	Ag(3)-S(4)#1	2.534(3)			
	Ag(3)-S(6)	2.563(3)	$P(2)S_4$	P(2)-S(2)	2.049(4)
	Ag(3)-S(2)	2.658(3)		P(2)-S(3)	2.054(4)
	Ag(3)-S(11)	2.685(3)		P(2)-S(10)	2.071(4)
$Ag(4)S_3$	Ag(4)-S(7)	2.522(3)		P(2)-S(12)#10	2.023(4)
	Ag(4)-S(9)	2.538(3)			
	Ag(4)-S(11)	2.540(3)	$P(3)S_4$	P(3)-S(6)	2.074(4)
$Ag(5)S_3$	Ag(5)-S(7)#5	2.462(3)		P(3)-S(8)#1	2.050(4)
	Ag(5)-S(10)	2.471(3)		P(3)-S(9)#2	2.063(4)
	Ag(5)-S(1)#6	2.613(3)		P(3)-S(11)#12	2.024(4)

[a]Symmetry transformations used to generate equivalent atoms. (#1) -x,y+1/2,-z-1/2; (#2) x,y+1,z; (#3) -x-1,y-1/2,-z-1/2; (#4) -x,y-1/2,-z-1/2; (#5) x+1,-y-3/2,z+1/2; (#6) -x+1,-y-1,-z; (#7) x,y-1,z;

(#8) -x,-y-3,-z; (#9) -x+1,-y-2,-z; (#10) -x,-y-2,-z ; (#11) -x,-y-1,-z; (#12) -x-1,y+1/2,-z-1/2; (#13) x-1,-y-3/2,z-1/2.

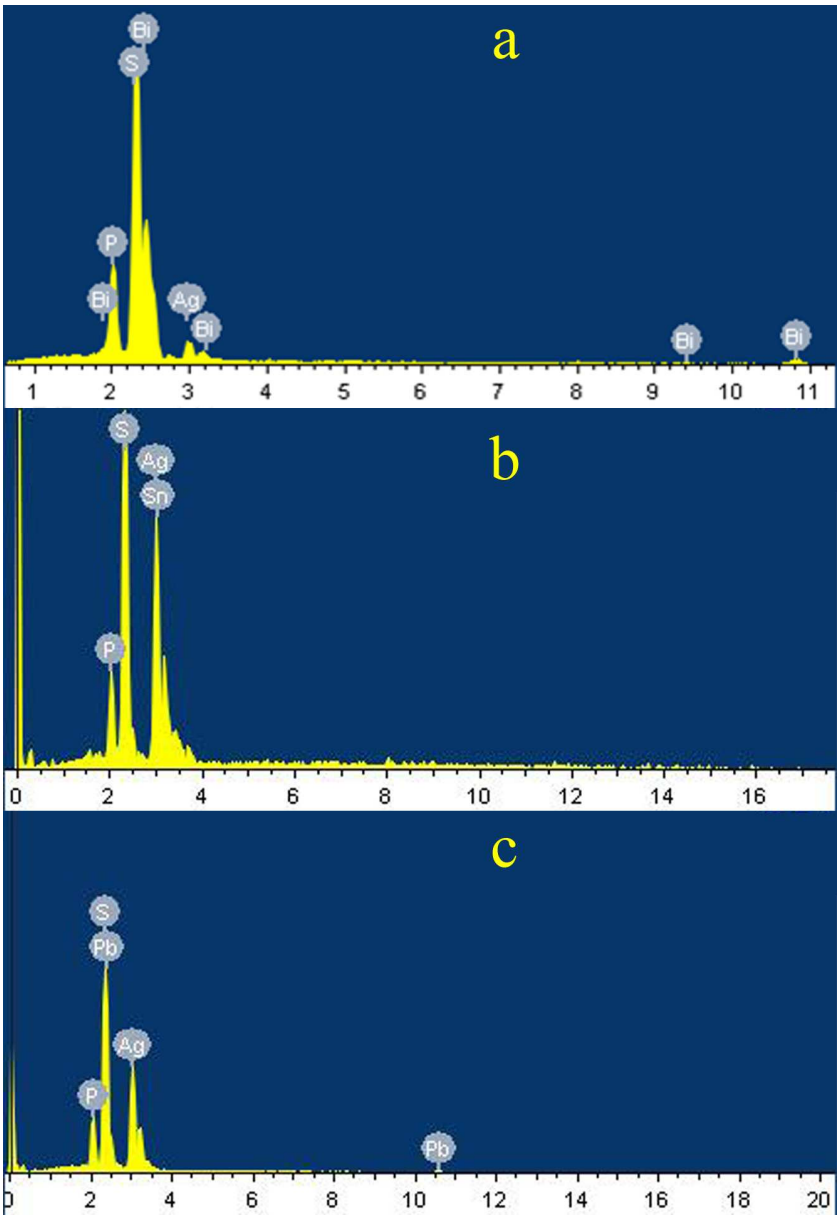

Figure S1. Microscopic elemental analyses of **1** (a), **2** (b) and **3** (c) by EDS.

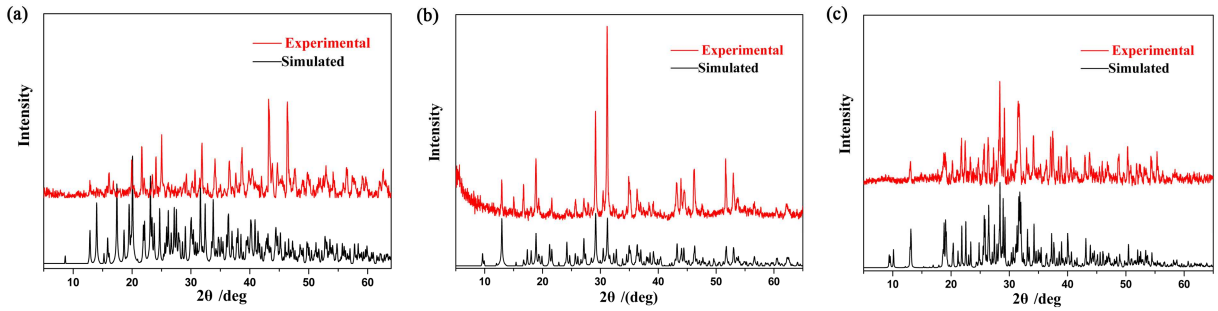

Figure S2. Simulated and experimental (~25 °C) XRD powder patterns of **1** (a), **2** (b) and **3** (c). Intensities of some peaks on the experimental patterns don't match those on the simulated ones because of the effect of preferred orientation.

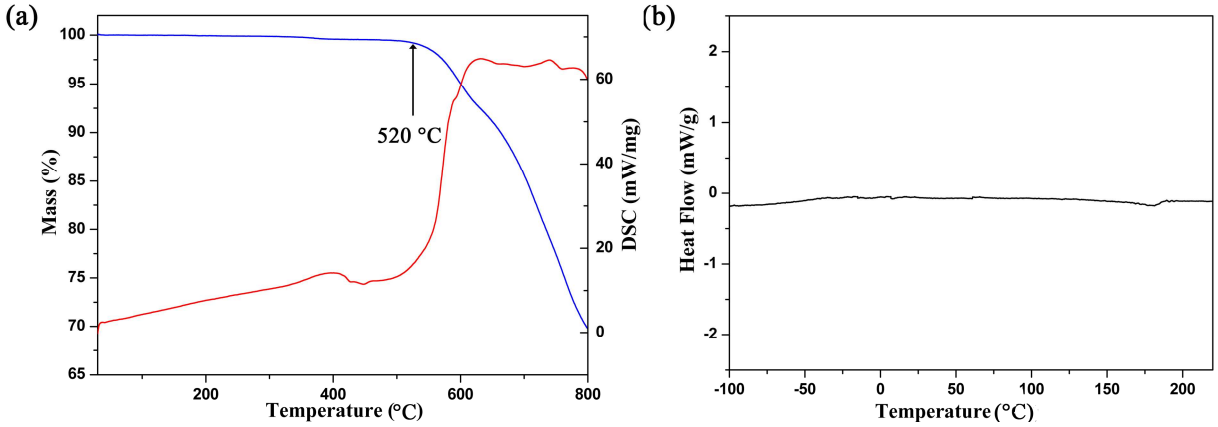

Figure S3. (a) TGA curve shows that compound **1** can be stable up to 520 °C. (b) DSC curve of **1** reveals no phase transition happens in the temperature region of –100~220 °C.

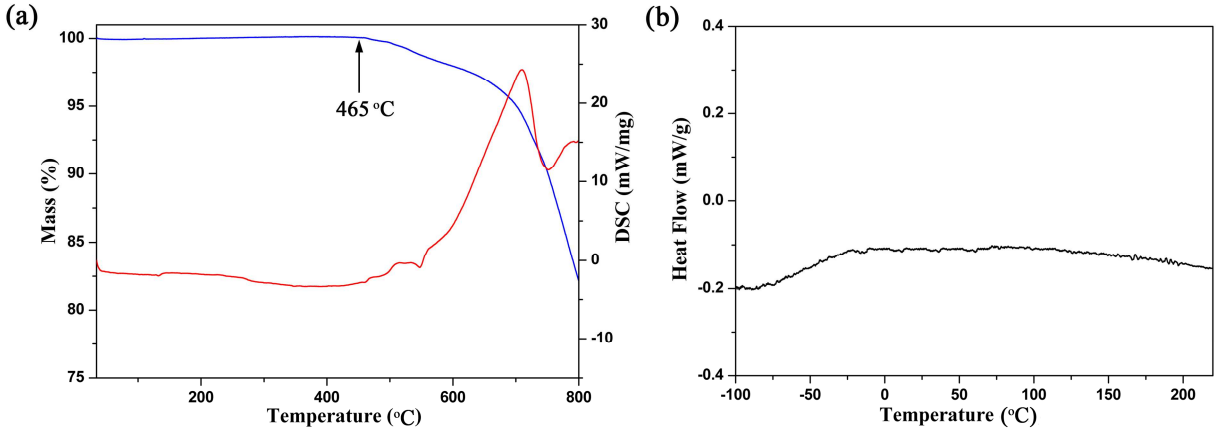

Figure S4. (a) TGA curve shows that compound **2** can be stable up to 465 °C. (b) DSC curve of **2** reveals no phase transition happens in the temperature region of –100~220 °C.

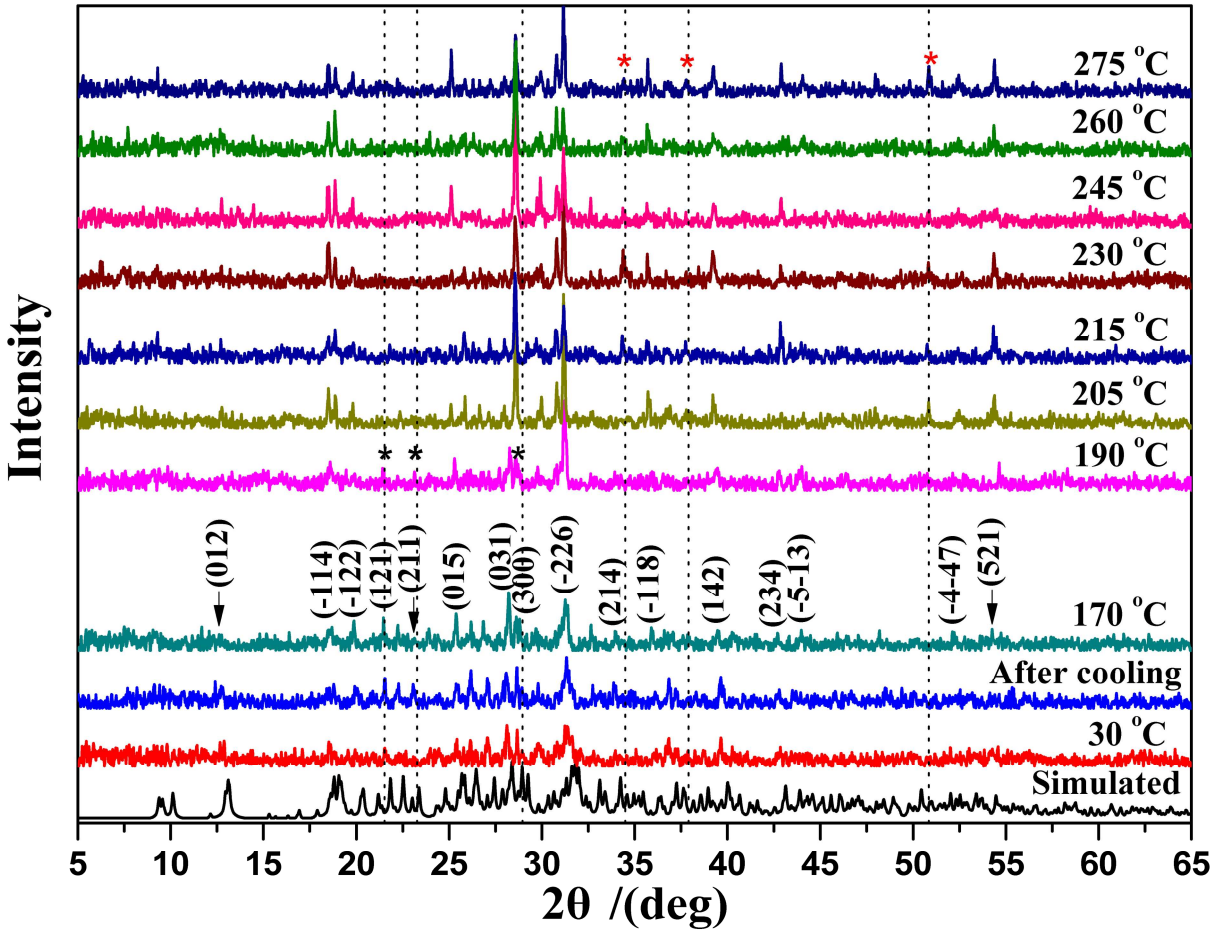

Figure S5. Simulated and variable-temperature XRD powder patterns of **3** from 170 to 275 °C. The powder diagram after cooling down undergone phase transition is labeled by 'After cooling'. The black and red asterisks respectively represent the disappeared and newly emerged Bragg peaks under structural phase transition at ~204 °C.

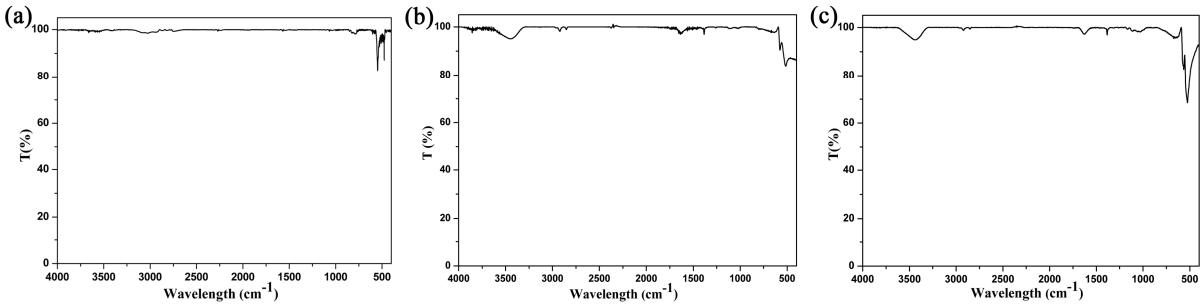

Figure S6. IR spectra of **1** (a), **2** (b) and **3** (c). The absorptions at around 550 cm^{-1} can be assigned to the *v* (P–S) vibrations. The minor peaks at ~1640 and ~3300 cm^{-1} can be attributed to water.

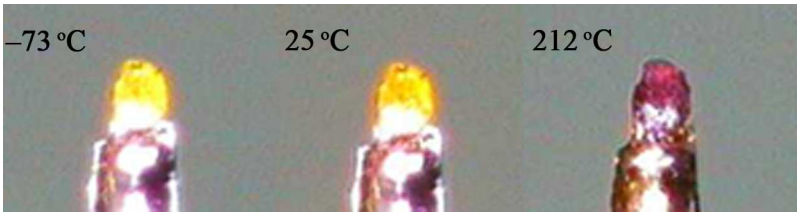

Figure S7. Photomicrographs of the same crystal of **3** mounted on a glass fiber, recorded at –73 °C, 25 °C and 212 °C from left to right.