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Electronic Supplementary Information

Solid-state Conversion of Double Helix Thallium(I) Coordination Polymer to Corrugated Tape Silver(I) Polymer

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Experimental

1. Materials and Physical Techniques.

All reagents for the synthesis and analysis were commercially available and used as received. PARSONIC 15S ultrasonic bath (with the frequency 28 KHz) was used for the ultrasonic irradiation. Microanalyses were carried out using a Vario EL III rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded using an Equinox 55 FT-IR spectrometer (Bruker, Bremen, Germany) in ATR form, in the range of 400-4000 cm^{-1} with 4.0 cm^{-1} resolution and the 16 scan's numbers. The molecular structure plot and simulated XRD powder pattern based on single crystal data were prepared using OLEX and Mercury software. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with mono chromatized Cu-k_α radiation. The thermal behavior was measured with a PL-STA 1500 apparatus in the static atmosphere of nitrogen. The samples were characterized with a scanning electron microscope (Philips XL 30) with gold coating.

2. Synthesis of $[Tl(\mu_2\text{-dcpa})]_n$ (1) nanostructures by a sonochemical process

To prepare nano-sized $[Tl(\mu_2\text{-dcpa})]_n$, 4 mmol (0.884 g) of the 2,4-dichlorophenoxyacetic acid was dissolved in 15 ml methanol and was mixed and stirred with solution of 4 mmol (0.228 g) KOH in 5 ml H_2O at 100 °C for about 45 minutes, then a solution of 4 mmol (1.064 g) $TlNO_3$ in 6 ml H_2O was added to the mixture and the heating and stirring process was continued for about one hour. Then the vessel of the reaction was positioned in an ultrasonic bath. After about 5 hours white precipitate was obtained which was filtered and dried at room temperature. d.p. = 177 °C, yield: 1.331 g, 78.4 % based on final product, IR (selected bands; in cm^{-1}): 447.9 vs, 480.0 vs, 549.6 m, 612.8 m, 688.0 s, 751.0 vs, 795.6 m, 865.7 m, 935.8 m, 1059.8 s, 1105.7 m, 1159.0 w, 1240.9 s, 1340.5 m, 1416.1 s, 1476.2 vs, 1555.5 m, 1598.2 w and 1735.9 w, Anal. calc. For $C_8H_5Cl_2O_3Tl$: C, 22.64; H, 1.19 found; C, 22.71; H, 1.10 %.

3. Mechanochemical reaction of 1 with $AgNO_3$ in order to synthesis of $[Ag_2(\mu_2\text{-dcpa})_2]_n$ (2).

This reaction was performed between 2 mmol (0.849 g) of [Tl(μ_2-dcpa)]$_n$ (**1**) nano-structure with 2.5 mmol (0.424 g) of $AgNO_3$. These two reactants were mixed in mortar and ground up for 30 minutes. The XRD pattern of resulting mixture approved the existence of compound **2** and produced $TlNO_3$ (Figure S1c in the SI). Then the mixture was four times washed with distilled water until the unreacted $AgNO_3$ and produced $TlNO_3$ removed from it and the pure product was separated. d.p. = 222 °C, yield: 0.626 g, 95.4 % based on final product, IR (selected bands; in cm^{-1}): 432.2 m, 465.4 s, 563.5 s, 606.2 s, 648.8 s, 698.1 s, 762.8 s, 824.0 s, 864.6 m, 948.2 m, 1039.5 s, 1066.7 s, 1100.7 m, 1239.8 s, 1339.8 s, 1415.0 s, 1450.6 s, 1478.3 s, 1559.9 vs and 1732.6 w, Anal. calc. For $C_{16}H_{10}Ag_2Cl_4O_6$: C, 29.30; H, 1.54 found; C, 29.18; H, 1.48 %.

4. Checking the reversibility of this solid state structural transformation with $TlNO_3$

This reaction was performed between 0.25 mmol (0.164 g) of **2** with 0.75 mmol (0.200 g) of $TlNO_3$. These two reactants were mixed in mortar and ground up for 30 minutes. The XRD pattern of resulting precipitate approved that this transformation is irreversible (Figure S1f in the SI) and [Ag_2(μ_2-dcpa)$_2$]$_n$ (**2**) was not converted back to **1** upon solid-state reaction with $TlNO_3$. IR (selected bands; in cm^{-1}): 432.1 m, 465.3 s, 563.4 s, 606.2 s, 648.7 s, 698.1 s, 762.9 s, 824.0 s, 864.5 m, 948.2 m, 1039.5 s, 1066.6 s, 1100.7 m, 1239.7 s, 1339.7 s, 1375 s, 1415.0 s, 1450.6 s, 1478.2 s, 1560.0 vs and 1732.5 w.

5. Synthesis of [Tl(μ_2-dcpa)]$_n$ (1) and preparation of its single crystals.

2 mmol (0.442 g) of the 2,4-dichlorophenoxyacetic acid was dissolved in 20 ml methanol and was mixed and stirred with solution of 2 mmol (0.114 g) KOH in 5 ml H_2O at 100 C for about 45 minutes, then a solution of 2 mmol (0.532 g) $TlNO_3$ in 5 ml H_2O was added to the mixture and the heating and stirring process was continued for about one hour. After filtering it was allowed to evaporate for several days and then suitable crystals were obtained. The crystals was separated and kept in its mother liquid. d.p. = 177 °C, yield: 0.541 g, 63.7 % based on final product, IR (selected bands; in cm^{-1}): 447 vs, 481 vs, 549 m, 612 m, 688 s, 750 vs, 795 m, 865 m, 936 m, 1059 s, 1105 m, 1160 w, 1240 s, 1340 m, 1415 s, 1476 vs, 1556 m, 1598 w and 1735 w. Anal. calc. For $C_8H_5Cl_2O_3Tl$: C, 22.64; H, 1.19 found; C, 22.57; H, 1.15 %.

6. Thermal behavior studies

TGA data (Figure S3a) indicated that single crystal of **1** is stable up to 170 °C in a static atmosphere of nitrogen (Figure S3a). The TG curve also exhibits the thermolysis stage between 170 and 450 °C with a mass loss of 48.4% (calcd 50.0%) which is attributed to removal of dcpa^{-} from **1**. The DTA curve displays a very sharp exothermic peak at 300 °C (Figure S3a). Compound **1** nanostructures which prepared by sonochemical procedure, shows similar thermal behavior (Figure S3b). The thermal behaviour of compound **1** after solid-state mechanochemical reaction with excess $AgNO_3$ (Figure S3c) is different from **1** (Figure S3a,b) which approved formation of other new compound (**2**) from this conversion. Thermolysis of compound **1** is accompanied with an exothermic peak at 300 °C which do not observed in **2** (Figure S3c). TGA data indicated that compound **2** nanoparticles are stable up to 160 °C in a static atmosphere of nitrogen (Figure S3d). The TG curve also exhibits the decomposition and thermolysis stage between 160 and 350 °C with a mass loss of 63.5% (calcd 67.1%) which is attributed to removal of dcpa^{-} from **2**. The DTA curve displays a very sharp endothermic peak at 240 °C (Figure S3d). We also examined thermal behaviour of compound **2** after mechanochemical reaction of it with $TlNO_3$ (Figure S3e). The result is the same as that obtained from mechanochemiical reaction of **1** with excess $TlNO_3$ (Figure S3c). This observation also indicates that conversion of **1** to **2** is irreversible and in this stage we only have mixture of **2** and $TlNO_3$.

Table S1. Crystal data and structure refinement for compounds [Tl(μ_2-dcpa)]$_n$ (**1**).

Identification code	**1**
Empirical formula	$C_8H_5Cl_2O_3Tl$
Formula weight	424.39
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2_1/c
Unit cell dimensions	a = 17.903(2) Å b = 3.9651(5) Å c = 13.9329(16) Å α =90.00^o β = 98.904(4)^o γ =90.00^o
Volume	977.1(2) Å^3
Z	4
Density (calculated)	2.885 g.cm^{-3}
Absorption coefficient	17.049 mm^{-1}
F(000)	768
Crystal size	0.500 × 0.110 × 0.030 mm^3
Theta range for data collection	3.005 to 26.366^o
Index ranges	$-22 \leq h \leq 19$ $-4 \leq k \leq 4$ $-15 \leq l \leq 17$
Reflections collected	3238
Independent reflections	1362
Absorption correction	Multi-scan
Max. and min. transmission	0.7457 and 0.2283
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1748 / 0 / 127
Goodness-of-fit on F^2	1.003
Final *R* indices [I>2σ (*I*)]	R_1= 0.0628 wR_2= 0.1480
R Indices (all data)	R_1= 0.0913 wR_2= 0.1623
Largest diff. Peak, hole	4.271 and -3.016 e.Å^{-3}

Table S2. Selected bond lengths /Å and angles /° for compound [Tl(μ_2-dcpa)]$_n$ (**1**).

Tl(1)-O(2)	2.708(10)	O(2)-Tl(1)-O(2)	74.7(3)
Tl(1)-O(2)	2.786(10)		

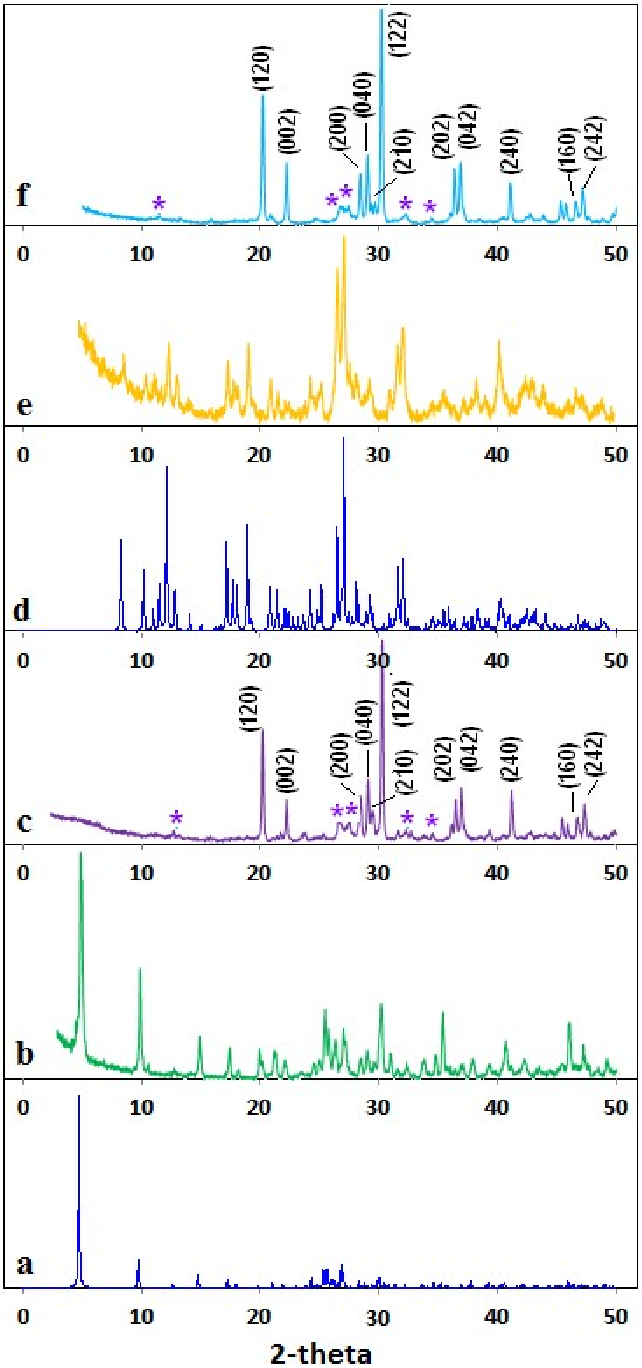


Figure S1. XRD patterns; a) simulated pattern based on single crystal data of compound [Tl(μ_2-dcpa)]$_n$ (**1**), b) compound **1** nanostructures synthesized under ultrasonic irradiations, c) compound **1** after solid-state mechanochemical reaction with excess $AgNO_3$, d) simulated pattern based on single crystal data of compound [Ag_2(μ_2-dcpa)$_2$]$_n$ (**2**), e) pure phase of **2** and f) compound **2** after mechanochemical reaction of it with excess $TlNO_3$. The two XRD patterns in c and f parts show that we have mixture of compound **1** (with low intensity peaks which characterized by * symbol) and $TlNO_3$ (with high intensity peaks which characterized by its crystallographic planes).

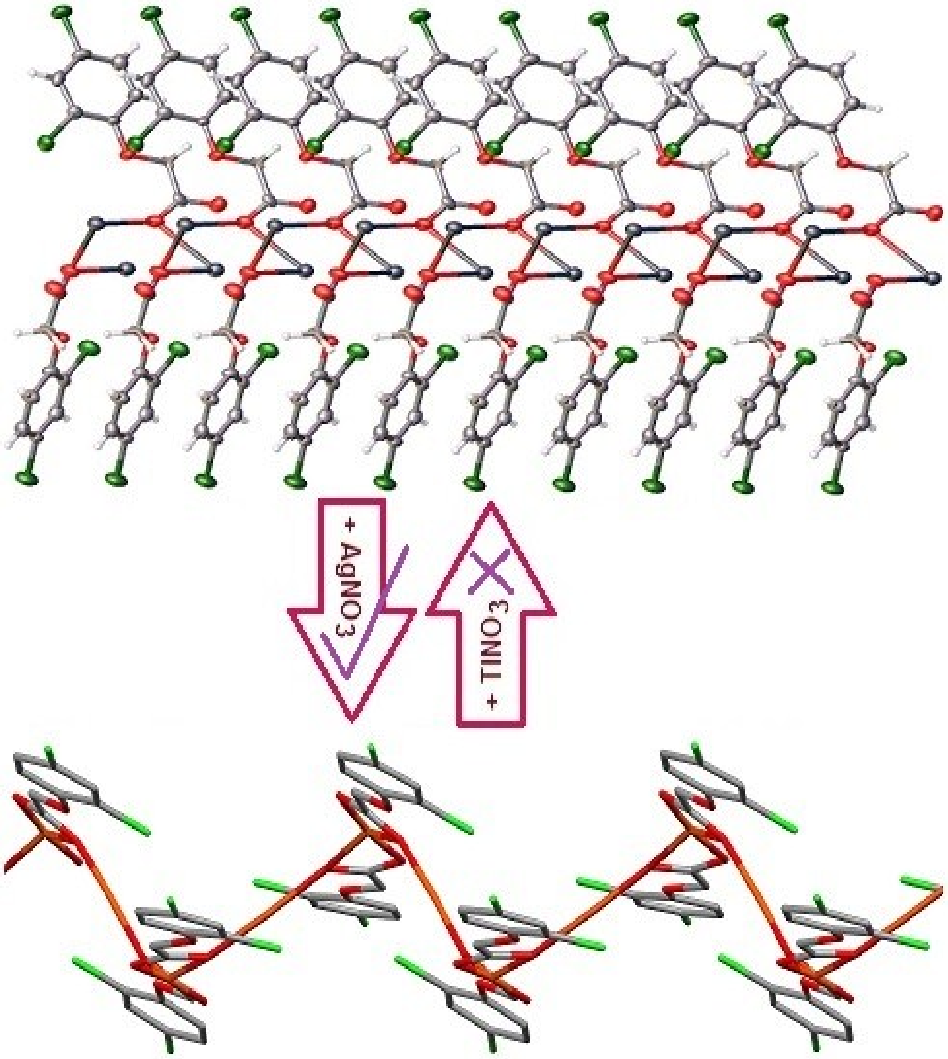
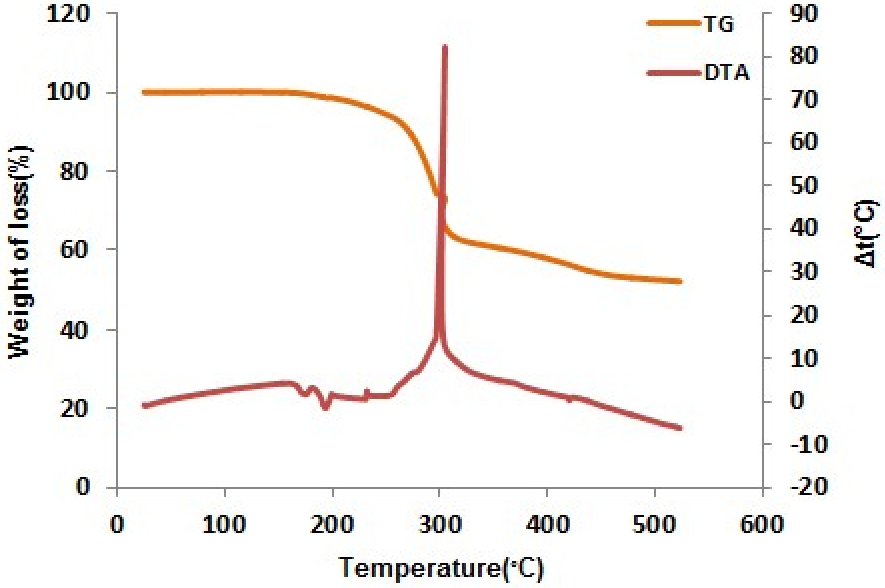


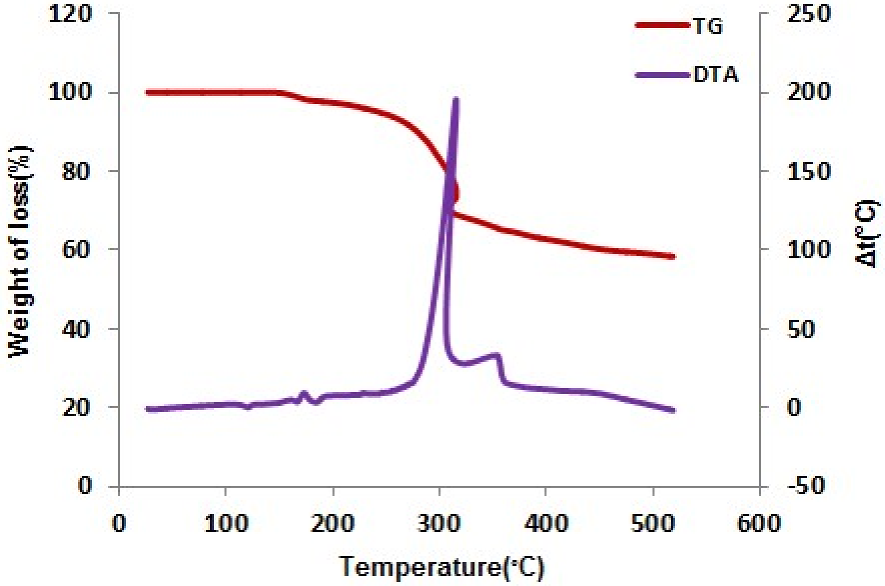
Figure S2. A schematic diagram illustrating the irreversible conversion of **1** (top) with helix chain structure to **2** (bottom) with corrugated tape structure upon mechanochemical reaction, (Tl = dark gray, Ag = orange, O = red, Cl = green, C = gray and H = white).

a)



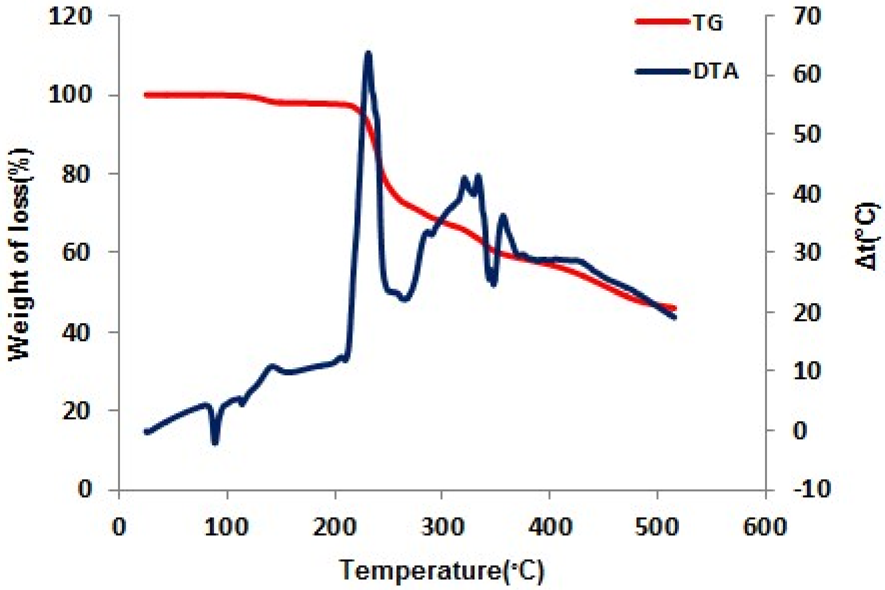
120
100
80
60
40
20
0
Weight of loss(%)
90
80
70
60
50
40
30
20
10
0
-10
-20
Δt(°C)
0
100
200
300
400
500
600
Temperature(°C)
TG
DTA

b)

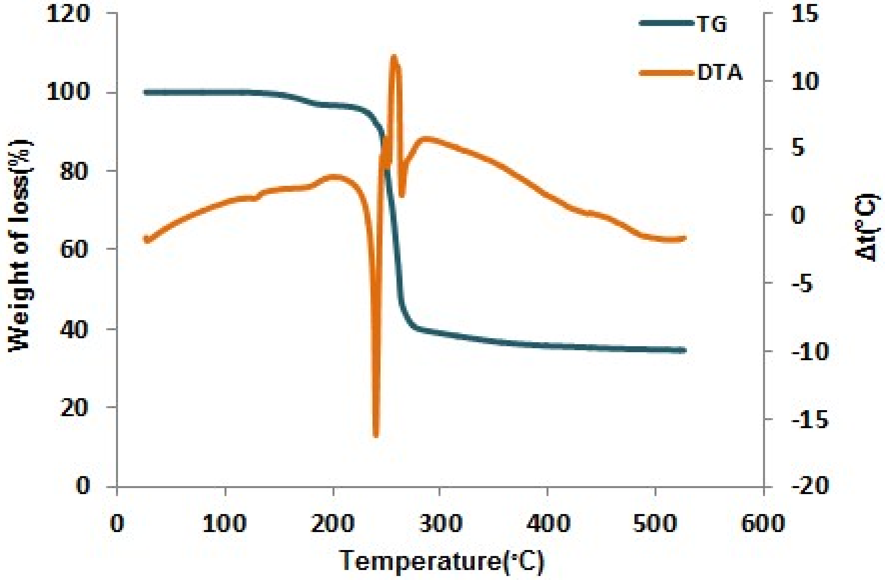


120
100
80
60
40
20
0
Weight of loss(%)
250
200
150
100
50
0
-50
Δt(°C)
0
100
200
300
400
500
600
Temperature(°C)
TG
DTA

c)


TG
DTA
Weight of loss(%)
Δt(°C)
Temperature(°C)
0
20
40
60
80
100
120
-10
0
10
20
30
40
50
60
70
0
100
200
300
400
500
600

d)


TG
DTA
Weight of loss(%)
Δt(°C)
Temperature(°C)
0
20
40
60
80
100
120
-20
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-10
-5
0
5
10
15
0
100
200
300
400
500
600

e)

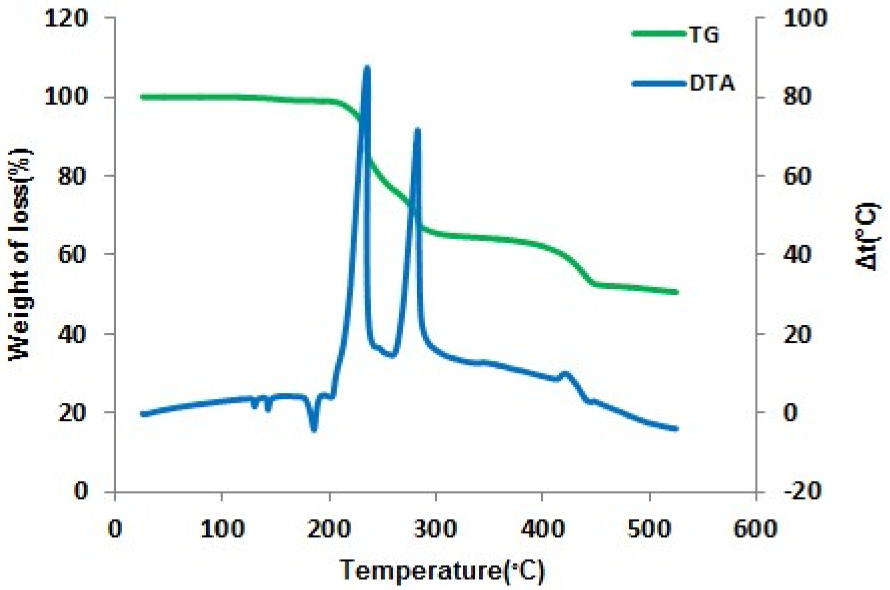

Figure S3. Thermal behaviour of a) compound [Tl(μ_2-dcpa)]$_n$ (**1**) single crystals, b) compound **1** nanostructures synthesized under ultrasonic irradiations, c) compound **1** after solid-state mechanochemical reaction with excess $AgNO_3$, d) compound [Ag_2(μ_2-dcpa)$_2$]$_n$ (**2**) after washing the mixture obtained from previous part and e) compound **2** after mechanochemical reaction of it with excess $TlNO_3$.