

## **Halogen Dipole Moment Effect of Phenolic Ring on Formation of Stair Like Polymers or Polymers with Tetranuclear Cubic Cage Units; New Precursors for Preparation of $\text{TiCl}$ and $\text{Ti}_2\text{O}_3$ Nanostructures**

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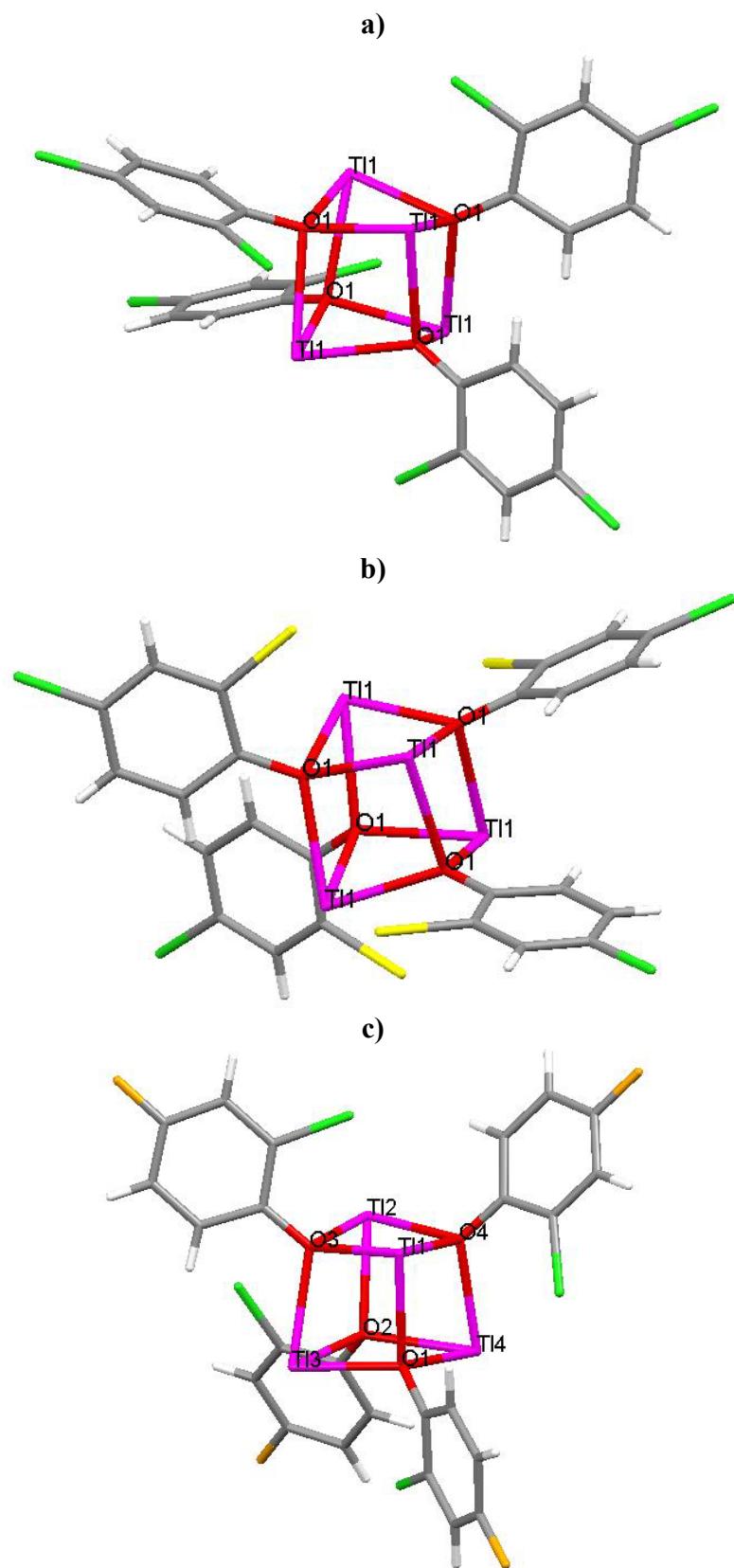
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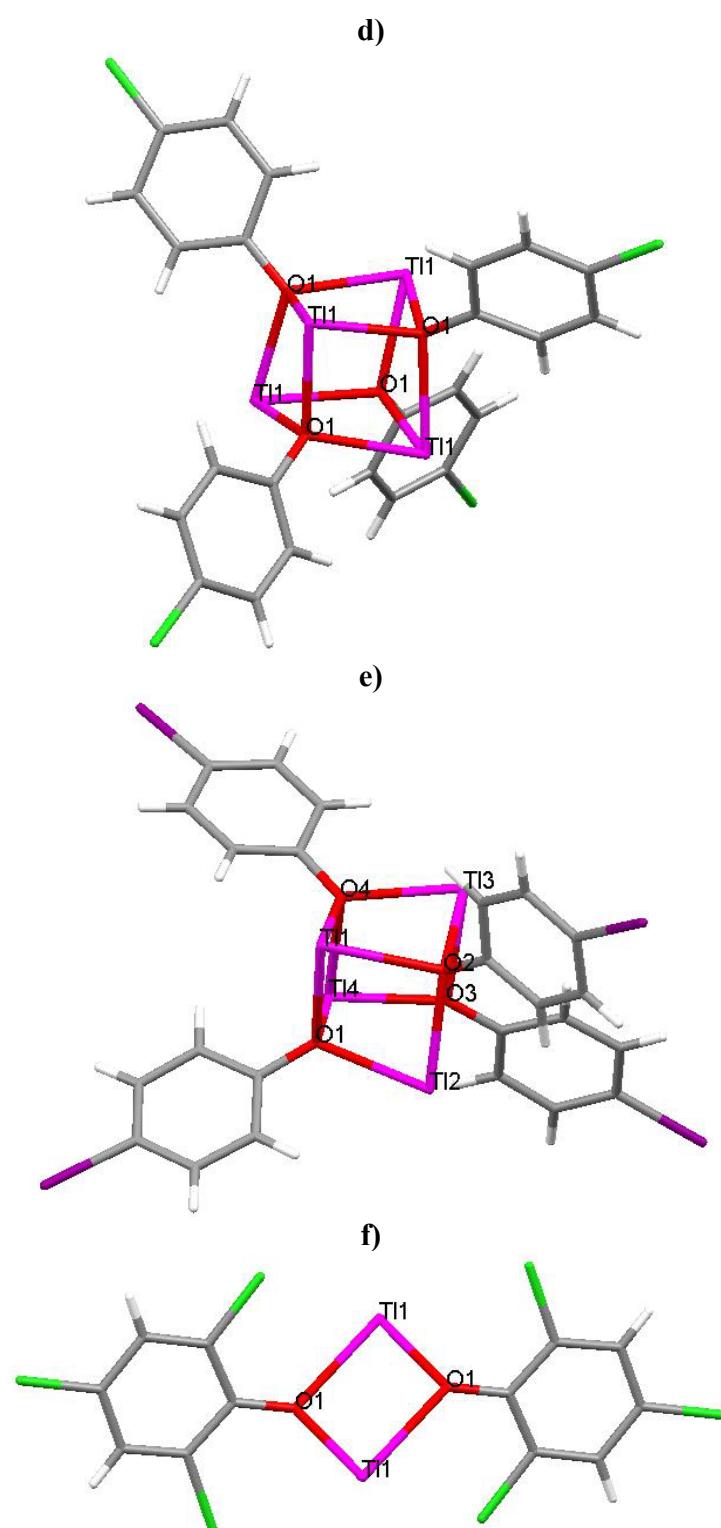
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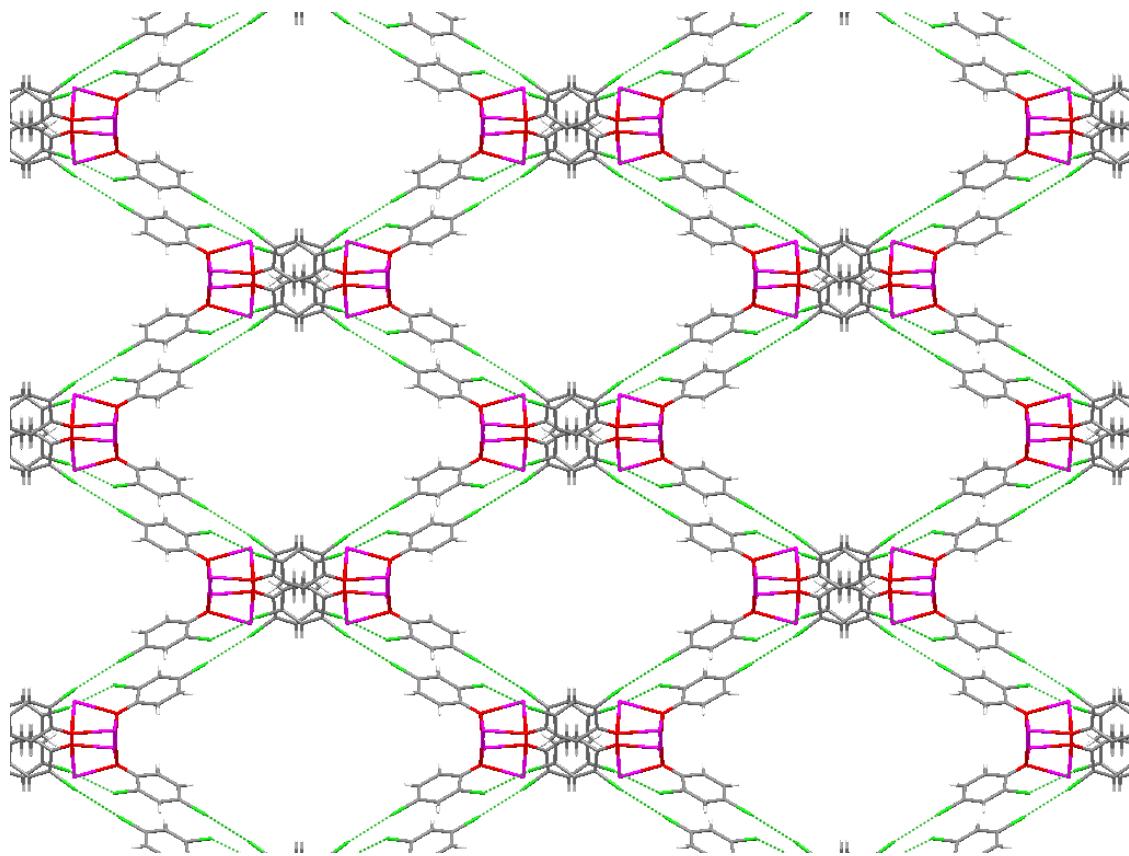
**Table S1.** Bond lengths /Å of secondary Tl···Tl, Tl···C, Tl···H, Tl···F, Tl···Cl and Tl···I interactions in compounds **1–9**.

[Tl <sub>4</sub> (μ <sub>3</sub> -2,4-dcp) <sub>4</sub> ] (1)		[Tl <sub>4</sub> (μ <sub>3</sub> -3,4-dcp) <sub>4</sub> ] (2)		[Tl(μ <sub>3</sub> -2,5-dcp)] (3)	
Tl1-Tl1	3.845	Tl1-C11	3.586	Tl1-C1	3.550
Tl1-Tl1	3.845	Tl1-Tl2	3.864	Tl1-C2	3.624
		Tl2-Tl1	3.970	Tl1-Tl1	3.888
[Tl(μ <sub>3</sub> -2,4,6-tcp)] (4)				Tl1-Tl1	3.888
Tl1-O1	2.828	[Tl <sub>4</sub> (μ <sub>3</sub> -2,4-bcp) <sub>4</sub> ] (5)		Tl1-Tl1	3.888
Tl1-Tl1	3.815	Tl1-Tl1	3.872	Tl1-H2	3.063
Tl1-Tl1	3.815	Tl1-Tl1	3.872	Tl1-Cl1	3.661
Tl1-Tl1	3.810			Tl1-Cl1	3.588
Tl1-Cl1	3.632	[Tl <sub>4</sub> (μ <sub>3</sub> -4-cp) <sub>4</sub> ] (7)		Tl1-Cl2	3.572
Tl1-Cl1	3.343	Tl1-C2	3.639		
Tl1-Cl3	3.544	Tl1-C5	3.654	[Tl <sub>4</sub> (μ <sub>3</sub> -4-ip) <sub>4</sub> ] (8)	
		Tl1-Tl1	3.986	Tl1-C4	3.609
[Tl <sub>4</sub> (μ <sub>3</sub> -2,4-cfp) <sub>4</sub> ] (6)		Tl1-Tl1	3.986	Tl2-C8	3.655
Tl1-C7	3.657	Tl1-Cl1	3.619	Tl4-C10	3.670
Tl1-C8	3.602			Tl4-C11	3.791
Tl1-C9	3.546	[Tl(μ <sub>3</sub> -4-fp)] (9)		Tl4-C12	3.710
Tl1-C10	3.464	Tl1-C1	3.858	Tl4-C15	3.509
Tl1-C11	3.516	Tl1-C2	3.834	Tl4-C22	3.613
Tl1-C12	3.606	Tl1-C3	3.561	Tl4-C25	3.530
Tl4-C3	3.599	Tl1-C4	3.344	Tl1-Tl2	3.883
Tl4-C4	3.481	Tl1-C5	3.415	Tl1-Tl3	3.884
Tl1-Tl3	3.801	Tl1-C6	3.668	Tl2-Tl4	3.878
Tl1-Tl1	3.861			Tl3-Tl4	3.916
Tl2-Tl4	3.838			Tl2-I6	3.816
Tl4-H21	3.113			Tl3-I7	3.663
Tl2-Cl3	3.709			Tl3-I8	3.877
Tl2-F1	3.268			Tl4-I7	3.801

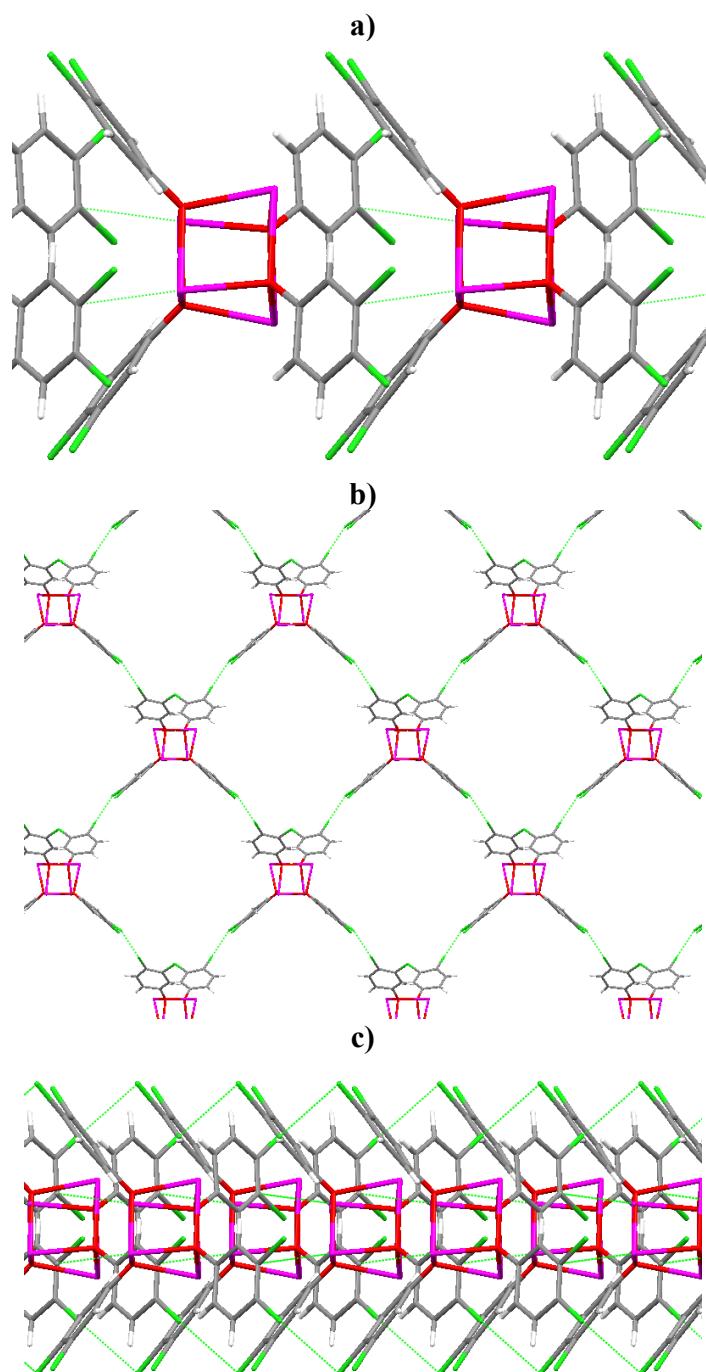




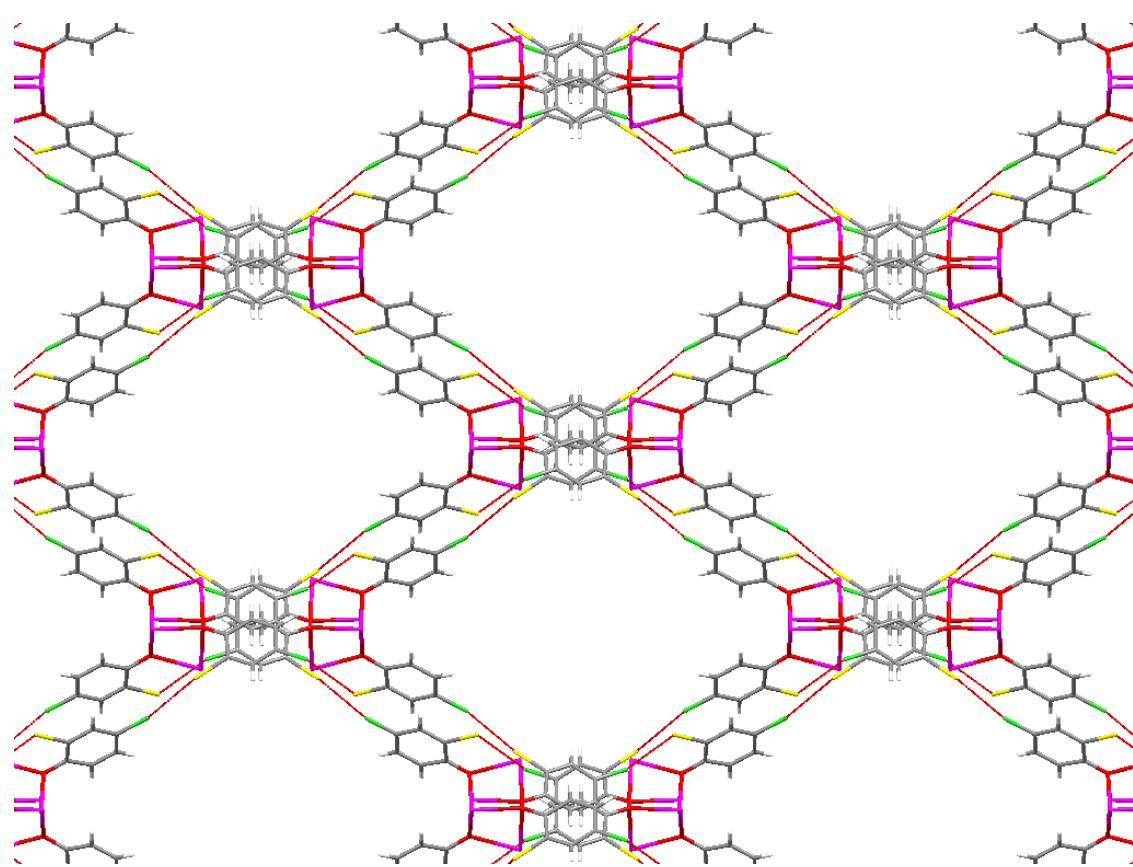
**Figure S1.** View of the two types of primary structural units; a-e) distorted tetranuclear cubic cage unit in compounds **1**, **5**, **6**, **7** and **8** and f) dimeric unit in compound **4** (Tl = purple, O = red, C = gray, F = orange, Cl = green, Br = yellow, I = dark purple and H = white).



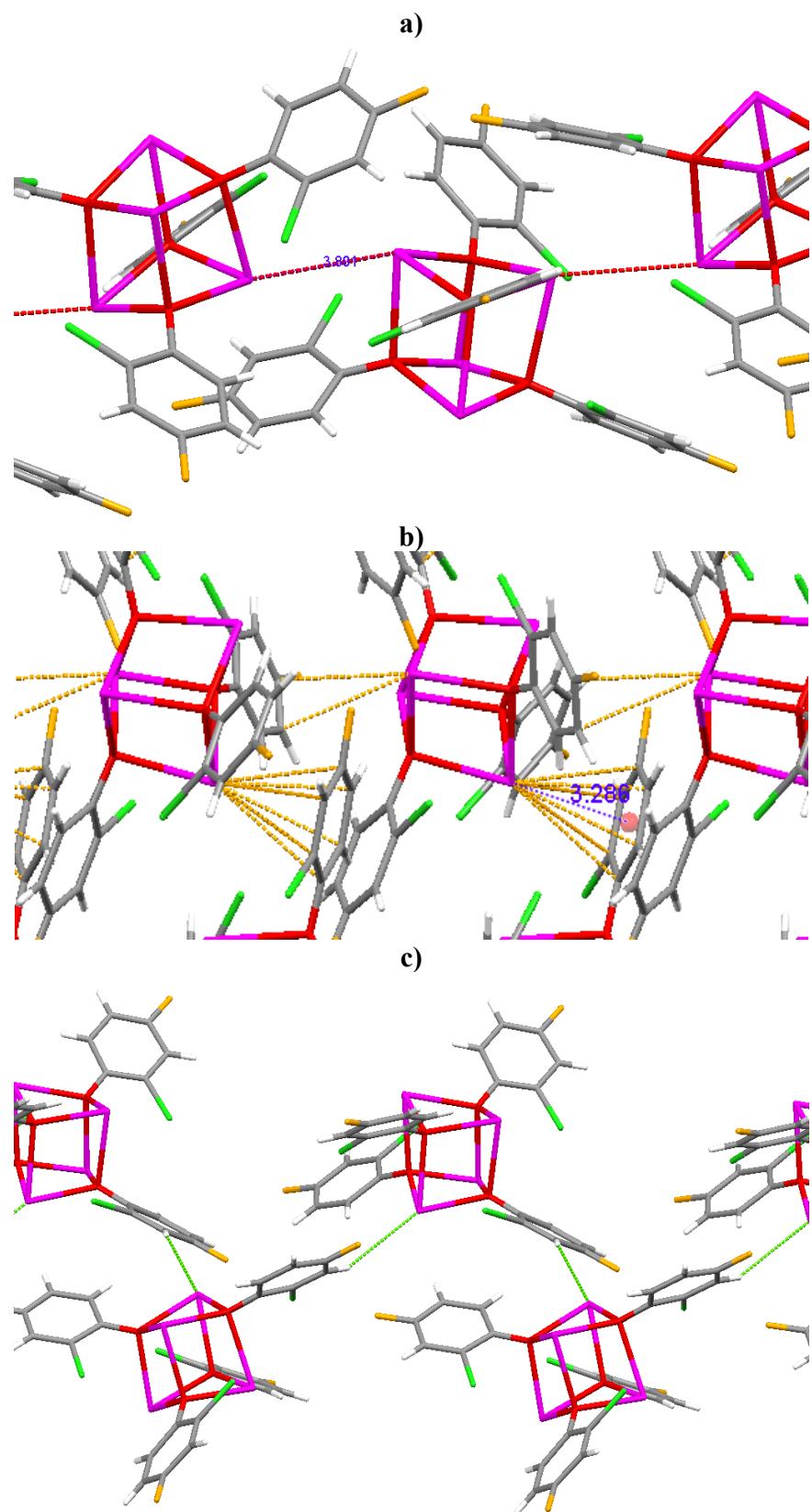
**Figure S2.** A fragment of three-dimensional supramolecular network in  $[\text{Tl}_4(\mu_3\text{-}2,4\text{-dcp})_4]$  (**1**) constructed from  $\text{Cl}\cdots\text{Cl}$  interactions (Tl = purple, O = red, C = gray, Cl = green and H = white).

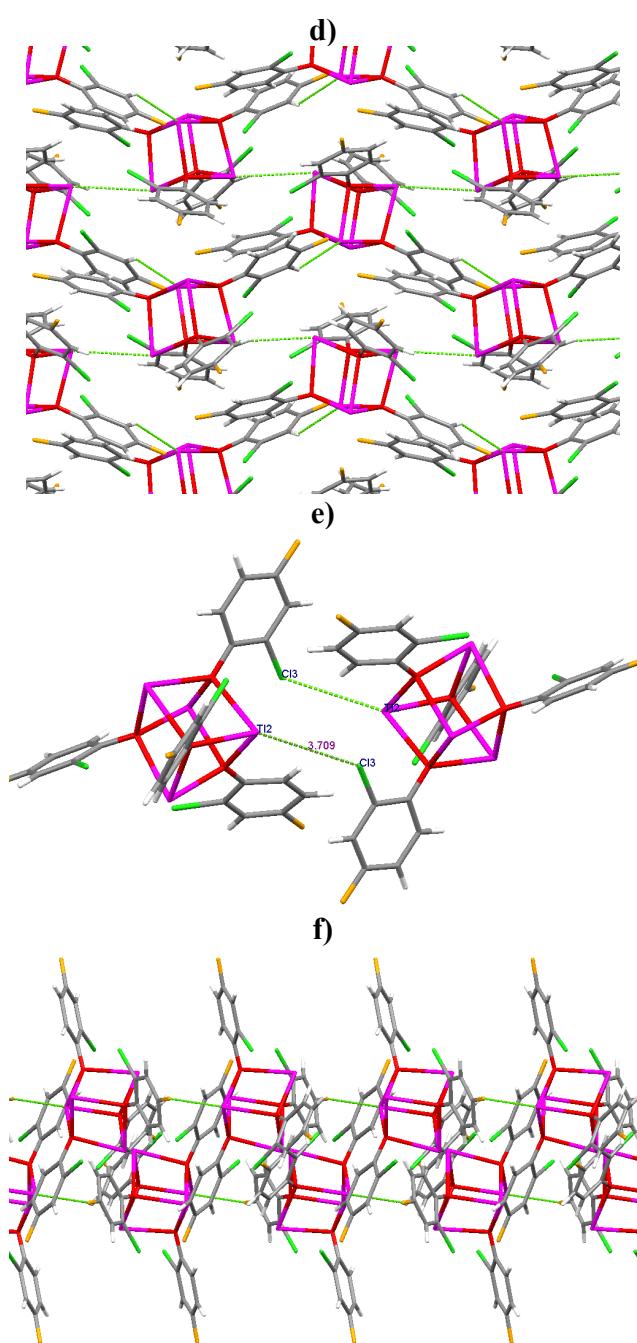


**Figure S3.** a) A fragment of one-dimensional supramolecular polymer of  $[\text{Tl}_4(\mu_3\text{-3,4-dcp})_4]$  (**2**) along the crystallographic *a* axis, constructed from short  $\text{Tl}\cdots\text{C}$  contacts, b) the role of  $\text{Cl}\cdots\text{Cl}$  interactions in formation of two-dimensional supramolecular polymer of **2** along the crystallographic *c* axis and c) side view of two-dimensional supramolecular polymer of **2** constructed from secondary  $\text{Tl}\cdots\text{C}$  and  $\text{Cl}\cdots\text{Cl}$  interactions along the crystallographic *a* axis ( $\text{Tl} = \text{purple}$ ,  $\text{O} = \text{red}$ ,  $\text{C} = \text{gray}$ ,  $\text{Cl} = \text{green}$  and  $\text{H} = \text{white}$ ).

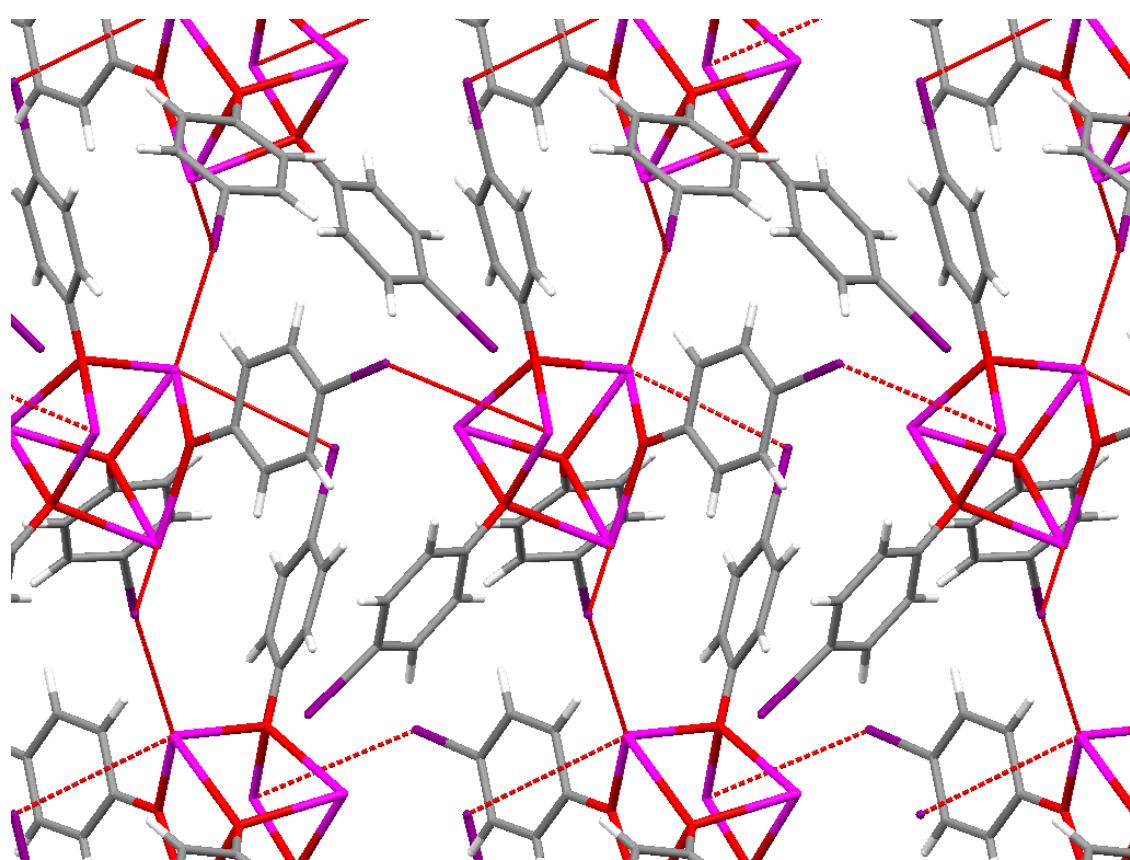


**Figure S4.** A fragment of three-dimensional supramolecular network in  $[\text{Tl}_4(\mu_3\text{-}2,4\text{-bcp})_4]$  (**5**) constructed from  $\text{Cl}\cdots\text{Br}$  interactions (Tl = purple, O = red, C = gray, Cl = green, Br = yellow and H = white).

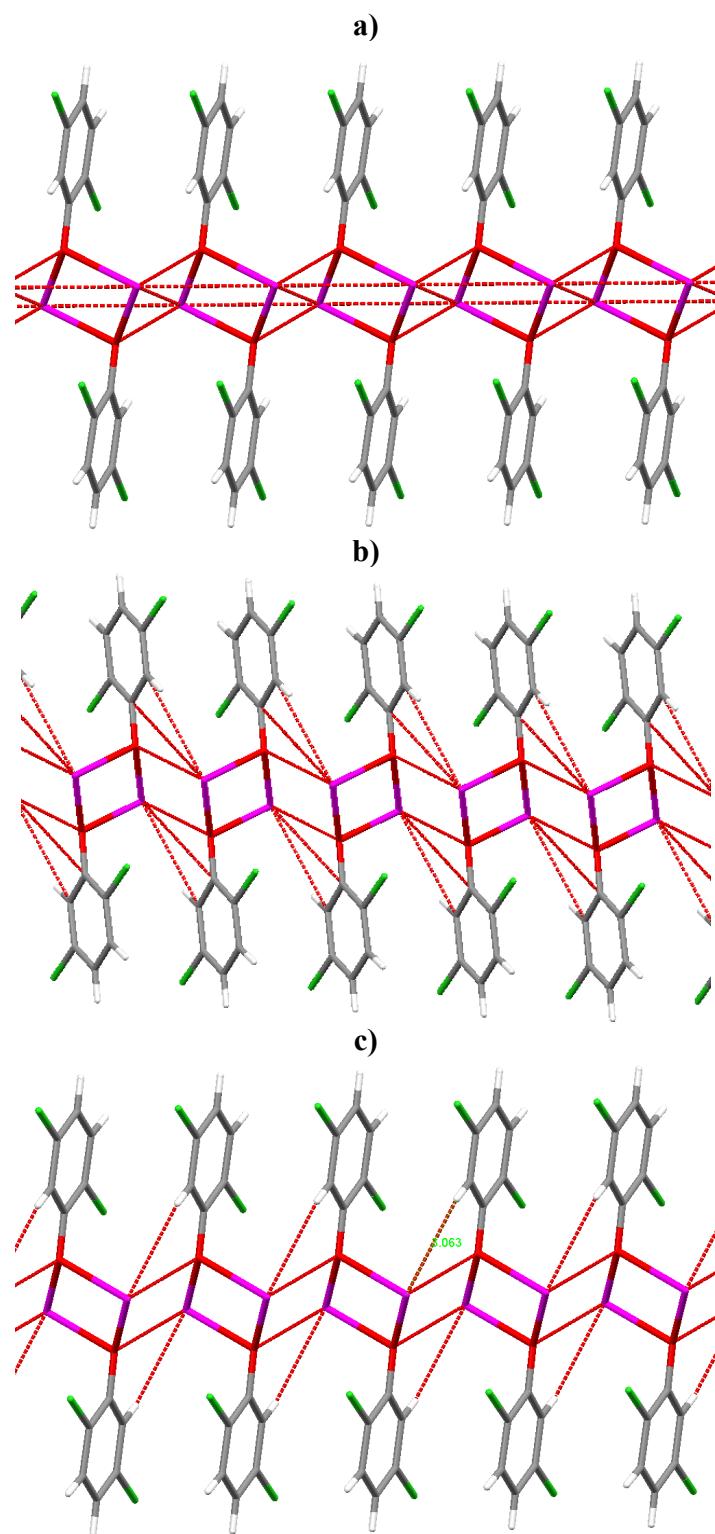




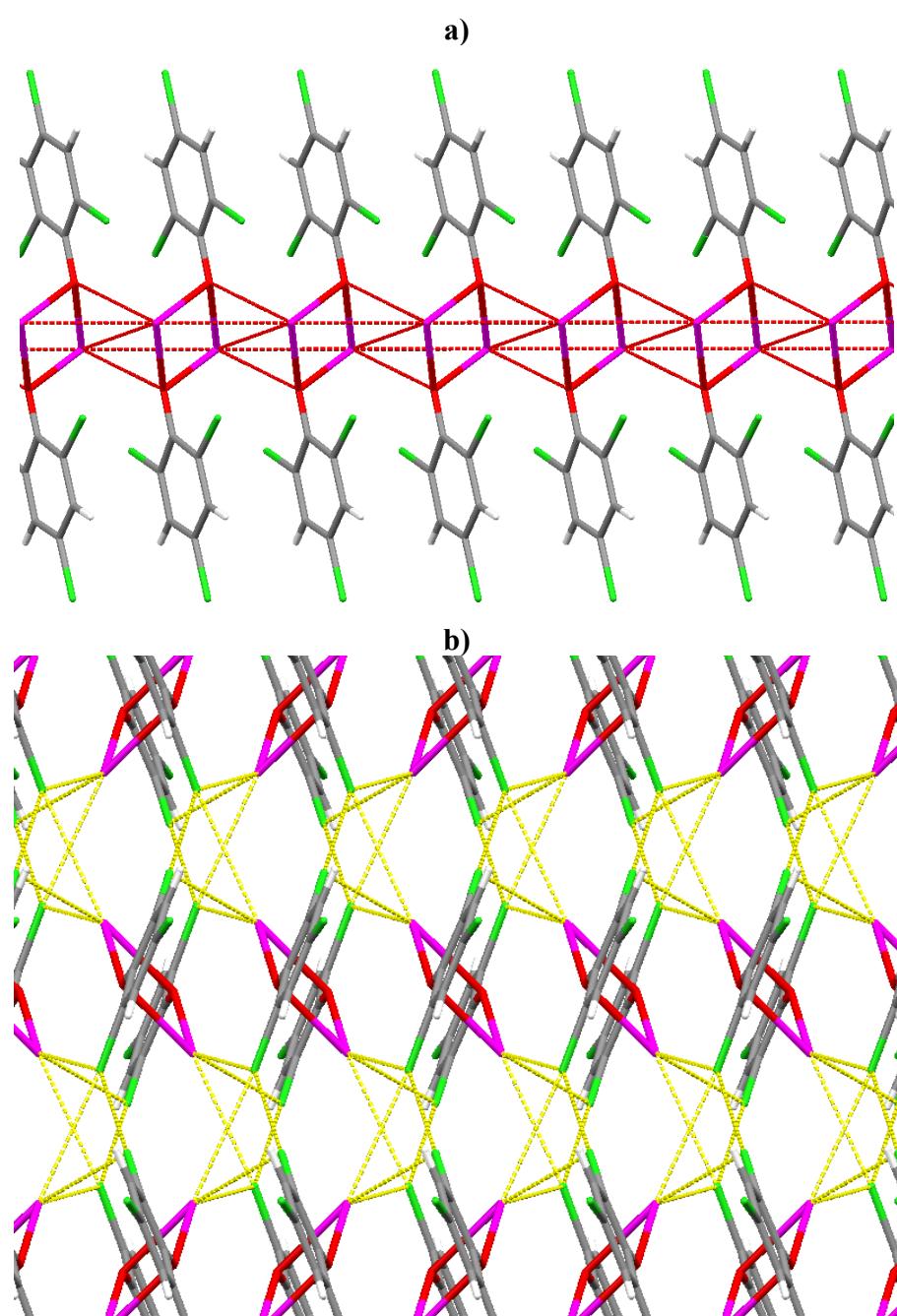
**Figure S5.** a) A fragment of one-dimensional supramolecular polymer in  $[\text{Tl}_4(\mu_3\text{-}2,4\text{-cfp})_4]$  (**6**) constructed from inter-cage  $\text{Tl}\cdots\text{Tl}$  interaction, b) representation of secondary  $\eta^6\text{-Tl}\cdots\text{C}$  and  $\eta^2\text{-Tl}\cdots\text{C}$  interactions in **6**, c) the role of agostic interaction in formation of one-dimensional supramolecular polymer in **6**, d) a fragment of two-dimensional supramolecular polymer in **6**, constructed from agostic  $\text{Tl}\cdots\text{H}$  and inter-cage thalophilic interactions, e) The role of  $\text{Tl}_2\cdots\text{Cl}_3$  short contact in connection of two tetranuclear cubic cage units to each other, f) A fragment of one-dimensional supramolecular polymer in **6** constructed from short  $\text{Tl}_2\cdots\text{F}_1$  contact along the crystallographic *c* axis (Tl = purple, O = red, C = gray, F = orange, Cl = green and H = white).



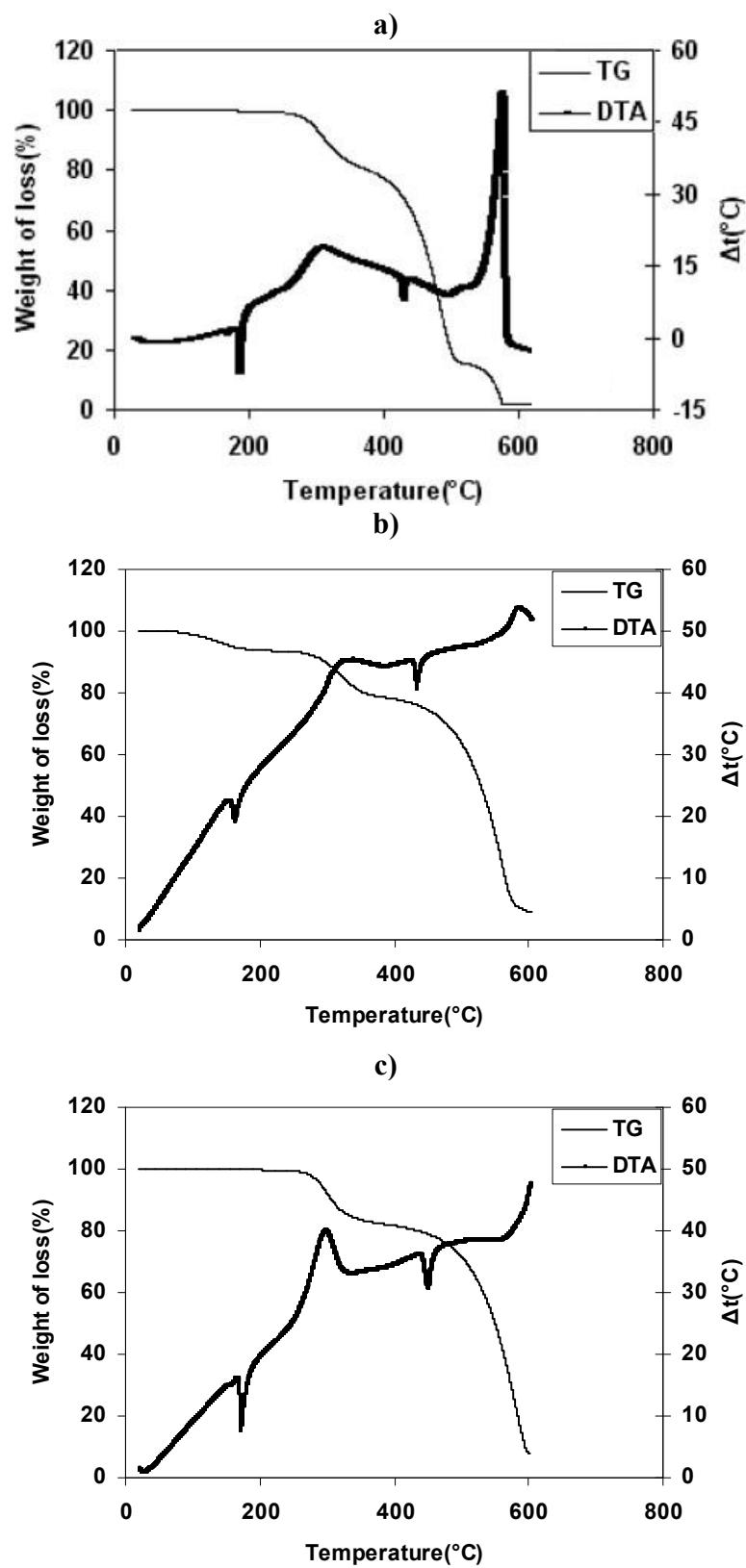
**Figure S6.** Represents the role of short  $\text{Tl}\cdots\text{I}$  contacts in formation of three-dimensional supramolecular network in **8** ( $\text{Tl}$  = purple,  $\text{O}$  = red,  $\text{C}$  = gray,  $\text{I}$  = dark purple and  $\text{H}$  = white).

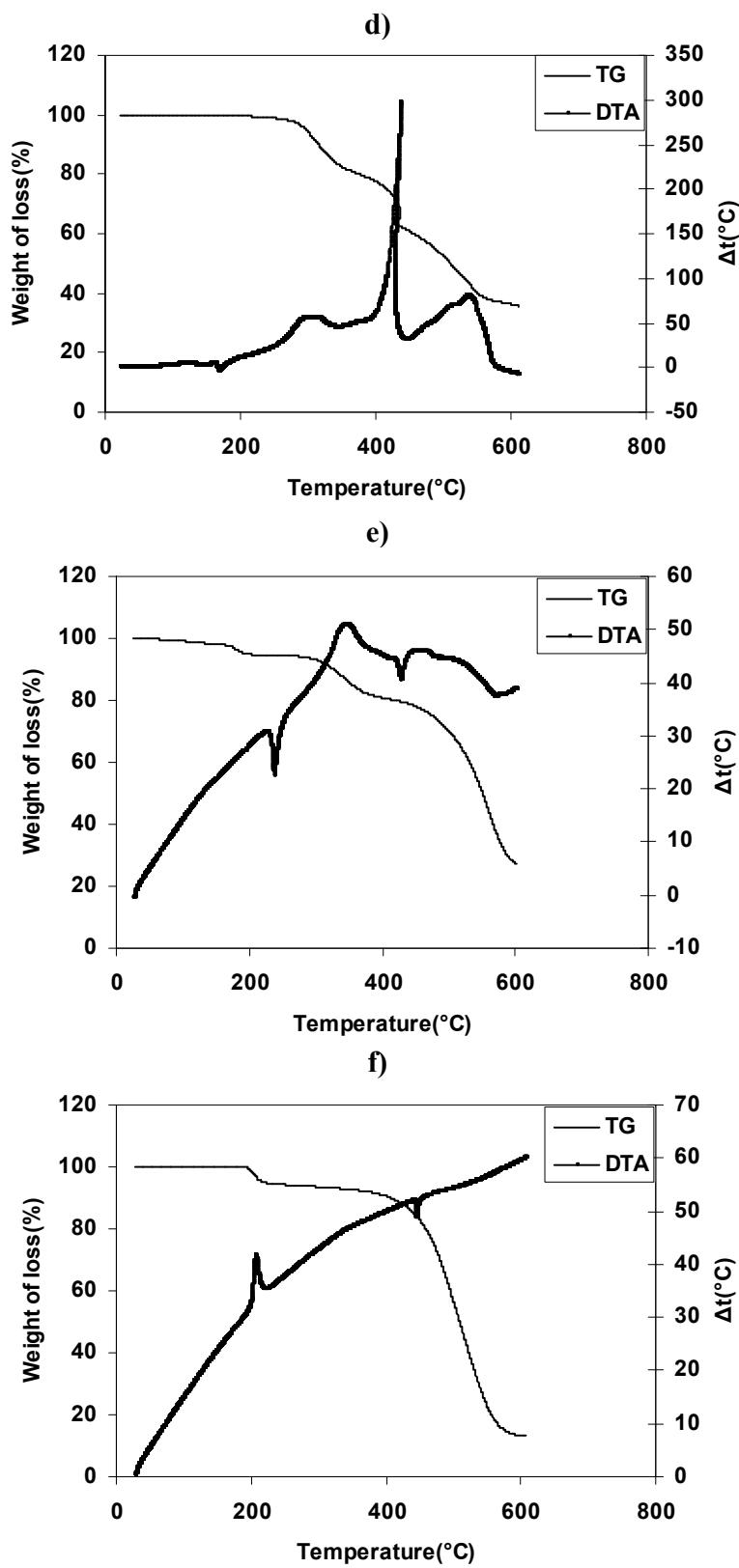


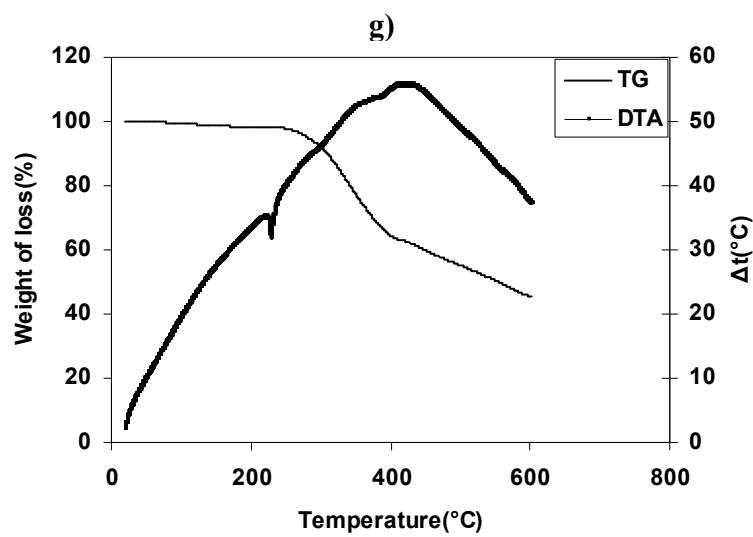
**Figure S7.** Representation of secondary intra-chain a)  $\text{Tl}\cdots\text{Tl}$ , b)  $\text{Tl}\cdots\text{C}$  and c)  $\text{Tl}\cdots\text{H}$  interactions in  $[\text{Tl}(\mu_3\text{-2,5-dcp})] \text{ (3)}$  ( $\text{Tl}$  = purple,  $\text{O}$  = red,  $\text{C}$  = gray,  $\text{Cl}$  = green and  $\text{H}$  = white).



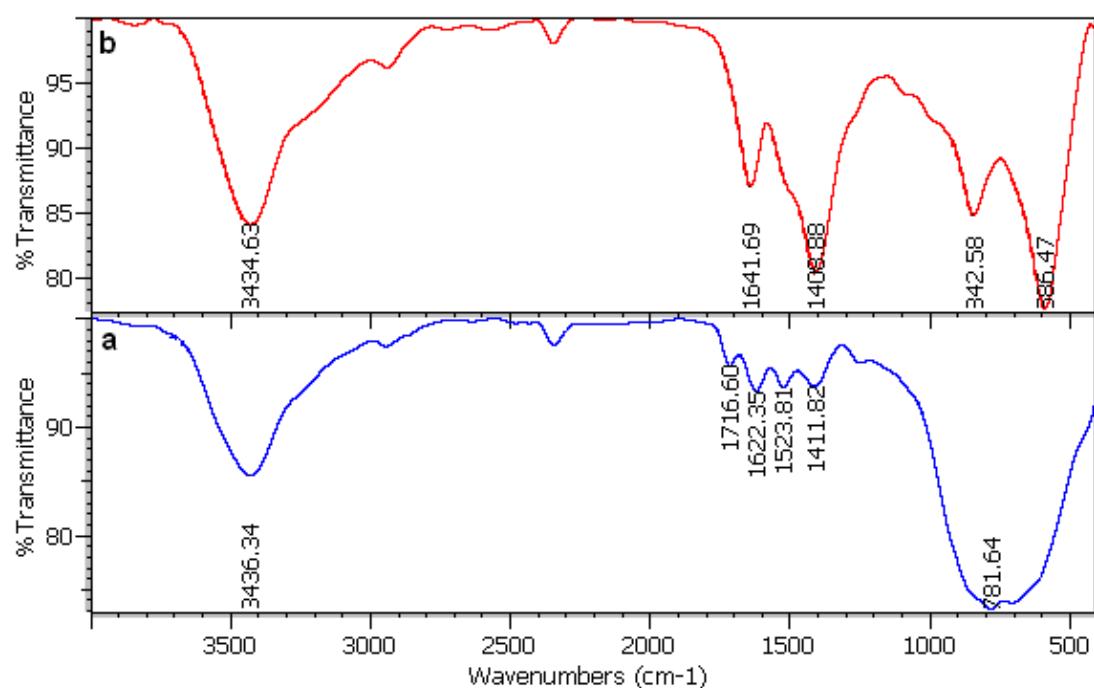
**Figure S8.** a) Intra-chain thalophilic interactions between the Tl(I) and three other thallium atoms in  $[\text{Tl}(\mu_3\text{-2,4,6-tcp})]$  (**4**) and b) the role of three inter-chain  $\text{Tl}\cdots\text{Cl}$  and one inter-chain  $\text{Cl}\cdots\text{Cl}$  interactions in connection of one-dimensional coordination polymers in **4**, resulting in a two-dimensional supramolecular network (Tl = purple, O = red, C = gray, Cl = green and H = white).



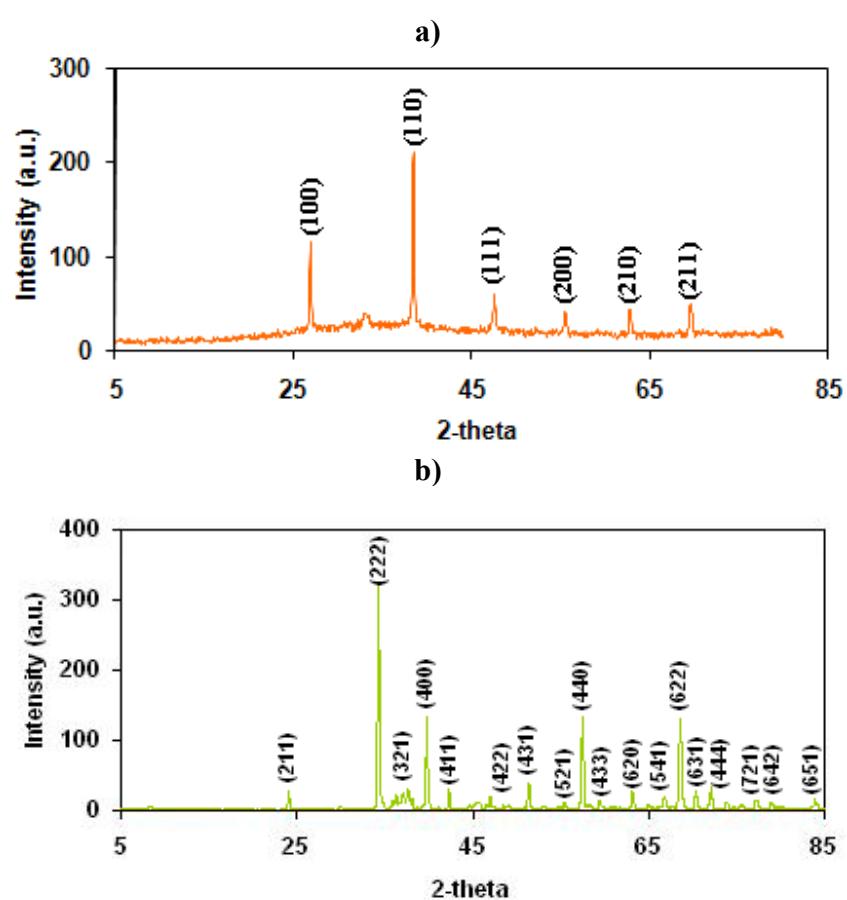




**Figure S9.** Thermal behavior of compounds a) 1, b) 3, c) 5, d) 6, e) 7, f) 8 and g) 9.



**Figure S10.** IR spectra of the residues obtained after calcination process of compounds **3** at 600 °C (a) and **9** at 400 °C (b) which attributed to TlCl and  $\text{Tl}_2\text{O}_3$ , respectively.



**Figure S11.** XRD pattern of the residue obtained after calcination process of compounds 3 (a) and 9 (b) at 600 and 400 °C, respectively.