Supporting Information for

Polymeric supertetrahedral InS clusters assembled by new linkages

Yu-Hong Wang, Jian-Bing Jiang, Peng Wang, Xiao-Lu Sun, Qin-Yu Zhu,* and Jie Dai*

Figure S1. Unit structure of compound **1** consists of an isolated $[H_2dach]^{2+}$ and a $[Ni(dach)_3]^{2+}$ cations. The $In_4(dach)_4S_6$ cluster is completed for clarity.

Figure S2. (a) Unit structure of compound **2** consists of an isolated and water molecules. (b) The one-dimensional chain structure of **2**, showing that the repeating unit consists of eight edge-sharing tetrahedra for a complete period.

Figure S3. (a) Unit structure of compound **3** with an isolated $[Ni(dach)_3]^{2+}$ cation. The incompletely solved solvent molecules are omitted for clarity. (b) The 2-D polyanionic framework of **3** assembled by T4 clusters, showing the –S–S–S– bridges.

Figure S4. (a) Unit structure of compound **4**. Some incompletely solved cations and solvent molecules are omitted for clarity. (b) The 2-D polyanionic framework of **4** assembled by complex bridges.

Figure S5. The structure of $(Hdach)_{10}\cdot[Co(dach)_3]_8\cdot\{[In_{17}Co_4S_{38}H_3]_2[Co(dach)_2]\}\cdot 2H_2O$, a known compound.

Figure S6. The XRD results of compounds **1**–**4** with those calculated from X-ray single-crystal diffraction data, (a), (b), (c) and (d), respectively.

Figure S7. The EDX results of **1**-**4**, showing the information of the elements and their relative contents of the compounds.

Figure S8. The solid-state UV-vis absorption spectra of the indium sulfides of (a) compounds **1**, **2**, and (b) compounds **3**, **4**.

Figure S9. The DSC-TG curves of the compound **1** and **3**.

Table S1 Crystal data and structural refinement parameters for **1**~**4**

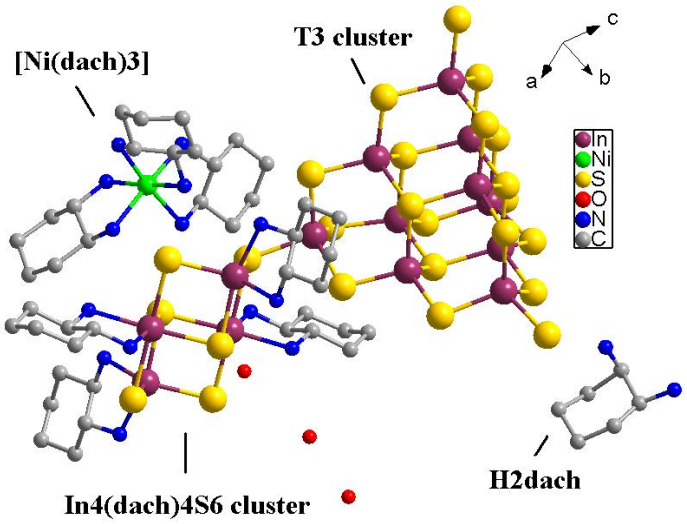
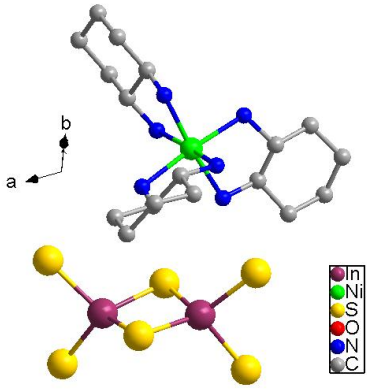
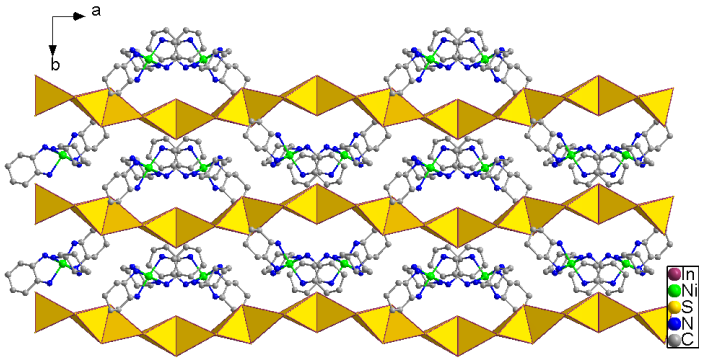


Figure S1. Unit structure of compound **1** consists of an isolated $[H_2dach]^{2+}$ and a $[Ni(dach)_3]^{2+}$ cations. The $In_4(dach)_4S_6$ cluster is completed for clarity.

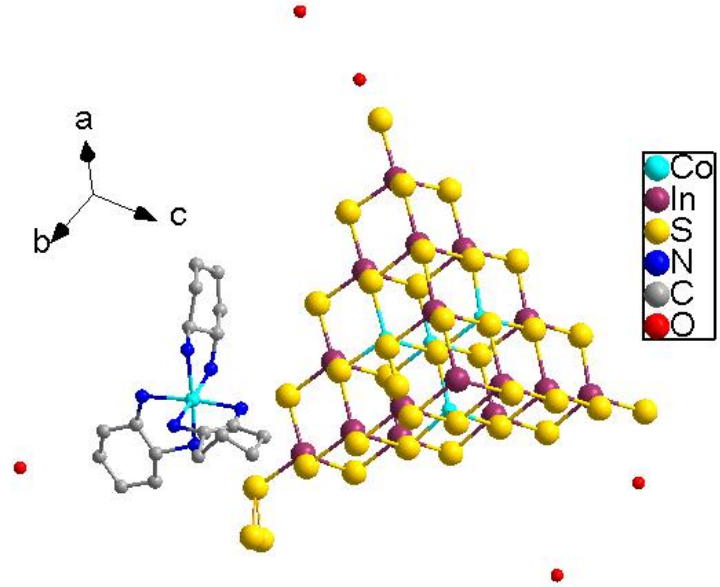


(a)

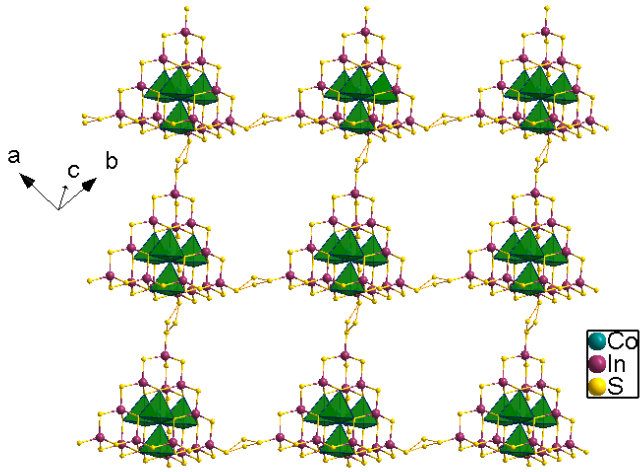


(b)

Figure S2. (a) Unit structure of compound **2** consists of an isolated and water molecules. (b) The one-dimensional chain structure of **2**, showing that the repeating unit consists of eight edge-sharing tetrahedra for a complete period.

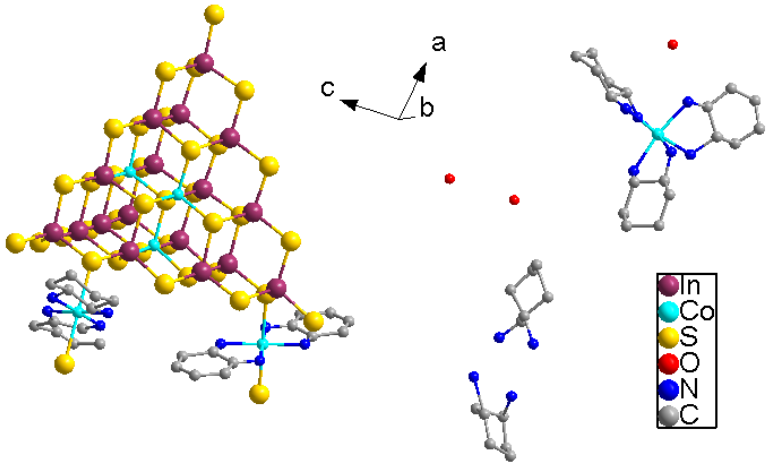


(a)

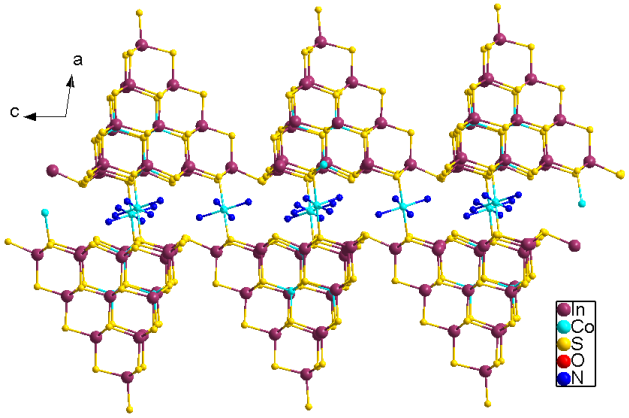


(b)

Figure S3. (a) Unit structure of compound **3** with an isolated $[Ni(dach)_3]^{2+}$ cation. The incompletely solved solvent molecules are omitted for clarity. (b) The 2-D polyanionic framework of **3** assembled by T4 clusters, showing the –S–S–S– bridges.

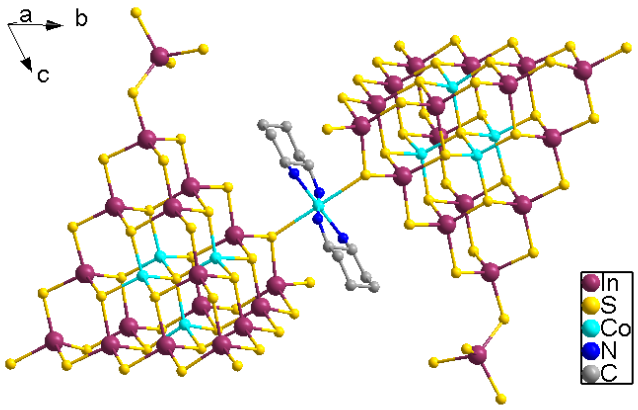


(a)



(b)

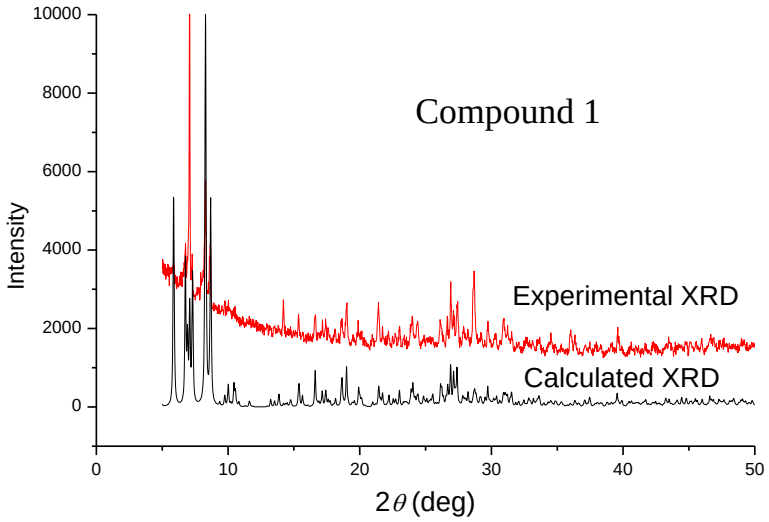
Figure S4. (a) Unit structure of compound **4**. Some incompletely solved cations and solvent molecules are omitted for clarity. (b) The 2-D polyanionic framework of **4** assembled by complex bridges.



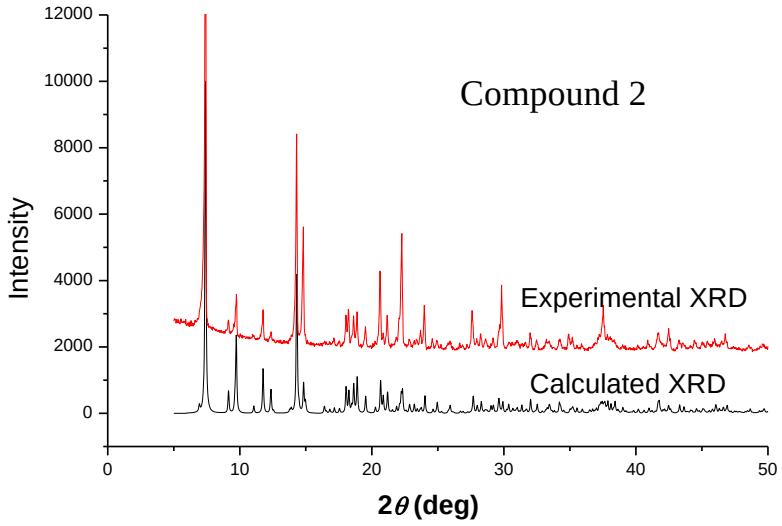
(b)

Figure S5. The structure of $(Hdach)_{10}\cdot[Co(dach)_3]_8\cdot\{[In_{17}Co_4S_{38}H_3]_2[Co(dach)_2]\}\cdot 2H_2O$, a known compound

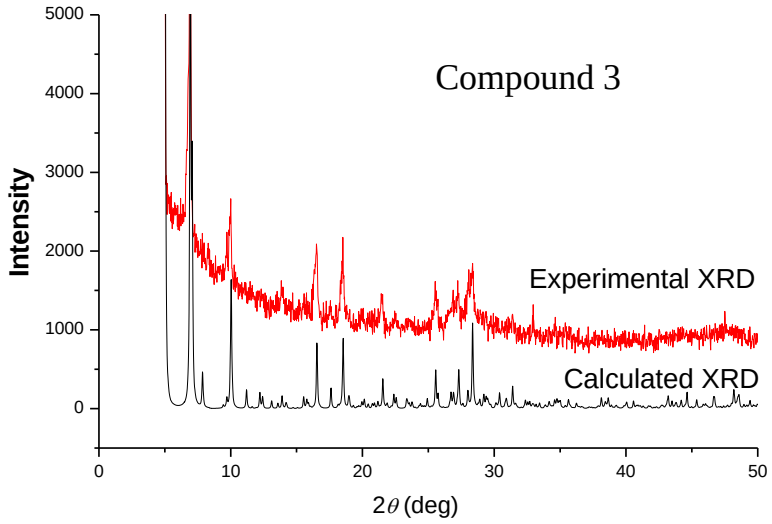
The compound was synthesized from elements Co (1.5 mg, 0.025 mmol), In (5.6 mg, 0.05 mmol) and L-cysteine (12.1 mg, 0.1 mmol) in a water solution of 1mL 75 % dach. The method is the same as that of the compound **3**, except that no (BMIm)Br and GeO_2 were added in. The mixture was heated to140 °C for 9 days in a sealed thick-walled Pyrex tube. After cooling to room temperature the block green crystals were obtained with 55% yield (based on In).



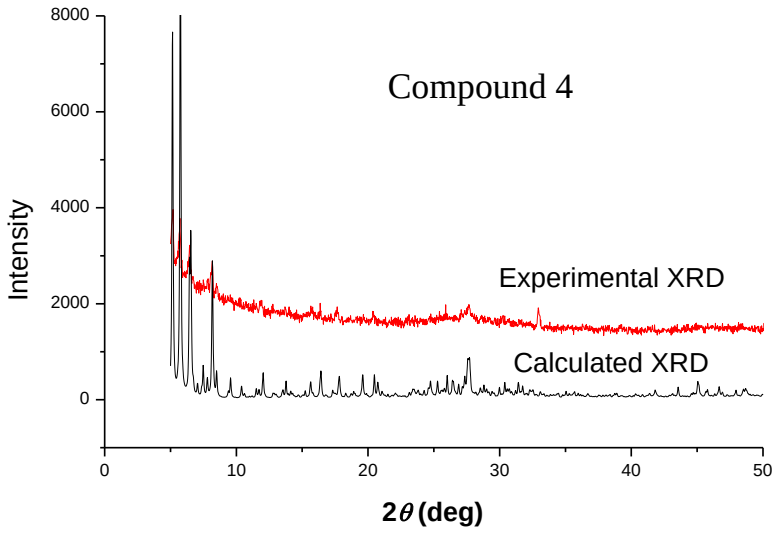
(a)



(b)

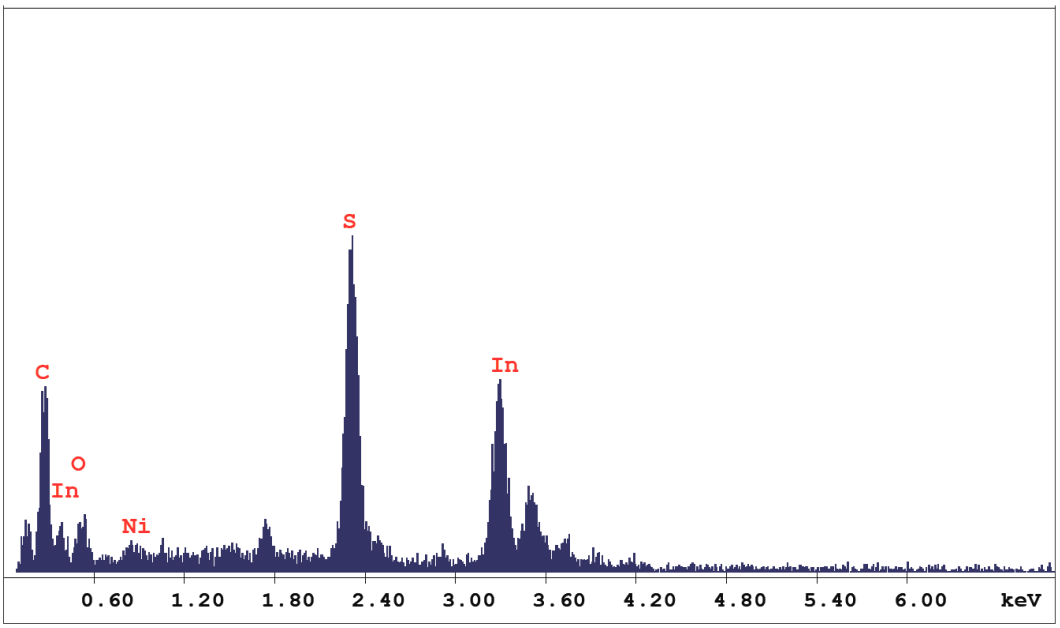


(c)

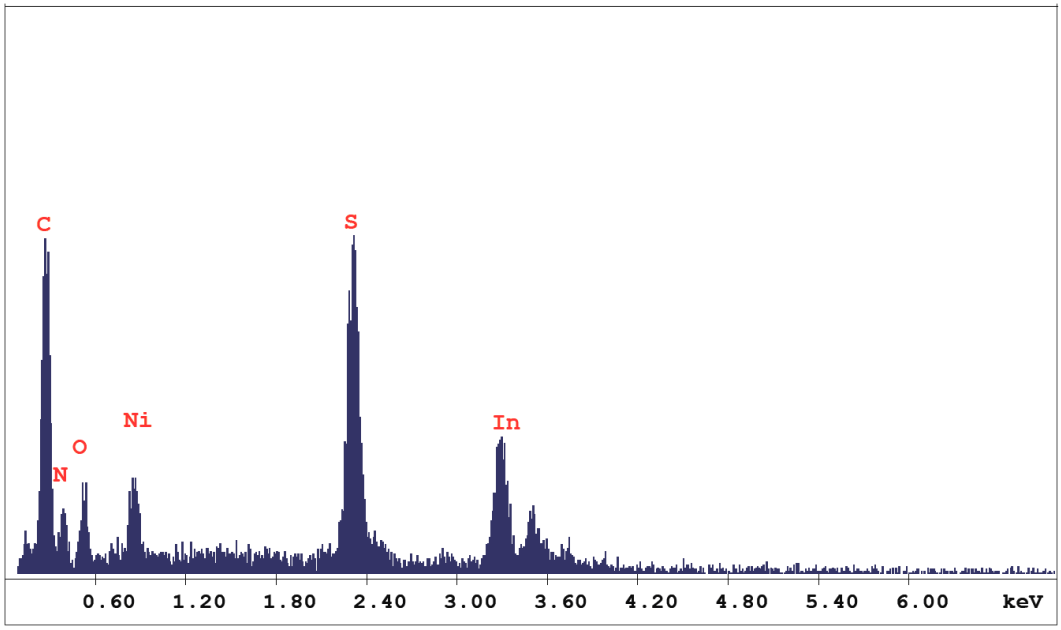


(d)

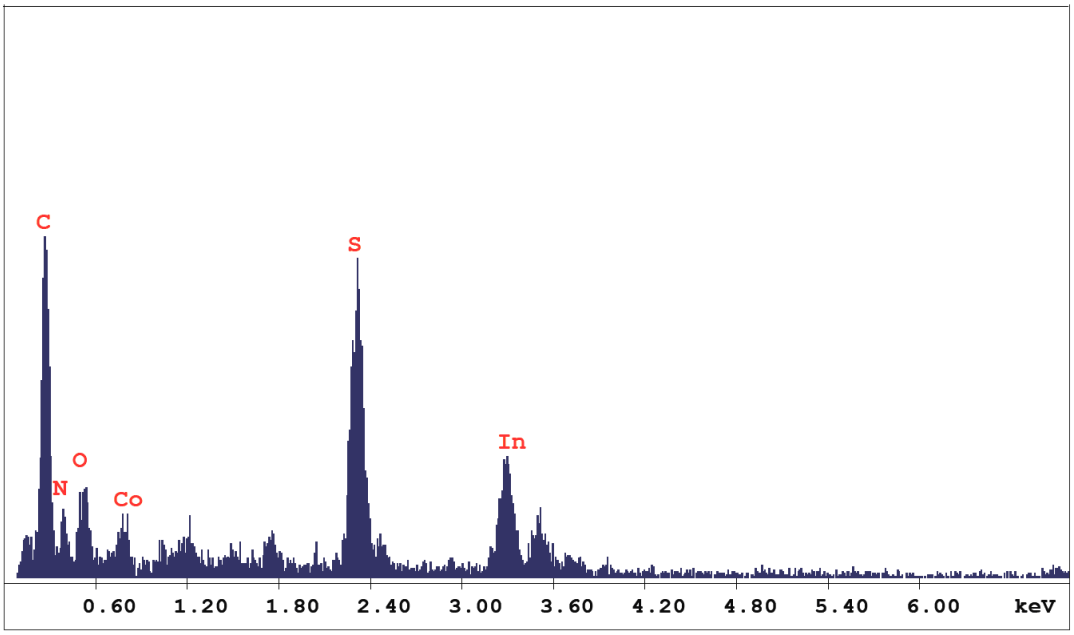
Figure S6. The XRD results of compounds **1**–**4** with those calculated from X-ray single-crystal diffraction data, (a), (b), (c) and (d), respectively.



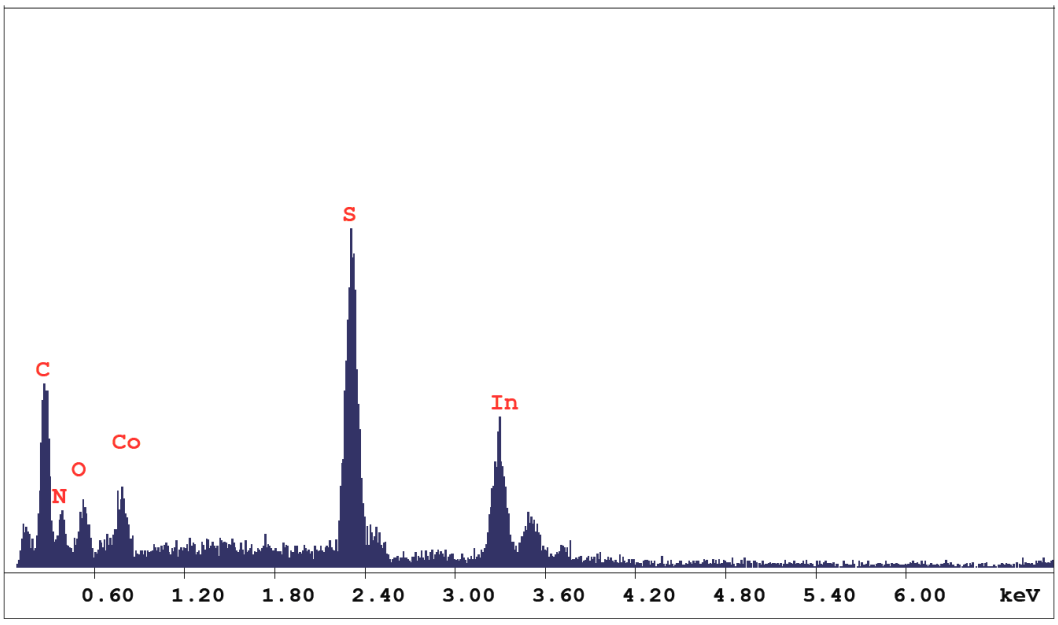
(a) Compound **1**, S:In:Ni, 18:12:1.0



(b) Compound **2**, S:In:Ni, 4.0:2.2:1.0

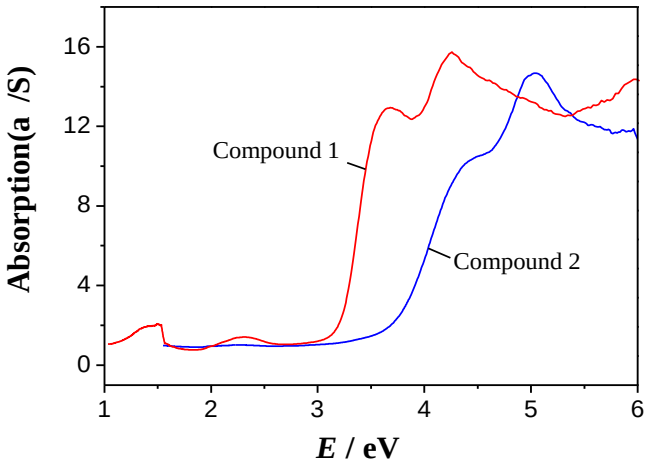


(c) Compound **3**, S:In:Co, 4.5:2.2:1.0

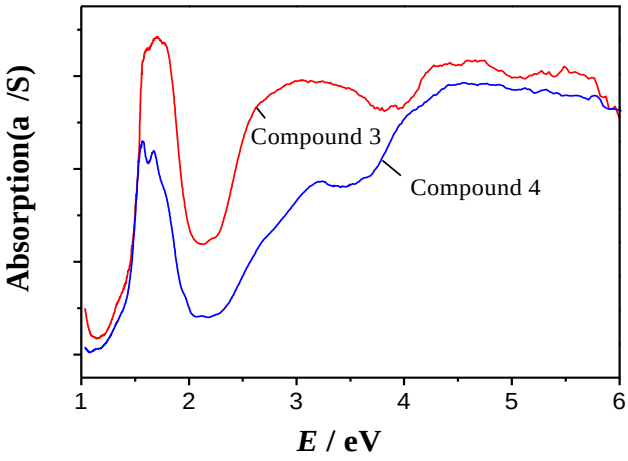


(d) Compound **4**, S:In:Co, 4.1:1.8:1.0

Figure S7. The EDX results of **1-4**, showing the information of the elements and their relative contents of the compounds.



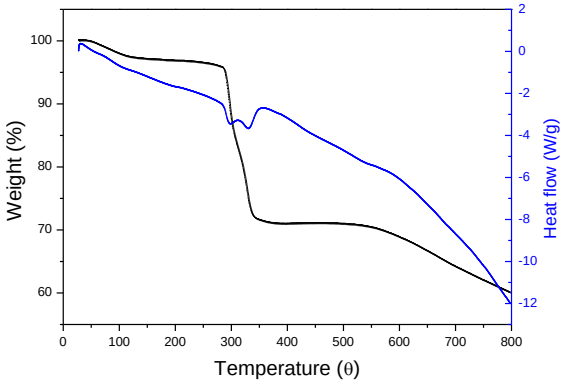
(a)



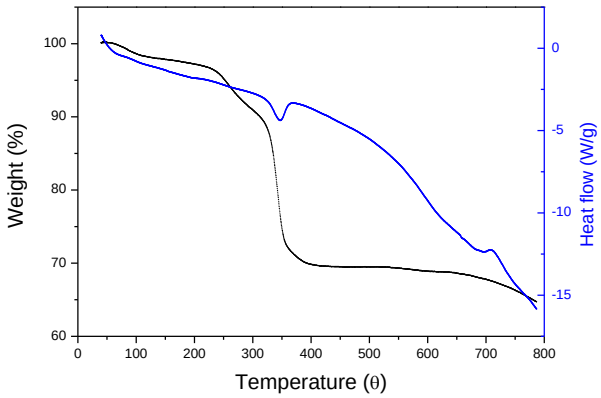
(b)

Figure S8. The solid-state UV-vis absorption spectra of the indium sulfides of (a) compounds **1**, **2**, and (b) compounds **3**, **4**.

Optical diffuse-reflection spectra of **1**–**4** were measured at room temperature using $BaSO_4$ as a standard reference. The absorption (α/S) data were calculated from the reflectance using the Kubelka-Munk function. The optical band gaps (onset) obtained by extrapolation of the linear portion of the absorption edges are estimated as 3.18, 2.57, 1.90 and 1.67eV for **1**–**4**, respectively (Figure S7). Compounds **3** and **4** have the metal centered transition of the Co(II) ion in the visible range that is different to the Ni(II) compounds, due to the tetrahedron Co(II) in the T4 cluster.



(a)



(b)

Figure S9. The DSC-TG curves of the compound **1** (a) and **3** (b).

The DSC-TG curves of the compound **1** were illustrated in Figure S9. The decomposition of **1** occurs in three distinct stages. The first weight loss from 57°C to 256°C corresponds to the release of isolated $[H_2dach]^{2+}$ and H_2O molecules. The weight loss of 5.8% is close to that calculated (5.9%) for the formula. In the temperature range 256–382°C the weight loss of 20.58% is attributed to the release of coordinated dach molecule (calcd. 20.39%). The experimental mass loss of 45.96% corresponds to the elimination of coordinated dach molecule (calcd. 45.04%). The thermal decomposition compound **3** is similar to compound **1** (Figure S9b). The first weight loss of 8.59% from 59 to 288°C corresponds to the release of isolated $[H_2dach]^{2+}$ and H_2O molecules (calcd. 8.11%). The second stage in the range 288-391°C the weight loss of 24.88% is attributed to release of the coordinated dach

molecule (calcd. 25.81%). The third stage in the range 391-800°C corresponds to incompletely decomposition of the cluster.

Table S1 Crystal data and structural refinement parameters for **1~4**

	1	**2**
Chemical formular	$C_{36}H_{92}In_{12}N_{12}NiO_3S_{20}$	$C_{72}H_{192}In_8N_{24}Ni_4O_{12}S_{16}$
Formula weight	2818.94	3252.86
Crystal system	monoclinic	monoclinic
Space group	P21/c	C2/c
a/Å	18.9686(10)	32.042(4)
b/Å	18.8743(9)	9.8206(8)
c/Å	26.1162(14)	24.305(2)
α/deg	90.00	90.00
β/deg	107.4360(10)	127.353(2)
γ/deg	90.00	90.00
V/Å^3	8920.5(8)	6079.7(10)
Z	4	2
Dc/g cm^{-3}	2.223	1.777
μ/mm^{-1}	3.757	2.422
F(000)	5776	3296
θ_{max}(^{o})	27.5	27.5
T(k)	223(2)	223(2)
Reflections collected	37861	16980
Unique reflections	15654	6838
Reflections (> 2 sigma *I*)	12921	6071
R_{int}	0.0569	0.0360
GOF	1.014	1.089
R^a (ref > 2 sigma *I*)	0.0563	0.0530
wR^b	0.1387	0.1409
Largest diff. peak and hole /e.A^{-3}	1.399 and -1.175	1.221 and -0.948
	3	**4**
Chemical formular	$C_{90}H_{222}Co_8In_{16}N_{30}O_5S_{37}$	$C_{168}H_{408}Co_{17}In_{32}N_{56}O_6S_{68}$
Formula weight	5299.76	10165.64
Crystal system	monoclinic	monoclinic

Space group	Fddd	P 2_1/c
a/Å	24.8713(15)	22.9417(10)
b/Å	28.3131(16)	26.2387(10)
c/Å	52.118(3)	27.3488(11)
α/deg	90.00	90.00
β/deg	90.00	99.4540(10)
γ/deg	90.00	90.00
V/Å^3	36701(4)	16239.3(11)
Z	8	2
Dc/g cm^{-3}	1.730	1.969
μ/mm^{-1}	3.134	3.543
F(000)	17924	9026
θ_{max}(^{o})	27.5	27.5
T (k)	296(2)	223(2)
Reflections collected	72053	86962
Unique reflections	4052	36866
Reflections (> 2 sigma *I*)	3154	25976
R_{int}	0.0518	0.0501
GOF	1.083	1.132
R^a(ref > 2 sigma *I*)	0.1170	0.0814
wR^b	0.1963	0.2020
Largest diff. peak and hole /e.A^{-3}	4.639 and -1.734	4.248 and -2.944

[a] $R = \Sigma(||F_0|-|F_C||)/\Sigma|F_0|$; [b] $wR = [\Sigma w(|F_0|^2-|F_C|^2)^2/\Sigma w(F_0^2)]^{1/2}$