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Indium−Sulfur Supertetrahedral Polymers Integrated with $[M(phen)_3]^{2+}$ Cations (M = Ni and Fe)

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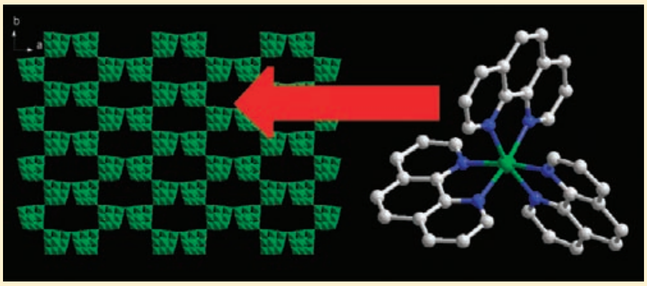
S *Supporting Information*

ABSTRACT: A series of supertetrahedral polymers of chalcogenometalates (T3 cluster compounds) integrated with M-phen complexes (phen =1,10-phenanthroline; M = Ni, Fe) was prepared by a similar solvothermal technique. Compound $[Fe(phen)_3]_4[H_4In_{20}S_{38}]\cdot Hphen\cdot 3HDMA\cdot 8H_2O$ (Mp-InS-**4**) (DMA = dimethylamine) is a 1-D straight chain. Compounds $[M(phen)_3]_4[In_{20}S_{37}]\cdot 6Hphen\cdot 4H_2O$ (M = Ni, Mp-InS-**5**; Fe, Mp-InS-**6**) are the first reported 2-D T*n* polymers integrated with complex cations of $[M(phen)_3]^{2+}$. Compound $[Ni(phen)_3]_4[H_4In_{20}S_{38}]\cdot 2Hphen\cdot 2HDMA\cdot 3H_2O$ (Mp-InS-**7**) shows a zigzag 1-D structure. We find that the reaction time is an important factor in assembling of the T3 clusters. Prolonging the reaction time seems favorable to the higher condensed phases (from 0-D to 2-D). However, a longer reaction time resulted in the crack of 2-D structure. Integrating M−phen complex cations with the chalcogenido anions can improve absorption of the materials in the visible range due to the charge transfers within the cations or between cations and anions.



INTRODUCTION

Substantial success on supertetrahedral clusters of chalcogenometalates denoted as T*n* clusters has been achieved because they can serve as building blocks for constructing crystalline porous frameworks with semiconductive property.[1−3] To further promote potential applications of chalcogenometalates in photoelectronic materials, it is highly desirable to develop the single-phase semiconducting materials cocrystallized with optically active guest species, such as metal−phen/bpy complex cations (phen = 1,10-phenanthroline; bpy = bipyridine).[4] The metal complexes of phen/bpy have been interesting until now for their application in photoelectronic materials. The Ru(II)−phen/bpy system offers extensive applications in solar light harvesting and energy conversion.[5,6] Besides the Ru(II)−phen/bpy complexes, Os(II)[6] and Fe(II)[7] complexes are also candidates for photochemical sensitizers. The Ru(II)−bpy complexes in the dye-sensitized TiO_2 materials are either surface modified on the TiO_2 substrate or embedded into the cavity of porous TiO_2 in uncertain composition, which belong to multicomponent materials.[6a,8] Our goal is to obtain single-phase crystal compounds integrated with M(II)−phen/bpy complexes. In such materials the dye molecules are dispersed and contact well with the anion structure in known composition. To date, examples of M(II)−phen/bpy complexes integrated with polymeric inorganic anion structures are not popular. Some oxo[9] or chalcogenido compounds[10] in which the phen/bpy bonded to anion structures have been reported, but their anions are not supertetrahedra based.

We reported the first example of InS-T3 clusters with cocrystallized Ni−phen complex cations, including two 0-D and one 1-D compounds denoted as Mp-InS-**1**−**3**.[11] It has been found that M(II)−phen complexes can change the band gap of the materials. Research is now faced with a challenge to expand the dimensions of the semiconducting anion and to find out the relationship between the products and the conditions of the synthetic reactions. The increase of the dimensions of the anion structure can enhance the stability of the hybrid materials and more importantly can improve the semiconductive property in multiorientations. However, based on our experiences in syntheses of such compounds, there seems to be a tendency to form low-dimensional structures due to the large size and the rigid structure of the complexes of M−phen. The 0-D cation−anion discrete compounds are the most preferable structure. For example, Mp-InS-**1** and Mp-InS-**2** can be easily prepared. Great effort has been made to prepare multidimensional compounds in which M−phen complex cations are integrated with polymeric T*n* clusters. We report herein new 1-D polymeric T3 clusters and the first example of 2-D InS-T3 clusters with cocrystallized Ni−phen and Fe−phen complex cations. Although a few 2-D extended structures of T*n* clusters have been reported previously, the counterions of them are protonated amines not the M−phen

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Table 1. Crystal Data and Structural Refinement Parameters for Mp-InS-4−7

	Mp-InS-**4**	Mp-InS-**5**	Mp-InS-**6**	Mp-InS-7
formula	$C_{162}H_{149}In_{20}N_{28}Fe_4O_8S_{38}$	$C_{216}H_{152}In_{20}N_{36}Ni_4O_4S_{37}$	$C_{216}H_{152}In_{20}N_{36}Fe_4O_4S_{37}$	$C_{172}H_{140}In_{20}N_{30}Ni_4O_3S_{38}$
fw	6368.22	7033.20	7021.76	6424.66
cryst size (mm^3)	0.40 × 0.24 × 0.19	0.10 × 0.10 × 0.03	0.25 × 0.15 × 0.10	0.28 × 0.20 × 0.16
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	P_1	$C\,2/c$	$C\,2/c$	$C\,2/c$
a (Å)	11.8680(6)	39.53(4)	39.346(3)	29.9641(16)
b (Å)	16.1506(8)	17.169(16)	17.2158(9)	18.4435(8)
c (Å)	28.9425(18)	35.34(2)	35.118(2)	41.506(2)
α (deg)	80.757(4)	90.00	90.00	90.00
β (deg)	87.066(4)	108.405(16)	108.280(2)	108.3060(10)
γ (deg)	80.195(4)	90.00	90.00	90.00
V ($Å^3$)	5393.9(5)	22753(35)	22587(2)	21777.2(19)
Z	1	4	4	4
ρ_{calcd} (g cm^{-3})	1.947	2.053	2.065	1.960
F(000)	3040	13 664	13 632	12 848
μ (mm^{-1})	2.771	2.707	2.650	2.829
T (K)	223(2)	223(2)	223(2)	223(2)
R_{int}	0.0470	0.1066	0.0939	0.0639
reflns collected	42 384	53 812	55 796	61 238
unique reflns	28 586	19 943	19 828	24 688
obsd reflns	21 160	11 336	13 251	17 063
no. params	1459	1129	1159	1037
GOF on F^2	0.917	0.984	1.062	1.046
R_1 [$I > 2\sigma(I)$]	0.0694	0.0758	0.0745	0.0684
$_wR_2$	0.1510	0.1554	0.1347	0.1235

or M−bpy complexes.[12] Structural and optical characteristics of these new Tn compounds are discussed.

EXPERIMENTAL SECTION

1. General. All analytically pure starting materials were purchased and used without additional purification. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr pellets. Elemental analysis was carried out on an EA 1110 elemental analyzer. Room-temperature optical diffuse reflectance spectra of the microcrystal samples were obtained with a Shimadzu UV-3150 spectrometer. The absorption (α/S) data were calculated from the reflectance using the Kubelka−Munk function, $\alpha/S = (1 - R)^2/2R$,[13] where R is the reflectance at a given energy, α is the absorption, and S is the scattering coefficient. XRD of the products was carried out on a D/MAX-3C X-ray diffraction meter with Cu Kα (λ = 1.5406 Å) radiation. Thermoanalytical measurement was performed using a DCS-TGA microanalyzer of SDT 2960 and was heated under a nitrogen stream of 100 mL min^{-1} with a heating rate of 5 °C min^{-1}.

2. Syntheses. *$[Fe(phen)_3]_4[H_4In_{20}S_{38}]\cdot Hphen\cdot 3HDMA\cdot 8H_2O$ (Mp-InS-**4**).* Analytically pure In powder (0.0114 g, 0.10 mmol), iron powder (0.0058 g, 0.10 mmol), Na_2S (0.0480 g, 0.20 mmol), and 1,10-phenanthroline (0.0600 g, 0.30 mmol) were mixed in a solvent of DMF/H_2O (1:2 in v/v). The mixture was sealed in a thick Pyrex tube (7 mm diameter, 180 mm length, and 1.2 mm thick) under ambient atmosphere and pressure. The tube was heated under autogenous pressure at about 140 °C for 18 days to yield dark-red block-shaped crystals (yield 30% based on In). The crystals were washed with ethanol, dried, and stored under vacuum. Anal. Calcd for $C_{162}H_{149}In_{20}N_{29}Fe_4O_8S_{38}$ (MW 6368.22): C, 30.55; H, 2.36; N, 6.38. Found: C, 30.32; H, 2.37; N, 6.28. IR data (KBr, cm^{-1}): 3432(s), 3042(w), 2926(w), 1635(s), 1577(w), 1514(m), 1429(s), 1337(w), 1147(m), 1019(m), 849(s), 720(s), 667(w), 475(s).

*$[Ni(phen)_3]_4[In_{20}S_{37}]\cdot 6Hphen\cdot 4H_2O$ (Mp-InS-**5**).* Analytically pure In powder (0.0114 g, 0.10 mmol), nickel powder (0.0060 g, 0.10 mmol), Na_2S (0.0480 g, 0.20 mmol), and 1,10-phenanthroline (0.0600 g, 0.30 mmol) were mixed in a solvent of DMF/H_2O (1:2 in v/v). The mixture was sealed in a thick Pyrex tube (7 mm diameter, 180 mm length, and 1.2 mm thick) under ambient atmosphere and pressure. The tube was heated under autogenous pressure at about 140 °C for 24 days to yield orange block-shaped crystals (yield 32% based on In). The crystals were washed with ethanol, dried, and stored under vacuum. Anal. Calcd for $C_{216}H_{152}In_{20}N_{36}Ni_4O_4S_{37}$ (MW 7033.20): C, 36.89; H, 2.18; N, 7.17. Found: C, 36.58; H, 2.31; N, 7.15. IR data (KBr, cm^{-1}): 3684(m), 3450(w), 3048(m), 2932(vw), 1623(s), 1573(m), 1512(vs), 1417(vs), 1306(w), 1220(m), 1144(m), 957(w), 841(vs),770(w), 725(vs), 638(m), 502(w).

*$[Fe(phen)_3]_4[In_{20}S_{37}]\cdot 6Hphen\cdot 4H_2O$ (Mp-InS-**6**).* Compound Mp-InS-**6** was prepared by a similar method used in the synthesis of Mp-InS-**5** except that nickel powder was replaced by iron powder (0.0058 g, 0.10 mmol). The mixture in DMF/H_2O (1:2 in v/v) was sealed in a thick Pyrex tube that was heated under autogenous pressure at about 140 °C for 24 days to yield red block-shaped crystals (yield 41% based on In). The crystals were washed with ethanol and diethyl ether, dried, and stored under vacuum. Anal. Calcd for $C_{216}H_{152}In_{20}N_{36}Fe_4O_4S_{37}$ (MW 7021.83): C, 36.95; H, 2.18; N, 7.18. Found: C, 36.77; H, 2.28; N, 7.02. IR data (KBr, cm^{-1}): 3421(s), 3045(w), 2924(w), 1624(w), 1574(w), 1509(m), 1423(vs), 1336(w), 1219(w), 1140(m), 844(vs), 722(vs), 628(w), 462(m).

*$[Ni(phen)_3]_4[H_4In_{20}S_{38}]\cdot 2Hphen\cdot 2HDMA\cdot 3H_2O$ (Mp-InS-**7**).* Compound Mp-InS-7 was prepared by a similar method used in the synthesis of Mp-InS-5 except that the reaction time was prolonged to 32 days at

about 140 °C to yield red block-shaped crystals (yield 21% based on In). The crystals were washed with ethanol, dried, and stored under vacuum. Anal. Calcd for $C_{172}H_{140}In_{20}N_{30}Ni_4O_3S_{38}$ (MW 6424.64): C, 32.16; H, 2.20; N, 6.54. Found: C, 32.46; H, 2.36; N, 6.25. IR data (KBr, cm^{-1}): 3410(s), 3049(w), 2918(vw), 1618(m), 1511(s), 1416(vs), 1337(w), 1222(w), 1142(m), 1050(w), 839(s), 718(vs), 636(w), 558(w).

3. Crystal Structure Determination. Data collections were performed on a Rigaku Mercury CCD diffractometer using a ω-scan method with graphite-monochromated Mo Kα radiation (λ = 0.071075 nm) at a temperature of 223(2) K. An absorption correction was applied for all the compounds using a multiscan correction method. The structures were solved with direct methods using the SHELXS-97 program, and the refinement was performed against F^2 using SHELXL-97. All non-hydrogen atoms of Mp-InS-**4**−**7** were refined anisotropically except for those disordered atoms which were restrained to be approximately isotropic. The hydrogen atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters. The small molecules, Hphen, and HDMA (a pyrolysate from DMF) are not all located because of the serious disorder problems that is usually encountered in this kind of T*n* compounds. The unlocated small molecules contribution to the scattering factors has been taken into account with PLATON/SQUEEZE for compounds Mp-InS-**4**−**7**. Relevant crystal data, collection parameters, and refinement results can be found in Table 1.

■ RESULT AND DISCUSSION

1. Preparation. Compounds Mp-InS-**4**−**7** were prepared by a similar solvothermal technique. The elements In and M (M = Ni or Fe) reacted with Na_2S and phen in a mixed solvent of DMF/H_2O. The optimized mole ratio of In:M:Na_2S:phen is 1:1:2:3, and the optimized reaction temperature is about 140 °C. We find that the reaction time is an important factor in assembling of the T3 clusters. The reaction time for the 0-D compounds, Mp-InS-**1** and Mp-InS-**2**, was about 12 days,[11] that for the 1-D compounds, Mp-InS-**3** (see Supporting Information) and Mp-InS-**4**, was about 18 days, and that for the 2-D compounds, Mp-InS-**5** and Mp-InS-**6**, was about 24 days under the same other conditions. Prolonging the reaction time seems favorable to the higher condensed phase. However, further prolonging the reaction time to hope to obtain the 3-D compound did not succeed. A new 1-D compound Mp-InS-**7** was accidentally obtained after 32 days. The purity of all samples Mp-InS-**4**−**7** for physical measurements is ensured by carefully hand-picked crystals. Since Mp-InS-**5** and Mp-InS-**7** were obtained under the same experimental condition, except the reaction time, and the XRD pattern of a sample of Mp-InS-**5** fitted well with that of the calculated one (pure phase, SI-Figure 3, Supporting Information), it is believable that there is a relationship between the two compounds, which is discussed in the structural section. The main parts of the compounds, the anion clusters and the M−phen cations, are determined by single-crystal data analysis. Other components in the formula are deduced from single-crystal data analysis (residual peaks), elemental microanalysis, IR measurement, and the charge balance rule. Vibration bands of IR at about 3400 and 1630 cm^{-1} indicate the presence of H_2O molecules, and those at about 3040, 840, and 720 cm^{-1} are assigned to C−H in phen. The bands at 1510 cm^{-1} are assigned to vibration of the C═N bond. The bands at about 1030 cm^{-1} indicate the presence of $-NH_2$ (HDMA) groups. The peaks at 3300 cm^{-1} of N−H bands are hidden in the broad absorption band of the water molecules. Anyway, the deduced components about the small molecules in these compounds are only the most possible results.

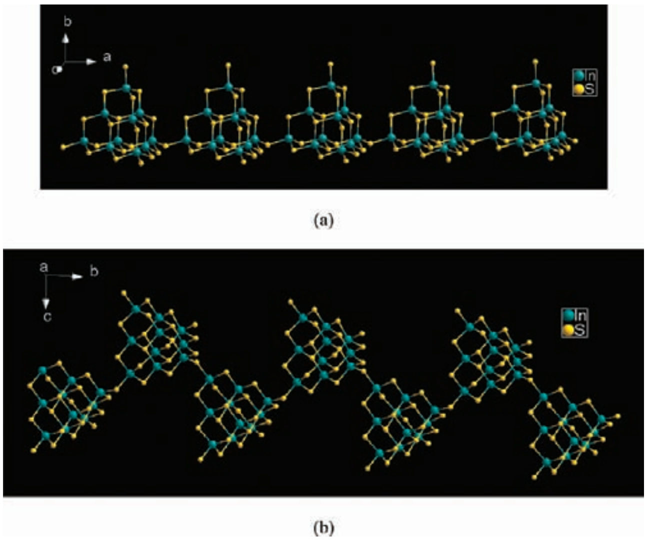


Figure 1. One-dimensional chains of the polymeric anion in Mp-InS-**4** (a) and Mp-InS-**7** (b) (complex cations are omitted for clarity).

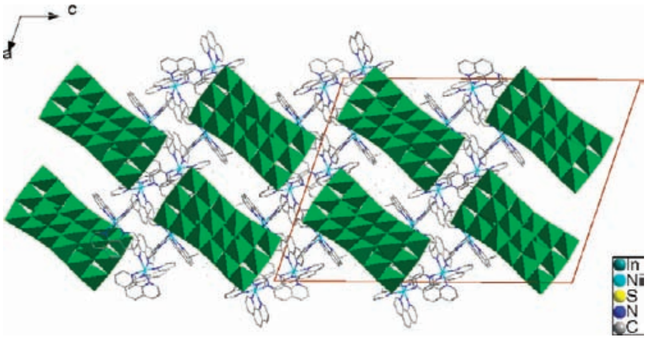


Figure 2. Chain packing in Mp-InS-**7** viewed along the *b* direction, showing the polyhedral view of the polymeric anion (small molecules are omitted for clarity).

The interest of this work is the fundamental structures of the anions and the M−phen cations.

2. Description of the Structures. *1-D Compounds Mp-InS-**4** and Mp-InS-**7**.* The crystal of Mp-InS-**4** is triclinic and belongs to the P_1 space group with one formula in a unit cell, showing a similar structure to Mp-InS-**3**, by comparing the data of the unit cells and the anion packing (SI-Figure 1, Supporting Information). The 1-D chain is assembled by $[In_{10}S_{19}]^{8-}$ clusters with cosharing two of the corner sulfur atoms (Figure 1a). The repeat unit of the chain is a single T3 cluster. The complex cations $[Fe(phen)_3]^{2+}$ (Fe1 and Fe2) and the free phen ligand were completely solved, except $[Fe(phen)_3]^{2+}$ (Fe3 and Fe4) that can only be solved partially for the disorder problems. The carbon atoms presented around Fe3 and Fe4 are evidence for the presence of two additional $[Fe(phen)_3]^{2+}$. The packing structure of compound Mp-InS-**4** is shown in the Supporting Information (SI-Figure 1). The crystal of Mp-InS-**7** is monoclinic and belongs to the *C*2/*c* space group with four formulas in a unit cell (SI-Figure 2, Supporting Information). Though the 1-D chain of Mp-InS-**7** is also assembled by T3 clusters with coshared two-connected sulfur atoms (Figure 1b), the structure shows a zigzag linkage. The repeated unit for the chain of Mp-InS-**7** is a T3 dimer that is different from that of 1-D Mp-InS-**4**. Figure 2 shows

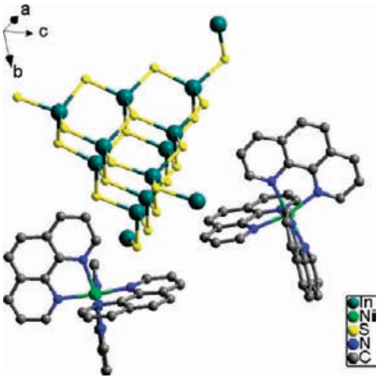
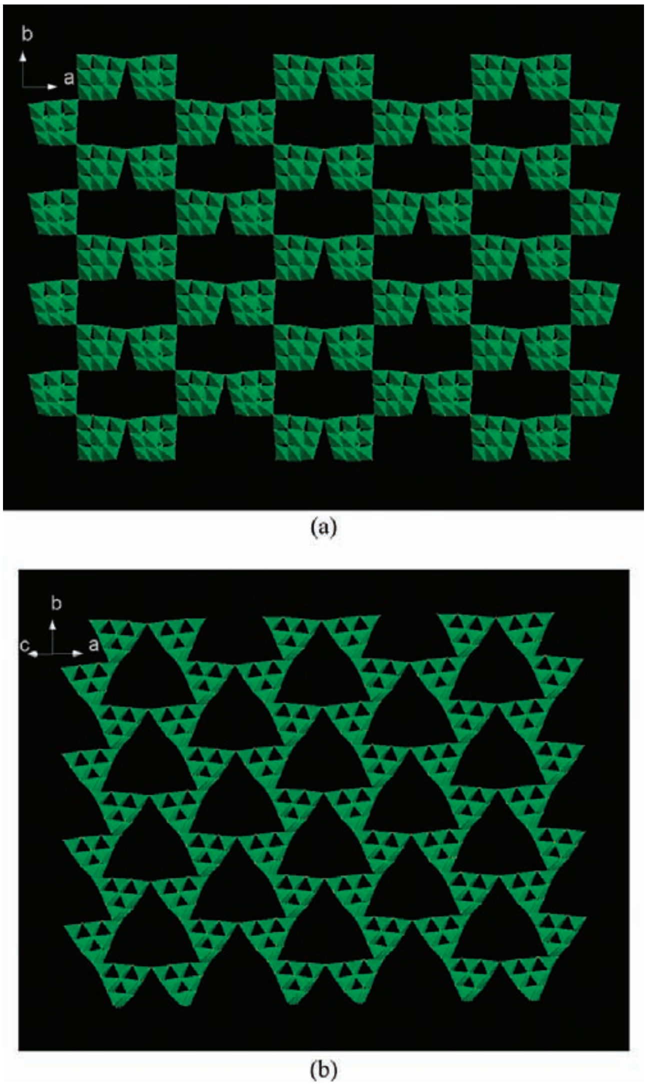


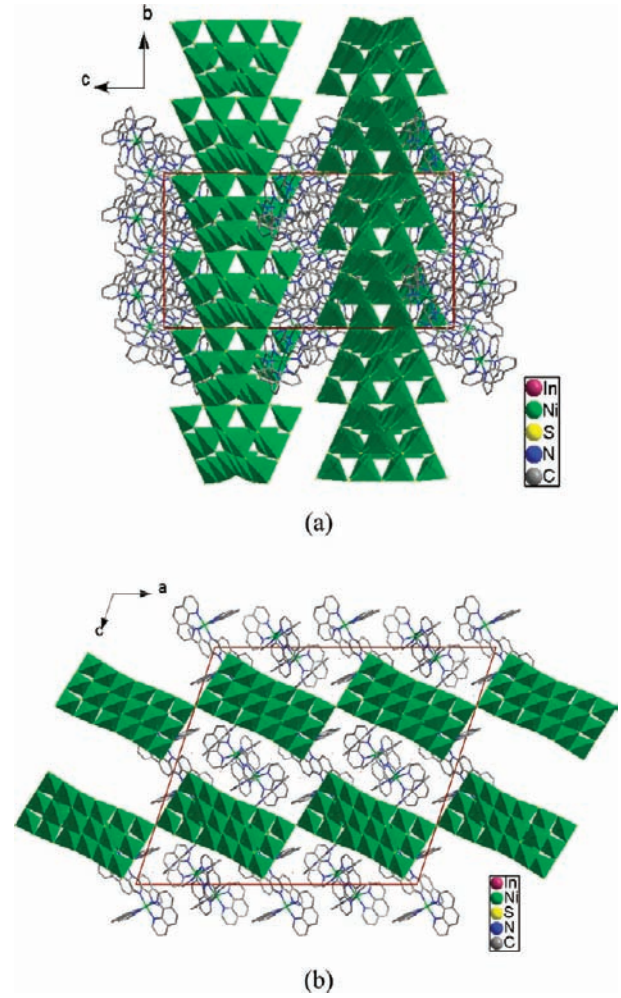
Figure 3. Fundamental structure of compound Mp-InS-**5**. The protonated phen, water, and hydrogen atoms have been omitted for clarity.



(a)

(b)

Figure 4. Two-dimensional structure of Mp-InS-**5**, viewed along the *c* direction (a) and along the {1/2 0 1} direction (b).



(a)

(b)

Figure 5. Molecular packing of Mp-InS-**5**, showing the layered structure. View along the *a* direction (a) and the *b* direction (b).

the chain packing of Mp-InS-**7**, viewed along the *b* direction. Four T3 cluster chains pass through a crystal cell along the *b* direction.

*2-D Compounds Mp-InS-**5** and Mp-InS-**6***. Since Mp-InS-**5** and Mp-InS-**6** are isomorphous structure, only the structure of Mp-InS-**5** is discussed in detail. The fundamental subunit of the anion of Mp-InS-**5** (Figure 3) is a T3 cluster of $[In_{10}S_{18.5}]^{7-}$ in which three of the corners are coshared by the neighboring clusters. The counterions are $[Ni(phen)_3]^{2+}$ and the protonated phen. The crystal belongs to the *C*2/*c* space group with four formulas, $[Ni(phen)_3]_4[In_{20}S_{37}]$, in one crystal unit. The average distances of In−S bonds are 2.437 Å for bibridging mode and 2.505 Å for tribridging mode in the order of bibridging < tribridging in accordance with those of Mp-InS-**1**−**3**.[11] The longer terminal In−S distances (In(1)−S(1), 2.472(5) Å) imply that the terminal sulfur atoms are likely to be protonated.

The framework of Mp-InS-**5** can be best visualized if each $[In_{10}S_{20}]^{10-}$ cluster is represented by a supertetrahedron with 10 small InS_4 tetrahedron. By this representation, the structure is shown in Figure 4. The 2-D T3 clusters are covalently connected in a layer parallel to the *ab* plane with a quadrate hole in size 1/2*a* × 1/2*b* (Figure 4a). While viewed along the {1/2 0 1} direction, the layer shows the trigonal holes with a side length of about 23.8 Å (twice the side distance of a T3 cluster) (Figure 4b). This pattern is similar to that of some 3-D T3 compounds.[2b] On the basis of our knowledge, compounds Mp-InS-**5** and Mp-InS-**6** are the first examples of 2-D T3 compounds with cocrystallized M−phen complexes.

Figure 5 shows the layered arrangement of the anions and cations, viewed along the *a* direction and the *b* direction.

The $[Ni(phen)_3]^{2+}$ cations serve as complex layers, sandwiched between the inorganic layers. Some cations are even embedded into holes of the T3 cluster layers. There are two types of important intermolecular interactions, S···H−C contacts between cations and anions and C···C stacking or contacts of phen planes. The S···H−C contacts range from 3.357 to 3.499 Å, and the C···C stacking ranges from 3.214 to 3.390 Å (Table 2). The S···H−C contacts and C···C stacking of Mp-InS-**6** range from 3.336 to 3.493 Å and from 3.166 to 3.384 Å, respectively (Table 3). These interactions pass over the whole crystal lattice and play an important role in cation−anion charge transfer (CACT) that affect the energy levels of the inorganic−organic hybrid material.

3. Proposed Relationship between the 2-D Structure of Mp-InS-5 and the 1-D Structure of Mp-InS-7. We discussed that a long reaction time would cause a crack of the 2-D structure. Since Mp-InS-**5** and Mp-InS-**7** were obtained under the same experimental condition, except the reaction time, and the sample of Mp-InS-**5** is a pure phase, it is believable that there is a relationship between the two compounds. The structural data in Table 1 clearly shows the similarity for 2-D structure of Mp-InS-**5** and 1-D structure of Mp-InS-**7**. The crystal of Mp-InS-**7** belongs to the *C*2/*c* space group, showing the same space symmetry as that of Mp-InS-**5**. The data of the unit cell of Mp-InS-**7** is similar to that of Mp-InS-**5** with a little elongation in sizes, *a*, *b*, and *c* of **7** corresponding to *c*, *b*, and *a* of **5**. The relationship can be understood directly from the cluster packings of Mp-InS-**7** and Mp-InS-**5** (Figures 5b and 2). On the basis of the discussion mentioned above, we proposed that the 1-D Mp-InS-**7** obtained afterward is formed by breaking the 2-D structure of Mp-InS-**5** along the (1 0 0) and (1/2 0 0) planes (Figure 6a and 6b).

Table 2. Important S···C and C···C Contacts in Mp-InS-5 (Å)[a]

$S(2)\cdots C(7)^{ii}$	3.632	$S(5)\cdots C(3)$	3.566
$S(5)\cdots C(7)$	3.406	$S(16)\cdots C(31)^{iii}$	3.356
$C(6)\cdots C(78)^{iv}$	3.305	$C(7)\cdots C(78)^{iv}$	3.227
$C(7)\cdots C(79)^{iv}$	3.286	$C(8)\cdots C(81)^{iv}$	3.341
$C(8)\cdots C(82)^{iv}$	3.310	$C(9)\cdots C(82)^{iv}$	3.359
$C(12)\cdots C(77)^{iv}$	3.383	$C(20)\cdots C(69)^{v}$	3.369
$C(20)\cdots C(70)^{v}$	3.390	$C(59)\cdots C(81)^{vi}$	3.214
$C(59)\cdots C(82)^{vi}$	3.240	$C(60)\cdots C(82)^{vi}$	3.273

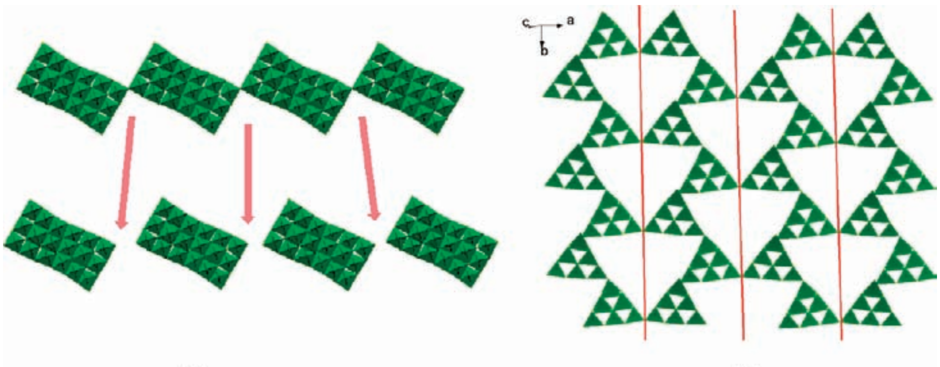
[a] Symmetry: (i) $x, -1+y, z$; (ii) $x, 1-y, -1/2+z$; (iii) $1.5-x, 1/2-y, 1-z$; (iv) $2-x, 1+y, 1/2-z$; (v) $x, 1-y, 1/2+z$; (vi) $-1+x, 1+y, z$.

Table 3. Important S···C and C···C Contacts in Mp-InS-6 (Å)[a]

$S(1)\cdots C(43)^{i}$	3.336	$S(5)\cdots C(71)^{ii}$	3.493
$S(19)\cdots C(55)^{iii}$	3.369		
$C(11)\cdots C(78)$	3.299	$C(11)\cdots C(82)$	3.229
$C(12)\cdots C(81)$	3.166	$C(12)\cdots C(82)$	3.256
$C(28)\cdots C(68)^{iv}$	3.384	$C(54)\cdots C(78)^{iv}$	3.241
$C(55)\cdots C(78)^{iv}$	3.182	$C(55)\cdots C(79)^{iv}$	3.260
$C(56)\cdots C(81)^{iv}$	3.347	$C(56)\cdots C(82)^{iv}$	3.309
$C(57)\cdots C(82)^{iv}$	3.349		

[a] Symmetry: (i) $x, -y, -1/2+z$; (ii) $1/2-x, 1/2+y, 1/2-z$; (iii) $1/2-x, 1/2-y, 1-z$; (iv) $-x, -y, 1-z$.

4. Electronic Spectra in the Solid State. Optical diffuse-reflection spectra of Mp-InS-**5** and **6** were measured at room temperature using $BaSO_4$ as a standard reference (Figure 7). In order to assign the energy bands, the absorption spectra observed for $(HDMA)_6In_{10}S_{18}$, a 3-D T_3 compound, and $[M(phen)_3]Cl_2$ (M = Ni, Fe) are illustrated in Figure 7a and 7b. The broad bands in the area larger than about 3.2 eV (387 nm) for Mp-InS-**5** and Mp-InS-**6** are assigned to anion-centered bands overlapped with $\pi\cdots\pi^*$ transitions of the phen ligand. The small shoulder band at about 2.30 eV for Mp-InS-**5** is assigned to a d−d transition of the $[Ni(phen)_3]^{2+}$ cation in comparison with the spectrum of $[Ni(phen)_3]Cl_2$. Besides the bands mentioned above, a new intense absorption in the range of 2.5−3.2 eV for Mp-InS-**5** is assigned to the cation−anion charge-transfer band (CACT). The reddish orange color of the compound Mp-InS-**5** also supports that there is a strong charge transfer between cations and anions, because the color of $[Ni(phen)_3]^{2+}$ is pink and $[In_xS_y]^{n-}$ is colorless or pale yellow. The onset energy of Mp-InS-**5** (about 2.20 eV) was estimated by extrapolation of the linear portion of the absorption edge of the CACT band if the weak d−d transition is not considered. The intense absorption band at about 2.4 eV for Mp-InS-**6** is assigned to the metal to ligand charge transfer (MLCT) of $[Fe(phen)_3]^{2+}$ in comparison with the spectrum of $[Fe(phen)_3]Cl_2$. The onset energy of Mp-InS-**6** is about 1.9 eV, estimated by extrapolation of the linear portion of the absorption edge of the intense MLCT band. There is no such MLCT band for $[Ni(phen)_3]^{2+}$ compounds. Therefore, the band gap of Mp-InS-**6** has a larger red shift than that of Mp-InS-**5**. The intense absorption in the range of 2.5−3.2 eV for Mp-InS-**6** can also be assigned to the CACT band that overlaps



(a) (b)

Figure 6. Relationship between the 2-D structure of Mp-InS-**5** and the 1-D structure of Mp-InS-**7**: the red arrows in a and red lines in b marked the points of crystal cracking.

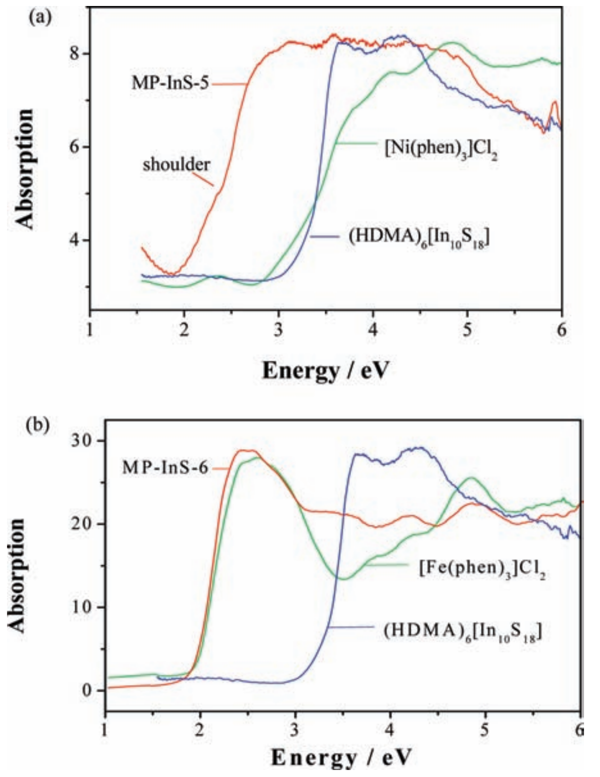


Figure 7. (a) Solid-state electronic spectra of Mp-InS-**5**, $(HDMA)_6In_{10}S_{18}$, and $[Ni(phen)_3]Cl_2$. (b) Solid-state electronic spectra of Mp-InS-**6**, $(HDMA)_6In_{10}S_{18}$, and $[Fe(phen)_3]Cl_2$.

with the MLCT band and anion-centered bands forming a platform. The charge transfer between cations and anions is very important for metal complex dye-sensitized semiconductors, which narrows the energy gap of the material and can be pre-excited by sunlight in a broad range.[14] The result of the spectral studies is helpful to understand the photoabsorption mechanism of such materials.

CONCLUSION

Despite some metal−phen complexes being well-known optically active dyes, only a few chalcogenido T*n* compounds integrated with M−phen are known. We prepared a series of organic−inorganic hybrid compounds Mp-InS-**4**−**7** that integrated with the M−phen complex by a solvothermal technique. We find that the reaction time plays an important role in assembling of the T*n* clusters. Prolonging the reaction time seems favorable to the higher condensed phase (from 0-D to 2-D). However, further prolonging the reaction time resulted in the crack reaction of the 2-D structure. Compounds Mp-InS-**5** and Mp-InS-**6** are two first obtained porous 2-D T3 compounds integrated with complex cations of $[M(phen)_3]^{2+}$. The new single-phase materials with layered $[In_xS_y]^{n-}$ anions show intense MLCT absorption (Fe−phen compound) and CACT absorption bands. For this reason, integrating M−phen cations into the chalcogenido materials can improve the absorption of visible sunlight. In particular, the $S\cdot\cdot\cdot H-C$ interaction between the metal complex cation and the chalcogenometalate anion is important in energy conversion. Although the cation used in this work is not a real complex dye as Ru−phen/bpy, this research leads to a new development in the synthesis of such materials, which will provide useful guidance for future exploration on the intriguing chalcogenides with Ru−phen/bpy dyes, a new material with photophysical applications.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** CIF tables, figures of XRD, TG and IR. This material is available free of charge via the Internet at http://pubs.acs.org.

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