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Photoelectroactive Ternary Chalcogenido-Indate-Stannates with a Unique 2-D Porous Structure

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A lot of ternary In-Sb-Q (Q = S, Se) chalcogenido-metalates with amine or complex cations have been recently reported for their diverse structures, however, such type of In-Sn-Q chalcogenido-metalates has been rarely announced. Herein we report a series of 2-D In-Sn-Q compounds prepared using metal-phenanthroline cationic template, $[M(Phen)_3](In_2Sn_2Q_8)\cdot(amine)\cdot nH_2O$ (M = Ni(II), Fe(II) or Co(II); amine = cyclohexylamine (Cha) or 1,6-diaminohexane (Dah); Q = S or Se). Their anions are isostructural and are 2-D porous network with large 16-tetrahedron-rings. The 2-D network joint of the In-Sn-Q is a $(In/Sn)_3Q_3$ six-membered ring, which is different from the Sn_3Q_4 pseudosemicube of most 2-D Sn-Q binary compounds. The materials exhibit photocurrent response property measured by photoelectrochemical cell. The result shows that (1) the selenides exhibit more intense photocurrents than the sulfides and (2) the current intensity is related to the metal-phenanthroline cations.

Introduction

Significant attention has been re-focused in the hydro- or solvothermal syntheses of 2-D main-group metal chalcogenides with protonated organoamines or transition metal complex cations due to their layered porous structures and potential applications in anisotropic conductivity, ion exchange in layers, and nonlinear optical properties.[1] As the familiar examples, two types of 2-D structures of thiostannates were reported (Fig. S1†), the first one is constructed by fused hexagonal 24-atom rings that is formed from six Sn_3S_4 pseudosemicube clusters with $(\mu\text{-S})_2$ bridges; the second one is also constructed by six Sn_3S_4 units, which form elliptically shaped 32-atom rings with the $(\mu\text{-S})_2$ and $\mu\text{-}(SnS_4)$ bridges in 1:2. A series of such porous layered compounds were characterized.[2,3] Despite that the cations were exchanged, the 2-D anion structures were hardly changed. Most of the 2-D selenidostannates also take the hexagonal 24-atom rings,[4] while some more complicated structures are reported recently.[5]

Ternary or even quaternary metal chalcogenide compounds are attractive to enhance the structural diversity and hence enrich the physical properties. A family of ternary (anion) transition-metal-thiostannate compounds were reported,[6] such as $A^IM^ISnQ_3$, $A^I_2M^I_2SnQ_4$, $A^{II}M^I_2SnQ_4$, $A^I_2M^I_2Sn_2Q_6$ and $A^I_2M^{II}Sn_2Q_6$ (A = alkali metal ions, M = transition metal ions, and Q = S, Se). Recently a lot of ternary In-Sb-Q compounds with protonated organoamines or transition metal complex cations have been reported and their structures and properties have spurred increasing interest.[7] Hydro- or solvothermal syntheses of main-group metal chalcogenides have been performed about more than two decades, however, inorganic-organic hybrid ternary In-Sn-Q compounds are inconceivably rare in contrast to those of In-Sb-Q compounds. To the best of our knowledge only very few reports about main group ternary M^{III}-M^{IV}-Q (M^{III} = Ga, In; M^{IV} = Ge, Sn) compounds (microporous 3-D structures), having amine cations, were documented.[8]

We have been devoting to the study of chalcogenido compounds with M-phen complex cations (Phen = 1,10-phenanthroline). The M-Phen cations can not only act as the structure directing ions, but also give additional charge-transfer properties to the metal chalcogenides.[9] In this work, we present five new 2-D In-Sn-S and In-Sn-Se main-group metal chalcogenides with formula $[M(Phen)_3](In_2Sn_2Q_8)\cdot(amine)\cdot nH_2O$ (M = Ni(II), Fe(II) or Co(II); amine = cyclohexylamine (Cha) or 1,6-diaminohexane (Dah); Q = S or Se). Unique 2-D structure features of the $(M^{III}M^{IV})Q_4$ type In-Sn-Q anions are found, which are discussed in comparison with those of the reported 2-D Sn-Q binary compounds. Based on our knowledge, the 2-D In-Sn-Q with amines or amine complexes have not been obtained until now. Spectral and photocurrent conversion properties of these compounds are measured and discussed.

Experimental

General remarks

Starting materials in analytical purity were purchased commercially and used without further purification. The IR spectra were recorded as KBr pellets on a Nicolet Magna 550 FT-IR spectrometer. Elemental analyses of C, H, and N were performed using an EA1110 elemental analyzer. Solid-state room-temperature optical diffuse reflectance spectra of the microcrystal samples were obtained with a Shimadzu UV-3150 spectrometer using $BaSO_4$ as a standard reference. Thermal analysis was conducted on a TGA-DCS 6300 microanalyzer. The samples were heated under a nitrogen stream of 100 mL·min^{-1} with a heating rate of 20 °C·min^{-1}. Room-temperature powder X-ray diffraction data were collected on a D/MAX-3C diffractometer using a Cu tube source (CuKα, λ = 1.5406 Å). Fluorescence spectra of the solid samples were obtained with an Edinburgh FLS920 spectrometer. The In:Sn ratio was measured by Varian 710-ES ICP spectrometer.

Synthesis

[Ni(Phen)$_3$](In$_3$SnS$_8$)·(Cha)·4H$_2$O (1). The reagents of In (0.0057 g, 0.05 mmol), S (0.0064 g, 0.20 mmol), Sn (0.0059 g, 0.05 mmol), Ni (0.0030 g, 0.05 mmol), Phen (0.0300 g, 0.15mmol), Cha (cyclohexylamine, 1.5 mL) and H$_2$O (0.5 mL) were mixed in a thick Pyrextube (ca.15 cm long). The sealed tube was heated at 160 °C for 5 days to yield pink plate crystals. The crystals were washed with ethanol, dried, and stored under vacuum (45% yield based on In). Elemental analysis (C$_{42}$H$_{45}$N$_7$In$_2$NiO$_4$Sn$_2$S$_8$, MW 1494.05). Calcd: C, 33.76; H, 3.04; N, 6.56. Found: C, 33.43; H, 3.16; N, 6.79. IR (cm^{-1}): 3424(vs), 3076(w), 2931(w), 2821(w), 1623(w), 1580(w), 1514(s), 1421(s), 1384(m),1102(m), 843(s), 768(w), 723(vs), 641(w), 479(w).

[Ni(Phen)$_3$][(In/Sn)$_4$Se$_8$]·(Cha)·4H$_2$O (2). Compound **2** was obtained by following a similar procedure to that of **1**, but element Se (0.0158g, 0.20 mmol) was used instead of S. The sealed tube was heated at 160 °C for 5 days to yield orange plate crystals. (40% yield based on In). Elemental analysis (C$_{42}$H$_{45}$N$_7$In$_2$NiO$_4$Sn$_2$Se$_8$, MW 1869.25). Calcd: C, 26.99; H, 2.43; N, 5.25. Found: C, 26.91; H, 2.37; N, 5.09. IR (cm^{-1}): 3424(s), 3076(w), 2921(m), 2850(w), 1621(m), 1580(m), 1514(s), 1421(s), 1382(m),1141(m), 1101(m), 842(vs), 768(w), 768(m), 722(vs), 641(w), 474(w).

[Fe(Phen)$_3$][(In/Sn)$_4$S$_8$]·0.5(Dah)·2H$_2$O (3). Compound **3** was obtained by following a similar procedure to that of **1**, but element Fe (0.0028g, 0.05 mmol) was used instead of Ni and Dah (1,6-diaminohexane, 0.25g, 2.15 mmol) was used instead of Cha. The sealed tube was heated at 160 °C for 7 days to yield dark red crystals. The crystals were washed with ethanol, dried, and stored under vacuum (50% yield based on In). Elemental analysis (C$_{39}$H$_{36}$N$_7$In$_2$FeO$_2$Sn$_2$S$_8$, MW 1414.11). Calcd: C, 33.13; H, 2.57; N, 6.93. Found: C, 33.48; H, 3.21; N, 7.40. IR (cm^{-1}): 3423(s), 3040(w), 2921(w), 2848(w), 1628(m), 1597(w), 1574(w), 1508(m), 1453(w), 1423(vs), 1408(w), 1338(w), 1310(w), 1203(w), 1141(w), 1053(w), 909(w), 840(vs), 797(w), 768(m), 735(w), 720(vs), 558(w), 524(w), 423(w).

[Fe(Phen)$_3$][(In/Sn)$_4$Se$_8$]·0.5(Dah)·2H$_2$O (4). Compound **4** was obtained by following a similar procedure to that of **3**, but element Se (0.0158g, 0.20 mmol) was used instead of S. The sealed tube was heated at 180 °C for 7 days to yield dark red crystals. The crystals were washed with ethanol, dried, and stored under vacuum (50% yield based on In). Elemental analysis (C$_{39}$H$_{36}$N$_7$In$_2$FeO$_2$Sn$_2$Se$_8$, MW 1789.31). Calcd: C, 26.18; H, 2.03; N, 5.48. Found: C, 26.66; H, 2.46; N, 6.07. IR (cm^{-1}): 126(w), 3036(w), 2920(w), 2845(w), 1627(m), 1574(w), 1508(w), 1452(w), 1422(vs), 1407(w), 1337(w), 1310(w), 1203(m), 1143(w), 1052(w), 909(w), 839(vs), 796(w), 768(w), 733(w), 720(vs), 644(w), 476(w), 423(w).

[Co(Phen)$_3$][(In/Sn)$_4$Se$_8$]·(Cha)·4H$_2$O (5). Compound **5** was obtained by following a similar procedure to that of **2**, but element Co (0.0030g, 0.05 mmol) was used instead of Ni. The sealed tube was heated at 160 °C for 7 days to yield orange crystals. The crystals were washed with ethanol, dried, and stored under vaccuum (50% yield based on In). Elemental analysis (C$_{42}$H$_{45}$N$_7$In$_2$CoO$_4$Sn$_2$Se$_8$, MW 1869.50). Calcd: C, 26.98; H, 2.43; N, 5.24. Found: C, 27.32; H, 2.61; N, 5.45. IR (cm^{-1}): 3442(s), 3133(w), 3042(w), 2921(w), 2847(w), 1622(m), 1577(w), 1514(s), 1493(w), 1447(w), 1421(vs), 1339(w), 1305(w), 1219(w), 1141(m), 1100(m), 1006(w), 956(w), 866(w), 842(vs), 768(w), 723(vs), 642(w), 539(w), 496(w), 450(w), 423(w).

X-ray Crystallographic Study

Data collections were performed on a Rigaku Mercury CCD diffractometer using a ω-scan method with graphite monochromated MoKα radiation (λ= 0.071075 nm) at room temperature. The collected data were reduced by using the program *CrystalClear*, and an absorption correction (multi-scan) was applied for all the compounds.[10] The reflection data were also corrected for Lorentz and polarization effects. The structures were solved with direct methods using the SHELXS-97 program and the refinement was performed against F^2 using SHELXL-97.[11] All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms on Phen were positioned with idealized geometry and refined with fixed isotropic displacement parameters. All the atoms of anion and complex cations were refined anisotropically. The solvent amines have not been completely solved due to the serious disorder. The small molecules, one cyclohexylamine molecule and four water molecules for **1**, **2** and **5** and half of a 1,6-diaminohexane molecule and two water molecules for **3**, contribution to the scattering factors, have been taken into account with PLATON/SQUEEZE. Relevant crystal data, collection parameters, and refinement results can be found in Table 1.

Electrode preparation and photocurrent measurement

The photoelectrodes of the compounds were prepared using the powder coating method. As a typical procedure, the crystals of compounds were ground and pressed uniformly on the ITO glass (0.5 cm^2, 100 Ω/□). A 150 W high pressure xenon lamp, located 20 cm away from the surface of the ITO electrode, was used as a light source. The photocurrent experiments were performed on a CHI650E electrochemistry workstation in a three-electrode system, the sample coated ITO glass as the working electrode with an area of 0.385 cm^2 (Φ = 0.7 cm), a Pt plate as auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode. The supporting electrolyte solution was a 0.1 mol·L^{-1} sodium sulfate aqueous solution (100 mL). The lamp was kept on continuously, and a manual shutter was used to block exposure of the sample to the light. The sample was typically irradiated with intervals of 20 s.

Results and discussion

Synthesis and characterization

Compounds **1**–**5** are prepared under similar solvothermal conditions from a mixture of elements In, Sn, Q, transition metal M, Phen and amines, which were sealed in a thick Pyrextube, heated at 160 °C for 5–7 days. The added amines are important to adjust the alkalinity of the reaction system and to accelerate the reaction. The quantity of the water is also important to obtain high quality crystals (Experimental section). The solvothermal technique has been proven to be a successful method in situ synthesis of $[M(Phen)_3]^{2+}$ cations for charge balance and structural directing of the formation of chalcogenidoindate-stannates. It is difficult to distinguish Sn and In atoms only based on crystal analysis (next section). Formulas of the as-prepared compounds are deduced with the assistances of EDS, ICP measurements and the charge-balance law. The EDS scan of a single crystal face clearly confirmed the uniform distribution of In and Sn elements (Fig. 1). The In:Sn ratio is approximately 1:1 based on ICP and EDS (Table S1, Fig. S2†). Single crystal analysis proved that one asymmetric anion unit $(In/Sn)_4Q_8$ corresponds to one $[M(Phen)_3]^{2+}$ cation, which defined the atom number of main-group metals (4) and the anion's charge (2–). The only algebraic solution of x and y for $(In_xSn_yQ_8)^{2-}$ is: x=2 and y=2 based on the charge balance and atom sum. Therefore the formula should be $[M(Phen)_3](In_2Sn_2Q_8)$, if ignored the solvent molecules.

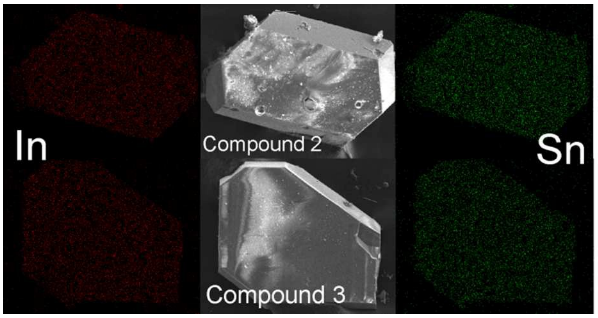

Fig. 1. The EDS scan of a single crystals of **2** and **3** clearly confirmed the uniform distribution of In and Sn elements

The FTIR spectra of **1**–**5** in 400–1700 cm^{-1} rang and Raman spectra of **1–3** in 250–1700 cm^{-1} are showed in Figure 2a and 2b. The IR bands at 1515, 1420, 845 and 725 cm^{-1} indicate the C-H stretches of the Phen rings. Different ν_{C-H} vibrations of **1**, **2**, **5** (1115 cm^{-1}, Cha) and **3**, **4** (1204 cm^{-1}, Dah) due to the different amines can be distinguished in IR spectra. The O–H bend vibrations of cocrystallized water are found at about 1625 cm^{-1}. The bands around 1600 cm^{-1} of Raman are attributed to the ring stretches of the Phen. The evidence of the thio or selenido compounds can be distinguished by the finger characteristic bands below 400 cm^{-1} of Raman spectra (M–Se or M–S vibrations). Optical diffuse-reflection spectra of **1**–**4** were measured and the absorption data are calculated from the reflectance (Fig. 2c and 2d). The spectra of **1** (InSnSNi) and **2** (InSnSeNi) are similar and can be assigned to two main parts. The first weak peak, about 2.36 eV, in the visible area, is assigned to the *d–d* transition of the $[Ni(Phen)_3]^{2+}$ cation and the intense absorption (> 2.5 eV) results from the metal chalcogenide anion including the charge-transfer between cation and anion. The very intense bands of **3** (InSnSFe) and **4** (InSnSeFe) at around 2.3 eV are attributed to the cation-centered Fe to Phen charge transfer (MLCT), which extend the absorption of the chalcogenide to 1.9 eV. The CT bands are important character for main-group metal chalcogenide with Phen complexes,[9] but they are overlapped with cation or anion centered bands and not easy to be distinguished from the curves.

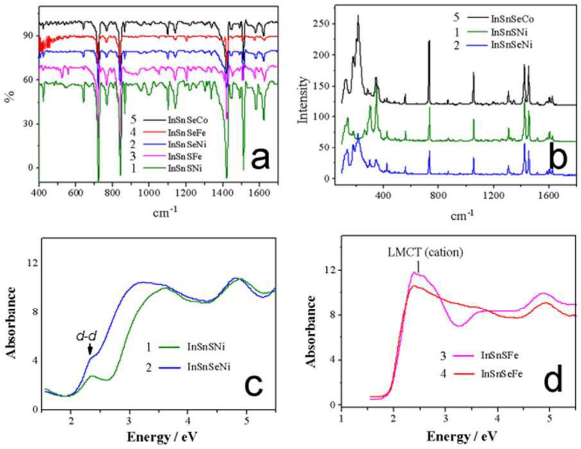

Fig. 2. FT-IR, Raman and solid-state absorption spectra.

Thermogravimetic (TG) analysis of **1-5** showed that their behaviors undergo about three decomposition steps from room temperature to 680 °C (Fig. S3†). The first step, before 200–250 °C, lost the cocrystallized water molecules (4 H_2O for Cha compounds and 2 H_2O for Dah compounds); The second step, from 200–250 °C to 350–370 °C, lost the cocrystallized amine molecules (one Cha for **1**, **2** and **5** and half of a Dah for **3** and **4**); The third step with vigorous weight loss, between about 350 and 680 °C, corresponds to the decomposition of the metal-phenanthroline cations. The chalcogenido anions are slowly decomposed above 680 °C. Since the solvent amines have not been completely solved due to the serious disorder, the formulas of these compounds are based on the elemental analysis and the thermal analysis data. The experimental data and calculated data of TG are listed in Figure S3 and the caption.

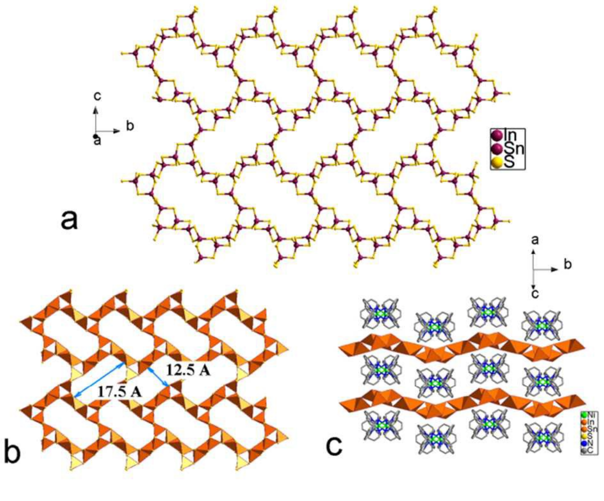

Fig. 3. (a) The 2-D anion structure of **1**. (b) Porous 2-D anion structure of 1 in polyhedron view. (c) Molecular packing of crystal **1**, showing the sandwiched cation-anion arrangement.

Structure of compounds

Single-crystal X-ray crystallography (**1**–**3**, **5**, Fig. S4†, Table 1) and XRD analysis (**1**–**5**, Fig. S5, S6†) reveal that all the compounds are monoclinic and belong to $P2_1/n$ space group and their anions are isostructural. The asymmetric unit of **1** includes a disordered free amine (Cha) and four water molecules. The anion is a two-dimensional porous framework of $\{[In_2Sn_2S_8]^{2-}\}_n$, which form elliptically shaped 16-tetrahedron (T)-membered rings (also called 32-atoms ring) (Fig. 3a). The large 16 T-memberd ring has nano scale windows in size of ca. 17.5 × 12.5 Å^2 measured using the interatomic distances of the inner opposite sulfur atoms. All the In or Sn atoms are in MQ_4 tetrahedron geometry and are connected by sharing the corners or edges. According to the literatures, the In–S bond distances are somewhat longer than those of the Sn–S bonds in average. However in many cases they are hard to be distinguished. The metal atom sites may be statistically occupied with In and Sn,[8] Based on this consideration, the Sn and In atoms are not distinguished in crystallographic treatment, and all the labels of In and Sn are labeled as In/Sn. Figure 3b shows polyhedron view of the herringbone-like arrangement of the fused 16 T-membered ring structure. The arrangement of the 2-D fused elliptically shaped 16 T-membered rings is also different from that of the similar SnS binary compounds reported, in which the rings are fused in the same direction.

These layers are stacked in an -AA- fashion parallel to (1 0 -1) plane. The $[Ni(Phen)_3]^{2+}$ cations are sandwiched between layered anions and one of the Phen planes of the cation extends into the 1-D tunnel formed by the porous windows of the anions (Fig. 3c and Fig. S7†). There are a lot of C–H···S weak hydrogen bonds between the cations and anions, which play the role of structural directing. It is worth noting that all the anion structures of the four ternary InSnQ compounds **1**–**3** and **5** are characterized with the same structure if ignoring the effect of different chalcogen atoms and disorder.

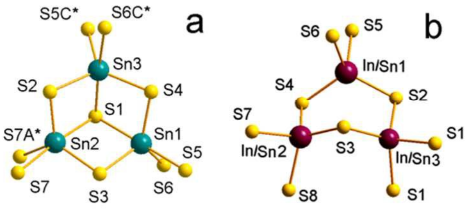

Fig. 4 Different three direct joints in (a) binary SnQ compounds and (b) ternary InSnQ compounds.

It should be noticed that the network joints of the two types of 2-D compounds (binary and ternary, shown in Figure 4) are different. The joints of the porous structures of all the four new compounds are not the $[(In/Sn)_3S_4]$ pseudosemicubes, which is familiar in binary chalcogenido stannates as $[Sn_3S_4]$ (Fig. 4a), but the heterometallic $[(In/Sn)_3S_3]$ ring units (Fig. 4b). Now we can consider two problems: (1) the role of the indium atoms played in the formation of 2-D structure that is different from the tin atoms in 2-D SnQ compounds; (2) the structural directing effect of the $[Ni(Phen)_3]^{2+}$ cations. The Sn atom can take fivefold coordination, while the In atom prefer the tetrahedral fourfold coordination geometry. For these natures the Sn_3S_3 six-membered ring takes *trans* chair-like structure and the chair-like ring structure allows the three Sn atoms coordinated by an additional S atom to form a pseudosemicube cluster in most cases.[2–4] The $(In/Sn)_3S_3$ six-membered ring takes *cis* boat-like structure. Very recently, the *cis* boat-like Sn_3S_3 ring unit has been reported in binary SnQ compounds,[5a,b] but it should be noticed that the 2-D network joints in these compounds are invariable the Sn_3S_4 pseudosemicubes. Although main-group metal chalcogenides with amine complexes have been explored for a long period,[12] attempts to obtain the single crystals as **1–5** with metal amine complex cations, such as $[M(en)_3]^{2+}$ (en = ethylenediamine), were unsuccessful. For this reason, the templating function of the rigid $[M(Phen)_3]^{2+}$ is obvious. The size and rigidity of the cation just fitting the corrugated layered structure might be considered.

Photocurrent response

Main-group metal chalcogenides usually have semiconducting property and some $[M(Phen)_3]^{2+}$ cations have been widely used as photochemical and photoelectric active complex ions.[13] The photocurrent responsive properties of **1**–**5** were investigated using a three electrode photoelectrochemical cell with the microcrystal sample modified ITO working electrode (Fig. 5). A more detailed description is given in experimental section. Upon repetitive irradiation with xenon light on and off, clear photocurrent responses are observed, which are repeatable with only slightly shift of the base line. Especially, the response rates are very fast, because the photogenerated current can reach the saturated state immediately (showing square waves). Comparing with those of the sulfides modified electrode, about 0.7 μA·cm^{-2} for **3**, the photocurrent intensity of the selenides exhibit more intense photocurrents, about 6.0 μA·cm^{-2} for **4** (Figure 5a). Similar results are found for **1** and **2** (Fig. S8†). Figure 5b shows the photocurrent intensity of the three selenides **2**, **4** and **5** under the same experiment condition. It shows that the selenides with redox active $[Fe(Phen)_3]^{2+}$ and $[Co(Phen)_3]^{2+}$ cations are more sensitive to the irradiation than that with $[Ni(Phen)_3]^{2+}$ cation. The photoexcitation mechanism may be explained as follows. As the material is photoexcited, the $[M(Phen)_3]^{2+}$ cation, acting as a photosensitizer, quickly transfers the electron from the excited band of the cation to the chalcogenide layers and the hole in ground state obtains electron from the ITO electrode (applied potential −0.5 V), and then the cathodic current is generated.

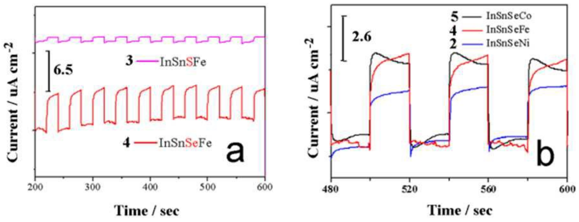

Fig. 5 Photocurrent responses in the presence of a 0.1 mol·L^{-1} Na_2SO_4 aqueous solution with −0.5 V applied potential of (a) the Fe-Phen compounds **3** and **4** and (b) the selenide compounds **2**, **4** and **5**.

Conclusions

In summary, a series of 2-D ternary chalcogenido-indate-stannates have been isolated by solvothermal method using metal-phenanthroline rigid templates. It is a great progress in this discipline, since rare ternary In-Sn-S compounds were reported. Their anions are isostructural and 2-D porous network with large 16-tetrahedron-rings. Because the In atom prefers tetrahedral coordination unlike the Sn atom that favors both four and five coordination, structure of the network joint of the 2-D In-Sn-Q is a $(In/Sn)_3Q_3$ six-membered ring that is different from the Sn_3S_4 pseudosemicube of most 2-D Sn-Q binary compounds. The materials exhibit photocurrent response property. The result shows that (1) the selenides exhibit more intense photocurrents than the sulfides; (2) the current intensity is related to the metal-phenanthroline cations.

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Notes and references

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† Electronic Supplementary Information (ESI) available: the experiment details, Figures of asymmetric units of **1**-**3** and **5**, XRD patterns, photocurrent response of nickle compounds, Table of crystallographic data and structure refinement parameters, See DOI: 10.1039/b000000x/. Crystallographic data of **1**-**3** and **5** in CIF format contain the supplementary crystallographic data for this paper, CCDC 1017772-1017775.

1 (a) N. Pienack, A. Puls, C. Näther, W. Bensch, *Inorg. Chem.*, 2008, **47**, 9606−9611; (b) Q. Zhang, I. Chung, J. I. Jang, J. B. Ketterson, M. G. Kanatzidis, *Chem. Mater.*, 2009, **21**, 12–14; (c) M. Wu, J. Rhee, T. J. Emge, H. Yao, J.-H. Cheng, S. Thiagarajan, M. Croft, R. Yang, J. Li, *Chem. Commun*., 2010, **46**, 1649–1651; (d) W.-W. Xiong, J. Miao, P.-Z. Li, Y. Zhao, B. Liu, Q. Zhang, *CrystEngComm*, 2014, **16**, 5989–5992; (e) M.-L. Feng, X.-H. Qi, B. Zhang, X.-Y. Huang, *Dalton Trans.*, 2014, **43**, 8184−8187.

2 (a) J. B. Parise, Y. Ko, J. Rijssenbeek, D. M. Nellis, K. Tan, S. Koch, *Chem. Commun.,* 1994, 527−527; (b) K. Tan, Y. Ko, J. B. Parise, *Acta Crystallogr. C*, 1995, **51**, 398−401; (c) T. Jiang, A. Lough, G. A. Ozin, R. L. Bedard, R. Broach, *J. Mater. Chem.,* 1998, **8,** 721−732; (d) T. Jiang, A. Lough, G. A. Ozin, *Adv. Mater.,* 1998, **10,** 42−46; (e) H. Ahari, A. Lough, S. Petrov, G. A. Ozin, R. L. Bedard, *J. Mater. Chem.*, 1999, **9**, 1263−1274.

3 (a) T. Jiang, G. A. Ozin, R. L. Bedard, *Adv. Mater.,* 1994, **6**, 860−865; (b) Y. Ko, K. Tan, D. M. Nellis, S. Koch, J. B. Parise, *J. Solid State Chem.,* 1995, **114**, 506−511; (c) T. Jiang, A. J. Lough, G. A. Ozin, D. Young, R. L. Bedard, *Chem. Mater.,* 1995, **7,** 245−248; (d) T. Jiang, G. A. Ozin, *J. Mater. Chem.*, 1998, **8**, 1099−1108.

4 (a) W. S. Sheldrick, H. G. Braunbeck, *Z. Anorg. Allg. Chem.,* 1993, **619**, 1300−1306; (b) J. B. Parise, Y. Ko, K. Tan, D. M. Nellis, S. Koch *J. Solid State Chem.,* 1995, **117**, 219−228; (c) H. Ahari, A. Lough, S. Petrov, G. A. Ozin, R. L. Bedard, *J. Mater. Chem.,* 1999, **9**, 1263−1274; (d) A. Loose, W. S. Sheldrick, *Z. Anorg. Allg. Chem.,* 1999, **625**, 233−240; (e) A. Fehlker, R. Blachnik, *Z. Anorg. Allg. Chem.,* 2001, **627**, 1128−1134; (f) S. Lu, Y. Ke, J. Li, S. Zhou, X. Wu, W. Du, *Struct.Chem.,* 2003, **14**, 637−641; (g) Y. Lin, S. Dehnen, *Inorg. Chem.,* 2011, **50**, 7913−7915; (h) G.-N. Liu, G.-C. Guo, M.-J. Zhang, J.-S. Guo, H.-Y. Zeng, J.-S. Huang, *Inorg. Chem.,* 2011, **50**, 9660−9669; (i) Y. Lin, D. Xie, W. Massa, L. Mayrhofer, S. Lippert, B. Ewers, A. Chernikov, M. Koch, S. Dehnen, *Chem. Eur. J.,* 2013, **19**, 8806−8813.

5 (a) J.-R. Li, Z.-Z. Xie, X.-W. He, L.-H. Li, X.-Y. Huang, *Angew. Chem. Int. Ed.,* 2011, **50**, 11395−11399; (b) Y. Lin, W. Massa, S. Dehnen, *Chem. A Eur. J.,* 2012, **18**, 13427−13434; (c) Y. Lin, W. Massa, S. Dehnen, *J. Am. Chem. Soc.,* 2012, **134**, 4497−4500; (d) J.-R. Li, W.-W. Xiong, Z.-L. Xie, C.-F. Du, G.-D. Zou, X.-Y. Huang, *Chem. Commun.,* 2013, **49**, 181−183.

6 (a) W. S. Sheldrick, M. Wachhold, *Coord. Chem. Rev.*, 1998, **176**, 211−322; (b) C. D. Morris, H. Li, H. Jin, C. D. Malliakas, J. A. Peters, P. N. Trikalitis, A. J. Freeman, B. W. Wessels, M. G. Kanatzidis, *Chem. Mater.*, 2013, **25**, 3344−3356.

7 (a) N. Ding, M. G. Kanatzidis, *Chem. Mater.,* 2007**, 19**, 3867–3869; (b) J. Zhou, X.-H. Yin, F. Zhang, *Inorg. Chem.,* 2010, **49**, 9671–9676; (c) M.-L. Feng, P.-X. Li, K.-Z. Du, X.-Y. Huang, *Eur. J. Inorg. Chem.,* 2011, 3881–3885; (d) J. Zhou, L. An, *CrystEngComm,* 2011, **13**, 5924–5928; (e) J. Zhou, L. An, F. Zhang, *Inorg. Chem.*, 2011, **50**, 415–417; (f) J. Zhou, X. Liu, L. An, F. Hu, Y. Kan, R. Li, Z. Shen, *Dalton Trans*., 2013, **42**, 1735–1742; (g) K.-Y. Wang, M.-L. Feng, J.-R. Li, X.-Y. Huang, *J. Mater. Chem. A,* 2013, **1**, 1709–1715; (h) C.-Y. Yue, X.-W. Lei, Y.-X. Ma, N. Sheng, Y.-D. Yang, G.-D. Liu, X.-R. Zhai, *Cryst. Growth Des.,* 2014, **14**, 101−109.

8 N. Zheng, X. Bu, B. Wang, P. Feng, *Science*, 2002, **298**, 2366–2369.

9 (a) Z.-X. Lei, Q.-Y. Zhu, M.-H. Zhang, J.-B. Jiang, Y.-P. Zhang, J. Dai, *Inorg. Chem*., 2010, **49**, 4385–4387; (b) X. Zhang, W. Luo, Y.-P. Zhang, J.-B. Jiang, Q.-Y. Zhu, J. Dai, *Inorg. Chem.,* 2011**, 50**, 6972–6978; (c) J.-B. Jiang, G.-Q. Bian, Y.-P. Zhang, W. Luo, Q.-Y. Zhu, J. Dai, *Dalton Trans.,* 2011, **40**, 9551–9556; (d) Y.-P. Zhang, X. Zhang, W.-Q. Mu, W. Luo, G.-Q. Bian, Q.-Y. Zhu, J. Dai, *Dalton Trans.,* 2011, **40**, 9746–9751; (e) W.-Q. Mu, Q.-Y. Zhu, L.-S. You, X. Zhang, W. Luo, G.-Q. Bian, J. Dai, *Inorg. Chem.*, 2012, **51**, 1330–1335; (f) J.-B. Jiang, Y.-Y. Wu, P. Wang, P. Huo, Q.-Y. Zhu, J. Dai, *Dyes & Pigments,* 2014, **107**, 153–160.

10 *CrystalClear software,* Rigaku Corporation, 2001**,** Ver. 1.3.

11 a) G. M. Sheldrick, *SHELXS-97 and SHELXL-97*, *Program for structure solution and refinement*, Universität of Göttingen, Germany, 1997. b) G. M. Sheldrick, *SHELXS-2013 and SHELXL-2013*, *Program for structure solution and refinement*, Universität of Göttingen, Germany, 2013. c) G. M. Sheldrick, SHELX programs for structure solution, *Acta Cryst. A* 2008, **64**, 112.

12 J. Zhou, J. Dai, G.-Q. Bian, C.-Y. Li, *Coord. Chem. Rev.,* 2009, **253,** 1221−1247.

13 A. S. Polo, M. K. Itokazu, N. Y. M. Iha, *Coord. Chem. Rev.*, 2004, **248**, 1343; B. Happ, A. Winter, M. D. Hager, U. S. Schubert, *Chem. Soc. Rev.*, 2012, **41**, 2222−2255.

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ARTICLE TYPE

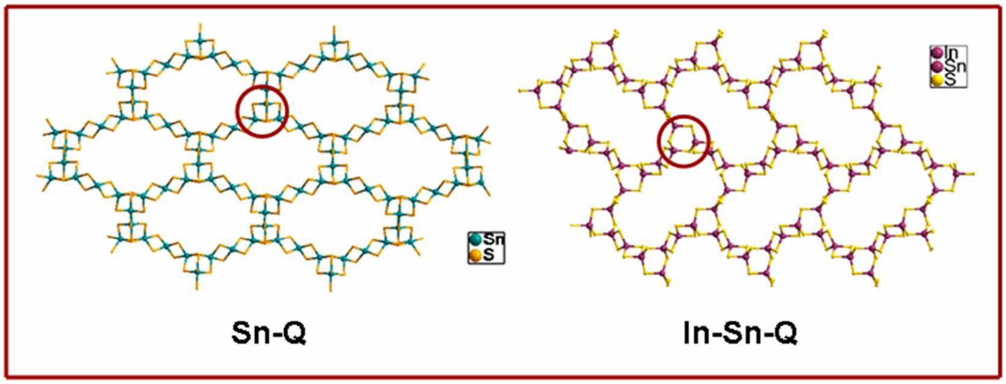
Table 1. Crystallographic Data and Structural Refinement Parameters for **1**–**3** and **5**

	1	**2**	**3**	**5**
formula	$C_{42}H_{45}In_2N_7NiO_4S_8Sn_2$	$C_{42}H_{45}In_2N_7NiO_4Se_8Sn_2$	$C_{39}H_{36}FeIn_2N_7O_2S_8Sn_2$	$C_{42}H_{45}CoIn_2N_7O_4Se_8Sn_2$
fw	1494.16	1869.26	1414.11	1869.50
cryst size (mm^3)	0.10×0.20×0.30	0.10×0.20×0.25	0.15×0.60×1.00	0.20 × 0.40 × 0.65
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\,2_1/n$	$P\,2_1/n$	$P\,2_1/n$	$P\,2_1/n$
a (Å)	15.281(3)	15.574(3)	15.130(3)	15.610(3)
b (Å)	23.918(5)	24.083(5)	23.728(5)	24.238(5)
c (Å)	15.657(3)	15.804(3)	15.450(3)	15.828(3)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	107.63(3)	107.11(3)	107.46(3)	107.04(3)
γ (deg)	90.00	90.00	90.00	90.00
V ($Å^3$)	5454 (2)	5665(2)	5291.5(18)	5726(2)
Z	4	4	4	4
ρ_{calcd} (g cm^{-3})	1.820	2.192	1.893	2.169
F(000)	2928	3504	2960	3500
μ (mm^{-1})	2.427	7.181	2.421	7.066
T (K)	293(2)	293(2)	293(2)	293(2)
reflns collected	51970	34016	43446	21988
unique reflns	12452	11456	9271	10001
observed reflns	9484	6449	7145	6729
GOF on F^2	0.937	1.157	1.059	1.100
R_1 [I>2σ(I)]	0.0552	0.0804	0.0798	0.0918
$_wR_2$ [I>2σ(I)]	0.1502	0.1322	0.1407	0.1820

Photoelectroactive ternary chalcogenido-indate-stannates with a unique 2-D porous structure

Jing Wu, Ya-Yang Pu, Xiao-Wei Zhao, Li-Wen Qian, Guo-Qing Bian, Qin-Yu Zhu* and Jie Dai*

SYNOPSIS and TOC



A series of photoelectroactive 2-D In-Sn-Q ternary compounds are prepared using metal-phenanthroline complex templates. The 2-D network joint of the In-Sn-Q is a $(In/Sn)_3Q_3$ six-membered ring, which is different from the Sn_3S_4 pseudosemicube of most 2-D Sn-Q binary compounds.