Review

Main-group metal chalcogenidometalates with transition metal complexes of 1,10-phenanthroline and 2,2'-bipyridine

Qin-Yu Zhu^a, Jie Dai^{a*}

^a College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China

Contents

1. Introduction
2. A survey of main-group metal chalcogenidometalates with phen/bpy complexes
 - 2.1. *The role of phen/bpy complexes in solvothermal syntheses*
 - 2.2. *The structures of the chalcogenidometalates with phen/bpy complexes*
 - 2.3. *The properties of the chalcogenidometalates with phen/bpy complexes*
 - 2.3.1. *Charge-transfer properties*
 - 2.3.2. *Photocurrent response properties*
 - 2.3.3. *Magnetic and SHG properties*
3. Structures of main-group metal chalcogenidometalates with phen/bpy complexes
 - 3.1. *Structures of Group 13 chalcogenidometalates (Ga, In)*
 - 3.2. *Structures of Group 14 chalcogenidometalates (Ge, Sn)*
 - 3.3. *Structures of Group 15 chalcogenidometalates (As, Sb)*
4. Summary

Acknowledgements

References

*Corresponding author. E-mail address: daijie@suda.edu.cn (J. Dai)

ABSTRACT Inorganic-organic hybrid main-group metal chalcogenidometalates have attracted considerable interest due to their various topologic structures and their potential applications in solid electrolytes, non-oxygen zeolites, and photo- or electro-catalyzers. The syntheses of these compounds are typically carried out under hydro(solvo)thermal conditions at relatively low temperature using various organic amines. Some comprehensive reviews have summarized the preparation and structures of these main-group metal chalcogenidometalates. One of the extended researches in this field is the challenge using the chelating imines, such as 1,10-phenanthroline (phen) and 2,2'-bipyridine (bpy), in the synthesis of inorganic-organic hybrid main-group metal chalcogenidometalates, because their transition metal complexes can add new optical or electronic properties to the host [chalcogenide](#) compounds. A series of [unique chalcogenidometalates with M-phen and M-bpy complexes](#) (M = metal ions) have been successfully isolated in recent decade. Unusual optic and photoelectronic properties of these compounds were found in comparison with those of amine series. This review focuses on the developments in the synthesis, structures and properties of these chalcogenidometalates. A comprehensive outline of the chalcogenidometalate compounds with discrete M-phen/bpy complex cations or covalently bonded M-phen/bpy moieties is presented. A section about the new functional properties of these compounds is specially compiled.

Keywords: chalcogenidometalates, main-group metals, solvothermal synthesis, phenanthroline complexes, bipyridine complexes

Abbreviations for various amines appeared in this review:

phen = 1,10-phenanthroline

bpy = 2,2'-bipyridine

mbpy = 4,4'-methyl-2,2'-bipyridine

terpy = 2,2',6',2''-terpyridine

MA = methylamine

EA = ethylamine

dien = diethylenetriamine,

en = ethylenediamine,

tren = tris(2-aminoethyl)amine,

EG =ethylene glycol

aep =N-(2-aminoethyl)piperazine

dba = di-*n*-butylamine

cha = cyclohexylamine

dah =1,6-diaminohexane

W = water

1. Introduction

Considerable attention has been paid and substantial successes have been achieved in inorganic-organic hybrid main-group metal chalcogenidometalates. It has been revealed that the integration of organic components with inorganic chalcogenide structures can produce materials with well-defined various topological structures and hold promise for applications in ion exchange, nonlinear optics, electronics and catalysis [1-6]. According to the classification of cation components, the inorganic-organic hybrid main-group metalchalcogenidometalates can be generally divided into three categories. The first is the chalcogenidometalates with organic quaternary ammonium or phosphonium cations, such as R_4N^+ and R_4P^+ ($R = Me, Et, Pr$, etc). These compounds were early developed originating from solvothermal preparation of artificial non-oxygen zeolites. Comprehensive reviews of the preparation and structures of these compounds were given by Sheldrick and Wachhold [7,8]. The second is the chalcogenidometalates with various protonated organic amines. The synthetic approaches of numerous chalcogenidometalates were developed mainly using non-chelating amines [8-10]. The organic amines play important roles for the reaction system in offering a chalcogenide source by reacting with chalcogen elements and in acting as templating or structure-directing agents. Yaghi, Feng and others reported a series of porous supertetrahedral chalcogenidometalates by using non-chelating amines [9-11], which was summarized in an important review article by Feng in 2005 [11]. Solvothermal synthesis using chelating amines, such as ethylenediamine (en) and diethylenetriamine etc, in the presence of transition/lanthanide metals, has launched a new type of chalcogenidometalates with metal-amine complex cations, which can be classified as the third class. Numerous such main-group metal chalcogenidometalates with transition metal amine complex cations or the decorated complex moieties have been reported. An early review of corresponding compounds was presented by Li in 1999 [12] and some subsequent reviews were presented by ours and Dehnen groups [13,14]. Very recently, Zhou has summarized the synthesis, crystal structures, and optical properties of heterometallic chalcogenides containing lanthanide-amine complexes [15].

Recently, Kanatzidis, Dehnen and Huang groups explored a new synthetic system of chalcogenidometalates using ionic solvents, for example [BMIm]Br (BMIm = 1-butyl-3-methyl-imidazolium), and some compounds with unusual structures were obtained [16-20]. A very recent review on the ionothermal synthesis of chalcogenidometalates was contributed by Dehnen [21]. Zhang group demonstrated and reviewed that surfactants can serve as promising reaction media for the preparation of crystalline chalcogenides and can also act as counterions and templates in the formation of chalcogenide frameworks [22-24]. Our group and some others have been interested in solvothermal synthesis of main group chalcogenidometalates in the presence of conjugated organic chelating imines, mainly 1,10-phenanthroline (phen) and 2,2'-bipyridine (bpy) and their metal complexes (M-phen/bpy). Subsequent developments have been made [in the synthesis, structural analysis](#)

and especially in the study of their unique optical and photoelectro chemical properties.

1,10-phenanthroline and 2,2'-bipyridine are classic chelating ligands for transition metal ions and have played an important role in the development of coordination chemistry. The detailed discussion about phen/bpy and their metal complexes can be found in reference [25]. They and their complexes are now still continuously interesting as the versatile ligands for organic-metal frameworks, supramolecular chemistry [26-28] and molecular biology as DNA cleaving or insertion reagent [29,30]. Phen/bpy is a rigid planar, hydrophobic and electron-conjugated heteroaromatic system. Taking the feature of their empty π^* orbital, some of their transition metal complexes, such as Ru(II), Co(II) and Fe(II), show an intense metal-to-ligand charge-transfer (MLCT) characteristic in visible spectra. These complexes have been used as photoelectronic [31-34] and photoactive catalysis materials [35-39], because they have narrow gap between ground and excited states, and the energy of the excited state matches well with that of the conductive band of the semiconductors. Many recent efforts have focused on the design and synthesis of novel photoactive M-phen/bpy derivatives, especially, the Ru(II)-phen/bpy system. The Ru(II)-phen/bpy dye-sensitized solar cells have attracted significant attention during the past decade due to the high efficiency in the conversion of sunlight to electricity [40-45]. However, most metal complexes sensitized inorganic semiconductors belong to multicomponent assemblies. They are either surface-modified materials in which the metal complexes ride on the surface of inorganic semiconductors or embedded materials in which the metal complexes are embedded in the cavity of the mesoporous inorganic oxides with uncertain composition. The fundamental study devoted to the single phase semiconductive materials with co-crystallized M-phen/bpy complex cations or fused complex moieties is a particular challenge.

The transition metal and lanthanide metal complexes of various amines as counterions or structure-directing agents may provide complementary synergistic effects with the host inorganic chalcogenide frameworks on both the structures and the properties, such as magnetic [46,47] and luminescent features [48]. Despite extensive research on such metal chalcogenidometalates, it was relatively less known about photoelectro active properties of such chalcogenidometalates in comparison with those of the inorganic chalcogenides. Integrated amine complexes usually broke the polymeric structures of chalcogenides, which expands the energy gap of the materials. To promote the photoelectronic properties of chalcogenidometalates of main-group metals or potential applications as photoactive materials, it is highly desirable to develop hybrid materials that allow molecular-level uniform integration of semiconducting frameworks with optically and electrically active metal-phen/bpy species. The onset absorption energy of chalcogenidometalates can be significantly improved by replacing the amine complexes with photo active M-phen/bpy complexes. The early example using $[M(\text{phen})_3]^{2+}$ as cation templates to organize tetrahedral chalcogenido clusters into unique crystals was reported by Feng group [49] and low energy charge-transfer between the cation and anion was demonstrated. We have proved that current intensities of the M-phen/bpy complex cations

functionalized chalcogenido clusters are greatly increased in comparison with those of the chalcogenido clusters with quaternary ammonium cations [50]. We and others have explored chalcogenidometalates, in which the M-phen/bpy cations are integrated with the chalcogenide anions or the complex moieties are fused with the skeletons of the chalcogenide, respectively. Substantial successes on such chalcogenidometalates have been achieved.

This review focuses on main-group metal chalcogenidometalates with phen/bpy metal complexes. As a comprehensive information, starting materials and typical reaction conditions that have been employed for the preparation and the structural information are summarized in Tables 1 and 2. The structures for group 13–15 chalcogenidometalates are described respectively as compounds with discrete M-phen/bpy cations or covalently bonded phen/bpy complexes. The directing effects of phen/bpy complexes on the formation of anion structures of group 13–15 chalcogenidometalates are discussed. More valuable, the roles of the transition metal phen/bpy complexes on promoting the optical and photoelectronic properties of the chalcogenidometalates are demonstrated, which is the advantage of the chalcogenidometalates with M-phen/bpy and is different from those with chelating amine complexes. Hopefully this review will inspire more interest in exploring new materials of chalcogenidometalates.

Table 1. Structural and preparative information for main-group chalcogenometalates with discrete M-phen/bpy complexes

No.	Compounds	Reactants	Solvent	D	T / time (d)	Space group	Ref
1	[Ni(bpy) ₃] ₃ [H ₄ In ₁₀ S ₂₀]·bpy·2EG·6H ₂ O	In + Ni + S	EG + W	0	140/10	<i>P2₁/c</i>	[51]
2	[Ni(bpy) ₃] ₂ [H ₂ In ₁₀ S ₁₉]·bpy·2HEA·2H ₂ O	In + Ni + S	aep + W	1	140/10	<i>Pbcn</i>	[51]
3	[Ni(bpy) ₃] ₇ [H ₄ In ₄₀ S ₇₄]·7(Hbpy)·3HEA·8H ₂ O	In + Ni + S	EA + W	2	140/12	<i>C2</i>	[51]
4	[Ni(phen) ₃] ₃ [H ₂ In ₁₀ S ₂₀]·2(NH ₂ Me ₂)·7H ₂ O	In + Ni + S + Cys	DMF + W	0	145/12	<i>P2₁/c</i>	[52]
5	[Ni(phen) ₃] ₃ [H ₄ In ₁₀ S ₂₀]·14.5H ₂ O	In + Ni + S + Na ₂ S	DMF + W	0	145/12	<i>Pt</i>	[52]
6	[Ni(phen) ₃] ₃ [H ₂ In ₁₀ S ₁₉]· <i>n</i> H ₂ O	In + Ni(phen) + Na ₂ S	DMF + W	1	140/12	<i>Pt</i>	[52]
7	[Ni(phen) ₃] ₄ [In ₂₀ S ₃₇]·6(Hphen)·4H ₂ O	In + Ni + Na ₂ S	DMF + W	2	140/24	<i>C2/c</i>	[53]
8	[Fe(phen) ₃] ₄ [In ₂₀ S ₃₇]·6(Hphen)·4H ₂ O	In + Fe + Na ₂ S	DMF + W	2	140/24	<i>C2/c</i>	[53]
9	[Fe(phen) ₃] ₃ [In ₁₀ S ₁₉]·2(Hphen)·3(NH ₂ Me ₂)·8H ₂ O	In + Fe + Na ₂ S	DMF + W	1	140/18	<i>P1</i>	[53]
10	[Ni(phen) ₃] ₄ [In ₁₀ S ₁₉]·2(Hphen)·2(NH ₂ Me ₂)·3H ₂ O	In + Ni + Na ₂ S	DMF + W	1	140/32	<i>C2/c</i>	[53]
11	[Ni(phen) ₃] ₃ [In ₂ Se ₅]·H ₂ O	In + Ni + Se	dba + W	1	140/4	<i>P2₁2₁2₁</i>	[54]
12	[Fe(phen) ₃] ₃ [In ₂ Se ₅]·H ₂ O	In + Fe + Se	dba + W	1	140/4	<i>P2₁2₁2₁</i>	[54]
13	[Ni(phen) ₃] ₂ [Ge ₄ S ₁₀]·4CH ₃ OH·12H ₂ O	Ni(phen) + Ge ₄ S ₁₀	MeOH + W	0	r/0.5	<i>C2/c</i>	[55]
14	[Ni(phen) ₃] ₂ [Ge ₄ S ₁₀]·3.5H ₂ O	Ni(phen) + Ge ₄ S ₁₀	DMF + W	0	r/0.5	<i>C2/c</i>	[55]
15	[H ₂ (4,4'-bpy)] ₂ [Ge ₄ S ₁₀]·2(4,4'-bpy)·7H ₂ O	Cu(NO ₃) ₂ + Ge ₄ S ₁₀	W	0	140/3	<i>C2/c</i>	[56]
16	[Fe(phen) ₃] ₂ [Sn ₆ Se ₁₄]·2.5H ₂ O	SnCl ₄ + FeCl ₃ + Se	MA + W	2	185/5	<i>R-3c</i>	[57]
17	[Fe(phen) ₃] ₃ [Hg ₂ Sn ₂ Se ₇]·1.5Et ₃ N·0.25H ₂ O	Fe(SCN) + HgO + Sn + Se	EA + W	1	150/6	<i>Pt</i>	[58]
18	[Ni(Phen) ₃] ₃ [In/Sn ₄ S ₈]·(cha)·4H ₂ O	In + Sn + Ni + S	cha + W	2	160/5	<i>P2₁/n</i>	[59]
19	[Ni(Phen) ₃] ₃ [In/Sn ₄ Se ₈]·(cha)·4H ₂ O	In + Sn + Ni + Se	cha + W	2	160/5	<i>P2₁/n</i>	[59]
20	[Co(Phen) ₃] ₃ [In/Sn ₄ Se ₈]·(cha)·4H ₂ O	In + Sn + Co + Se	cha + W	2	160/7	<i>P2₁/n</i>	[59]
21	[Fe(Phen) ₃] ₃ [In/Sn ₄ S ₈]·0.5(dah)·2H ₂ O	In + Sn + Fe + Se	dah + W	2	160/7	<i>P2₁/n</i>	[59]

22	[Fe(phen) ₃][As ₃ S ₆]·dien·7H ₂ O	As ₂ O ₃ + FeCl ₃ +S	dien+W	0	140/5	<i>P</i> $\bar{1}$	[60]
23	[Co(phen) ₃][As ₂ Se ₁₀]	As ₂ O ₃ + CoCl ₂ +Se	en+MeOH	1	130/5	<i>C</i> 2	[61]
24	[Co(phen) ₃] ₂ [As ₈ Se ₁₄]	As ₂ O ₃ + CoCl ₂ +Se	en+W	0	130/5	<i>P</i> $\bar{1}$	[61]
25	[Fe(phen) ₃][As ₂ Se ₆]	As ₂ O ₃ + FeCl ₃ +Se	dien+MeOH	0	130/5	<i>P</i> $\bar{1}$	[62]
26	[Zn(phen)(dien)][As ₂ Se ₆]·2phen	As ₂ O ₃ + ZnCl ₂ +Se	dien+MeOH	0	130/5	<i>P</i> $\bar{1}$	[62]
27	[Ni(phen) ₃][As ₂ Se ₂ (μ -Se ₃)(μ -Se ₅)]	As ₂ O ₃ + NiCl ₂ +Se	dien+MeOH	1	130/5	<i>C</i> 2	[62]
28	[Ni(phen) ₃] ₂ [Sb ₁₈ S ₂₉]	Ni(OAc) ₂ +Sb ₂ S ₃	EA+W	3	170/7	<i>P</i> 2 ₁	[63]
29	[Ni(bpy) ₃][Sb ₆ S ₁₀]	Na ₃ SbS ₄ +Ni(bpy)	W	2	140/1	<i>Pbcn</i>	[64]
30	[Fe(bpy) ₃][Sb ₆ S ₁₀]	Na ₃ SbS ₄ +Fe(bpy)	W	2	140/1	<i>Pbcn</i>	[64]
31	[Ni(mbpy) ₃][Sb ₆ S ₁₀]	Na ₃ SbS ₄ +Ni(mbpy)	W	2	140/1	<i>C</i> 2/ <i>c</i>	[64]

Table 2. Structural and preparative information for main-group chalcogenometalates with covalently bonded phen/bpy complexes

No.	Compounds	Reactants	Solvent	D	T / time(d)	Space group	Ref.
32	[InS(phen)Cl] ₄ ·1.5(C ₂ H ₆ O ₂)·0.5H ₂ O	InCl ₃ +S	EG+W	0	180/8	<i>P</i> $\bar{1}$	[65]
33	[InSe(phen)Cl] ₄	InCl ₃ +Se	EG+W	0	180/8	<i>P</i> 4 ₁	[65]
34	[InSCl(bpy)] ₄ ·H ₂ O	InCl ₃ +S	EG+W	0	140/14	<i>I</i> 4 ₁ / <i>a</i>	[66]
35	[InSeCl(bpy)] ₄	InCl ₃ +Se	EG+W	0	140/8	<i>P</i> $\bar{1}$	[66]
36	[Mn ₂ Sn ₂ Se ₆ (phen) ₄]·2H ₂ O	SnCl ₄ +MnCl ₂ +Se	MA+W	0	185/5	<i>P</i> 2 ₁ / <i>n</i>	[57]
37	[Fe ₂ Sn ₂ Se ₆ (phen) ₄]	SnCl ₄ +FeCl ₃ +Se	MA+W	0	185/5	<i>C</i> 2/ <i>c</i>	[57]
38	[MnSnSe ₃ phen]	SnCl ₄ +MnCl ₂ +Se	MA+W	1	175/6	<i>P</i> $\bar{1}$	[57]
39	[MnSn ₂ Se ₅ (phen) ₂]	SnCl ₄ +MnCl ₂ +Se	MA+W	1	185/5	<i>C</i> 2/ <i>c</i>	[57]
40	[Mn ₂ Sn ₄ (phen) ₂]·H ₂ O	Sn+MnCl ₂ +S	MA+W	1	170/5	<i>C</i> 2m	[67]
41	{[Fe(phen) ₂] ₂ Sn ₂ S ₆ }	Fe+Sn+S	MA+W	0	120/3	<i>P</i> $\bar{1}$	[68]
42	{[Fe(phen) ₂] ₂ Sn ₂ S ₆ }·(phen)·H ₂ O	Fe+Sn+S	MA+W	0	120/9	<i>P</i> 2 ₁ / <i>n</i>	[68]
43	{[Co(phen) ₂] ₂ Sn ₂ S ₆ }	CoCl ₂ +Sn+S	MA+W	0	120/5	<i>P</i> $\bar{1}$	[68]
44	{[Co(phen) ₂] ₂ Sn ₂ S ₆ }·(phen)·H ₂ O	Co+Sn+S	MA+W	0	120/5	<i>P</i> 2 ₁ / <i>n</i>	[68]
45	{[Ni(phen) ₂] ₂ Sn ₂ S ₆ }·4,4'-bipy·0.5H ₂ O	Sn+NiCl ₂ +S	MA+W	0	120/7	<i>C</i> 2/ <i>c</i>	[69]
46	{[Ni(phen) ₂] ₂ Sn ₂ S ₆ }·2,2'-bipy	Sn+NiCl ₂ +S	MA+W	0	120/7	<i>P</i> 2 ₁ / <i>n</i>	[69]
47	[Mn ₂ Sn ₂ Se ₆ (terpy) ₂]	Mn(terpy)+Sn+Se	en+W(CaCO ₃)	0	150/0.5	<i>P</i> $\bar{1}$	[70]
48	[MnSnSe ₃ (terpy)] _n	Mn(terpy)+Sn+Se	en+W(CaCO ₃)	0	150/0.5	<i>P</i> $\bar{1}$	[70]
49	[Mn ₂ (phen) ₄ (As ₂ S ₃)·phen·2H ₂ O]	As ₂ O ₃ + MnCl ₂ +S	dien+W	0	140/5	<i>P</i> 2 ₁ / <i>c</i>	[60]
50	{[Mn(phen) ₂] ₂ (AsSe ₄) ₂][As ₂ Se ₆]·H ₂ O}	As ₂ O ₃ + MnCl ₂ +Se	dien+MeOH	0	130/5	<i>P</i> $\bar{1}$	[62]
51	[Mn(phen) ₂ As ₂ Se ₃ (Se ₂)]	As+Mn+Se	en+W	1	150/5	<i>Pccn</i>	[71]
52	[Mn ₂ As ₂ S ₅ (phen)]	As+Mn+S	en+W	2	150/5	<i>P</i> 2 ₁ / <i>c</i>	[72]
53	[Mn ₃ As ₂ S ₈ (phen) ₃]·H ₂ O	As+Mn+S	en+W	1	150/5	<i>Pbcn</i>	[72]
54	[Mn ₂ As ₂ S ₅ (phen)]	As+MnCl ₂ +S	MA+W	1	150/5	<i>P</i> 2 ₁	[73]
55	[Mn ₃ As ₂ S ₈ (bpy) ₃]·H ₂ O	As+MnCO ₃ +S	W	1	180/7	<i>Pbcn</i>	[74]
56	[Mn ₂ As ₂ S ₅ (bpy)]	As+MnCl ₂ +S	dien+W	2	180/7	<i>P</i> 2 ₁ / <i>c</i>	[74]
57	(HMA) ₂ {[Mn(phen) ₂](AsS ₄)·phen}	As+MnCl ₂ +S	MA+W	0	150/6	<i>P</i> $\bar{1}$	[75]
58	(HMA) ₂ {[Mn(phen) ₂](AsS ₄) ₂ }	As+MnCl ₂ +S	MA+W	0	150/6	<i>P</i> 2 ₁ / <i>c</i>	[75]
59	{[Mn(phen) ₂](As ₂ S ₄) _n }	As+MnCO ₃ +S	MA+W	1	150/6	<i>P</i> 2 ₁ / <i>c</i>	[75]
60	{[Mn(phen) ₃](AsS ₃) ₂ }·H ₂ O	As+MnCl ₂ +S	MA+W	1	170/6	<i>P</i> 2 ₁ / <i>c</i>	[75]
61	[AsS(S ₃)]{[Mn(bpy) ₂] ₂ (AsS ₄) ₂ }	As+MnCO ₃ +S	W	0	150/5	<i>P</i> $\bar{1}$	[75]
62	{[Mn(bpy) ₂ SCN][Mn(bpy) ₂ AsS ₄]} ₂	As+MnCO ₃ +S+SCN	W	0	150/5	<i>P</i> $\bar{1}$	[76]

63	$\{[\text{Mn}(\text{bpy})_2\text{SCN}]\text{AsS}_3\}_2$	As+MnCO ₃ +S+SCN	W	0	150/6	$P\bar{1}$	[76]
64	$\{[\text{Mn}(\text{terpy})]_2(\text{As}_4\text{S}_8)\}_n$	As ₂ S ₃ +Mn(terpy)+S	tren+W(CaCO ₃)	0	150/0.5	$P\bar{1}$	[76]
65	$\{[\text{Mn}(\text{terpy})]_2(\text{As}_2\text{S}_4)\}_n$	As+Mn(terpy)+S	tren+W	1	150/0.5	$C2/c$	[77]
66	$\{[\text{Mn}(\text{terpy})]_2(\text{As}_2\text{Se}_5)\}_{2n}$	As+Mn(terpy)+Se	tren+W(CaCO ₃)	0	150/0.5	$P\bar{1}$	[77]
67	$\{[\text{Mn}(\text{terpy})]_2(\text{As}_4\text{Se}_8)\}_n$	As+Mn(terpy)+Se	tren+W(CaCO ₃)	0	150/0.5	$P\bar{1}$	[77]
68	$[\text{Mn}_3\text{As}_2\text{Se}_8(\text{terpy})_3]_n$	As+Mn(terpy)+Se	tren+W(CaCO ₃)	0	150/1	Cc	[78]
69	$[\text{Mn}_2\text{As}_2\text{Se}_4(\text{terpy})_2]\cdot 2(\text{H}_2\text{O})$	As+Mn(terpy)+Se	tren+W(CaCO ₃)	0	150/1	$P2_1/n$	[79]
70	$[\text{Mn}_2\text{Sb}_2\text{S}_3(\text{phen})]_n$	Sb +Mn+S	en+W	2	150/5	$P2_1/c$	[80]
71	$[\text{Mn}_2\text{Sb}_2\text{S}_3(\text{bpy})]_n$	Sb + MnCl ₂ +S	MA+W	2	120/7	$P\bar{1}$	[81]
72	$(\text{HMA})_2\{[\text{Mn}(\text{phen})]_2(\text{SbSe}_4)\}\cdot \text{phen}$	Sb+MnCl ₂ +Se	MA+W	0	120/5	$P2_1/n$	[82]

2. A survey of main-group metal chalcogenidometalates with phen/bpy complexes

2.1. The role of phen/bpy complexes in solvothermal syntheses

Solvothermal synthesis at relatively low temperature ($T \approx 100\text{--}200^\circ\text{C}$) in amines or amines/water has been proved to be a useful technique for the preparation of crystal-state chalcogenidometalates. The amines can act as template agents or structure directing agents in crystallization [11-14]. Ethylenediamine (en) is an excellent reaction medium with appropriate boiling point and low viscosity. It is not only an excellent solvent, but also can chelate metal ions forming [coordination saturated](#) $[\text{M}(\text{en})_3]^{n+}$ counterions to stabilize the large metal chalcogenide anions or forming [unsaturated](#) $[\text{M}(\text{en})_x]^{2+}$ ($x = 1$ or 2) complex moieties [to covalently bond with](#) various structures of chalcogenides. As a well known chelating ligands, phen/bpy forms stable $[\text{M}(\text{phen/bpy})_x]^{n+}$ complexes similar to those of en. The conjugated imine nitrogen atoms of phen/bpy have strong coordination ability with transition metal ions and can also be protonated in acidic media. However, there are some different aspects between phen/bpy and en. Table 3 lists the physical constants of en, phen and bpy. The basicity of phen/bpy is remarkable lower than that of aliphatic diamines due to the electron-withdrawing characteristic of the heteroaromatic rings. The phen/bpy [can accept an electron back donating](#) from d orbitals of transition metal ions. Due to the rigidity of phen/bpy, unlike the $[\text{M}(\text{en})_x]^{n+}$ ions, the $[\text{M}(\text{phen/bpy})_x]^{n+}$ complex ions have fixed space and conformation. They are either clockwise Δ or anticlockwise Λ configurations.

Because of the features of high melting and boiling points and weak basicity, phen and bpy in general cannot directly replace the amines in the syntheses of chalcogenidometalates and another amines need to be added (Table 1 and 2). The auxiliary organic [amines play](#) an important role in synthetic reaction. [They](#) create an alkaline system and offer a source of chalcogenide anions through the reaction with chalcogen elements (the usual reactant in solvothermal synthesis). Otherwise, carbonate salt should be added to increase the basicity to generate S^{2-} anion [Table 1 and 2]. The methylamine (MA) is a common solvent for solvothermal synthesis of chalcogenidometalates with phen/bpy complexes. However, reaction of higher percentage of MA system should be in Teflon lined stainless steel

autoclaves but not be in the [sealed glass tube](#), because MA is a volatile amine with very low boiling point [that is explosive at the reaction temperature](#). The DMF-water is also an excellent solvent system for solvothermal synthesis of such chalcogenidometalates. Although DMF is not an organic amine, it can in situ generate dimethylamine under the solvothermal condition [52,53]. As a general reaction medium, water is an indispensable solvent that plays the roles in adjusting the solubility, viscosity and boiling point of the solvent mixtures. Recently, Bensch and co-workers reported a new synthesis route of chalcogenidometalates containing transition metal complexes with aromatic ligands. In this synthetic approach, simple chalcogenidometalate [and metal complex](#) salts are directly used as the source so that the usage of elemental chalcogen as well as amines is avoided. The reaction time could be significantly reduced while maintaining good product yields [64]. The phen and bpy mainly act as the coordination ligands of transition metal ions in the reaction systems and only a few examples were reported that the synthetic reaction using chalcogen element happened in excess phen/bpy without adding additional amine [56,65,66].

In addition, due to the large size in radii, phen/bpy complex cations can match well with the large chalcogenide anions, which in some cases is favorable for the crystallization. For instance, although main-group metal chalcogenides with en complexes have been explored for a long period, attempts to obtain the single crystals of 2-D chalcogenidostannates with $[M(en)_3]^{2+}$ cations were unsuccessful. In contrast, five compounds with the rigid $[M(phen)_3]^{2+}$ were isolated. The templating function of the rigid $[M(phen)_3]^{2+}$ is obvious [59].

Table 3. Selected physical and chemical constants of en, phen and bpy.

	en	phen	bpy
molecular formula	C ₂ H ₈ N ₂	C ₁₂ H ₈ N ₂	C ₁₀ H ₈ N ₂
formula weight(g·mol ⁻¹)	60.10	180.21	156.19
melting point (°C)	8.5	116	70
boiling point (°C)	117.3	>300	272
protonation (log K ₁)	10.65	4.95	4.80
coordination (log K _{Cu})		9.25	
solubility	misc-w, al	misc-w, al	misc-w, al

misc = miscible, w = water, al = ethanol.

2.2. The structures of the chalcogenidometalates with phen/bpy complexes

As the metal-organic components, phen/bpy complexes in the structures of main-group chalcogenidometalates act as discrete counterions (saturated complexes $[M(phen/bpy)_3]^{2+}$) and structure-decorating moieties (unsaturated complexes $[M(phen/bpy)_2]$ or $[M(phen/bpy)]$). The transition-metal ions involved are [Mn\(II\)](#), [Fe\(II\)](#), [Co\(II\)](#), and [Ni\(II\)](#) etc. Consequently, the main-group

chalcogenidometalates can be classified as salts with charge balanced phen/bpy complex cations and compounds with structure-decorated phen/bpy complex moieties. Sometimes the phen/bpy molecules or their protonated cations also incorporate into the final products for space filling or charge balance [53,68]. Due to the large size (about 12 Å in diameter) and rigidity of the phen/bpy complex cations, almost no 3-D chalcogenide anion has been found for such kind of compounds and low dimensional 0-D to 2-D structures are preferred (Table 1) except one thioantimonate, in which the M-phen complex enters the channel of a 3D thioantimonate $[\text{Ni}(\text{phen})_3]_2\text{Sb}_{18}\text{S}_{29}$ [63]. The M-phen/bpy complex cations in 2-D compounds are usually sandwiched between the layered structures, for example in $[\text{Ni}(\text{phen})_3][\text{In}/\text{Sn}_4\text{S}_8]\cdot(\text{Cha})\cdot 4\text{H}_2\text{O}$ (**18**) (Fig. 1a) [59]. Only one example was reported in which $[\text{Ni}(\text{bpy})_3]^{2+}$ cations completely sit in the pores of the 2-D network (**3**), as the template with C-H...S weak hydrogen bonds (Fig. 1b,c) [51]. The unsaturated $[\text{M}(\text{phen}/\text{bpy})]$ or $[\text{M}(\text{phen}/\text{bpy})_2]$ complex moieties are invariably coordinated by the chalcogenidometalate anions via chalcogenide atoms to compensate the coordination geometry, which usually terminates the polymerization of chalcogenido anions. This is one of the reasons why these compounds take low dimensional structures in general. These π conjugated ligands are easily self-arranged to a stacking structure with strong $\pi\cdots\pi$ interactions, forming high dimensional supramolecular structures. For instance, there are lots of such $\pi\cdots\pi$ stacking (3.32 Å) between the phen planes along two directions giving the most regular arrangement of $[\text{InS}(\text{phen})\text{Cl}]_4$ cluster (**32**) (Fig. 2) [65, 66].

(a)

Fig.1. (a) Molecular packing of crystal **18**, showing the sandwiched cation-anion arrangement [59].
(b) and (c) The templating role of $[\text{Ni}(\text{bpy})_3]^{2+}$ cation in a 2-D compound **3** [51].

Fig.2. (a) Strong $\pi \cdots \pi$ interactions between the phen ligands, and (b) the regular arranged molecules forming higher dimensional supramolecular structure in compound **32** [65].

Because there is no symmetry plane in $[\text{M}(\text{phen/bpy})_3]^{2+}$, as a result, such complex ions adopt either of two optical forms (Δ or Λ) and have optical activity. However, a racemic mixture of the two forms usually exists in most of the compounds, namely both the Δ and Λ configurations coexist in a crystals. Only limited single enantiomer crystals were reported. For instance, two chiral selenidoindate crystals $\{[\text{M}(\text{phen})_3]\text{In}_2\text{Se}_5 \cdot \text{H}_2\text{O}\}_n$ ($\text{M} = \text{Ni}, \text{Fe}$) (**11**) and (**12**) were obtained using solvothermal method [54]. The chalcogenidoindates crystallize as mechanical racemic mixtures of single enantiomer crystals

in a chiral space group $P2_12_12_1$, in which either the R-helix of 1-D InSe anion is directed by clockwise (Δ) cations of $[\text{M}(\text{phen})_3]^{2+}$ (**11**) or the L-helix of 1-D anion is directed by anticlockwise (Λ) cation (**11'**) (Fig. 3). The $\pi\cdots\pi$, $\text{C}\cdots\text{Se}$ and $\text{C-H}\cdots\text{Se}$ oriented interactions of metal complex cations with selenidoindate anions play an important role in the chiral recognition in forming the crystals. A similar homochiral amine complex was reported [83].

Fig.3. The chiral Λ - $[\text{Ni}(\text{phen})_3]^{2+}$ and Δ - $[\text{Ni}(\text{phen})_3]^{2+}$ cations and the related R-helical and L-helical 1-D anions in **11** and **11'** [54].

The phen/bpy metal complexes possess both hydrophilic and hydrophobic structure-directing effects, namely its positive charge favors the formation of ionic structures, whereas its hydrophobic aromatic ligand tend to favor the hydrophobic assembly. Such an ‘amphiphilic’ structure-directing effect may play a role in the formation of layered structures. The layered complex cation structure is usually sandwiched between the anion layers, in which small organic molecules or water molecules are enwrapped. A one-dimensional water chain was observed in the structure of $[\text{Fe}(\text{phen})_3][\text{As}_3\text{S}_6]\cdot\text{dien}\cdot 7\text{H}_2\text{O}$ (**22**) (Fig. 4a) [60], which is stabilized by anion-water hydrogen-bonding interactions. Another example is $[\text{Ni}(\text{phen})_3]_2[\text{Ge}_4\text{S}_{10}]\cdot 3.5\text{H}_2\text{O}$ (**14**) (Fig. 4b) [55]. A 2-D $[\text{Ge}_4\text{S}_{10}]^{4-}/\text{H}_2\text{O}$ hydrogen-bonding net is stabled by the complex cation layers. In recent years there has been considerable interest in water chains or clusters in biochemical sense [84]. Also, the water aggregates gusted in chalcogenometalate compounds are of interest related to the ion conduction [11].

Fig.4. (a) The 1-D H₂O chains stabilized by $[As_3S_6]^{3-}$ via O–H···S and O–H···O H-bonds in compound **22** [60]. (b) The 2-D structure assembled by $[Ge_4S_{10}]^{4-}$ and water via O–H···S H-bonds in compound **14** [55].

2.3. The properties of the chalcogenidometalates with phen/bpy complexes

The phen and bpy have empty π^* orbitals that can accept electron from metal centers. Therefore, different from the complexes of aliphatic chelating amines, some of their transition metal complexes in low valence state show intense MLCT absorption. The phen/bpy complexes as counterions or structure-decorating moiety of the inorganic chalcogenometalates may provide fascinating additional functions for the host materials. For this reason, main-group metal chalcogenides with M-phen/bpy complexes have garnered considerable attention from inorganic chemists not only for their various structures, but also for their unique optical, magnetic and photoelectronic properties. It can be expected to develop new functional materials.

2.3.1. Charge-transfer properties. Compounds displaying charge-transfer (CT) absorption have been interesting until now for their applications in optical and photoelectronic materials [85-87]. The UV-vis-NIR spectra are useful technique to characterize the CT bands for various main-group metal chalcogenide materials with M-phen/bpy complexes. Besides the solution spectra, solid-state optical diffuse-reflection spectra are the useful method to estimate the band gap energy for the CT materials. The absorption (α/S) data of solid state samples can be calculated from the reflection spectra [88]. The strong metal-to-ligand CT (MLCT) bands for Ru(II), Fe(II) and Co(II) compounds extend the absorption range of the chalcogenides to low energy area, which can increase the photo energy absorption from near ultraviolet to visible range [25].

In compound $[Ni(phen)_3]_4[In_{20}S_{37}]$ (**7**), the anion is a 2-D porous InS polymer with T3 tetrahedral clusters. Figure 5 shows the solid-state absorption spectra of $[Ni(phen)_3]Cl_2$, $[HDMA]_2[In_{10}S_{18}]$ (1-D) and $[Ni(phen)_3]_4[In_{20}S_{37}]$ (2-D) (**7**) (DMA = dimethyl amine), which clearly demonstrates that a new

ACCT band exists at about 2.8 eV for (7) [53]. The results of the spectroscopic study are useful for exploring new ACCT functional materials. The observation of anion to cation CT absorption confers special properties on the species of chalcogenidometalate compounds, such as optical and photoelectric properties based on the ACCT induced excitation (see below).

Fig.5. Solid-state absorption spectra of $[\text{Ni}(\text{phen})_3]\text{Cl}_2$, $[\text{HDMA}]_2[\text{In}_{10}\text{S}_{18}]$ and $[\text{Ni}(\text{phen})_3]_4[\text{In}_{20}\text{S}_{37}]$ (7) demonstrating the ACCT band [53] (α is the absorption, and S is the scattering coefficient).

The band energy of ACCT transition between M-phen/bpy cation and chalcogenidometalate anion is sensitive to the polarity of solvents. Fast and reversible solvent-induced chromic effect was found for ACCT compound $\{[\text{Ni}(\text{phen})_3]_2\text{Ge}_4\text{S}_{10}\} \cdot 3.5\text{H}_2\text{O}$ (14). When the crystals were immersed in alcohol solvent and then in water alternately, the color immediately changes between pink and yellow (Fig. 6a) [55]. The speed of the solvent-induced color change relates to the molecular size and the structure of alcohols (Fig. 6b). The smaller the alcohol molecule is, the faster the color change will be. The fastest color change was found by using methanol solvent that took only about one second. The molecule (solvent) exchange speed is important for the application in molecular detection and separation. For example, it might be used as an alcohol detection material.

Fig.6. (a) solvent-induced chromic effect found for compound $\{[\text{Ni}(\text{phen})_3]_2\text{Ge}_4\text{S}_{10}\} \cdot 3.5\text{H}_2\text{O}$ (**14**). (b) The minimum percent of alcohol in a mixed solvent with water for the complete color change from red to yellow form within 5 seconds. (1) methanol, (2) ethanol, (3) *i*-propanol, (4) *n*-propanol and (5) *n*-butanol [55].

A series of cubic $[\text{InQ}(\text{phen/bpy})\text{Cl}]_4$ ($\text{Q} = \text{S}$ and Se) compounds **32–35** were reported. Spectroscopic study and theoretical calculation indicate that introducing phen/bpy to chalcogenido $[\text{InQCl}]_4$ clusters significantly decreases the energy gap of the frontier orbitals (from HOMO to LUMO) due to the cluster to ligand charge-transfer (CLCT) (Fig. 7). Increasing the π -conjugated system of the aromatic ligand or using the heavier chalcogenido element might reduce the energy gap and consequently could control the energy of photophysical absorption of the materials [65,66], which is useful in

application concerned with electron excitation, electron-transfer etc.

(a)

(b)

Fig.7. (a) A sketch illustrating the energy levels of the frontier orbitals and energy gap of compounds $[\text{InQ}(\text{phen/bpy})\text{Cl}]_4$ (**32–35**), comparing with those of the non coordinated cubic cores [66]. (b) The calculated HOMO and LUMO orbitals of compound **32** [65].

2.3.2. Photocurrent response properties. Main-group metal chalcogenides usually have semiconducting properties and $[\text{M}(\text{phen/bpy})_3]^{2+}$ cations ($\text{M} = \text{Ru}, \text{Co}$ and Fe) as photochemical and photoelectric active complex ions have been used for solar energy conversion studies [31–34]. The photocurrent response properties of some main-group metal chalcogenides with M-phen/bpy complexes were investigated using a photoelectrochemical cell with the microcrystal sample modified ITO working electrode. Photocurrent responses were observed upon irradiation with xenon light for a series of 2-D

In-Sn-Q compounds $[M(\text{Phen})_3](\text{In}/\text{Sn}_4\text{Q}_8) \cdot (\text{amine}) \cdot n\text{H}_2\text{O}$ (**18–21**) ($M = \text{Ni(II)}$, Fe(II) or Co(II) ; amine = cyclohexylamine (Cha) or 1,6-diaminohexane (Dah); $Q = \text{S}$ or Se) (Fig. 8) [59]. The photocurrent intensity of the selenide modified electrodes is higher than that of the sulfides. For the selenides, the photocurrent conversion of those with redox active $[\text{Fe}(\text{Phen})_3]^{2+}$ and $[\text{Co}(\text{Phen})_3]^{2+}$ cations is more effective than those with non redox active $[\text{Ni}(\text{Phen})_3]^{2+}$ cation.

Fig.8. Photocurrent responses of the 2-D $[M(\text{Phen})_3](\text{In}/\text{Sn}_4\text{Q}_8)$ compounds ($M = \text{Fe}$, Co and Ni ; $Q = \text{S}$ and Se), (a) $[\text{Fe}(\text{phen})_3](\text{In}/\text{Sn}_4\text{S}_8)$ and $[\text{Fe}(\text{phen})_3](\text{In}/\text{Sn}_4\text{Se}_8)$, (b) $[M(\text{Phen})_3](\text{In}/\text{Sn}_4\text{Se}_8)$ ($M = \text{Co}$, Fe , Ni) [59].

2.3.3. Magnetic and SHG properties. Effective exchange interactions between $\text{Mn} \cdots \text{Mn}$ ions have been investigated on polynuclear manganese compounds by the use of the Heisenberg spin Hamiltonian. Guo group has prepared a series of thioarsenates fused with Mn-bpy complexes and studied their second harmonic generation (SHG) and magnetic behaviors [73,74,78,79]. The $\text{Mn} \cdots \text{Mn}$ distances and linkage modes of the thioarsenate anions with paramagnetic Mn(II) complexes determine the magnetic exchange pathways, which finally influence the types and the strengths of the magnetic exchange coupling. In general, antiferromagnetic coupling are reported for these compounds. The $(-\text{SAsSAsS}-)$ or $(-\text{SAsS}-)$ bridge links the Mn(II) ions to generate a weaker superexchange pathway with longer $\text{Mn} \cdots \text{Mn}$ distance, which finally lead to weaker antiferromagnetic coupling. In contrast, the tetrahedral $(\text{AsS}_4)^{3-}$ anions and the pyramidal $(\text{AsS}_3)^{3-}$ anion chelating with Mn(II) ions lead to shorter $\text{Mn} \cdots \text{Mn}$ distances about 3.3–3.8 Å. A stronger superexchange pathway, *via* $(\mu_3\text{-S})$ bridge, gives relatively stronger antiferromagnetic coupling (Table 4). Of particular interest is $\{[\text{Mn}(\text{phen})_3](\text{AsS}_3)_2\} \cdot \text{H}_2\text{O}$ (**60**) [75], which is the manganese thioarsenate with the shortest $\text{Mn} \cdots \text{Mn}$ distance showing the strongest antiferromagnetic coupling and spin-canting characteristic. Given that some compounds crystallize in non-centrally symmetric space groups, second-order nonlinear optical effects were expected. Studies of powder samples indicate that compounds $[\text{Mn}_2\text{As}_2\text{S}_5(\text{phen})]$ (**54**) and $(\text{HMA})\{[\text{Mn}(\text{phen})_2](\text{AsS}_4)\} \cdot \text{phen}$ (**57**) are weakly SHG active with a response being about 1/15 times of that of AGS (AgGaS_2) and being about

1/21 times of that of KTP (KTiOPO₄), respectively [73,75]. On the basis of structural data, the NLO behavior should originate from the cooperation of the polarizations of the polar units, including the unsaturated phen complexes, (As^{III}S₃) pyramids and so on.

Table 4 Magnetic properties of transition metal complexes decorated chalcogenidometalates

Compounds	Bridging units	Exchange pathways	Distances (Mn···Mn)	θ [k]	J [cm ⁻¹]
54	As ^{III} S ₃	-(μ_3 -S) ₂ -	3.686-4.520	-140.1	$J_1(-9.24)$ $J_2(-24.4)$ $zJ'_3(2.8)$
55	As ^V S ₄	-(μ_3 -S) ₂ -	3.812-4.784	-97.4	
56	As ^{III} S ₃	-(μ_3 -S) ₂ -	3.615-3.874	-115.8	
58	As ^V S ₄	-(μ_3 -S) ₂ -	3.696	-44.9	$J(-3.27)$ $zJ'(-0.95)$
59	As ^{III} ₂ S ₅	-SAsSAsS-	10.543	-4.3	$J(-0.15)$ $zJ'(-0.14)$
60	As ^{III} S ₃	-(μ_3 -S)-	3.345-4.719	-311.4	
61	As ^V S ₄	-SAsS-	6.429	-6.0	$J(-0.56)$ $zJ'(-0.01)$
62	As ^V S ₄	-(μ_3 -S) ₂ -	3.769	-17.75	$J(-3.17)$ $zJ'(-0.07)$
63	As ₂ ^{III} S ₆	-(SAsS ₂) ₂ -	10.842	-0.35	

3. Structures of main-group chalcogenidometalates with phen/bpy complexes

The structural characteristics of chalcogenidometalate anions have been summarized in previous reviews [11–20]. The general structures of chalcogenidoindates are usually simple 1-D [InQ₂]_n chains in the presence of chelating amine complex cations, [M(amine)₃]²⁺ [13], while when the cations are [M(phen/bpy)₃]²⁺ complexes, supertetrahedral clusters are preferred [51–53]. The general structures of chalcogenidostannates are mainly 0-D compounds with separated [Sn₂Q₆]⁴⁻ anion and [M(amine)₃]²⁺ cations [13], while when the cations are [M(phen/bpy)₃]²⁺ complexes, 2-D [Sn₃Q₇]_n anions are found [57,59]. These examples mean that the templating effect of [M(phen/bpy)₃]²⁺ is different to some extent from that of chelating amine complexes [M(amine)₃]²⁺, which features in structural dimension of chalcogenidometalates. In this survey, the structure discussions are focused on chalcogenidometalates of 13, 14, 15 groups in two aspects: the [main-group chalcogenidometalates with saturated and unsaturated M-phen/bpy complexes](#), respectively. [From this review, people can know the structural characteristics and bonding informations of these compounds.](#)

3.1 . Structures of Group 13 chalcogenidometalates (Ga, In)

The most common chalcogenide clusters of gallium and indium are a series of supertetrahedral clusters denoted as T_n (n=2–5, the number of metal layers). Substantial success on these types of clusters has been achieved. They can serve as building blocks for construction of crystalline porous frameworks with properties of ion exchange and ion conduction etc [11]. To further promote the potential applications of chalcogenidometalates in photoelectronic materials, it is desirable to develop hybrid materials with optically active guest species, such as [M(phen/bpy)₃]²⁺ cations. Our group

reported a series of chalcogenidoindates co-crystallized with $[M(\text{phen/bpy})_3]^{2+}$ cations. The structures of these chalcogenidoindates anions vary from 0-D to 2-D that is quite different from those with the chelating amine complexes, such as $[M(\text{en})_3]^{2+}$ [13].

Discrete T_n ($n > 3$) clusters are unstable because of their higher negative charges. Through sharing the corner chalcogen atoms, these T_n clusters usually form a polymeric framework, especially the 3-D porous structures. Compounds **1**, **4** and **5** (see Table 1) contain uncommon discrete T3 clusters with $[M(\text{phen/bpy})_3]^{2+}$ cations [51,52]. The T3 $[\text{H}_x\text{In}_{10}\text{S}_{20}]^{(10-x)-}$ clusters embed in the packing of $[M(\text{phen/bpy})_3]^{2+}$ cations (Fig. 9a). The stability of these discrete T3 clusters is ascribed to the wrapping effect of the aromatic cations and the anion-cation balances in charge and size, along with the inter ion's interactions. The corner chalcogen atoms of a discrete T3 cluster are sometimes protonated to balance the charge. Although the protons are unable to be observed directly from the Fourier map in crystal structure analysis, the longer terminal In-S distances imply that the terminal sulfur atoms are likely to be protonated. In general, the distance of protonated In-S_{terminal} bond is longer than that of the In-S_{bridged}. For example, the four terminal In-S distances of **4** are 2.462(3), 2.476(3), 2.495(3), and 2.491(3) Å, in which two are protonated, $[\text{H}_2\text{In}_{10}\text{S}_{20}]^{8-}$.

By sharing two or three of the terminal sulfur atoms of T3 clusters, 1-D and 2-D polymeric structures are formed (Fig. 9b-d) [53], but no 3-D structure has been obtained due to the steric hindrance of the $[M(\text{phen/bpy})_3]^{2+}$ cations. According to the arrangement of T3 clusters there are two types of 1-D structures $[\text{In}_{10}\text{S}_{19}]^{8-}$, uniform or zigzag arrangements in chains of **9** and **10**, respectively. The T3 clusters in 2-D compounds **7** and **8** are covalently connected by cosharing three corner atoms forming a layered structures $[\text{In}_{20}\text{S}_{37}]^{14-}$. Quadrate hole in size 19.7×8.6 Å (Fig. 9c) and trigonal holes with a side length of about 23.8 Å (Fig. 9d) are formed viewed along the *c* and $\{1/2\ 0\ 1\}$ directions. The $[\text{Ni}(\text{phen})_3]^{2+}$ cations serve as complex layers, sandwiched between the inorganic layers. A similar 2-D compound is **3**, in which the counterion is $[\text{Ni}(\text{bpy})_3]^{2+}$ cation [51]. However, the arrangement of the T3 clusters takes a different up and down fashion.

Fig. 9. (a) The molecular packing of **1**, showing polyhedral view of the anions [51]. (b) One-dimensional chains of the polymeric anion in **9** and **10** [53]. (c) and (d) Two-dimensional structures of **7** and **3** viewed along different direction [53, 51].

In addition to the Tn clusters as discrete anions or subunits of porous chalcogenidoindates, a series of unique In_4Q_4 ($Q = S, Se$) clusters coordinated with phen/bpy ligand were prepared, $[InQ(phen/bpy)Cl]_4$, **32-35** [65,66]. The cluster structure of $[InSe(phen)Cl]_4$ (**33**) is shown in Fig. 10a and Fig. 10b with space-filling model. The In_4Q_4 cluster is a distorted cube and the corners of the cluster are alternatively occupied by In and Se/S atoms. Each of the indium(III) atoms takes an octahedral coordination mode, coordinated by three $\mu-3$ bridged Se/S atoms, one chelating phen/bpy and one chloride ion. The symmetry of the cluster belongs approximately to S_4 group Fig. 10c. The crystal structure of **33** belongs to a chiral space group $P4_1$, and the clusters interact each other with strong $\pi \cdots \pi$ stackings of the phen ligands. By the strong $\pi \cdots \pi$ stacking, the clusters assemble to a helical chain around a 4_1 helical axis that parallels with the c axis (Fig.10d). The crystal structure of compound **33** is chiral, in which all of the helical chains take a clockwise mode and parallel each other with interchain's $\pi \cdots \pi$ stacking.

Fig.10. Structure of compound **33** (a) and the space-filling model (b). Helical chain structure of **33** assembled by strong $\pi\cdots\pi$ stacking around a 4_1 axis viewed along the c axis (c), and the a axis (d) [65].

3.2. Structures of Group 14 chalcogenidometalates (Ge, Sn)

The tetrahedral ortho-anions GeQ_4^{4-} ($\text{Q} = \text{S}, \text{Se}$) are easily condensed by cosharing the Q atoms to afford tetrameric $[\text{Ge}_4\text{Q}_{10}]^{4-}$ subunit, which is stable and can be dissolved in water. A series of polymeric thio/selenidogermanates have been prepared by several groups by introducing transition metal ions as the linkages of the $[\text{Ge}_4\text{Q}_{10}]^{4-}$ subunits. The only example of the chalcogenidogermanates with M-phen/bpy complexes is the $[\text{M}(\text{phen})_3]_2[\text{Ge}_4\text{S}_{10}] \cdot x\text{Sol}$ ($\text{Sol} = 4\text{MeOH} \cdot 12\text{H}_2\text{O}$ (**13**) and $24\text{H}_2\text{O}$ (**14**)) [55]. The fundamental structure of compound **14** consists of a discrete T2 cluster of $[\text{Ge}_4\text{S}_{10}]^{4-}$ and two $[\text{Ni}(\text{phen})_3]^{2+}$ cations. The molecular packing is shown in Fig.11a and 11b. The most remarkable structural feature of **14** is that the arrangement of anions and cations forms large cavities (Fig. 11b). There are a lot of cocrystallized water molecules in the cavities of **14** (24 water molecules per anion), more than those in **13**. The water molecules are assembled by hydrogen bonds ($\text{O}-\text{H}\cdots\text{S}$ and $\text{O}\cdots\text{H}-\text{O}-\text{H}\cdots\text{O}$) to be a square water tunnel with side length of about $1/2 b$. The unusual cavity structure constructed by the $[\text{Ge}_4\text{Q}_{10}]^{4-}$ cluster and $[\text{Ni}(\text{phen})_3]^{2+}$ cations is presumably the key to understanding the matter of solvent exchange induced chromic property (see 2.3.) [55].

Fig.11. The molecular packing of **13** (a) and **14** (b), showing the water occupied cavities [55].

Chalcogenidostannates in lamellar $[\text{Sn}_3\text{Q}_7]_n$ anion have been reported with various cations. Compound $[\text{Fe}(\text{phen})_3]_2[\text{Sn}_6\text{Se}_{14}] \cdot 2.5\text{H}_2\text{O}$ (**16**) represents the first example of chalcogenidostannate with π -conjugated ligand complex cations [57]. The 2-D binary anion is constructed by fused 24-atom hexagonal rings that is formed by six Sn_3Se_4 pseudosemicube clusters with double (μ_2 -Se) bridges (Fig. 12a). All the Sn atoms are five-coordinated by Se atoms which are two- or three-coordinated. If the Sn(IV) is partially replaced by In(III), unique 2-D structure features of the $(\text{M}^{\text{III}}\text{M}^{\text{IV}})\text{Q}_4$ type of In-Sn-Q ternary anions are found with formula $[\text{M}(\text{Phen})_3][(\text{In}/\text{Sn})_4\text{Q}_8] \cdot (\text{amine})$ ($\text{M} = \text{Ni}(\text{II}), \text{Fe}(\text{II})$ or $\text{Co}(\text{II})$) (**18-21**) [59]. The anion is also a two-dimensional porous framework of $[(\text{In}/\text{Sn})_4\text{Q}_8]_n$, constructed by elliptically shaped 16-tetrahedron (T)-membered rings (also called 32-atoms ring) (Fig. 12b). The large 16 T-membered ring has nano scale windows in size of ca. $17.5 \times 12.5 \text{ \AA}^2$. All the In or Sn atoms are in MQ_4 tetrahedron geometry and are connected by sharing the corners or edges. It should be noticed that the network joint is different from that of the 2-D binary chalcogenidostannates. The joints of all the four In/Sn compounds are not the $[(\text{In}/\text{Sn})_3\text{S}_4]$ pseudosemicubes, which is familiar in binary chalcogenidostannates as $[\text{Sn}_3\text{S}_4]$, but the heterometallic $[(\text{In}/\text{Sn})_3\text{S}_3]$ ring units, because the Sn atom can take five-fold coordination, while the In atom prefer the tetrahedral four fold coordination geometry. Although the amine complex system has been explored for a long period, attempts to obtain the similar products as **18-21** with metal amine complex cations such as $[\text{M}(\text{en})_3]^{2+}$ were unsuccessful [59]. The templating function of the rigid $[\text{M}(\text{Phen})_3]^{2+}$ is therefore obvious.

Fig.12. The frameworks and joints in 2-D binary thiostannate of **16** (a), and in 2-D ternary thiostannate of **18** (b), showing the different porous structures [59].

A ternary mercury chalcogenidostannate **17** incorporating $[\text{Fe}(\text{phen})_3]^{2+}$ as counter cation was synthesized, which features a 1-D ribbon structure of $[\text{Hg}_2\text{Sn}_2\text{Se}_7]_n^{2n-}$ based on the $\{\text{Hg}_2\text{Sn}_2\text{Se}_9\}$ secondary building unit (Fig. 13) [58]. All the Se^{2-} ions act as bridging linkers. Each planar triangle HgSe_3 shares the Se^{2-} corners with three tetrahedral SnSe_4 and the alternating arrangement of two HgSe_3 and two SnSe_4 results in a tetra-metal nuclear $\{\text{Hg}_2\text{Sn}_2\text{Se}_9\}$ subunit.

Fig.13. A 1-D ribbon structure of $[\text{Hg}_2\text{Sn}_2\text{Se}_7]_n^{2n-}$ in **17**, incorporating $[\text{Fe}(\text{phen})_3]^{2+}$ as counter cation [58].

The Sn_xS_y anions can also fuse with unsaturated $[\text{M}(\text{phen})]^{2+}$ or $[\text{M}(\text{phen})_2]^{2+}$ complex moieties, which brings a series of novel covalently linked organic-inorganic hybrid chalcogenidostannates. Theoretical calculations indicate that transition metal complexes with large π -conjugated ligands, such as $[\text{Mn}(\text{phen})]^{2+}$, can serve as an excellent electron reservoir to stabilize the Sn_xS_y anion. The stable $[\text{Sn}_2\text{Q}_6]^{4-}$ anion can act as a tetradentate ligand to coordinate to unsaturated $[\text{M}(\text{phen/bpy})_2]^{2+}$ or $[\text{M}(\text{phen/bpy})]^{2+}$ cations ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}$), forming metal complex fused chalcogenidostannates **36–38**

(Fig. 14a,b) [57] and **41–44** [68]. The $[\text{Sn}_2\text{Se}_6]^{4-}$ dimer can be extended to 1-D structure by cosharing the Se^{2-} corners with neighboring units **39** (Fig. 14c) [57]. Similar compounds with terpyridine ligand were also reported **47**, **48** [70]. An unusual 1-D Sn(IV) compound was reported as an ortho-anion SnS_4^{4-} coordinated Mn-phen compound **40** (Fig. 14d) [67].

Fig.14. A series of covalently linked organic-inorganic hybrid chalcogenidostannates coordinated by $[\text{M}(\text{phen})]^{2+}$ or $[\text{M}(\text{phen})_2]^{2+}$ complex moieties, (a) **36**, (b) **38**, (c) **39** and (d) **40** [57, 67].

3.3. Crystal structures of Group 15 chalcogenidometalates (*As*, *Sb*)

The basic structure of thio/selenidoarsenates(V) is a tetrahedral ortho-anions $[\text{MQ}_4]^{3-}$ ($\text{Q} = \text{S}, \text{Se}$). The

$[\text{As}^{\text{V}}\text{Q}_4]^{3-}$ anion has been structurally characterized as a chelating ligand coordinating to $[\text{M}(\text{phen/bpy})]^{2+}$ or $[\text{M}(\text{phen/bpy})_2]^{2+}$ moieties **53**, **55**, **57-59** and **62**. The structures of these compounds are all unsaturated Mn-phen/bpy complexes coordinated by chalcogenidoarsenates(V) [72,74,75,76]. The **58** is a dimer of $[\text{Mn}(\text{phen})\text{AsS}_4]$ unit (Fig. 15a). The dimer can further coordinate to additional $[\text{Mn}(\text{phen/bpy})]$ moieties to form 1-D structure as found in **53** and **55** (Fig. 15b).

Fig.15. The dimer of $[\text{Mn}(\text{phen})\text{AsS}_4]$ unit in **58** (a) [75] and 1-D structure in **53** (b) [72].

The basic structure of trivalent thio/selenidoarsenates(III) is the trigonal pyramid $\text{As}^{\text{III}}\text{S}_3$ unit. Through coordinating with $[\text{Mn}(\text{phen})]$ fragments, a polymeric 1-D structure **60** was isolated (Fig. 16a) [75]. The $(\text{As}^{\text{III}}\text{S}_3)^{3-}$ anion is stabilized by coordinating to Mn(II) complex moieties. The $\text{As}^{\text{III}}\text{S}_3$ units easily condensed to form various polymeric anionic structures. Corner-sharing $\text{As}^{\text{III}}\text{Q}_3$ trigonal pyramids leads to a common dimeric saddle anion $[\text{As}_2\text{Q}_5]^{4-}$ ($\text{Q} = \text{S}, \text{Se}$), in which two AsS_3 trigonal pyramids are in *cis*-or *trans*-conformations, for example in $[\text{Mn}_2(\text{phen})_4(\text{As}_2\text{S}_5)]$ (**49**) [60]. As a polydentate ligand, $[\text{As}^{\text{III}}_2\text{Q}_5]^{4-}$ anions coordinate to Mn(II) ions with coligands phen/bpy form unique 2-D structures of $[\text{Mn}_2\text{As}_2\text{S}_5(\text{phen/bpy})]_n$ (**52**), (**56**) (Fig. 16b) [72, 74]. The $[\text{As}^{\text{III}}_2\text{Q}_5]^{4-}$ anions can be connected by sharing corner S atoms to be a 1-D chain, such as in $\{[\text{Mn}(\text{phen})_2](\text{As}_2\text{S}_4)\}_n$ (**59**) and $\{[\text{Mn}(\text{terpy})_2](\text{As}_2\text{Se}_4)\}_{2n}$ (**66**) (Fig. 17a.b). By further inserting $(-\text{Se}-)$ or $(-\text{Se}_x-)$ to $[\text{As}^{\text{III}}_2\text{Se}_5]^{4-}$, 1-D chain structures with $(-\text{Se}-\text{Se}-)$ bonds are constructed, such as in $[\text{Mn}(\text{phen})_2\text{As}_2\text{Se}_3(\text{Se}_2)]$ (**51**) (Fig. 17c), **23** and **27**. Connection of pyramidal AsSe_3 units by two Se-Se bonds can afford dimeric cycle anions $[\text{As}_2\text{Se}_6]^{2-}$, which have been found as discrete, **22**, **25**, **26** [60,62], and coordinated, **63** [76], compounds. Similar to bpy some terpy Mn-thio/selenidoarsenates were prepared **64-67**, **68** and **69** [77,78,79]. It is interesting that the reported manganese-phen/bpy complexes are unsaturated and directly coordinated by thio/selenidoarsenate anions, whereas the other transition metal complexes are in saturated state, $\text{M}(\text{phen/bpy})_3$, acting as the cations of thio/selenidoarsenates **22-26** (Table 1 and 2) [60-62].

(a)

(b)

Fig.16.(a) The 1-D structure of **60** showing the Mn-phen stabilized noncondensed $(As^{III}S_3)^{3-}$ anions [75]. (b) Unique 2-D structures in **52** and **56** coordinated with Mn-phen moiety [72, 74].

(a)

(b)

(c)

Fig.17. A series of covalently linked organic-inorganic hybrid chalcogenidoarsenates(III) coordinated by $[M(\text{phen})]^{2+}$ or $[M(\text{phen})_2]^{2+}$ complex moieties, (a) **59** [75], (b) **66** [77], and (c) **51** [71].

The research on thioantimonates has been very fruitful in the past decades. Despite that many thioantimonates (III) have been reported, however, only a few thioantimonate compounds with phen/bpy complexes were reported. Similar to the arsenates, the reported manganese-phen/bpy complexes of thioantimonates are unsaturated and coordinated by the anions [80-82], whereas the other transition metal complexes are in saturated state acting as the cations of thioantimonates [63, 64] (Table 1 and 2). Compound $[\text{Mn}_2\text{Sb}_2\text{S}_5(\text{phen})]_n$ (**70**) is a 2-D phen coordinated polymer and isostructural with **52** (an As compound). Compound **72** is a mononuclear compound with formula of $(\text{HMA})[\text{Mn}(\text{phen})_2\text{SbSe}_4]$. By directly using $\text{Na}_3[\text{SbS}_4]$ salt and metal complexes as the source materials, three layered thioantimonate(III) compounds formulated as $[\text{M}(\text{L})_3][\text{Sb}_6\text{S}_{10}]$ ($\text{M} = \text{Ni}, \text{Fe}; \text{L} = \text{bpy}, \text{mbpy}$) (**29-31**) were obtained featuring two different thioantimonate(III) network topologies [64]. Huang group recently reported a $[\text{Ni}(\text{phen})_3]_2\text{Sb}_{18}\text{S}_{29}$ (**28**), which represents a porous thioantimonate with the largest channels filled with M-phen complexes (Fig. 18) [63]. Significantly, it is also the first example of 3-D chalcogenidometalates integrated with M-phen/bpy complexes that is attributed to the variable structures of thioantimonate.

Fig.18. A unusual 3-D porous thioantimonate with the largest channels **28** [63].

4. Summary

In this review we focus on a survey of recent developments of main group metal chalcogenidometalates integrated with discrete M-phen/bpy complex cations or covalently bonded M-phen/bpy moieties. A comprehensive outline in synthesis, structural characteristics and properties with potential applications of these chalcogenidometalate compounds is presented. Due to the features of high melting and boiling points and weak basicity, phen and bpy usually cannot directly replace the amines in the syntheses of chalcogenidometalates and other amines need to be added. Due to the large size and rigidity of the M-phen/bpy complex cations, 0-D to 2-D low dimensional structures are preferred for such kind of compounds except one 3-D thioantimonate. In most cases the M-phen/bpy complex cations act as charge and space compensating ions, only in a few cases the M-phen complex enters into the 2-D and 3-D network acting as the cavity templates. These π -conjugated M-phen/bpy complex cations are easily self-arranged with $\pi \cdots \pi$ interactions to form supramolecular structures. Charge-transfer from metal to ligand (MLCT) within M-phen/bpy cation, from anion to cation (ACCT) in anion-cation separated salts, and from cluster to ligand (CLCT) in chalcogenidometalates with directly coordinated phen/bpy ligands is the characteristics for such compounds, which give the material unique photo and electro properties, such as chromic, non-linear optical and photoelectric effects. With the successful achievements reported here in M-phen/bpy chalcogenidometalates, we anticipate further breakthrough in the new syntheses, crystal structures and in their real applications as photo- and photoelectro-active materials.

Acknowledgements

We gratefully acknowledge financial support by the NSF of China (21371125 and 21571136), the Priority Academic Program Development of Jiangsu Higher Education Institutions and by State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials.

References

- [1] Q. C. Zhang, Y. Liu, X. H. Bu, T. Wu, P. Y. Feng, *Angew. Chem. Int. Ed.* 47 (2008) 113.
- [2] M. L. Feng, D. N. Kong, Z. L. Xie, X. Y. Huang, *Angew. Chem. Int. Ed.* 47 (2008) 8623.
- [3] M. G. Kanatzidis, N. Ding, *Nat. Chem.* 2 (2010) 187.
- [4] Y. Shim, B. D. Yuhas, S. M. Dyar, A. L. Smeigh, A. P. Douvalis, M. R. Wasielewski, M. G. Kanatzidis, *J. Am. Chem. Soc.* 135(2013), 2330.
- [5] T. Wu, Q. Zhang, Y. Hou, L. Wang, C. Mao, S.-T. Zheng, X. Bu, P. Feng *J. Am. Chem. Soc.* 135 (2013) 10250.
- [6] J. Lin, Q. Zhang, L. Wang, X. Liu, W. Yan, T. Wu, X. Bu, P. Feng, *J. Am. Chem. Soc.* 136 (2014) 4769;
- [7] W.S. Sheldrick, M. Wachhold, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 206.
- [8] W. S. Sheldrick, M. Wachhold, *Coord. Chem. Rev.* 176 (1998) 211.
- [9] H. Li, J. Kim, M. O’Keeffe, O. M. Yaghi, *Angew. Chem., Int. Ed.* 42 (2003) 1819.
- [10] J. Lin, Q. Zhang, L. Wang, X. Liu, W. Yan, T. Wu, X. Bu, P. Feng, *J. Am. Chem. Soc.* 136 (2014) 4769;
- [11] P.Y. Feng, X.H. Bu, N.F. Zheng, *Acc. Chem. Res.* 38 (2005) 293.
- [12] J. Li, Z. Chen, R.-J. Wang, D. M. Proserpio, *Coord. Chem. Rev.* 190–192 (1999) 707.
- [13] J. Zhou, J. Dai, G.-Q. Bian, C.-Y. Li, *Coord. Chem. Rev.* 253 (2009) 1221.
- [14] S. Dehnen, M. Melullis, *Coord. Chem. Rev.* 251 (2007) 1259.
- [15] J. Zhou, *Coord. Chem. Rev.* 315 (2016) 112.
- [16] Q. Zhang, I. Chung, J. I. Jang, J. B. Ketterson, M. G. Kanatzidis, *J. Am. Chem. Soc.* 131 (2009) 9896.
- [17] K. Biswas, Q. Zhang, I. Chung, J.-H. Song, J. Androulakis, A. J. Freeman, M. G. Kanatzidis, *J. Am. Chem. Soc.* 132 (2010) 14760.
- [18] J.-R. Li, Z.-L. Xie, X.-W. He, L.-H. Li, X.-Y. Huang, *Angew. Chem. Int. Ed.* 50 (2011) 11395.
- [19] Y. Lin, W. Massa, S. Dehnen, *J. Am. Chem. Soc.* 134 (2012) 4497.
- [20] S. Santner, J. Heine, S. Dehnen, *Angew. Chem. Int. Ed.* 55 (2016) 876.
- [21] M. S. S. Santner, J. Heine, S. Dehnen, *Angew. Chem. Int. Ed.* 55 (2016) 876.

- [22] W. W. Xiong, E. U. Athresh, Y. T. Ng, J. F. Ding, T. Wu, Q. C. Zhang, *J. Am. Chem. Soc.* 135 (2013) 1256.
- [23] W.-W. Xiong, Q. Zhang, *Angew. Chem. Int. Ed.* 54 (2015) 11616.
- [24] W.-W. Xiong, J. Miao, K. Ye, Y. Wang, B. Liu, Q. Zhang, *Angew. Chem. Int. Ed.* 54 (2015) 546.
- [25] A. Juris, V. Balzani, F. Barigelli, S. Campagna, P. Belser, A. V. Zelewsky, *Coord. Chem. Rev.* 84 (1988) 85.
- [26] R. Haldar, R. Matsuda, S. Kitagawa, S. J. George, T. K. Maji, *Angew. Chem. Int. Ed.* 54 (2014) 11772.
- [27] G.-L. Zhang, L.-P. Zhou, D.-Q. Yuan, Q.-F. Sun, *Angew. Chem. Int. Ed.* 54 (2015) 9844.
- [28] K. Manna, T. Zhang, F. X. Greene, W. Lin, *J. Am. Chem. Soc.* 137 (2015) 2665.
- [29] D. R. Boer, L. Wu, P. Lincoln, M. Coll, *Angew. Chem. Int. Ed.* 53 (2014) 1949.
- [30] S. Stimpson, D. R. Jenkinson, A. Sadler, M. Latham, D. A. Wragg, A. J. H. M. Meijer, J. A. Thomas, *Angew. Chem. Int. Ed.* 54 (2015) 3000.
- [31] T. A. White, S. L. H. Higgins, S. M. Arachchige, K. J. Brewer, *Angew. Chem. Int. Ed.* 50 (2011) 12209.
- [32] C.-C. Chou, F.-C. Hu, H.-H. Yeh, H.-P. Wu, Y. Chi, J. N. Clifford, E. Palomares, S.-H. Liu, P.-T. Chou, G.-H. Lee, *Angew. Chem. Int. Ed.* 53 (2014) 178.
- [33] C. Browning, J. M. Hudson, E. W. Reinheimer, F.-L. Kuo, R. N. McDougald, H. Rabâ, H. Pan, J. Bacsá, X. Wang, K. R. Dunbar, N. D. Shepherd, M. A. Omary, *J. Am. Chem. Soc.* 136 (2014) 16185.
- [34] Y. Kageshima, H. Kumagai, T. Minegishi, J. Kubota, K. Domen, *Angew. Chem. Int. Ed.* 54 (2015) 7877.
- [35] T. A. White, S. L. H. Higgins, S. M. Arachchige, K. J. Brewer, *Angew. Chem. Int. Ed.* 50 (2011) 12209.
- [36] K. Gao, N. Yoshikai, *Angew. Chem. Int. Ed.* 50 (2011) 6888.
- [37] T. R. Canterbury, S. M. Arachchige, R. B. Moore, K. J. Brewer, *Angew. Chem. Int. Ed.* 54 (2015) 12819.
- [38] L. D. Wickramasinghe, R. Zhou, R. Zong, P. Vo, K. J. Gagnon, R. P. Thummel, *J. Am. Chem. Soc.* 137 (2015) 13260.
- [39] M. D. Sampson, C. P. Kubiak, *J. Am. Chem. Soc.* 138 (2016) 1386.
- [40] A. Hagfeldt, M. Grätzel, *Acc. Chem. Res.* 33 (2000) 269.
- [41] M. Grätzel, *Nature* 414 (2001) 338.
- [42] M. K. Nazeeruddin, S. M. Zakeeruddin, J.-J. Lagref, P. Liska, P. Comte, C. Barolo, G. Viscardi, K. Schenk, M. Grätzel, *Coord. Chem. Rev.* 248 (2004) 1317.
- [43] A. S. Polo, M. K. Itokazuand, N. Y. M. Iha, *Coord. Chem. Rev.* 248 (2004) 1343.
- [44] C.-Y. Chen, H.-C. Lu, C.-G. Wu, J.-G. Chen, K.-C. Ho, *Adv. Funct. Mater.* 17 (2007) 29.

- [45] V. M. Blas-Ferrando, J. Ortiz, V. González-Pedro, R. S. Sánchez, I. Mora-Seró, F. Fernández-Lázaro, Á. Sastre-Santos, *Adv. Funct. Mater.* 25 (2015) 3220.
- [46] C.-Y. Yue, X.-W. Lei, Y.-X. Ma, N. Sheng, Y.-D. Yang, G.-D. Liu, X.-R. Zhai, *Cryst. Growth Des.* 14 (2014) 101.
- [47] J. Zhou, R.-Q. Zhao, T. Yang, X. Liu, H.-P. Xiao, H.-H. Zou, X.-F. Tan, *Dalton Trans.* 44 (2015) 7203.
- [48] J. Zhou, L. An, X. Liu, H. Zou, F. Hua, C. Liua, *Chem. Commun.* 48 (2012) 2537.
- [49] N. Zheng, H. Lu, X. Bu, P. Feng, *J. Am. Chem. Soc.* 128 (2006) 4528.
- [50] J.-B. Jiang, Y.-Y. Wu, P. Wang, P. Huo, Q.-Y. Zhu, J. Dai, *Dyes & Pigments* 107 (2014) 153.
- [51] Y.-P. Zhang, X. Zhang, W.-Q. Mu, W. Luo, G.-Q. Bian, Q.-Y. Zhu, J. Dai, *Dalton Trans.* 40 (2011) 9746.
- [52] Z.-X. Lei, Q.-Y. Zhu, X. Zhang, W. Luo, W.-Q. Mu, Jie Dai, *Inorg. Chem.* 49 (2010) 4385.
- [53] X. Zhang, W. Luo, Y.-P. Zhang, J.-B. Jiang, Q.-Y. Zhu, J. Dai, *Inorg. Chem.* 50 (2011) 6972.
- [54] X. Zhang, Z.-X. Lei, W. Luo, W.-Q. Mu, X. Zhang, Q.-Y. Zhu, J. Dai, *Inorg. Chem.* 50 (2011) 10872.
- [55] W.-Q. Mu, Q.-Y. Zhu, L.-S. You, X. Zhang, W. Luo, G.-Q. Bian, J. Dai, *Inorg. Chem.* 51 (2012) 1330.
- [56] M.-S. Wang, W.-T. Chen, L.-Z. Cai, G.-W. Zhou, G.-C. Guo, J.-S. Huang, *J. Cluster Science*, 14 (2003) 495.
- [57] G.-N. Liu, G.-C. Guo, M.-J. Zhang, J.-S. Guo, H.-Y. Zeng, J.-S. Huang, *Inorg. Chem.* 50 (2011) 9660.
- [58] Y.-L. Wang, M.-L. Feng, K.-Y. Wang, J.-R. Li, Z.-P. Wang, G.-D. Zou, X.-Y. Huang, *Inorg. Chem. Commun.* 33 (2013) 10.
- [59] J. Wu, Y.-Y. Pu, X.-W. Zhao, L.-W. Qian, G.-Q. Bian, Q.-Y. Zhu, J. Dai, *Dalton Trans.* 44 (2015) 4520.
- [60] Y. Pan, Qi. Jin, J. Chen, Y. Zhang, D. Jia, *Inorg. Chem.* 48 (2009) 5412.
- [61] J. Zhao, J. Liang, J. Chen, Y. Pan, Y. Zhang, D. Jia, *Inorg. Chem.* 50 (2011) 2288.
- [62] D. Jia, J. Zhao, Y. Pan, W. Tang, B. Wu, Y. Zhang, *Inorg. Chem.* 50 (2011) 7195.
- [63] K.-Z. Du, M.-L. Feng, L.-H. Li, B. Hu, Z.-J. Ma, P. Wang, J.-R. Li, Y.-L. Wang, G.-D. Zou, X.-Y. Huang, *Inorg. Chem.* 51 (2012) 3926.
- [64] C. Anderer, N. D. Alalacón, C. Näther, W. Bensch, *Chem. Eur. J.* 20 (2014) 16953.
- [65] Z.-X. Lei, Q.-Y. Zhu, M.-H. Zhang, J.-B. Jiang, Y.-P. Zhang, J. Dai, *Inorg. Chem.* 49 (2010) 353.
- [66] Y.-P. Zhang, Z.-X. Lei, J.-B. Jiang, Q.-Y. Zhu, X. Zhang, G.-Q. Bian, J. Dai, *Inorg. Chim. Acta* 376 (2011) 645.
- [67] G.-N. Liu, G.-C. Guo, F. Chen, S.-P. Guo, X.-M. Jiang, C. Yang, M.-S. Wang, M.-F. Wu, J.-S. Huang, *CrystEngComm* 12 (2010) 4035.

- [68] A. Kromm, W. S. Sheldrick, *Z. Anorg. Allg. Chem.* 634 (2008) 1005.
- [69] J. Hilbert, C. Näther, W. Bensch, *Dalton Trans.* 44 (2015) 11542.
- [70] J. Hilbert, C. Näther, W. Bensch, *Z. Anorg. Allg. Chem.* 640 (2014) 2858.
- [71] H. Jiang, X. Wang, T.-L. Sheng, S.-M. Hu, R.-B. Fu, X.-T. Wu, *Inorg. Chem. Commun.* 17 (2012) 5.
- [72] X. Wang, T.-L. Sheng, S.-M. Hu, R.-B. Fu, Ji.-S. Chen, X.-T. Wu, *J. Solid State Chem.* 182 (2009) 913.
- [73] G.-N. Liu, X.-M. Jiang, M.-F. Wu, G.-E Wang, G.-C. Guo, J.-S. Huang, *Inorg. Chem.* 50 (2011) 5740.
- [74] M.-L. Fu, G.-C. Guo, X. Liu, M.-F. W.-T. Chen, B. Liu, J.-S. Huang, *Inorg. Chem.* 45 (2006) 5793.
- [75] G.-N. Liu, G.-C. Guo, F. Chen, S.-H. Wang, J. Sun, J.-S. Huang, *Inorg. Chem.* 51 (2012) 472.
- [76] G.-N. Liu, G.-C. Guo, M.-S. Wang, J.-S. Huang, *Dalton Trans.* 43 (2014) 3931.
- [77] A. Kromm, W. S. Sheldrick, *Z. Anorg. Allg. Chem.* 634 (2008) 2948.
- [78] A. Kromm, W. S. Sheldrick, *Z. Anorg. Allg. Chem.* 635 (2009) 205.
- [79] A. Kromm, W. S. Sheldrick, *Z. Anorg. Allg. Chem.* 634 (2008) 121.
- [80] X. Wang, T.-L. Sheng, S.-M. Hu, R.-B. Fu, X.-T. Wu, *Inorg. Chem. Commun.* 12 (2012) 399.
- [81] C. Anderer, C. Näther, W. Bensch, *Inorg. Chem. Commun.* 46 (2014) 335.
- [82] G.-N. Liu, W.-J. Zhu, M.-J. Zhang, B. Xu, Q.-S. Liu, Z.-W. Zhang, C. Li, *J. Solid State Chem.* 218 (2014) 109.
- [83] Q. Zhang, X. Bu, Z. Lin, M. Biasini, W. P. Beyermann, P. Feng, *Inorg. Chem.* 46 (2007) 7262.
- [84] D. G. Wei, W. D. Wilson, S. Neidle, *J. Am. Chem. Soc.* 135 (2013) 1369.
- [85] Y. Li, T. Liu, H. Liu, M.-Z. Tian, Y. Li, *Acc. Chem. Res.* 47 (2014) 1186.
- [86] S. Ardo, G. J. Meyer, *Chem. Soc. Rev.* 38 (2009) 115.
- [87] D. B. Bucher, C. L. Kufner, A. Schlueter, T. Carell, W. Zinth, *J. Am. Chem. Soc.* 138 (2016) 186.
- [88] W. W. Wendlandt, H. G. Hecht, *Reflectance Spectroscopy*, Interscience Publishers, New York, 1966.