Electronic Supplementary Information

Hydrazine-solvothermal methods to synthesize polymeric thioarsenates from one-dimensional chain to three-dimensional framework

Jingyu Han,[a] Shufen Li, [a] Chunying Tang, [b] Wei Zheng, [a] Wenqing Jiang[a] and Dingxian Jia*[a]

[a] College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, People's Republic of China.

[b]Shandong Normal University, College of Chemistry,Chemical Engineering and Materials Scienc e, Jinan 250014, People's Republic of China.

1. Crystallographic data for **1–6.**

Table S1 Crystallographic and refinement data for **1–6.**

	1	**2**	**3**
CCDC	1856282	1856283	1856284
Empirical formula	$C_6H_{40}N_{14}S_{13}Mn_7As_4$	$CH_{17}N_7S_4MnAs$	$C_6H_{26}N_8S_6Mn_3As_2$
Fw	1409.56	385.32	717.37
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P\,2_1/c$ (no. 14)	P bca	$P\,\bar{1}$
a/ Å	10.378(2)	7.5398(15)	7.7875(16)
b/Å	27.244(5)	12.847(3)	8.0898(16)
c/ Å	17.662(5)	26.646(5)	10.072(2)
α/°	90	90	774.27(3)
β/°	120.57(2)	90	70.54(3)
γ/°	90	90	74.43
V/ Å^3	4299.6(17)	2581.0(9)	564.7(2)
Z	4	8	1
T/ K	293(2)	293(2)	293(2)
D_c/ Mg m^{-3}	2.178	1.983	2.109
F(000)	2756	1552	355
2θ(max)/°	50.70	50.70	50.70
Total reflns. collected	21029	7667	6300
Unique reflns	7861	2349	2075
R_{int}	0.0724	0.0750	0.0439
No. of parameters	376	128	138
R_1 [$I > 2\sigma$ (I)]	0.0406	0.0422	0.0426
wR_2 (all data)	0.0925	0.1016	0.1068
GOF on F^2	1.114	1.116	1.049
	4	**5**	**6**
CCDC	1856285	1856286	1856287
Empirical formula	$H_{24}N_{12}S_6Mn_3As_2$	$H_{24}N_{12}S_8Mn_3As_2$	$H_{24}N_8S_8Mn_3As_2$
Fw	699.33	763.45	707.41
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\,\bar{1}$	P2/n	$P\,\bar{1}$
a/ Å	9.3253(19)	11.798(2)	6.6881(13)
b/Å	9.5222(19)	8.3683(17)	7.9869(16)
c/ Å	11.863(2)	12.313(3)	10.966(2)
α/°	96.39(3)	90	78.68(3)
β/°	90.62(3)	112.66(3)	83.53(3)
γ/°	97.79(3)	90	77.92(3)
V/ Å^3	1036.9(4)	1121.8(4)	560.09(19)
Z	2	2	1
T/ K	293(2)	293(2)	293(2)
D_c/ Mg m^{-3}	2.240	2.260	2.097
F(000)	690	754	349
2θ(max)/°	50.70	50.70	50.70
Total reflns. collected	9044	10476	4629
Unique reflns	3780	2041	2041
R_{int}	0.0466	0.0308	0.0319
No. of parameters	211	116	101
R_1 [$I > 2\sigma$ (I)]	0.0376	0.0259	0.0291
wR_2 (all data)	0.0910	0.0567	0.0699
GOF on F^2	1.037	1.108	1.042

Table S2. Selected bond lengths (Å) and angles (°) for **1**

As(1)–S(2)	2.241(9)	As(1)–S(3)	2.243(10)
As(1)–S(4)	2.265(9)	As(2)–S(5)	2.253(9)
As(2)–S(6)	2.249(9)	As(2)–S(7)	2.262(8)
As(3)–S(8)	2.242(8)	As(3)–S(9)	2.278(8)
As(3)–S(10)	2.262(8)	As(4)–S(11)	2.268(9)
As(4)–S(12)	2.273(10)	As(4)–S(13)	2.273(9)
Mn(1)–N(1)	2.30(3)	Mn(1)–S(1)	2.675(7)
Mn(1)–S(2)	2.562(9)	Mn(1)–S(3)	2.608(8)
Mn(1)–S(8)	2.608(8)	Mn(1)–S(10)	2.643(8)
Mn(2)–N(3)	2.26(2)	Mn(2)–S(1)	2.540(7)
Mn(2)–S(3)	2.650(9)	Mn(2)–S(4)	2.675(9)
Mn(2)–S(5)	2.670(9)	Mn(2)–S(6)	2.643(9)
Mn(3)–N(5)	2.30(2)	Mn(3)–S(1)	2.594(7)
Mn(3)–S(6)	2.593(9)	Mn(3)–S(7)	2.609(8)
Mn(3)–S(8)	2.676(9)	Mn(3)–S(9)	2.602(9)
Mn(4)–N(4)#1	2.26(2)	Mn(4)–S(1)	2.594(7)
Mn(4)–S(9)	2.693(9)	Mn(4)–S(10)	2.663(9)
Mn(4)–S(11)	2.587(10)	Mn(4)–S(12)	2.584(10)
Mn(5)–S(1)	2.625(7)	Mn(5)–S(2)	2.616(9)
Mn(5)–S(4)	2.635(9)	Mn(5)–N(6)	2.25(2)
Mn(5)–S(12)	2.635(9)	Mn(5)–S(13)	2.654(9)
Mn(6)–S(1)	2.596(7)	Mn(6)–S(5)	2.614(9)
Mn(6)–S(7)	2.665(8)	Mn(6)–N(8)	2.363(16)
Mn(6)–S(11)	2.627(9)	Mn(6)–S(13)	2.591(9)
Mn(7)–N(9A)	2.297(19)	Mn(7)–N(9B)	2.287(19)
Mn(7)–N(10A)	2.257(19)	Mn(7)–N(10B)	2.257(19)
Mn(7)–N(11A)	2.26(2)	Mn(7)–N(11B)	2.275(19)
Mn(7)–N(12)	2.205(17)	Mn(7)–N(13A)	2.237(19)
Mn(7)–N(13B)	2.269(19)	Mn(7)–N(14A)	2.261(19)
N(1)–N(2)	1.439(18)	N(3)–N(4)	1.40(3)
N(5)–N(5) #3	1.45(4)	N(6)–N(7)	1.38(4)
N(8)–N(8)#4	1.45(5)		
Mn(7)–N(14B)	2.275(19)		
S(2)–As(1)–S(3)	101.3(3)	S(2)–As(1)–S(4)	97.9(3)
S(3)–As(1)–S(4)	99.7(3)	S(5)–As(2)–S(6)	99.9(3)
S(5)–As(2)–S(7)	100.7(3)	S(6)–As(2)–S(7)	99.6(3)
S(8)–As(3)–S(9)	101.6(3)	S(8)–As(3)–S(10)	99.0(3)
S(10)–As(3)–S(9)	100.0(3)	S(11)–As(4)–S(12)	97.9(3)
S(11)–As(4)–S(13)	99.3(3)	S(12)–As(4)–S(13)	100.3(3)
N(1)–Mn(1)–S(1)	175.4(7)	N(1)–Mn(1)–S(2)	93.3(7)

N(1)–Mn(1)–S(3)	95.7(6)	N(1)–Mn(1)–S(8)	89.3(7)
N(1)–Mn(1)–S(10)	87.6(6)	S(1)–Mn(1)–S(2)	89.6(3)
S(1)–Mn(1)–S(3)	88.1(3)	S(1)–Mn(1)–S(8)	87.9(2)
S(1)–Mn(1)–S(10)	88.3(3)	S(2)–Mn(1)–S(3)	84.2(3)
S(2)–Mn(1)–S(8)	176.7(3)	S(2)–Mn(1)–S(10)	100.7(3)
S(3)–Mn(1)–S(8)	93.5(3)	S(3)–Mn(1)–S(10)	173.9(3)
S(8)–Mn(1)–S(10)	81.4(3)	N(3)–Mn(2)–S(1)	176.9(7)
N(3)–Mn(2)–S(3)	91.3(6)	N(3)–Mn(2)–S(4)	86.1(6)
N(3)–Mn(2)–S(5)	87.1(6)	N(3)–Mn(2)–S(6)	89.6(6)
S(1)–Mn(2)–S(3)	90.1(2)	S(1)–Mn(2)–S(4)	91.4(3)
S(1)–Mn(2)–S(5)	91.5(3)	S(1)–Mn(2)–S(6)	92.8(3)
S(3)–Mn(2)–S(4)	80.6(3)	S(3)–Mn(2)–S(5)	178.4(3)
S(3)–Mn(2)–S(6)	99.0(3)	S(4)–Mn(2)–S(5)	99.3(3)
S(4)–Mn(2)–S(6)	175.7(3)	S(5)–Mn(2)–S(6)	80.9(3)
N(5)–Mn(3)–S(1)	170.3(5)	N(5)–Mn(3)–S(6)	87.4(5)
N(5)–Mn(3)–S(7)	98.2(5)	N(5)–Mn(3)–S(8)	82.3(5)
N(5)–Mn(3)–S(9)	90.5(5)	S(1)–Mn(3)–S(6)	92.8(3)
S(1)–Mn(3)–S(7)	91.5(2)	S(1)–Mn(3)–S(8)	88.1(2)
S(1)–Mn(3)–S(9)	89.9(3)	S(6)–Mn(3)–S(7)	82.9(3)
S(6)–Mn(3)–S(8)	100.3(3)	S(6)–Mn(3)–S(9)	175.7(3)
S(7)–Mn(3)–S(8)	176.8(3)	S(7)–Mn(3)–S(9)	93.7(3)
S(8)–Mn(3)–S(9)	83.2(3)	N(4)#1–Mn(4)–S(1)	174.8(7)
N(4)#1–Mn(4)–S(9)	87.2(7)	N(4)#1–Mn(4)–S(10)	87.8(7)
N(4)#1–Mn(4)–S(11)	89.6(7)	N(4)#1–Mn(4)–S(12)	93.6(7)
S(1)–Mn(4)–S(9)	87.9(2)	S(1)–Mn(4)–S(10)	89.6(2)
S(1)–Mn(4)–S(11)	92.9(3)	S(1)–Mn(4)–S(12)	91.3(3)
S(9)–Mn(4)–S(10)	80.9(3)	S(9)–Mn(4)–S(11)	97.9(3)
S(9)–Mn(4)–S(12)	178.9(3)	S(10)–Mn(4)–S(11)	177.2(3)
S(10)–Mn(4)–S(12)	98.3(3)	S(11)–Mn(4)–S(12)	82.9(3)
N(6)–Mn(5)–S(1)	174.9(7)	N(6)–Mn(5)–S(2)	95.5(7)
N(6)–Mn(5)–S(4)	90.4(7)	N(6)–Mn(5)–S(12)	89.8(8)
N(6)–Mn(5)–S(13)	84.7(7)	S(1)–Mn(5)–S(2)	89.6(3)
S(1)–Mn(5)–S(4)	90.5(3)	S(1)–Mn(5)–S(12)	89.5(3)
S(1)–Mn(5)–S(13)	90.2(3)	S(2)–Mn(5)–S(4)	80.6(3)
S(2)–Mn(5)–S(12)	97.5(3)	S(2)–Mn(5)–S(13)	179.7(3)
S(4)–Mn(5)–S(12)	178.1(3)	S(4)–Mn(5)–S(13)	99.3(3)
S(12)–Mn(5)–S(13)	82.6(3)	N(8)–Mn(6)–S(1)	178.2(7)
N(8)–Mn(6)–S(5)	89.8(7)	N(8)–Mn(6)–S(7)	88.8(7)
N(8)–Mn(6)–S(11)	86.7(7)	N(8)–Mn(6)–S(13)	88.8(8)
S(1)–Mn(6)–S(5)	91.6(3)	S(1)–Mn(6)–S(7)	90.2(2)
S(1)–Mn(6)–S(11)	92.0(3)	S(1)–Mn(6)–S(13)	92.2(3)
S(5)–Mn(6)–S(7)	82.4(3)	S(5)–Mn(6)–S(11)	176.5(3)
S(5)–Mn(6)–S(13)	97.1(3)	S(7)–Mn(6)–S(11)	97.3(3)

S(7)–Mn(6)–S(13)	177.6(3)	S(11)–Mn(6)–S(13)	83.1(3)
N(9A)–Mn(7)–N(9B)	46.8(19)	N(9A)–Mn(7)–N(10A)	73.2(19)
N(9A)–Mn(7)–N(10B)	52.2(19)	N(9A)–Mn(7)–N(11A)	97(2)
N(9A)–Mn(7)–N(11B)	128.2(19)	N(9A)–Mn(7)–N(12)	76.2(16)
N(9A)–Mn(7)–N(13B)	132.8(19)	N(9A)–Mn(7)–N(14A)	94.8(17)
N(9A)–Mn(7)–N(14B)	125(2)	N(9B)–Mn(7)–N(10A)	73.0(19)
N(9B)–Mn(7)–N(10B)	80.9(18)	N(9B)–Mn(7)–N(11A)	141(2)
N(9B)–Mn(7)–N(11B)	174.4(19)	N(9B)–Mn(7)–N(12)	105.2(16)
N(9B)–Mn(7)–N(13A)	119.6(18)	N(9B)–Mn(7)–N(13B)	95(2)
N(9B)–Mn(7)–N(14A)	50.3(16)	N(9B)–Mn(7)–N(14B)	91.5(18)
N(10A)–Mn(7)–N(10B)	37.1(19)	N(10A)–Mn(7)–N(11A)	82.7(19)
N(10A)–Mn(7)–N(11B)	104(2)	N(10A)–Mn(7)–N(12)	137.9(16)
N(10A)–Mn(7)–N(13B)	69.1(17)	N(10A)–Mn(7)–N(14A)	100(2)
N(10A)–Mn(7)–N(14B)	135.7(17)	N(10B)–Mn(7)–N(11A)	62(2)
N(10B)–Mn(7)–N(11B)	94(2)	N(10B)–Mn(7)–N(12)	100.9(18)
N(10B)–Mn(7)–N(13A)	124(2)	N(10B)–Mn(7)–N(13B)	104.2(18)
N(10B)–Mn(7)–N(14A)	126.5(19)	N(10B)–Mn(7)–N(14B)	170.9(18)
N(11A)–Mn(7)–N(11B)	34(2)	N(11A)–Mn(7)–N(12)	73.0(16)
N(11A)–Mn(7)–N(13A)	93(2)	N(11A)–Mn(7)–N(13B)	105(2)
N(11A)–Mn(7)–N(14A)	168(2)	N(11A)–Mn(7)–N(14B)	127(2)
N(11B)–Mn(7)–N(13A)	64.9(15)	N(11B)–Mn(7)–N(13B)	88.1(18)
N(11B)–Mn(7)–N(14A)	135.2(17)	N(11B)–Mn(7)–N(14B)	94(2)
N(12)–Mn(7)–N(13A)	118.7(18)	N(12)–Mn(7)–N(14B)	85.8(14)
N(13A)–Mn(7)–N(9A)	164.2(19)	N(13A)–Mn(7)–N(10A)	96(2)
N(13A)–Mn(7)–N(13B)	31.7(18)	N(13A)–Mn(7)–N(14A)	75.3(14)
N(13A)–Mn(7)–N(14B)	56(2)	N(13B)–Mn(7)–N(12)	150.0(16)
N(13B)–Mn(7)–N(14A)	65.5(17)	N(13B)–Mn(7)–N(14B)	71.3(15)
N(14A)–Mn(7)–N(14B)	44.6(18)	Mn(1)–S(1)–Mn(2)	91.3(2)
Mn(1)–S(1)–Mn(3)	92.1(2)	Mn(1)–S(1)–Mn(4)	91.0(2)
Mn(1)–S(1)–Mn(5)	88.9(2)	Mn(1)–S(1)–Mn(6)	177.6(3)
Mn(2)–S(1)–Mn(3)	88.0(2)	Mn(2)–S(1)–Mn(4)	177.6(3)
Mn(2)–S(1)–Mn(5)	90.3(2)	Mn(2)–S(1)–Mn(6)	89.9(2)
Mn(3)–S(1)–Mn(4)	92.2(2)	Mn(3)–S(1)–Mn(5)	178.0(3)
Mn(3)–S(1)–Mn(6)	90.1(2)	Mn(4)–S(1)–Mn(5)	89.5(2)
Mn(4)–S(1)–Mn(6)	87.7(2)	Mn(5)–S(1)–Mn(6)	89.0(2)
Mn(1)–S(2)–Mn(5)	91.6(3)	As(1)–S(2)–Mn(1)	87.8(3)
As(1)–S(2)–Mn(5)	90.7(3)	Mn(1)–S(3)–Mn(2)	90.4(3)
As(1)–S(3)–Mn(1)	86.7(3)	As(1)–S(3)–Mn(2)	89.9(3)
Mn(2)–S(4)–Mn(5)	87.2(3)	As(1)–S(4)–Mn(2)	88.8(3)
As(1)–S(4)–Mn(5)	89.7(3)	Mn(2)–S(5)–Mn(6)	86.8(3)
As(2)–S(5)–Mn(2)	88.6(3)	As(2)–S(5)–Mn(6)	88.9(3)
Mn(2)–S(6)–Mn(3)	85.9(3)	As(2)–S(6)–Mn(2)	89.4(3)
As(2)–S(6)–Mn(3)	88.6(3)	Mn(3)–S(7)–Mn(6)	88.3(2)

As(2)–S(7)–Mn(3)	88.0(3)	As(2)–S(7)–Mn(6)	87.4(3)
Mn(1)–S(8)–Mn(3)	91.7(3)	As(3)–S(8)–Mn(1)	90.2(3)
As(3)–S(8)–Mn(3)	86.9(3)	Mn(3)–S(9)–Mn(4)	89.8(3)
As(3)–S(9)–Mn(3)	88.0(3)	As(3)–S(9)–Mn(4)	88.6(3)
Mn(1)–S(10)–Mn(4)	90.2(2)	As(3)–S(10)–Mn(1)	88.9(3)
As(3)–S(10)–Mn(4)	89.7(3)	Mn(4)–S(11)–Mn(6)	87.2(3)
As(4)–S(11)–Mn(4)	89.2(3)	As(4)–S(11)–Mn(6)	88.0(3)
Mn(4)–S(12)–Mn(5)	89.5(3)	As(4)–S(12)–Mn(4)	89.1(3)
As(4)–S(12)–Mn(5)	88.7(3)	Mn(5)–S(13)–Mn(6)	88.5(3)
As(4)–S(13)–Mn(5)	88.2(3)	As(4)–S(13)–Mn(6)	88.8(3)

Symmetry transformations used to generate equivalent atoms: #1 x–1, y, z; #2 x+1, y, z; #3 –x, –y+1, –z; #4 –x+1, –y+1, –z+1

Table S3. Selected bond lengths (Å) and angles (°) for **2**

As(1)–S(1)	2.218(4)	As(1)–S(2)	2.142(5)
As(1)–S(3)	2.139(4)	As(1)–S(4)	2.167(4)
Mn(1)–N(1)	2.292(13)	Mn(1)–N(2)#1	2.262(13)
Mn(1)–N(3)	2.303(12)	Mn(1)–N(4)#1	2.311(12)
Mn(1)–S(1)	2.617(4)	Mn(1)–S(1)#2	2.605(4)
S(1)–As(1)–S(2)	111.36(17)	S(1)–As(1)–S(3)	105.12(16)
S(1)–As(1)–S(4)	104.24(15)	S(2)–As(1)–S(3)	112.81(19)
S(2)–As(1)–S(4)	110.21(18)	S(3)–As(1)–S(4)	112.67(18)
N(1)–Mn(1)– N(2)#1	82.7(5)	N(1)–Mn(1)–N(3)	94.0(5)
N(1)–Mn(1)–N(4)#1	92.9(4)	N(2)#1–Mn(1)–N(3)	88.7(5)
N(2)#1–Mn(1)–N(4)#1	91.1(5)	N(3)–Mn(1)–N(4)#1	173.0(4)
N(1)–Mn(1)–S(1)	167.6(3)	N(1)–Mn(1)–S(1)#2	85.0(3)
N(2)#1–Mn(1)–S(1)	91.6(3)	N(2)#1–Mn(1)–S(1)#2	165.8(4)
N(3)–Mn(1)–S(1)	96.9(3)	N(3)–Mn(1)–S(1)#2	85.1(3)
N(4)#1–Mn(1)–S(1)	76.1(3)	N(4)#1–Mn(1)–S(1)#2	96.6(3)
S(1)#2–Mn(1)–S(1)	101.81(16)	As(1)–S(1)–Mn(1)	115.09(15)
As(1)–S(1)–Mn(1)#1	110.72(15)	Mn(1)#1–S(1)–Mn(1)	92.58(14)

Symmetry transformations used to generate equivalent atoms: #1 x–1/2, y, –z+1/2；#2 x+1/2, y, –z+1/2；#3 –x+1, –y+1, –z.

Table S4. Selected bond lengths (Å) and angles (°) for **3**

As(1)–S(1)	2.341(4)	As(1)–S(2)	2.350(4)
As(1)–S(3)	2.337(5)	S(1)–Mn(1)	2.735(4)
S(1)–Mn(2)	2.640(4)	S(2)–Mn(2)	2.635(4)
S(2)–Mn(3)	2.632(4)	S(3)–Mn(3)	2.562(4)
Mn(1)–N(1)	2.254(12)	Mn(1)–N(2)	2.307(14)

Mn(1)–N(1)#1	2.254(12)	Mn(1)–N(2)#1	2.307(14)
Mn(1)–S(1)#1	2.735(4)	Mn(2)–N(3)	2.262(13)
Mn(2)–N(3)#2	2.262(13)	Mn(2)–S(1)#2	2.640(4)
Mn(2)–S(2)#2	2.635(4)	Mn(3)–N(4)	2.280(14)
Mn(3)–N(4)#3	2.280(14)	Mn(3)–S(2)#3	2.632(4)
Mn(3)–S(3)#3	2.562(4)		
S(1)–As(1)–S(2)	97.21(15)	S(1)–As(1)–S(3)	101.40(17)
S(2)–As(1)–S(3)	95.87(16)	As(1)–S(1)–Mn(1)	107.53(15)
As(1)–S(1)–Mn(2)	88.28(13)	Mn(1)–S(1)–Mn(2)	154.3(2)
As(1)–S(2)–Mn(2)	88.21(14)	As(1)–S(2)–Mn(3)	88.03(14)
Mn(2)–S(2)–Mn(3)	100.36(16)	As(1)–S(3)–Mn(3)	89.99(16)
N(1)–Mn(1)–N(1)#1	180.000(1)	N(1)–Mn(1)–N(2)	79.4(5)
N(1)–Mn(1)–N(2)#1	100.6(5)	N(1)–Mn(1)–S(1)	93.1(3)
N(1)#1–Mn(1)–S(1)	86.9(3)	N(2)–Mn(1)–S(1)	90.8(3)
N(2)–Mn(1)–S(1)#1	89.2(3)	N(1)#1–Mn(1)–N(2)#1	79.4(5)
N(1)#1–Mn(1)–N(2)	100.6(5)	S(1)#1–Mn(1)–S(1)	180.0
N(3)#2–Mn(2)–N(3)	180.000(2)	N(3)–Mn(2)–S(1)	88.9(4)
N(3)–Mn(2)–S(1)#2	91.1(4)	N(3)–Mn(2)–S(2)	89.3(3)
N(3)#2–Mn(2)–S(2)	90.7(4)	N(3)–Mn(2)–S(2)#2	90.7(3)
N(3)#2–Mn(2)–S(2)#2	89.3(4)	S(1)#2–Mn(2)–S(1)	180.0
S(1)–Mn(2)–S(2)	83.68(13)	S(2)#2–Mn(2)–S(2)	180.000(1)
S(1)–Mn(2)–S(2)#2	96.32(13)	N(4)–Mn(3)–S(2)	93.1(4)
N(4)–Mn(3)–S(3)	88.9(4)	N(4)#3–Mn(3)–S(2)	86.9(3)
N(4)–Mn(3)–S(2)#3	86.9(3)	N(4)#3–Mn(3)–S(2)#3	93.1(3)
N(4)#3–Mn(3)–S(3)	91.1(4)	S(2)#3–Mn(3)–S(2)	180.000(1)
S(2)–Mn(3)–S(3)	84.11(14)	S(3)#3–Mn(3)–S(2)	95.89(14)
S(3)–Mn(3)–S(3)#3	180.000(1)		

Symmetry transformations used to generate equivalent atoms: #1 –x+1, –y+1, #2 –x, –y+1, –z+2; #3 –x, –y+2, –z+2; #4 x, y–1, z; #5 x, y+1, z; #6 –x, –y+1, –z+1–z+1

Table S5. Selected bond lengths (Å) and angles (°) for **4**

As(1)–S(1)	2.216(2)	As(1)–S(2)	2.266(2)
As(1)–S(3)	2.237(2)	As(2)–S(4)	2.234(2)
As(2)–S(5)	2.281(2)	As(2)–S(6)	2.218(2)
Mn(1)–N(1)	2.240(6)	Mn(1)–N(1)#1	2.240(6)
Mn(1)–S(1)	2.615(2)	Mn(1)–S(1)#1	2.615(2)
Mn(1)–S(2)	2.605(2)	Mn(1)–S(2)#1	2.605(2)
Mn(2)–N(2)	2.320(6)	Mn(2)–N(3)	2.291(6)
Mn(2)–N(5)	2.277(6)	Mn(2)–N(7)	2.333(6)
Mn(2)–S(2)	2.577(2)	Mn(2)–S(3)	2.614(2)
Mn(3)–N(4)	2.303(6)	Mn(3)–N(6)	2.291(6)

Mn(3)–N(9)	2.286(6)	Mn(3)–N(11)	2.313(6)
Mn(3)–S(4)	2.622(2)	Mn(3)–S(5)	2.583(2)
Mn(4)–N(10)	2.318(7)	Mn(4)–N(10)#2	2.318(7)
Mn(4)–S(5)	2.639(2)	Mn(4)–S(5)#2	2.639(2)
Mn(4)–S(6)	2.582(2)	Mn(4)–S(6)#2	2.582(2)
S(1)–As(1)–S(2)	100.29(8)	S(1)–As(1)–S(3)	106.85(10)
S(2)–As(1)–S(3)	98.39(8)	S(4)–As(2)–S(5)	99.98(8)
S(4)–As(2)–S(6)	106.31(9)	S(5)–As(2)–S(6)	98.67(8)
N(1)–Mn(1)–S(1)	84.46(18)	N(1)#1–Mn(1)–S(1)	95.54(18)
N(1)–Mn(1)–S(2)	87.85(17)	N(1)#1–Mn(1)–S(2)	92.15(17)
S(1)#1–Mn(1)–S(1)	180.0	S(1)–Mn(1)–S(2)	82.47(7)
S(1)–Mn(1)–S(2)#1	97.53(7)	S(1)#1–Mn(1)–S(2)	97.53(7)
S(2)–Mn(1)–S(2)#1	180.0	N(1)–Mn(1)–N(1)#1	180.000(2)
N(2)–Mn(2)–S(2)	92.18(17)	N(2)–Mn(2)–S(3)	93.85(17)
N(3)–Mn(2)–S(2)	91.33(17)	N(3)–Mn(2)–S(3)	92.17(16)
N(5)–Mn(2)–S(2)	172.26(15)	N(5)–Mn(2)–S(3)	90.21(15)
N(7)–Mn(2)–S(2)	97.10(17)	N(7)–Mn(2)–S(3)	177.71(18)
S(2)–Mn(2)–S(3)	82.09(8)	N(2)–Mn(2)–N(3)	173.4(2)
N(2)–Mn(2)–N(5)	87.6(2)	N(2)–Mn(2)–N(7)	88.3(2)
N(3)–Mn(2)–N(5)	89.6(2)	N(3)–Mn(2)–N(7)	85.7(2)
N(5)–Mn(2)–N(7)	90.6(2)	N(4)–Mn(3)–S(4)	93.98(16)
N(4)–Mn(3)–S(5)	177.07(16)	N(6)–Mn(3)–S(4)	90.25(15)
N(6)–Mn(3)–S(5)	95.41(17)	N(9)–Mn(3)–S(4)	87.66(18)
N(9)–Mn(3)–S(5)	90.98(17)	N(11)–Mn(3)–S(4)	174.83(17)
N(5)–Mn(3)–S(11)	94.88(17)	S(4)–Mn(3)–S(5)	83.26(8)
N(4)–Mn(3)–N(6)	85.6(2)	N(4)–Mn(3)–N(9)	87.9(2)
N(4)–Mn(3)–N(11)	88.0(2)	N(6)–Mn(3)–N(9)	173.0(2)
N(6)–Mn(3)–N(11)	85.1(2)	S(5)#2–Mn(4)–S(5)	180.000(1)
S(6)–Mn(4)–S(5)	81.61(7)	S(6)–Mn(4)–S(5)#2	98.39(7)
S(6)#2–Mn(4)–S(6)	180.0	N(10)–Mn(4)–N(10)#2	180.000(1)
As(1)–S(1)–Mn(1)	88.25(8)	As(1)–S(2)–Mn(1)	87.44(7)
As(1)–S(2)–Mn(2)	89.87(7)	Mn(2)–S(2)–Mn(1)	100.68(8)
As(1)–S(3)–Mn(2)	89.60(8)	As(2)–S(4)–Mn(3)	87.27(7)
As(2)–S(5)–Mn(3)	87.27(7)	As(2)–S(5)–Mn(4)	88.21(7)
Mn(3)–S(5)–Mn(4)	101.60(8)	As(2)–S(6)–Mn(4)	91.04(7)

Symmetry transformations used to generate equivalent atoms: #1 –x, –y+1, –z+2； #2 –x+1, –y+3, –z+1

Table S6. Selected bond lengths (Å) and angles (°) for **5**

As(1)–S(1)	2.1991(9)	As(1)–S(2)	2.1283(10)

As(2)–S(3)	2.1675(10)	As(2)–S(4)	2.1491(9)
Mn(1)–N(1)	2.277(3)	Mn(1)–N(3)	2.294(3)
Mn(1)–N(5)	2.321(3)	Mn(1)–N(6)#3	2.283(3)
Mn(1)–S(1)	2.6625(11)	Mn(1)–S(3)	2.5753(11)
Mn(2)–N(2)	2.220(3)	Mn(2)–N(4)	2.342(3)
Mn(2)–S(1)	2.6171(10)	N(6)–Mn(1)#3	2.283(3)
S(1)–As(1)–S(1)#1	103.38(5)	S(1)–As(1)–S(2)	111.30(4)
S(1)#1–As(1)–S(2)	108.28(4)	S(2)–As(1)–S(2)#1	113.81(6)
S(3)#2–As(2)–S(3)	107.46(6)	S(3)–As(2)–S(4)	113.11(4)
S(4)–As(2)–S(3)#2	107.81(4)	S(4)–As(2)–S(4)#2	107.65(5)
N(1)–Mn(1)–N(3)	91.02(11)	N(1)–Mn(1)–N(5)	91.52(10)
N(1)–Mn(1)–N(6)#3	179.49(10)	N(3)–Mn(1)–N(5)	170.00(10)
N(3)–Mn(1)–N(6)#3	89.36(11)	N(5)–Mn(1)–N(6)#3	88.16(10)
N(1)–Mn(1)–S(1)	88.73(7)	N(1)–Mn(1)–S(3)	88.96(7)
N(3)–Mn(1)–S(1)	88.63(8)	N(3)–Mn(1)–S(3)	102.91(8)
N(5)–Mn(1)–S(1)	81.76(8)	N(5)–Mn(1)–S(3)	86.81(8)
N(6)#3–Mn(1)–S(1)	91.62(8)	N(6)#3–Mn(1)–S(3)	90.62(7)
S(1)–Mn(1)–S(3)	168.27(3)	N(2)–Mn(2)–N(2)#1	105.05(15)
N(2)–Mn(2)–N(4)	87.27(10)	N(2)–Mn(2)–N(4)#1	90.99(10)
N(4)#1–Mn(2)–N(4)	177.14(14)	N(2)–Mn(2)–S(1)	86.79(8)
N(2)–Mn(2)–S(1)#1	166.15(7)	N(4)–Mn(2)–S(1)	96.84(7)
N(4)–Mn(2)–S(1)#1	85.33(8)	S(1)#1–Mn(2)–S(1)	82.50(4)
Mn(1)–S(1)–Mn(2)	87.39(3)	As(1)–S(1)–Mn(1)	116.45(4)
As(1)–S(1)–Mn(2)	87.06(3)	As(2)–S(3)–Mn(1)	110.57(4)

Symmetry transformations used to generate equivalent atoms: #1 –x+1/2, y, –z+3/2；#2 –x+1/2, y, –z+5/2；#3 –x, –y+2, –z+2.

Table S7. Selected bond lengths (Å) and angles (°) for **6**

As(1)–S(1)	2.1843(11)	As(1)–S(2)	2.1825(11)
As(2)–S(3)	2.1661(11)	As(2)–S(4)	2.1283(12)
Mn(1)–N(1)	2.162(3)	Mn(1)–S(1)	2.5356(11)
Mn(1)–S(1)#1	2.8936(14)	Mn(1)–S(2)	2.8746(14)
Mn(1)–S(2)#2	2.6468(14)	Mn(1)–S(3)#1	2.5531(13)
Mn(2)–N(2)	2.297(3)	Mn(2)–N(3)	2.253(3)
Mn(2)–N(4)	2.310(3)		
S(1)–As(1)–S(2)	102.51(5)	S(1)–As(1)–S(3)	105.11(4)
S(1)–As(1)–S(4)	112.99(5)	S(2)–As(1)–S(3)	111.03(4)
S(2)–As(1)–S(4)	113.84(4)	S(3)–As(1)–S(4)	110.78(5)
N(1)–Mn(1)–S(1)	156.09(9)	N(1)–Mn(1)–S(1)#1	83.79(9)
N(1)–Mn(1)–S(2)	81.85(9)	N(1)–Mn(1)–S(2)#2	98.16(9)
N(1)–Mn(1)–S(3)#1	103.65(10)	S(1)–Mn(1)–S(2)	77.75(4)

S(1)–Mn(1)–S(1)#1	85.83(4)	S(1)#1–Mn(1)–S(2)	95.41(4)
S(1)–Mn(1)–S(2)#2	95.95(4)	S(1)–Mn(1)–S(3)#1	95.25(4)
S(2)#2–Mn(1)–S(2)	95.04(4)	S(2)–Mn(1)–S(3)#1	171.10(3)
S(2)#2–Mn(1)–S(3)#1	91.13(4)	S(1)#1–Mn(1)–S(2)#2	169.54(4)
S(1)#1–Mn(1)–S(3)#1	78.44(4)	N(2)–Mn(2)–N(2)#3	180.0
N(2)–Mn(2)–N(4)	93.28(13)	N(2)–Mn(2)–N(4)#3	86.72(13)
N(3)–Mn(2)–N(2)	89.75(14)	N(3)#3–Mn(2)–N(2)	90.25(13)
N(3)–Mn(2)–N(2)#3	90.25(14)	N(3)#3–Mn(2)–N(3)	180.000(1)
N(3)–Mn(2)–N(4)	92.19(13)	N(3)–Mn(2)–N(4)#3	87.81(13)
As(1)–S(1)–Mn(1)	92.37(4)	As(1)–S(1)–Mn(1)#1	83.47(4)
Mn(1)–S(1)–Mn(1)#1	94.17(4)	As(1)–S(2)–Mn(1)	83.74(4)
As(1)–S(2)–Mn(1)#2	107.17(4)	Mn(1)#2–S(2)–Mn(1)	84.96(4)
As(1)–S(3)–Mn(1)#1	92.57(4)		

Symmetry transformations used to generate equivalent atoms: #1 –x, –y+1, –z+1； #2 –x+1, –y+1, –z+1； #3 –x, –y+2, –z.

Table S8. Hydrogen bond lengths (Å) and angles (°) for **1**–**6**

D–H···A	d(H···A)	d(D···A)	<(DHA)
1			
N(12)–H(12A)···S(2)	2.97	3.59(3)	128.2
N(12)–H(12A)···N(2)	2.52	3.33(5)	151.0
N(8)–H(8B)···S(11)#1	2.69	3.35(2)	131.7
N(8)–H(8A)···S(7)#1	2.76	3.43(2)	131.9
N(7)–H(7B)···S(4)	3.02	3.62(3)	127.0
N(6)–H(6B)···S(3)#2	2.76	3.62(3)	159.5
N(5)–H(5A)···S(8)#3	2.78	3.41(2)	128.3
N(4)–H(4B)···S(5)	2.89	3.51(3)	128.0
N(4)–H(4A)···S(4)	2.82	3.49(2)	131.9
N(3)–H(3B)···S(9)#4	2.83	3.45(2)	127.4
N(3)–H(3A)···S(10)#4	2.77	3.43(2)	130.8
N(2)–H(2B)···S(10)	2.86	3.55(4)	135.7
N(2)–H(2B)···N(14B)	2.69	3.34(5)	130.8
N(2)–H(2A)···S(4)#5	2.57	3.40(4)	155.2
N(1)–H(1B)···S(12)#6	2.68	3.56(3)	167.9
2			
N(1)–H(1A)···S(2)#1	2.58	3.427(15)	157.5
N(1)–H(1B)···S(4)#2	2.80	3.361(12)	121.6
N(2)–H(2A)···S(1)#3	2.81	3.493(14)	133.4
N(2)–H(2B)···S(3)#4	2.67	3.437(14)	143.1
N(3)–H(3A)···S(4)#3	2.68	3.443(14)	143.2

N(3)–H(3B)···S(3)	2.78	3.490(15)	137.3
N(4)–H(4B)···S(2)#5	2.72	3.455(11)	140.0
N(4)–H(4B)···S(4)#3	2.99	3.527(15)	120.4
N(5)–H(5A)···S(3)#3	2.71	3.462(17)	142.9
N(5)–H(5A)···S(4)#3	2.90	3.598(19)	136.5
N(5)–H(5B)···S(2)	2.70	3.507(17)	151.4
N(6)–H(6B)···S(2)#6	3.00	3.65(2)	131.1
N(7)–H(7A)···S(4)#5	2.56	3.339(19)	146.3
N(7)–H(7B)···N(5)#6	1.98	2.82(2)	157.8
3			
N(1)–H(1A)···S(3)	2.56	3.410(13)	158.8
N(1)–H(1B)···S(3)#1	2.51	3.347(13)	154.6
N(2)–H(2)···S(2)#2	2.72	3.536(15)	149.0
N(3)–H(3B)···S(3)#3	2.69	3.358(14)	131.4
N(4)–H(4B)···S(1)#4	2.68	3.413(15)	139.1
4			
N(1)–H(1A)···S(3)	2.71	3.435(7)	137.9
N(1)–H(1B)···S(4)#1	2.61	3.416(6)	150.3
N(2)–H(2B)···S(6)#1	2.67	3.460(7)	146.6
N(3)–H(3A)···S(4)	2.65	3.370(7)	138.3
N(3)–H(3B)···N(8)#2	2.18	3.035(9)	158.3
N(4)–H(4A)···S(3)	2.73	3.443(7)	137.4
N(5)–H(5A)···S(6)#1	2.74	3.515(6)	144.6
N(5)–H(5B)···S(4)	2.60	3.310(6)	136.6
N(6)–H(6A)···N(12)#3	2.14	2.982(9)	155.3
N(6)–H(6B)···S(3)	2.61	3.353(7)	140.5
N(6)–H(6B)···S(5)#3	2.95	3.402(6)	112.7
N(7)–H(7A)···S(2)#2	2.63	3.446(7)	151.7
N(8)–H(8A)···S(1)#4	2.61	3.431(7)	153.0
N(8)–H(8B)···S(3)#5	2.98	3.706(7)	140.2
N(9)–H(9A)···S(6)	2.90	3.457(7)	121.7
N(10)–H(10B)···S(3)#6	2.66	3.436(6)	145.4
N(11)–H(11B)···S(5)#3	2.69	3.536(7)	157.8
N(12)–H(12A)···S(4)#7	2.79	3.584(7)	149.8
N(12)–H(12B)···S(6)#8	2.76	3.448(7)	135.1
5			
N(6)–H(6A)···S(3)	2.60	3.288(3)	133.8
N(5)–H(5B)···S(4)#1	2.90	3.558(3)	131.8
N(5)–H(5B)···S(4)#2	2.88	3.707(3)	152.6
N(5)–H(5A)···S(3)#3	2.68	3.358(3)	132.9
N(4)–H(4B)···S(2)#4	2.61	3.439(3)	154.1
N(4)–H(4A)···S(4)	2.70	3.511(3)	151.0

N(3)–H(3A)···S(2)	2.92	3.741(3)	152.2
N(2)–H(2B)···S(2)#5	2.65	3.418(3)	143.2
N(2)–H(2A)···S(4)#2	2.55	3.378(3)	152.3
N(1)–H(1B)···S(3)#1	2.68	3.410(3)	138.8
N(1)–H(1A)···S(4)	2.49	3.356(3)	162.7
6			
N(1)–H(1B)···S(4)#2	2.54	3.372(3)	156.5
N(2)–H(2A)···S(2)	2.92	3.803(4)	169.7
N(2)–H(2B)···S(4)#4	2.59	3.458(4)	164.5
N(2)–H(2C)···S(3)#5	3.01	3.676(4)	133.1
N(3)–H(3B)···S(4)#6	2.91	3.739(4)	155.9
N(3)–H(3C)···S(4)#1	2.71	3.531(4)	154.1
N(4)–H(4A)···S(4)#1	2.72	3.596(4)	168.5
N(4)–H(4B)···S(3)#7	2.77	3.647(4)	169.6
N(4)–H(4C)···S(4)#4	2.86	3.685(4)	155.3

Symmetry transformations used to generate equivalent atoms: For **1**: #1 –x+1, –y+1, –z+1; #2 x, –y+1/2, z+1/2; #3 –x, –y+1, –z; #4 x+1, y, z; #5 x–1, –y+1/2, z–1/2; #6 x, –y+1/2, z–1/2. For **2**: #1 x+1/2, y, –z+1/2; #2 –x, y–1/2, –z+1/2; #3 –x+1/2, y–1/2, z; #4 –x+1, y–1/2, –z+1/2; #5 x+1, y, z; #6 x+1/2, –y+1/2, –z. For **3**: #1 –x+1, –y+2, –z+1; #2 x, y, z–1; #3 –x, –y+1, –z+2; #4 x, y+1, z For **4**: #1 x, y–1, z; #2 –x, –y+2, –z+2; #3 –x+1, –y+2, –z+1; #4 –x, –y+1, –z+2; #5 x–1, y, z; #6 x, y+1, z; #7 x+1, y, z; #8 –x+1, –y+3, –z+1. For **5**: #1 –x, –y+1, –z+2; #2 x–1/2, –y+1, z–1/2; #3 –x, –y+2, –z+2; #4 –x+1, –y+2, –z+2; #5 x, y–1, z. For **6**: #1 x, y+1, z; #2 –x+1, –y+1, –z+1; #3 –x, –y+1, –z+1; #4 –x+1, –y+1, –z; #5 –x, –y+1, –z; #6 x–1, y+1, z; #7 –x, –y+2, –z.

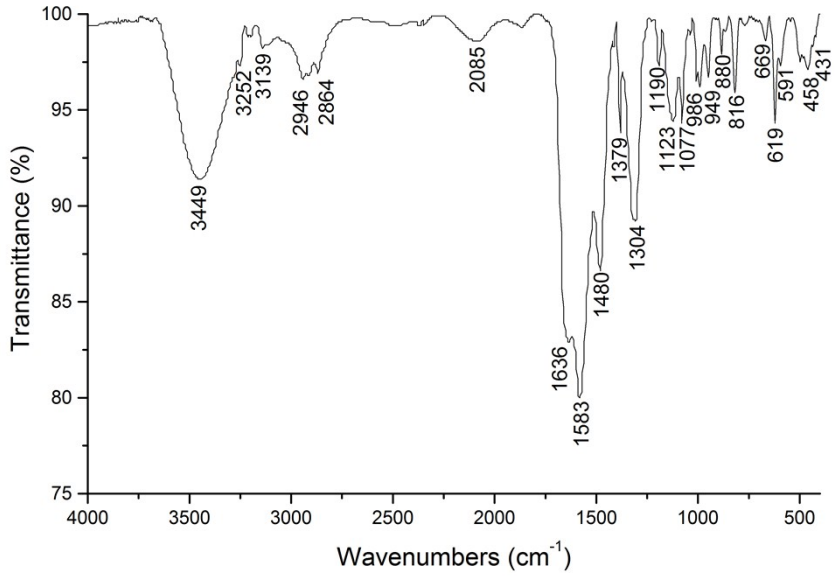


Fig. S1. IR spectrum of complex **1**.

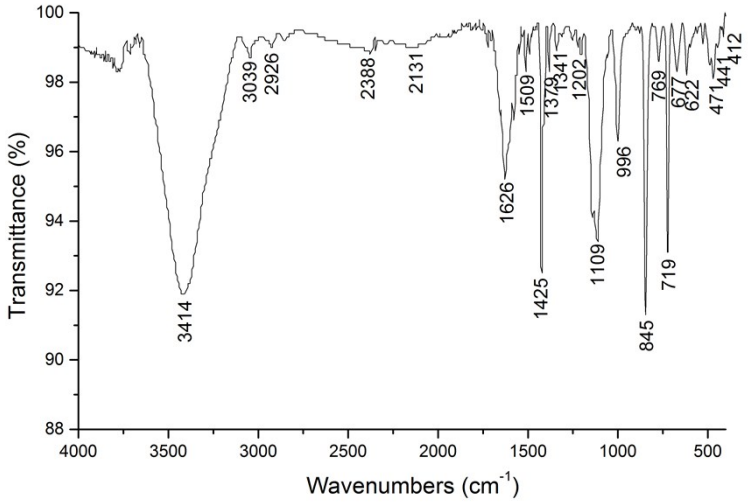


Fig. S2. IR spectrum of complex **2**.

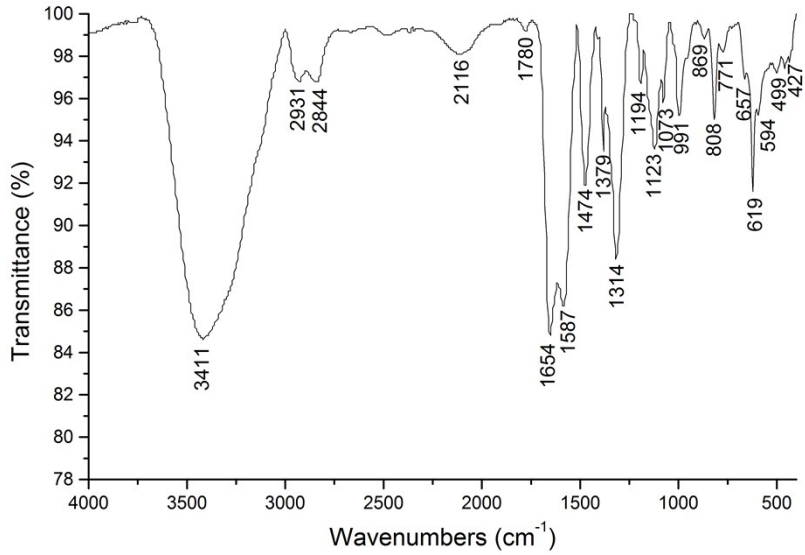


Fig. S3. IR spectrum of complex **3**.

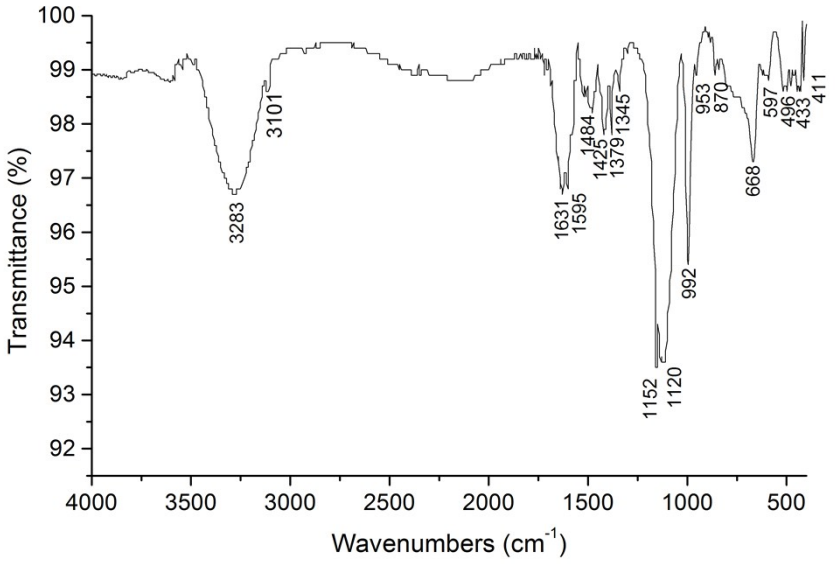


Fig. S4. IR spectrum of complex **4**.

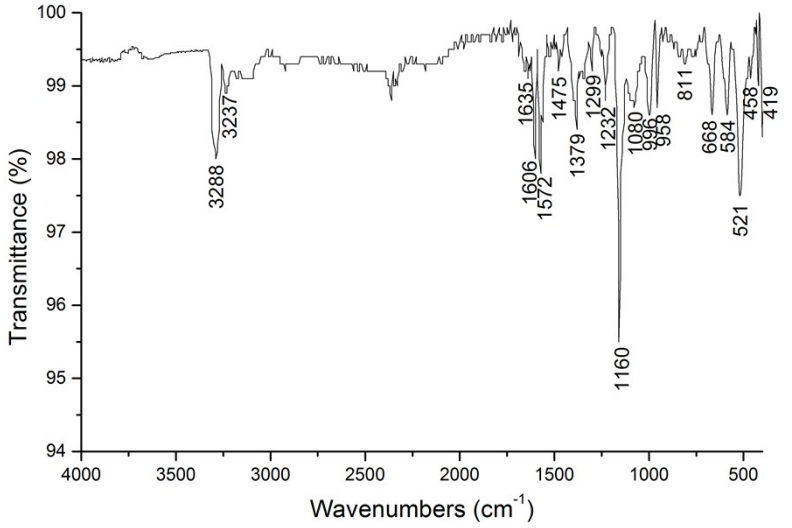


Fig. S5. IR spectrum of complex **5**.

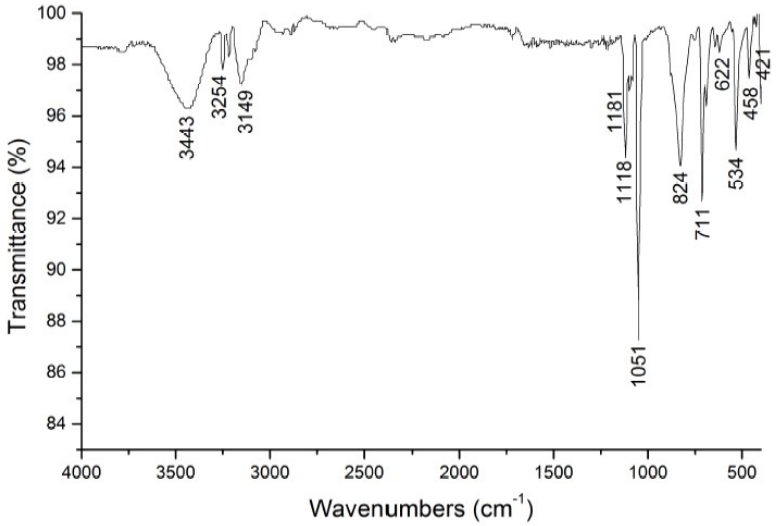
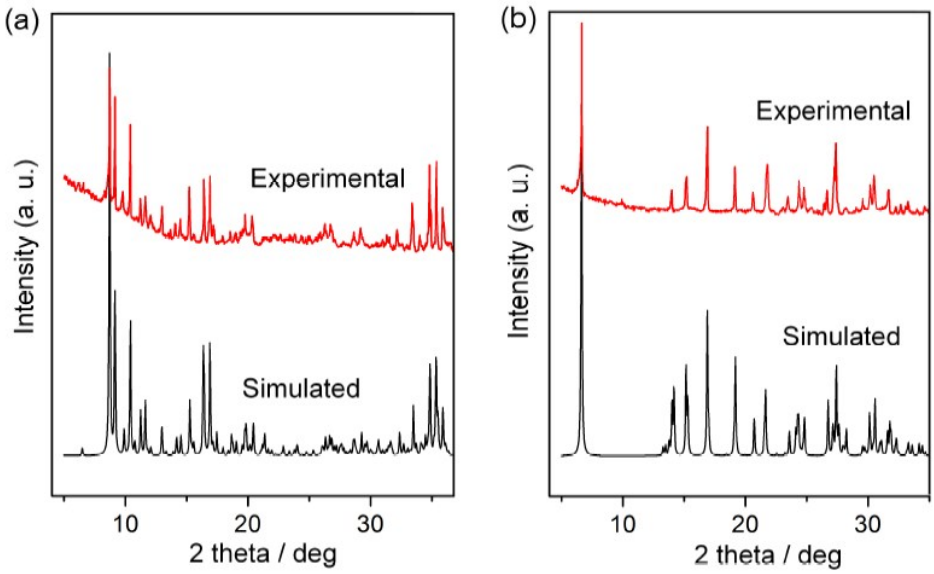


Fig. S6. IR spectrum of complex **6**.



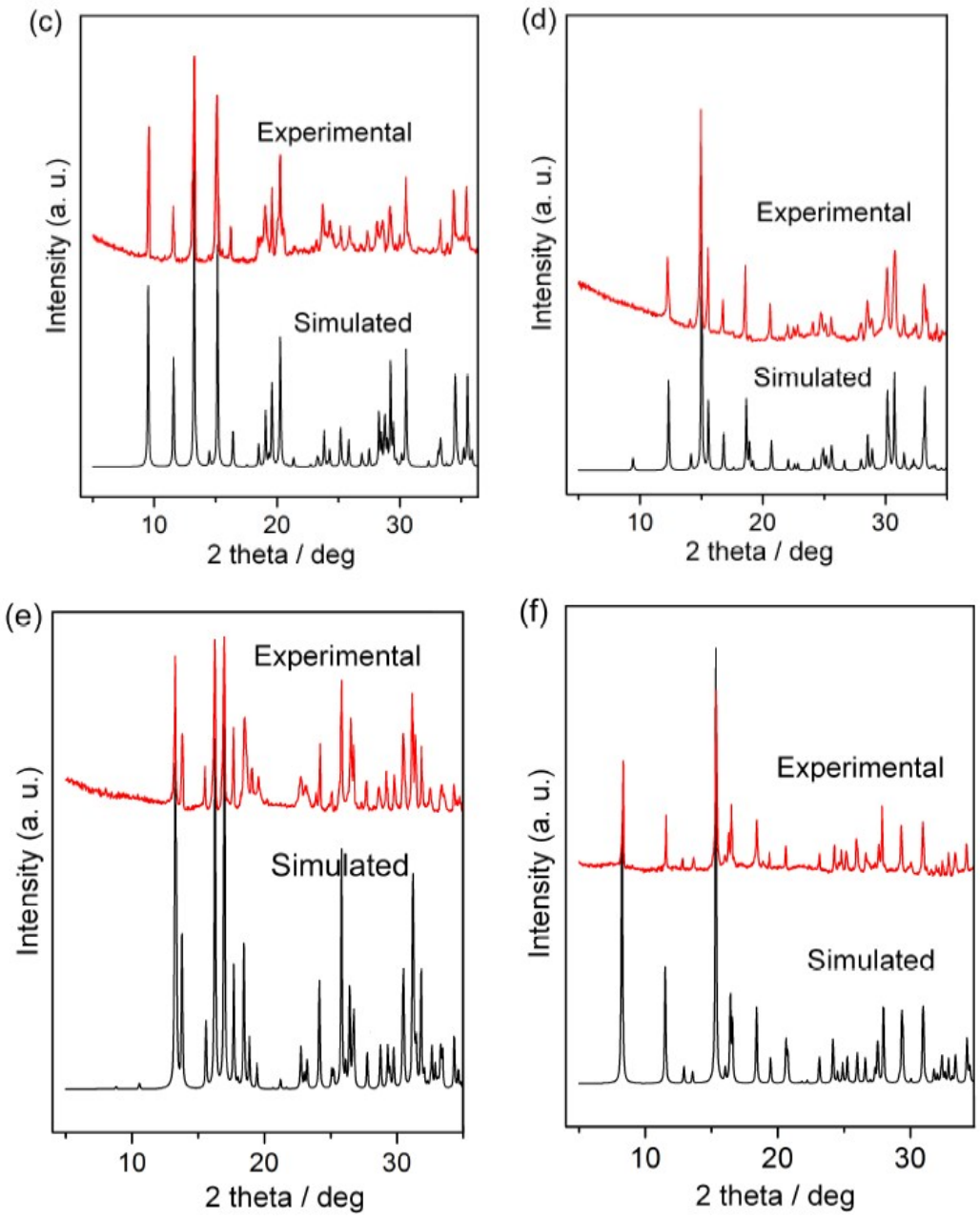


Fig. S7 Simulated and experimental powder XRD patterns of compound **1**(a), **2**(b), **3**(c), **4**(d), **5**(e) and **6**(f).

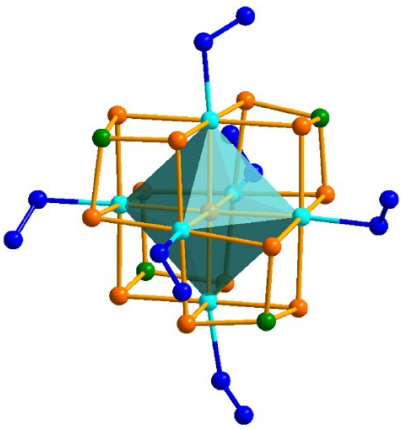


Fig. S8 Crystal structure of the $[(N_2H_4)_2Mn_6(\mu_6\text{-}S)(\mu\text{-}N_2H_4)_2(\mu_3\text{-}AsS_3)_4]^{2-}$ cluster in compound **1**, showing highlighted $Mn_6(\mu_6\text{-}S)$ octahedron.

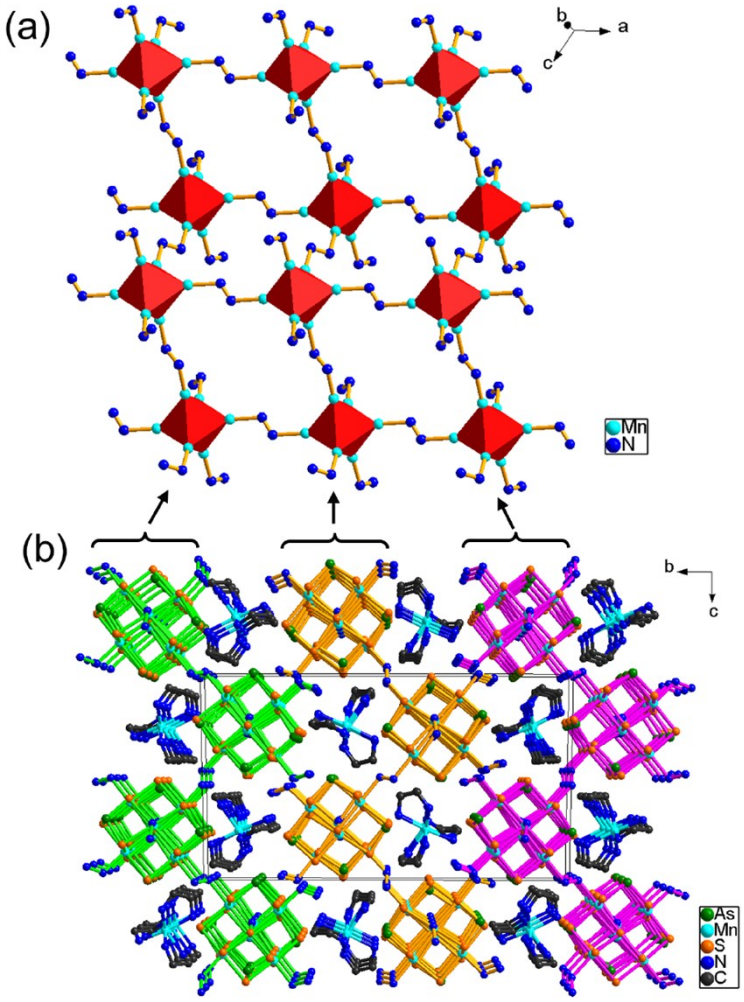


Fig. S9 (a) Schematic depiction of the waved layer constructed by $[Mn_6(\mu_6\text{-}S)(\mu_3\text{-}AsS_3)_4^{2-}]_n$ and N_2H_4 linkers in **1**. Red octahedra: Mn_6S core in the $[Mn_6(\mu_6\text{-}S)(\mu_3\text{-}AsS_3)_4]^{2-}$ cluster. (b) Packing diagram of **1** viewed the *a* axis, showing the parallel $[(N_2H_4)_2Mn_6(\mu_6\text{-}S)(\mu\text{-}N_2H_4)_2(\mu_3\text{-}AsS_3)_4^{2-}]_n$ waved layers.

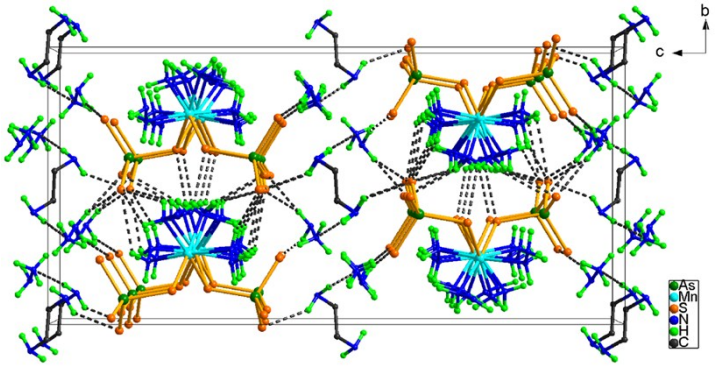


Fig. S10. Packing diagram of **2** viewed down the crystallographic *a* axis.

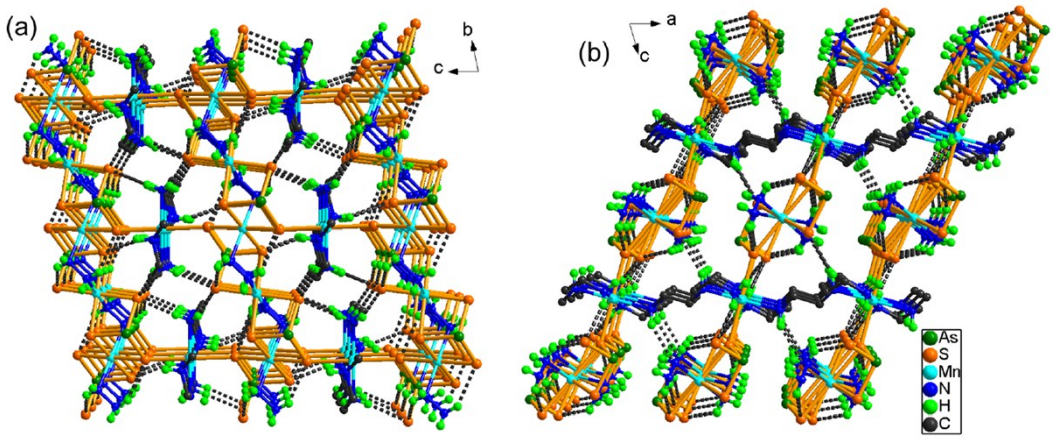


Fig. S11. Packing diagram of **3** viewed down the crystallographic *a* axis (a) and *b* axis (b), showing H···S hydrogen bonds. Hydrogen atoms of CH_2 are omitted for clarity.

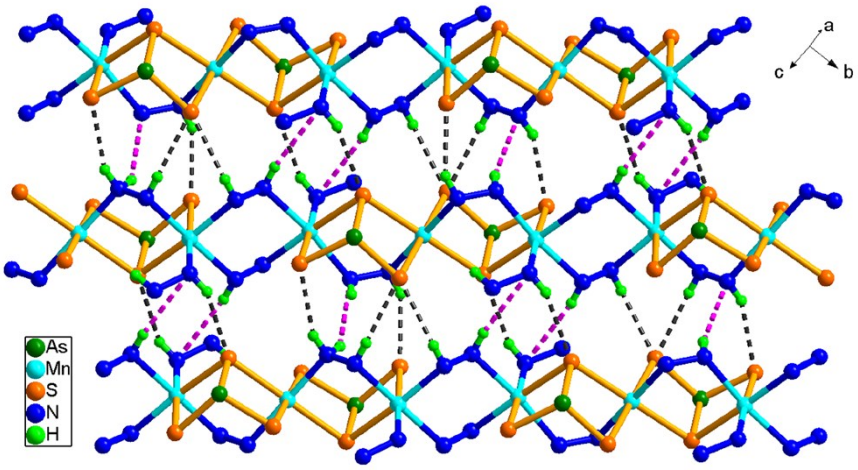


Fig. S12. A view of the layer constructed by $[\{Mn(N_2H_4)\}_2\{Mn(\mu\text{-}N_2H_4)_2(\mu\text{-}AsS_3)_2\}(\mu\text{-}N_2H_4)_2]_n$ chains via N–H···N (purple) and N–H···S (black) hydrogen bonds. Hydrogen atoms not involved in the hydrogen bonding formation are omitted for clarity.

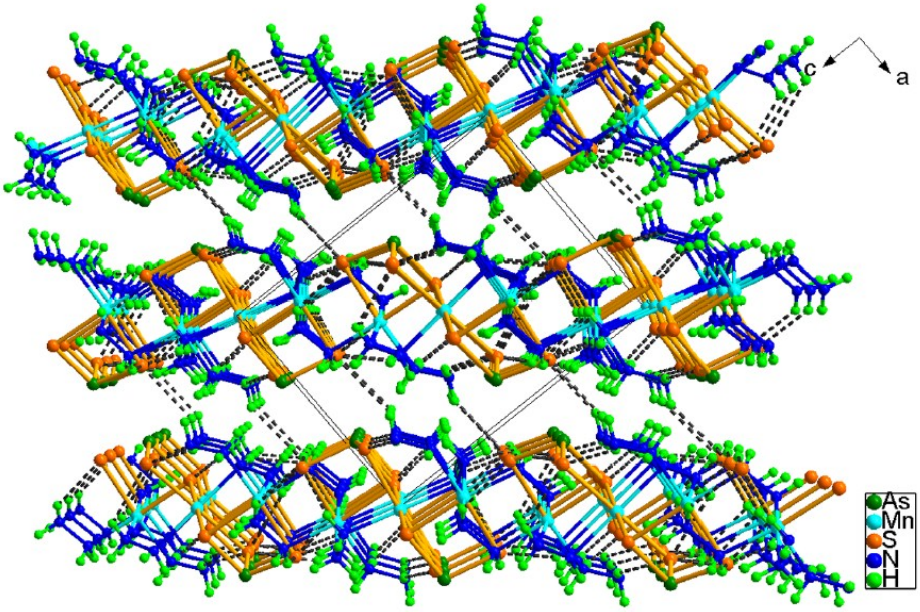


Fig. S13. Packing diagram of **4** viewed down the crystallographic *b* axis, showing H···S hydrogen bonds.

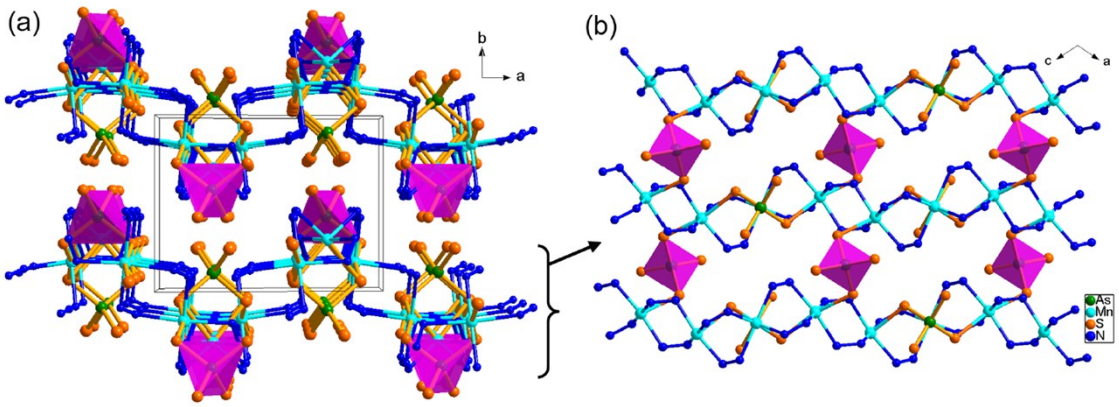


Fig. S14. (a) Packing diagram of **5** viewed down the *c* axis. (b) A view of the $[Mn_3(\mu\text{-}N_2H_4)_6(\mu_3\text{-}AsS_4)(\mu_2\text{-}AsS_4)]_n$ layer viewed down the *b* axis.

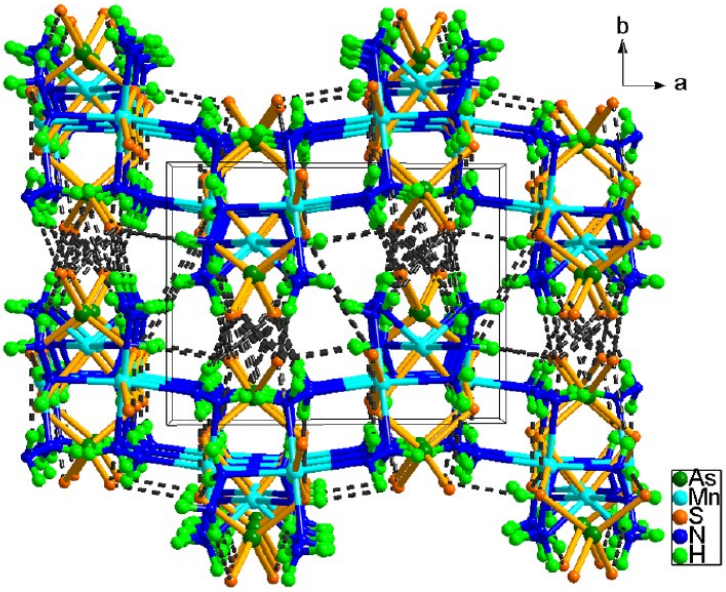


Fig. S15. Packing diagram of **5** viewed down the *c* axis, showing H···S hydrogen bonds.

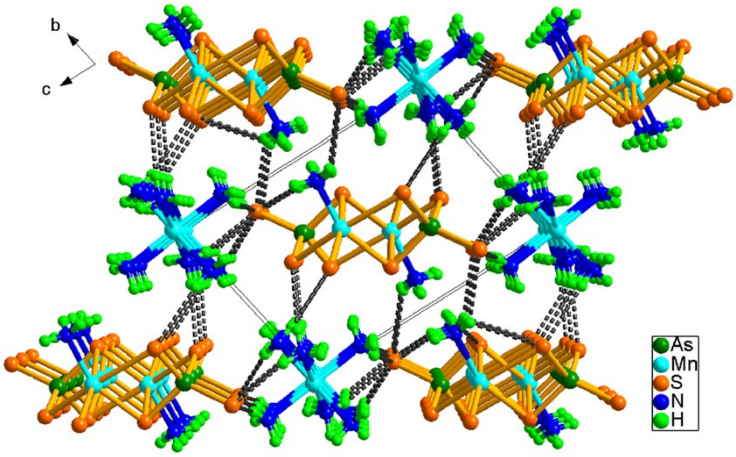


Fig. S16. Crystal packing diagram of **6** viewed down the crystallographic *a* axis. Carbon and hydrogen atoms are omitted for clarity.

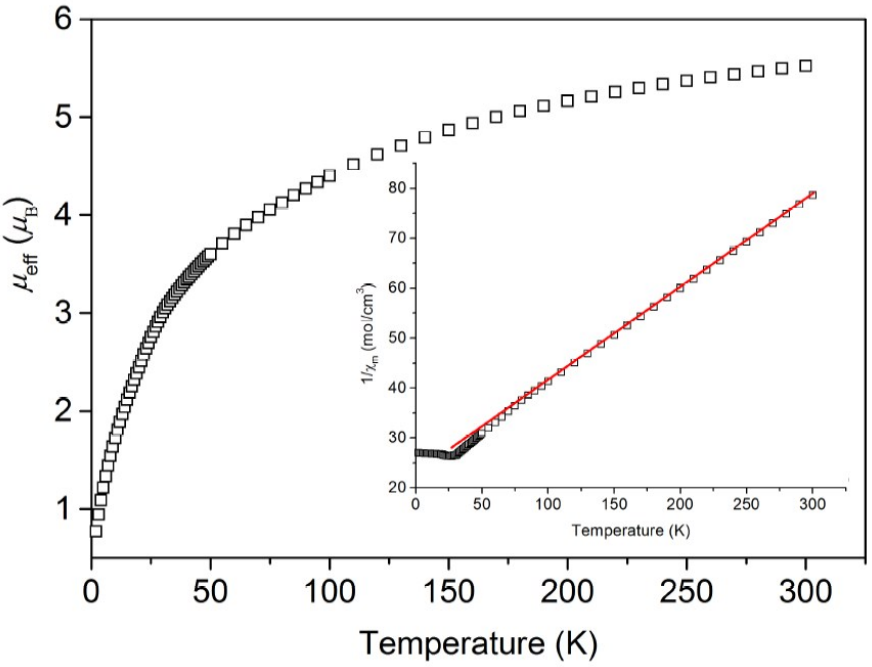


Fig. S17 Curves of μ_{eff} and $1/\chi_m$ (insert) versus T for compound **1**.

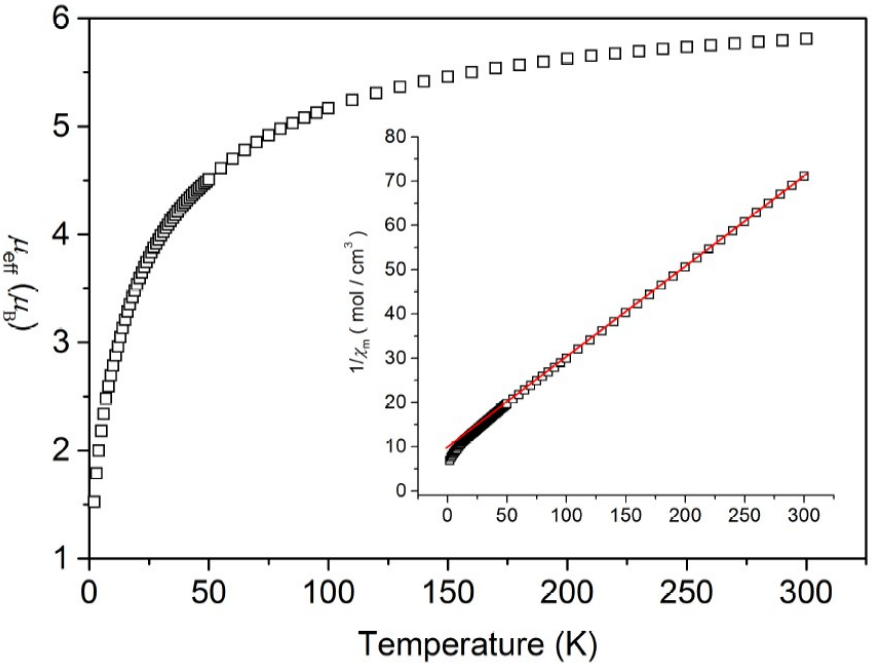


Fig. S18 Curves of μ_{eff} and $1/\chi_m$ (insert) versus T for compound **2**.

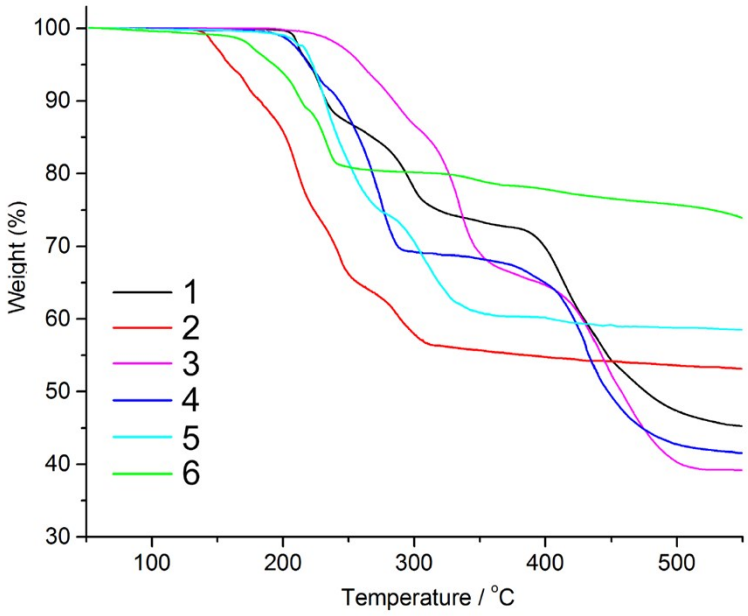


Fig. S19. TG curves of compounds **1**–**6**.

Thermal Properties:

Thermal stabilities of title compounds were investigated using thermogravimetric analysis (TGA) method under a nitrogen atmosphere in the temperature range of 25–550 °C (Fig. S19). TGA curve manifests that compound **1** decomposes in a multi-step process with a total weight loss of 54.2 %. The weight loss of 12.9 % in the first step between 210°C and 290 °C is consistent with the removal of four N_2H_4 and two H_2S molecules (theoretical value: 13.4%). The decomposition process is followed by a weight loss of 12.5% in the second step, and 28.8% in the third step, which are attributed to the losses of three en molecules (theoretical value: 12.8%) and two As_2S_2 units (theoretical value: 30.4%), respectively. Compound **2** exhibits a weight loss of 25.8% between 140°C and 260°C with overlapped steps, which corresponds with the release of a H_2S, a N_2H_4 and half an en molecule. The weight loss of 17.7% between 260°C and 290°C in the next step is attributed to the loss of two N_2H_4 ligands (theoretical value: 16.6 %). Compound **3** displays a three-step decomposition process with weight losses of 32.7 % in the first and second steps between 220°C and 390°C, which is accordant with the removal of a H_2S, two N_2H_4 and a trien molecule (theoretical value: 33.8 %). The weight loss 27.8 % in the third step between 420°C and 500°C is consistent with loss an As_2S_2 unit. Compound **4** shows a similar decomposition process to **3**. It has weight losses of 30.7 % in the first two steps between

190°C and 280°C, and 27.6 % in the third step between 380°C and 490°C. Compound **5** decomposes in distinct two steps with total weight loss of 38.9 % between 210°C and 330°C, which corresponds with the release of three H_2S (theoretical value: 12.6 %), six N_2H_4 (theoretical value: 25.2 %) molecules, respectively. Compound **6** displays a weight loss of 18.8 % between 170°C and 230°C in overlapped steps. The weight loss is consistent with release of all NH_3 molecules (theoretical value: 19.2 %) in **6**.