Electronic Supplementary Information

Temperature-Controlled Self-Assembly of a Series Inorganic-Organic Hybrid Arsenomolybdates †‡

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Fig. S1 SEM images and EDX spectra of single crystal of **1**.
Fig. S2 SEM images and EDX spectra of single crystal of **2**.
Fig. S3 SEM images and EDX spectra of single crystal of **3.**
Fig. S4 Polyhedral and ball-stick representation of the compounds of Ref.18 (a) and Ref.19 (b).
Fig. S5 Comparison of the simulated and experimental XRPD patterns of of **1-3**
Fig. S6 Polyhedral and ball-stick representation of the 3D supramolecular framework structure of **1** via hydrogen bond
Fig. S7 The IR spectra of **1-3.**
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Fig. S11 XPS spectra of **3.**
Fig. S12 Thermogravimetric curves of **1-3** in the flowing N_2 atmosphere.
Fig. S13 Temperature evolution of the inverse magnetic susceptibility χ_M^{-1} for 1 between 30 and 300 K.
Table.S1 The summary of detail synthetic information about some representative AM fragments originated from As^{III} atoms relevant to temperature.

1.EDX-SEM

EDX-SEM has been used to characterize the composition of the compounds. Figure. S1-3† show the SEM images of **1-3`** as well as the corresponding spectra recorded for the marked areas. According to the EDX spectra, the composition of the compounds were detected with approximate ratio of Cu: As: Mo found to be 1.9: 1: 2.9 for **1** (Fig. S1†); 1.6: 1: 4.4 for **2** (Fig. S2†); 1: 2.8 :2.9 for **3** (Fig. S3†). Owing to 1-8 % error estimated,[1] these results have been checked using multiple samples to reduce the error in the values. we selected four of them list in the Fig. S1-3†. Using both the structural data and analysis by EDX, XPS, BVS, charge balance arguments, we can estimate the formulae of compounds **1**, **2** and **3**. Using these approach , we can give the formula of **1** is **$[Cu_4(en)_4O_2(H_2O)_2][H_2As_2Mo_6O_{26}]$** (Cu: As: Mo = 2: 1: 3), **2** is **$[Cu(en)_2(H_2O)]_4[Cu(en)_2(H_2O)_2]\{[Cu(phen)(en)][As^{III}As^{V}Mo^{VI}_9O_{34}]_2\}$** (Cu: As: Mo = 3: 2: 9) and **3** is **$(H_2en)\ [Cu(en)_2][(CuO_6)Mo_6O_{18}(As_3O_3)_2]\cdot 10H_2O$** (Cu: As: Mo = 1: 3: 3).

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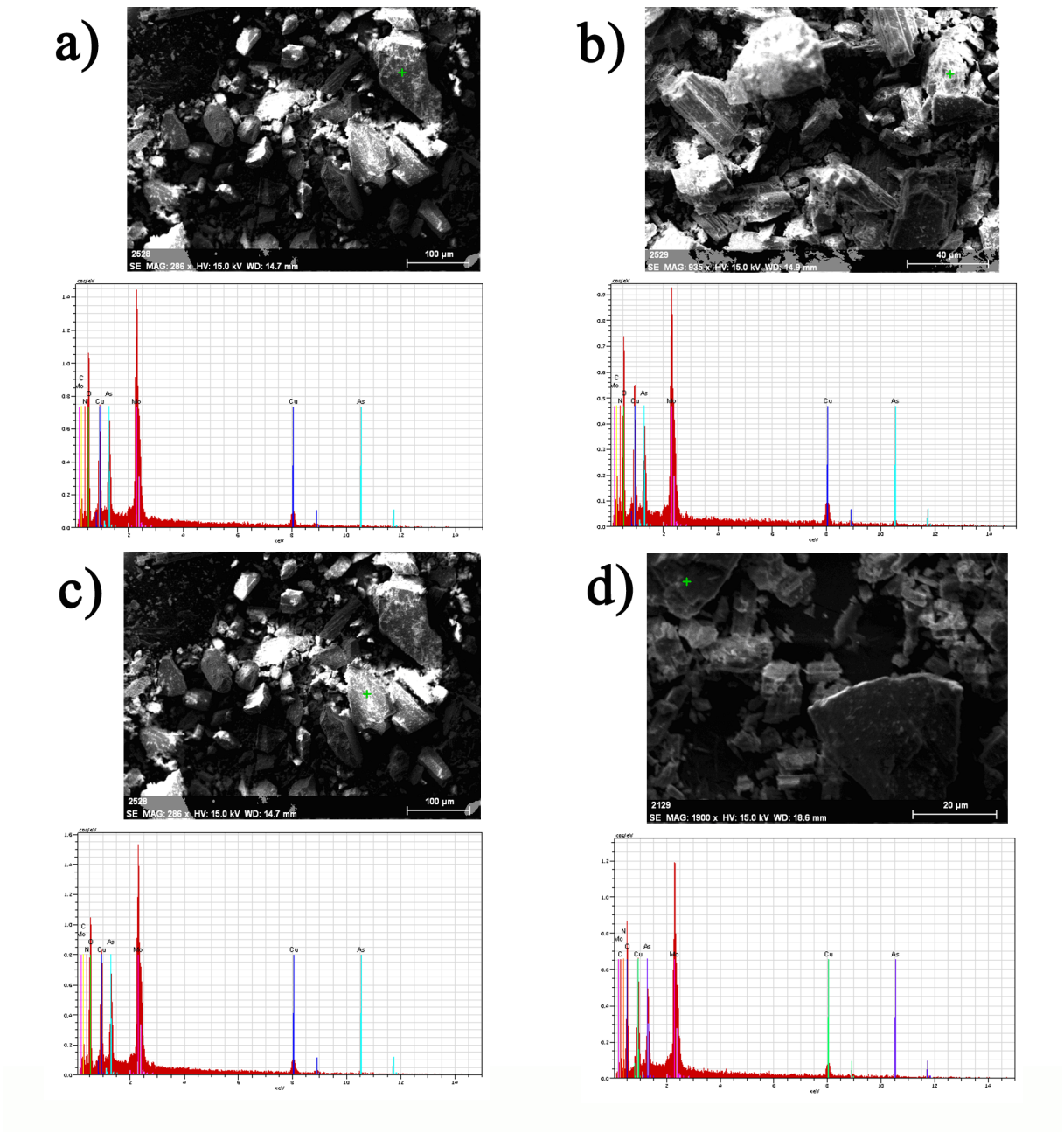

Fig. S1 SEM images and EDX spectra of single crystal of **1**.

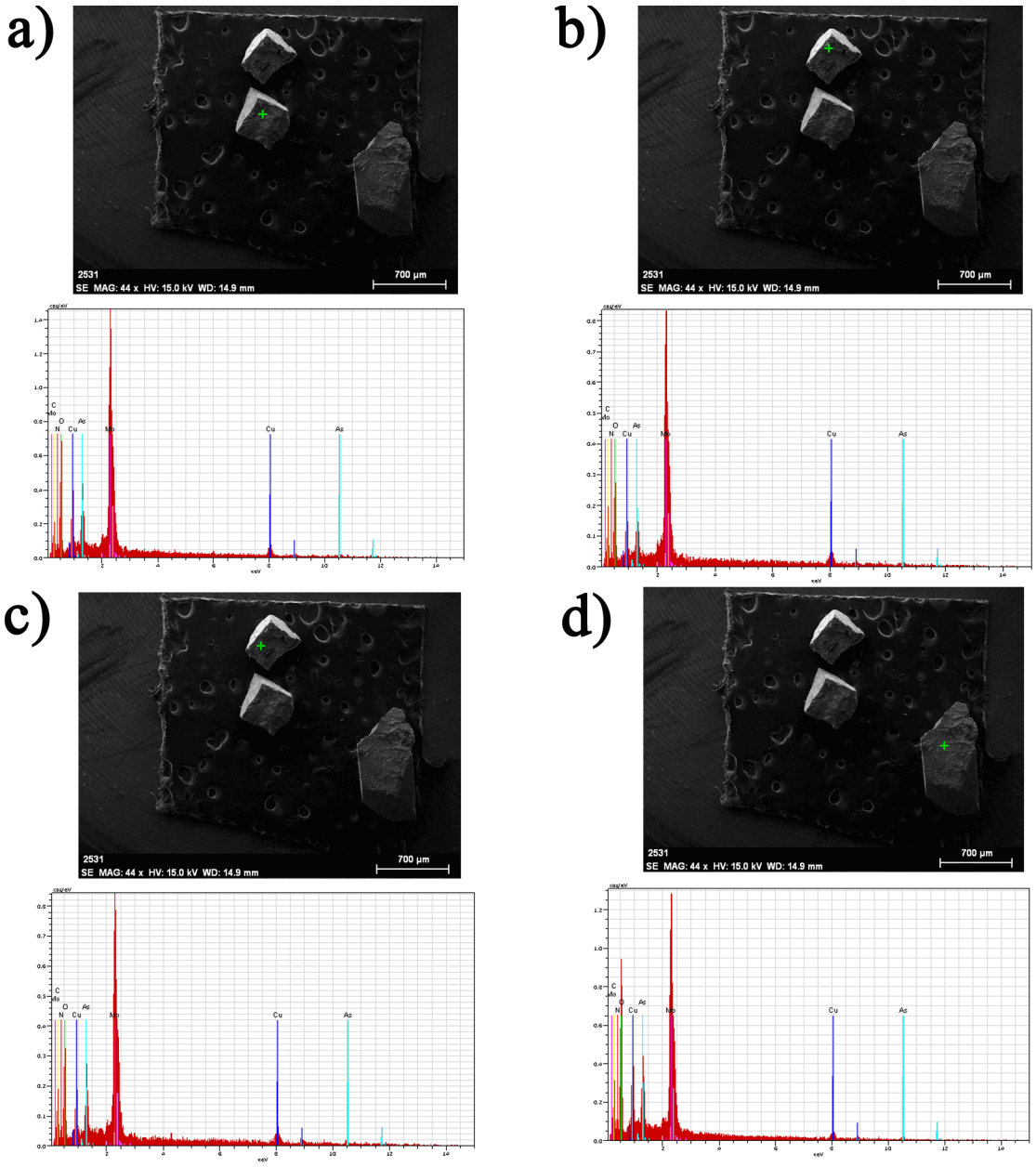

Fig. S2 SEM images and EDX spectra of single crystal of **2**.

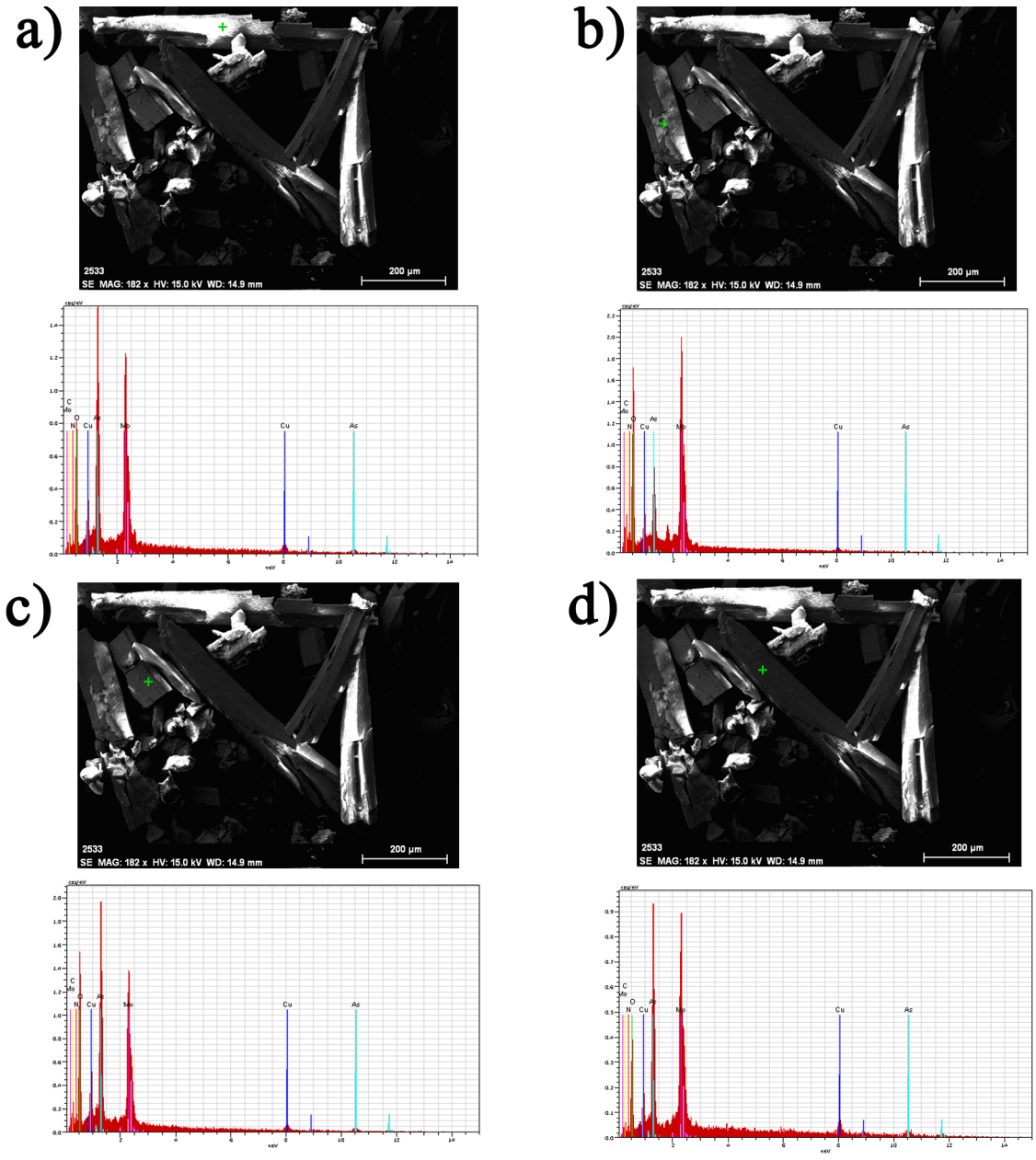

Fig. S3 SEM images and EDX spectra of single crystal of **3.**

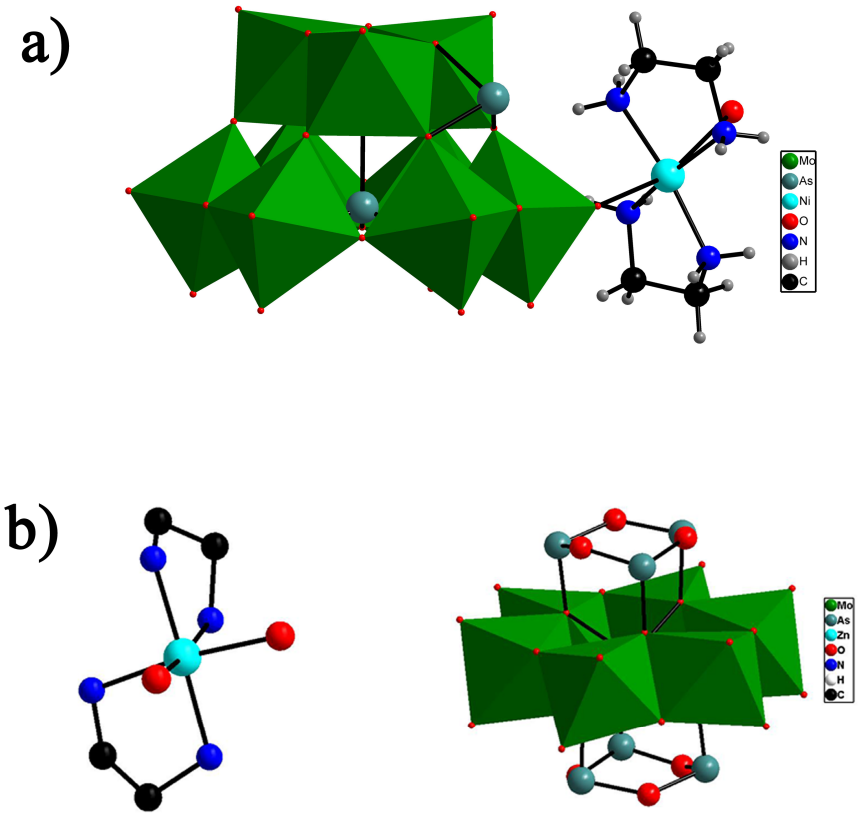

Fig. S4 Polyhedral and ball-stick representation of the compounds of Ref.18 (a) and Ref.19 (b).

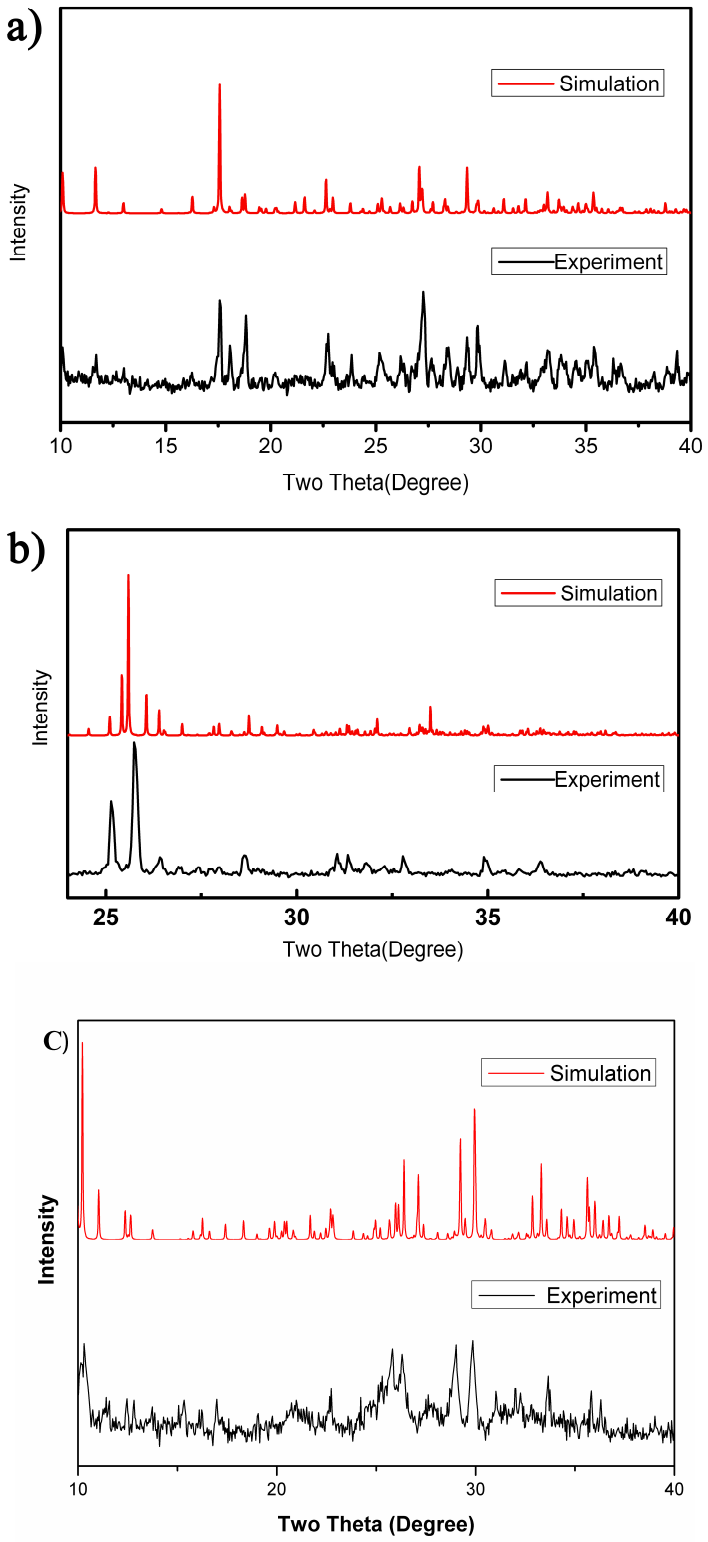

Fig. S5 Comparison of the simulated and experimental XRPD patterns of **1-3**: a) **1**; b) **2**; c) **3**.

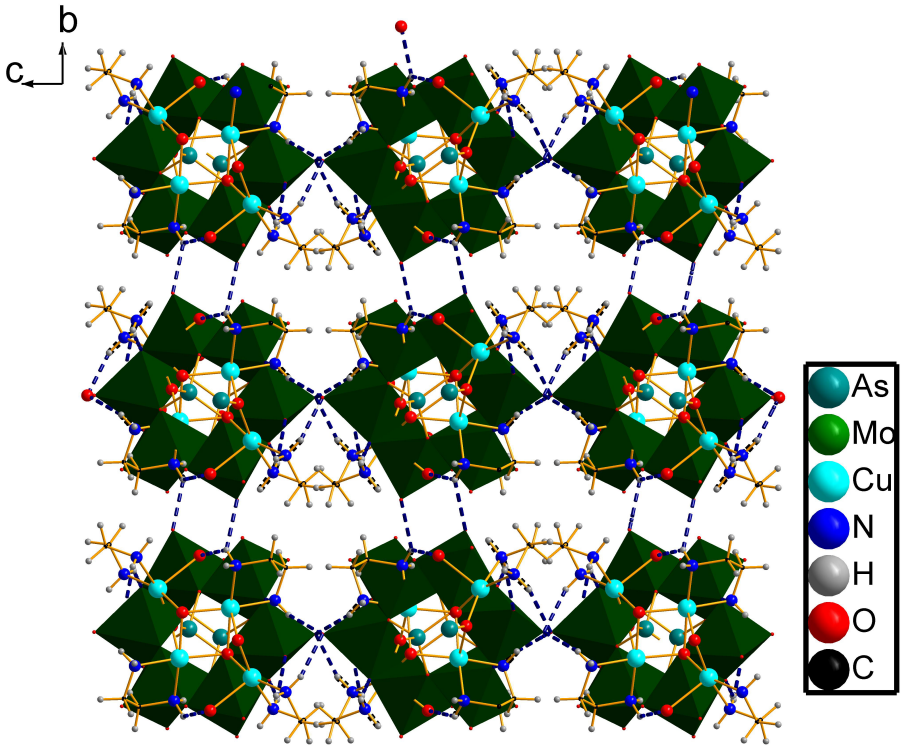

Fig. S6 Polyhedral and ball-stick representation of the 3D supramolecular framework structure of **1** via hydrogen bond.

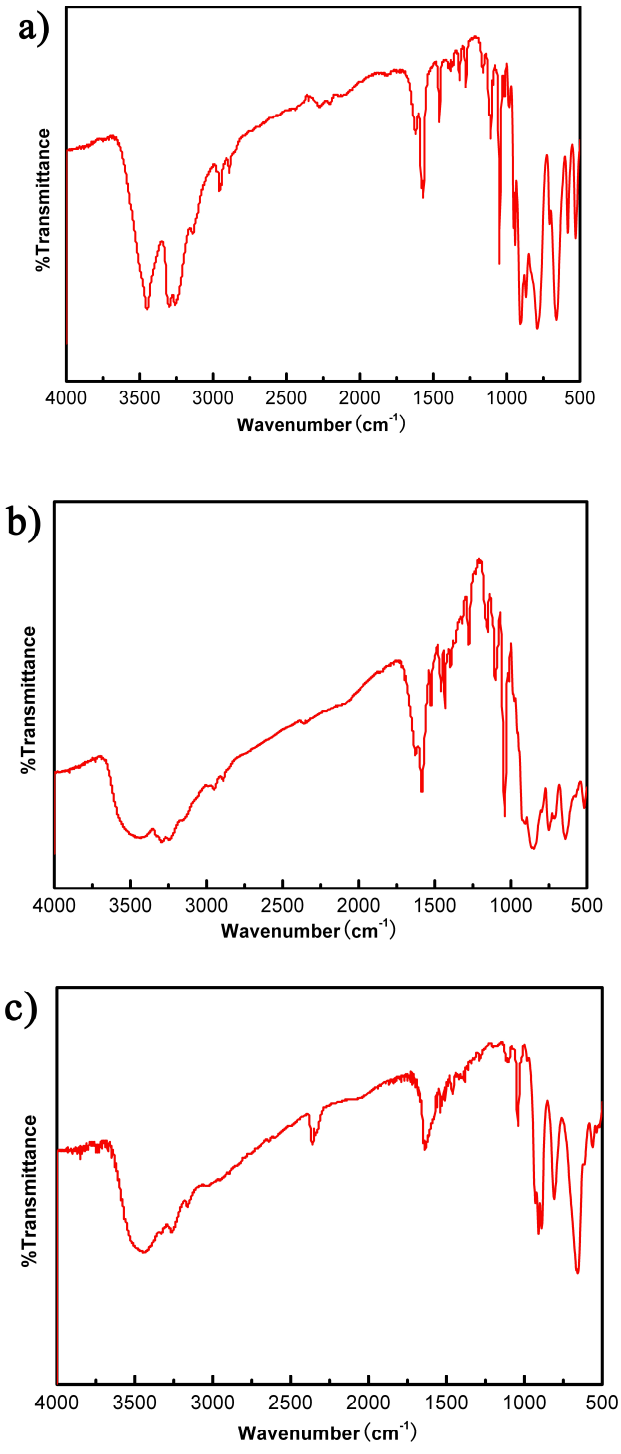

Fig. S7 The IR spectra of **1-3**: a) **1**; b) **2**; c) **3**.

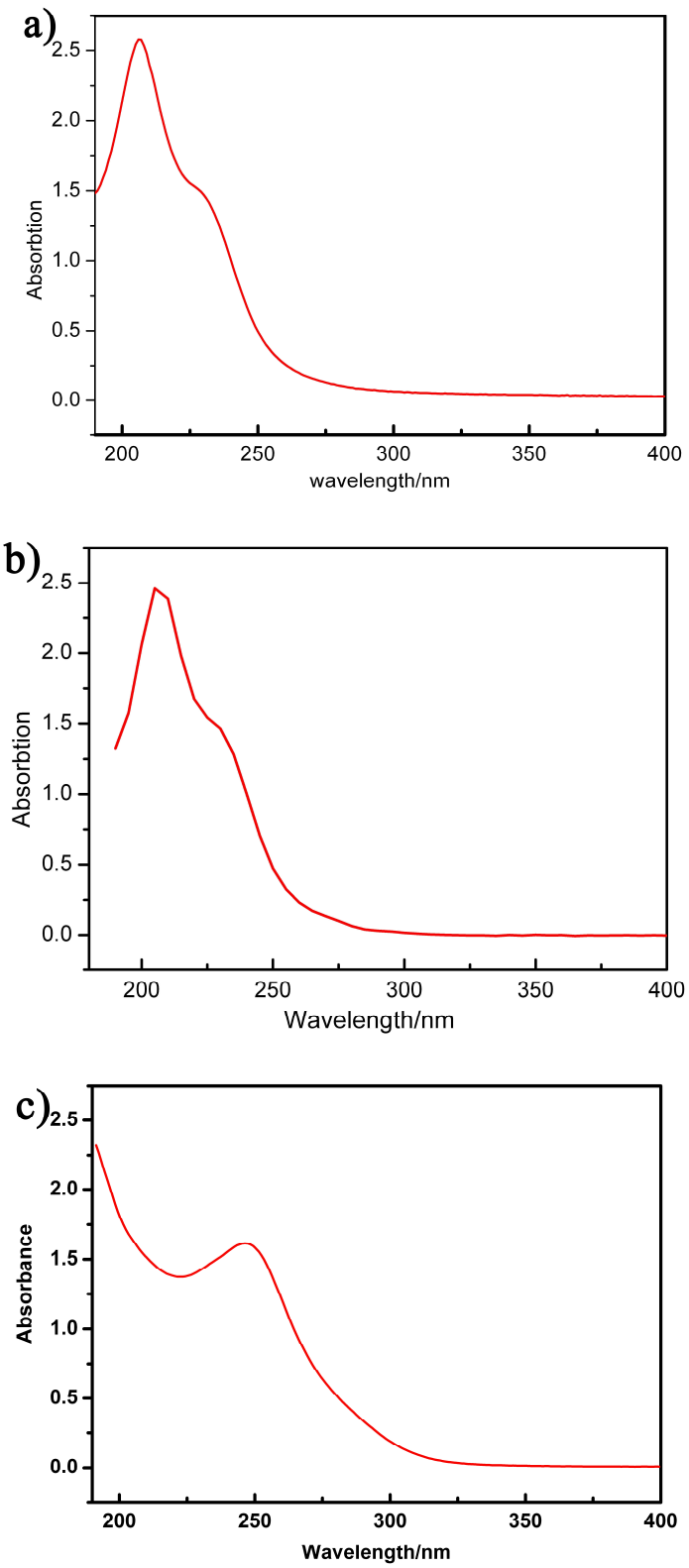

Fig. S8 The UV spectra of **1-3**: a) **1**; b) **2**; c) **3**.

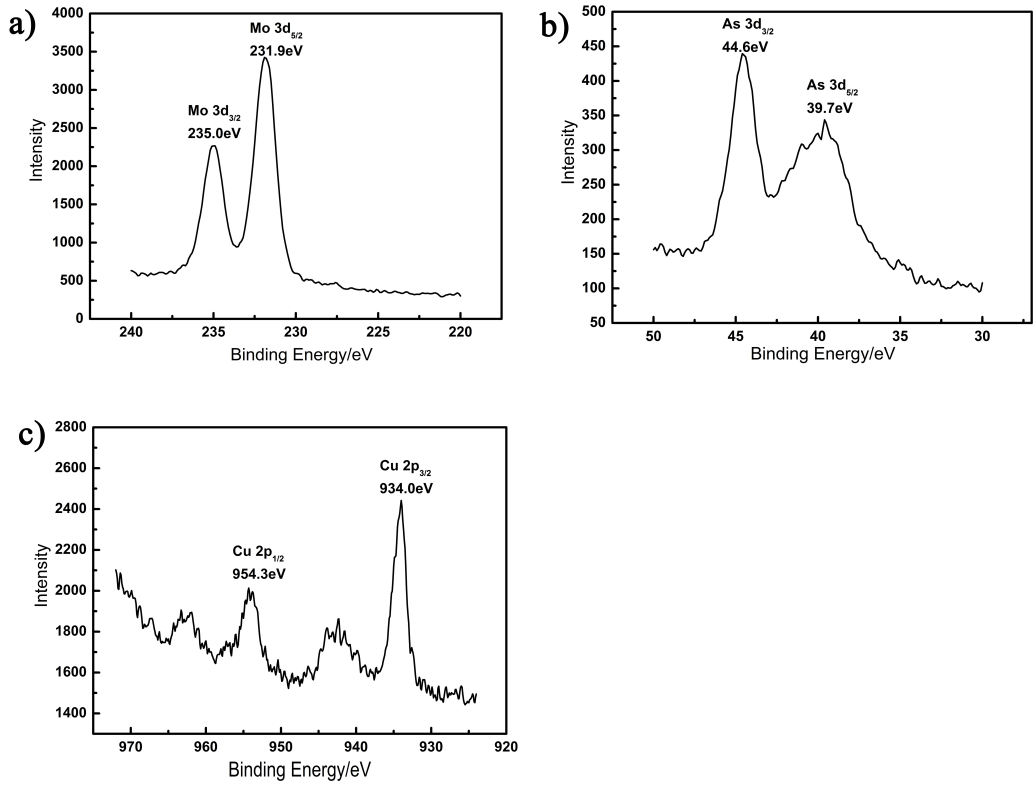

Fig. S9 (a) XPS spectra of **1** for Mo $3d_{5/2}$ and Mo $3d_{3/2}$. (b) XPS spectra of **1** for As $3d_{5/2}$ and As$3d_{3/2}$. (c) XPS spectra of **1** for Cu $2p_{3/2}$ and Cu $2p_{1/2}$.

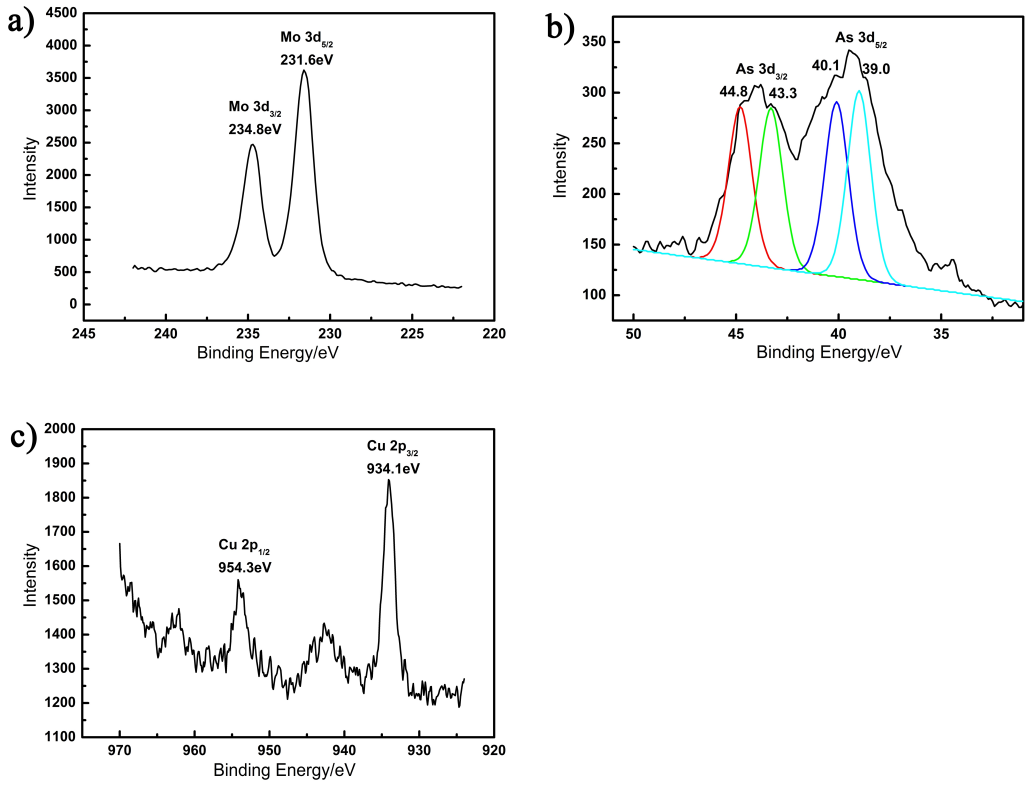

Fig. S10 (a) XPS spectra of **2** for Mo $3d_{5/2}$ and Mo $3d_{3/2}$. (b) XPS spectra of **2** for As $3d_{5/2}$ and As$3d_{3/2}$. (c) XPS spectra of **2** for Cu $2p_{3/2}$ and Cu $2p_{1/2}$.

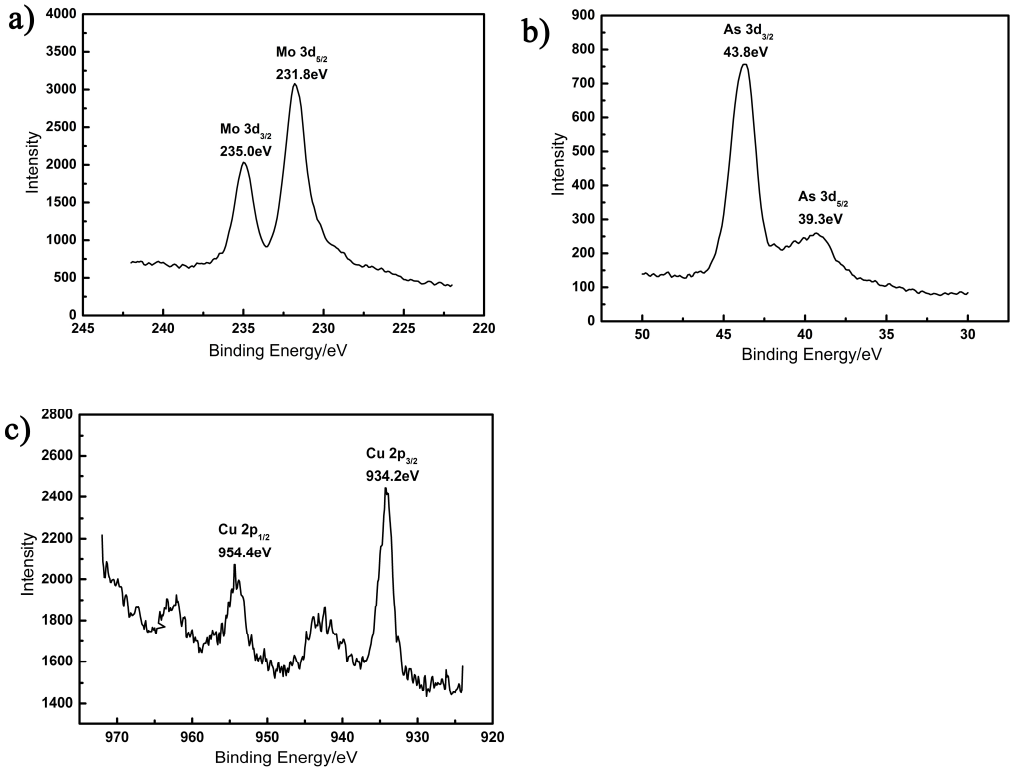

Fig. S11 (a) XPS spectra of **3** for Mo $3d_{5/2}$ and Mo $3d_{3/2}$. (b) XPS spectra of **3** for As $3d_{5/2}$ and As$3d_{3/2}$. (c) XPS spectra of **3** for Cu $2p_{3/2}$ and Cu $2p_{1/2}$.

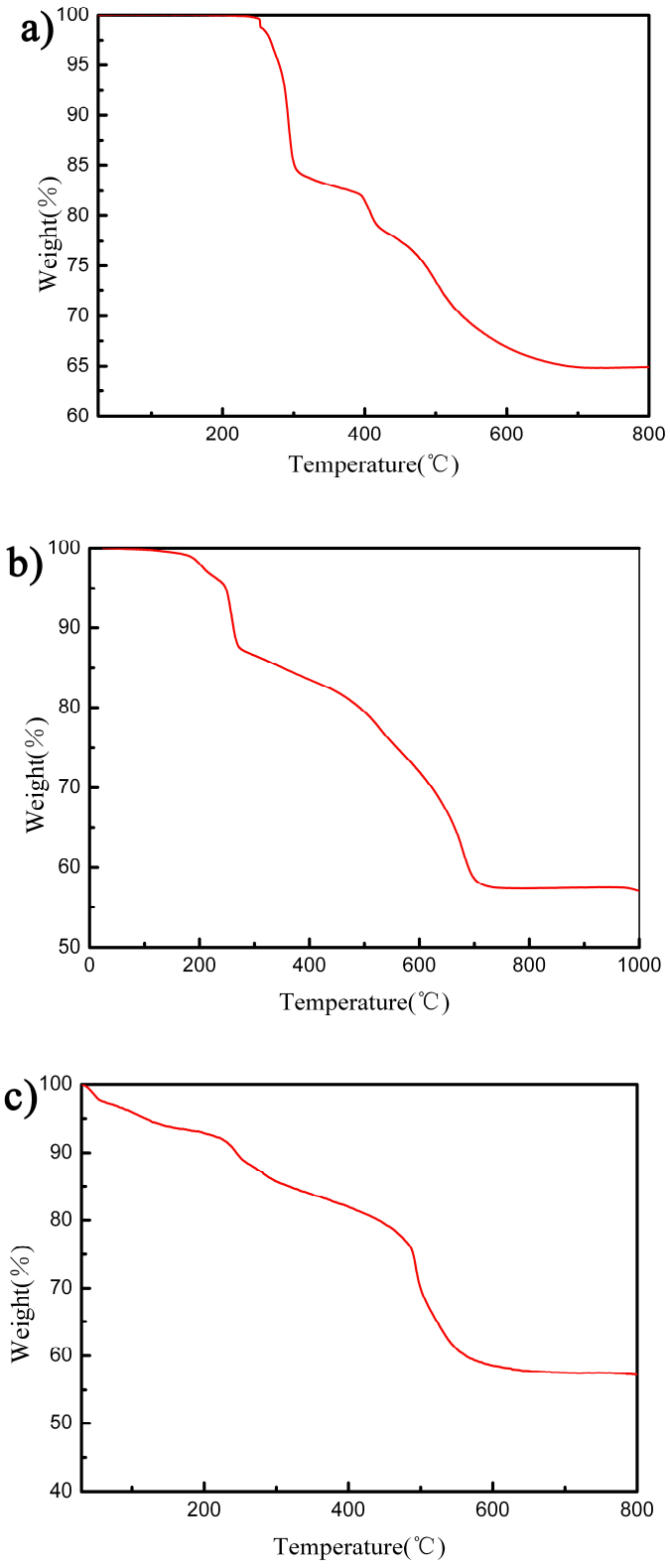

Fig. S12 Thermogravimetric curves of **1-3**: a) **1**; b) **2**; c) **3**.

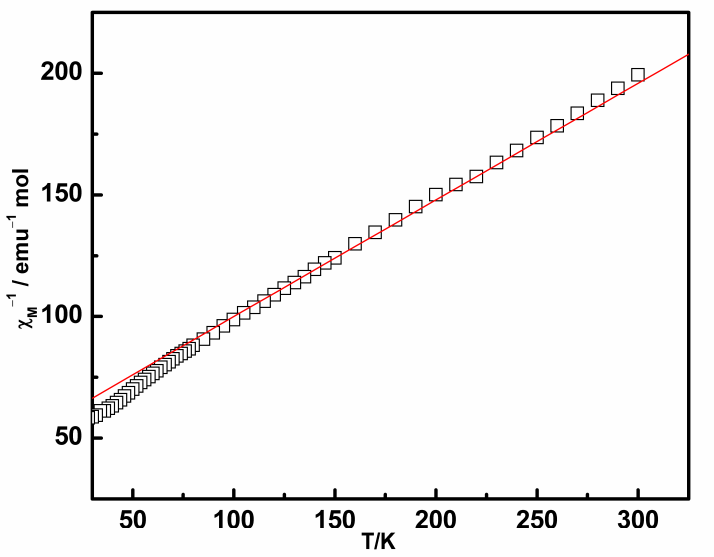

Fig. S13 Temperature evolution of the inverse magnetic susceptibility χ_M^{-1} for 1 between 30 and 300 K.

Table.S1: The summary of detail synthetic information about some representative AM fragments originated from As^{III} atoms relevant to temperature.

Formula	T (ºC)	Synthetic method	Molar ratio of some essential materials	pH
$[MM'(AsMo_7O_{27})_2]^{n-}$ (MM'=FeFe, CrFe and CrCr) [1]	80	solvent evaporation	As_2O_3:$(NH_4)_6Mo_7O_{24}\cdot 2H_2O$:TM =1:2:2	6.5
$(As_6CuMo_6O_{30})\{[Cu(imi)_4]_3[As_6CuMo_6O_{30}]\}_2\cdot 6H_2O$ [2] $[Cu(enMe)_2]_3[As_3Mo_3O_{15}]_3\cdot 2\ H_2O$ $(NH_4)_{10}\{Cu(H_2O)_4\}[AsMo_6O_{21}(OAc)_3]_2\cdot 12H_2O$	90	solvent evaporation	As_2O_3:$(NH_4)_6Mo_7O_{24}\cdot 2H_2O$:imidazole/ 1,2-propane diamine/ Acetic acid= 2.4:0.7:4.8	6.0
$[AgAs_2Mo_{15}O_{54}]^{11-}$ [3]	90	solvent evaporation	As_2O_3:$(NH_4)_6Mo_7O_{24}\cdot 2H_2O$: $AgNO_3$=1:2:1	7.0
$[As^{III}_2Fe^{III}_5MMo_{22}O_{85}(H_2O)]^{n-}$(M = Fe^{3+}, n = 14; M = Ni^{2+} and Mn^{2+}, n =15) [4]	90	solvent evaporation	As_2O_3:$(NH_4)_6Mo_7O_{24}\cdot 2H_2O$=1:2	6.0
$(H_2en)_3[(NiO_6)Mo_6O_{18}\ (As_3O_3)_2]Cl_2\cdot 6H_2O$ [5]	90	solvent evaporation	$NaAsO_2$:$Na_2MoO_4\cdot 2H_2O$:ethylenediamine=1.7:1.7:45	6.1
$(H_3NCH_2CH_2NH_3)_2(H_3O)_2[As^{III}As^{V}Mo^{VI}_9O_{34}]$ [6]	130	hydrothermal conditions	As_2O_3:$Na_2MoO_4\cdot 2H_2O$:ethylenediamine =1:1:1.5	4.4
$[C_5H_6N]_6[HAs^{III}As^{V}Mo^{V}Mo^{VI}_8O_{34}]\cdot 3H_2O$ [7]	130	hydrothermal conditions	$NaAsO_2$:$Na_2MoO_4\cdot 2H_2O$: pyridine=2:1:2	5.0
$[Cu(en)_2H_2O]_2\{[Cu(en)_2][Cu(en)_2As^{III}As^{V}Mo_9O_{34}]\cdot 4H_2O$ [8] $(H_2en)_{1.5}[Cu(en)(Hen)][As^{III}As^{V}Mo_9O_{34}]\cdot 2H_2O$ $[Cu(dap)_2]_4[Cu(dap)_2(H_2O)][Cu(dap)_2(As^{III}As^{V}Mo_9O_{34})_2]\cdot 2H_2O$	130	hydrothermal conditions	As_2O_3:$Na_2MoO_4\cdot 2H_2O$:TM: ethylenediamine/ 1,2-diaminopropane= =0.6:2.0:1.5/1.2:1.2	5.4 4.6 6.4
$Co^{III}(en)3H_3O[(Co^{II}O_6)Mo^{VI}_6O_{18}(As^{III}_3O_3)_2]\cdot 2H_2O$ [9]	135	hydrothermal conditions	As_2O_3:$MoO_3\cdot H_2O$:ethylenediamine =1.2:1:1.2	5.4
$[Cu(imi)_2]_2[(CuO_6)(As_3O_3)_2Mo_6O_{18}][Cu(imi)_2]_2$ [10]	140	hydrothermal conditions	$NaAsO_2$:$(NH_4)_6Mo_7O_{24}\cdot 2H_2O$:imidazole=3.1:1.0:4.0	--
$[H_4As^{III}_2As^{V}Mo^{V}_8Mo^{VI}_4O_{40}]^{-}$ [11]	150	hydrothermal conditions	As_2O_3:MoO_3:NaCl:H_2O = 5:10:10:380	--
$[\{Cu(imi)_2\}_3As_3Mo_3O_{15}]\cdot H_2O$ [12]	160	hydrothermal conditions	$NaAsO_2$:$(NH_4)_6Mo_7O_{24}\cdot 2H_2O$:imidazole=3.1:0.6:4.0	--
$[As(phen)]_2[As_2Mo_2O_{14}]$ [13]	180	hydrothermal conditions	$NaAsO_2$:H_2MoO_4:1,10-phenanthroline =1.6:1.2:1	---
(4,4′-bipy)$[Zn(4,4'\text{-bipy})_2(H_2O)_2]_2[(ZnO_6)(As^{III}_3O)Mo_6O_{18}]\cdot 7H_2O$(1) [14] $[Zn(phen)_2(H_2O)]_2[(ZnO_6)(As^{III}_3O_3)_2Mo_6O_{18}]\cdot 4H_2O$(2) $[Zn(2,2'\text{-bipy})2(H_2O)]_2[(ZnO_6)(As^{III}_3O_3)_2Mo_6O_{18}]\cdot 4H_2O$(3) $[Zn(H4,4'\text{-bipy})_2(H_2O)_4]\ [(ZnO_6)(As^{III}_3O_3)_2Mo_6O_{18}]\cdot 8H_2O$(4)	(1)-(4): 140 (5)-	hydrothermal conditions	$NaAsO_2$:$Na_2MoO_4\cdot 2H_2O$:4,4′-bipyridine/2,2′-bipyridine/1,10-phenanthroline =1:1:0.5	6.84 6.54 6.68 5.20

$(H_2$4,4′-bipy$)[Cu^I$(4,4′-bipy$)]_2[H_2As^V_2Mo_6O_{26}]\cdot H_2O$(5)	(8):			5.40
$(H_2$4,4′-bipy$)_3[H_2As^V_2Mo_6O_{26}]\cdot 4H_2O$(6)	130			3.25
$(H_2$4,4′-bipy$)_3[As^V_2Mo_6O_{26}]\cdot 4H_2O$(7)				3.46
$(H_2$4,4′-bipy$)_{2.5}(H_3O)[As^V_2Mo_6O_{26}(H_2O)]\cdot 1.25H_2O$ (8)				3.42

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