

**Electronic supplementary information (ESI) available for**  
**An unusual fan-type polyanion with a silver cation located at the**  
**axial center,  $[\text{AgAs}^{\text{III}}_2(\text{As}^{\text{III}}\text{As}^{\text{V}}\text{Mo}_4\text{O}_{18}(\text{OH})_2)_3]^{11-}$**

Ying Ma,<sup>a</sup> Qi Xue,<sup>b</sup> Suotian Min,<sup>b</sup> Yanping Zhang,<sup>a</sup> Huaiming Hu,<sup>a</sup> Shengli Gao<sup>a</sup> and  
Ganglin Xue<sup>a,\*</sup>

<sup>a</sup> *Key Laboratory of Synthetic and Natural Functional Molecule Chemistry (Ministry of Education), Department of Chemistry, Northwest University, Xi'an, 710069, China*

<sup>b</sup> *School of Material Science and Engineering, Shaanxi University of Technology, Hanzhong, 723000, China*

\*To whom correspondence should be addressed: [xglin707@163.com](mailto:xglin707@163.com)

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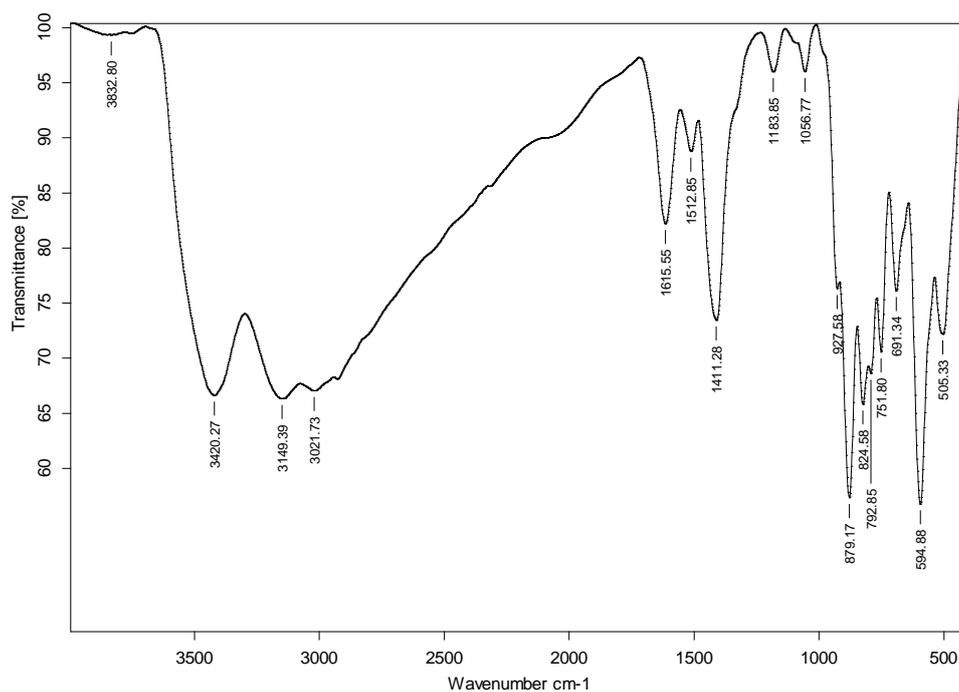
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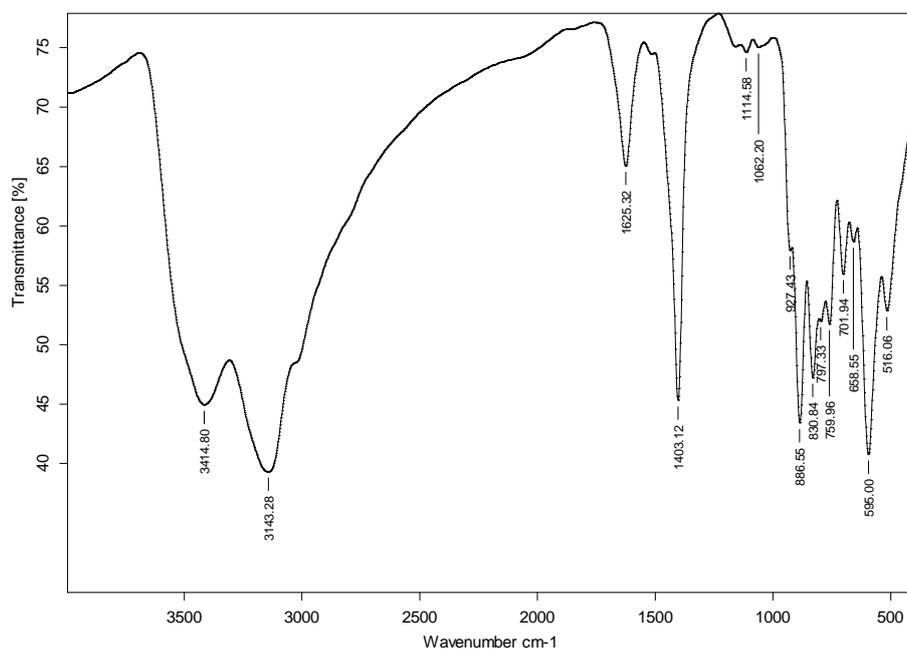
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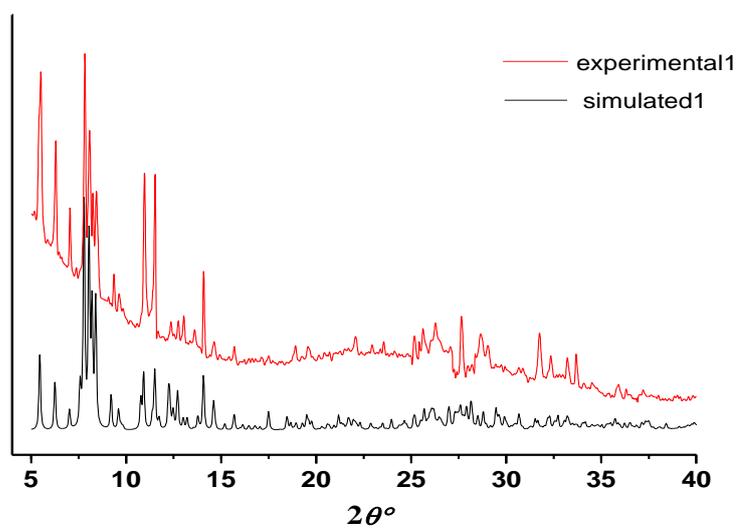


(a)

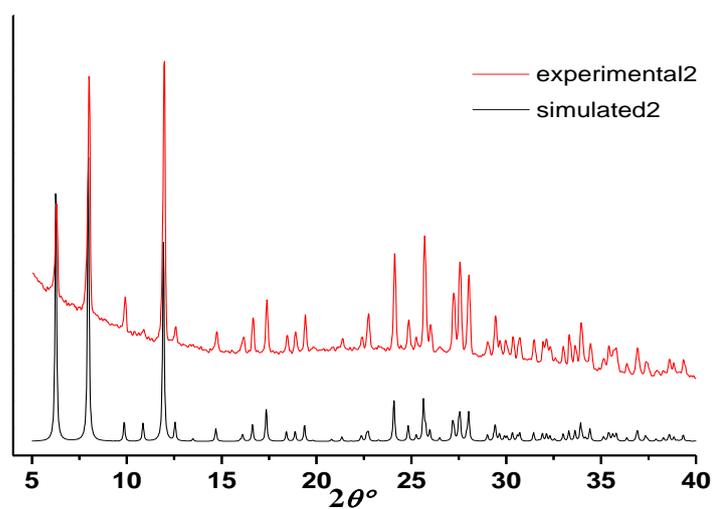


(b)

**Fig. S1** (a) IR spectra of compound 1; (b) IR spectra of compound 2.

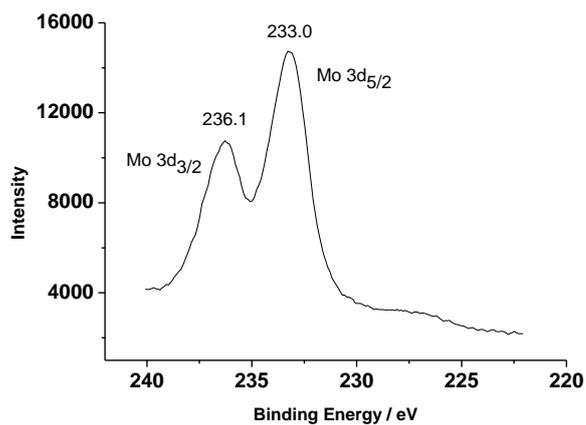


(a)

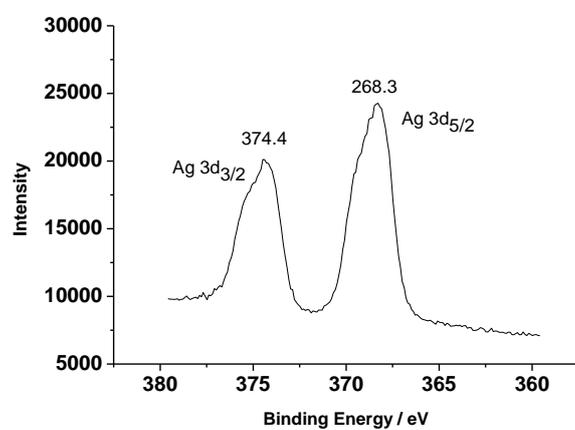


(b)

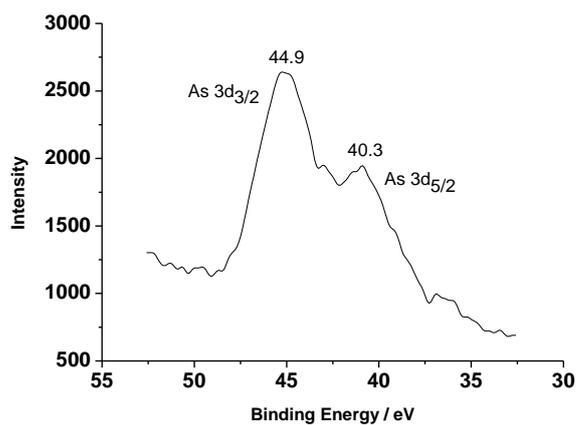
**Fig. S2** (a) Comparison of the simulated and experimental XRD patterns of compound **1**;  
(b) Comparison of the simulated and experimental XRD patterns of compound **2**.



(a)

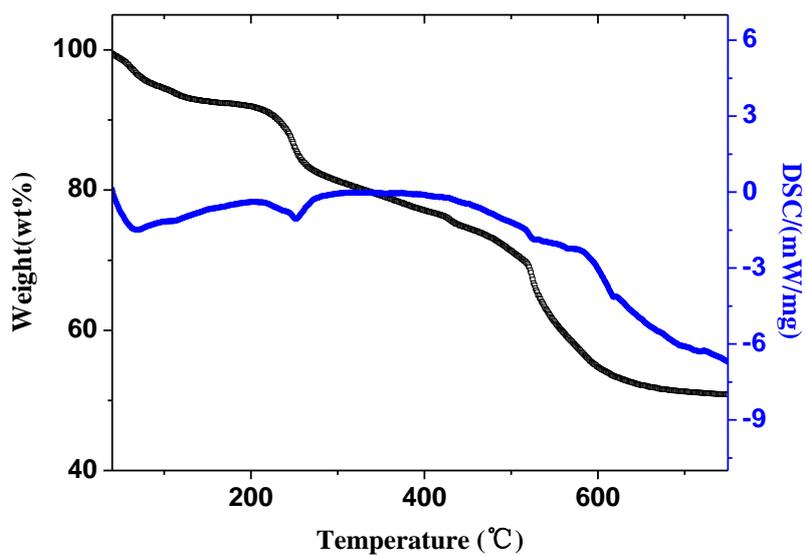


(b)

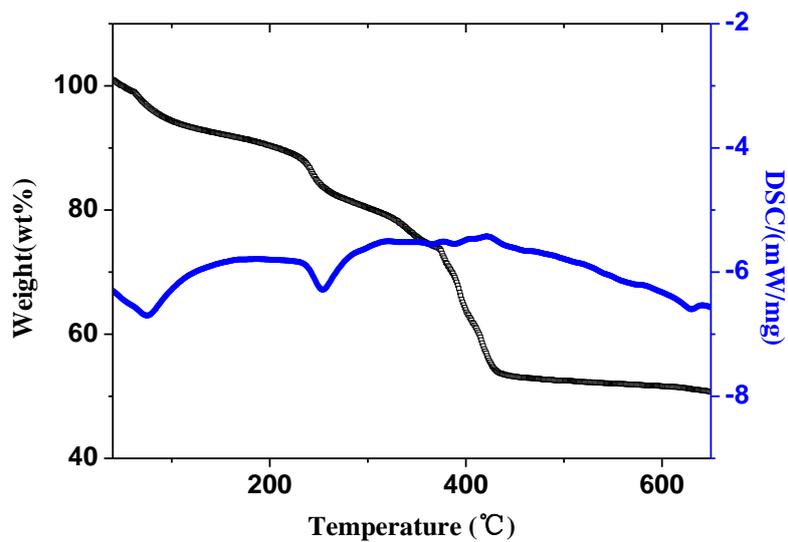


(c)

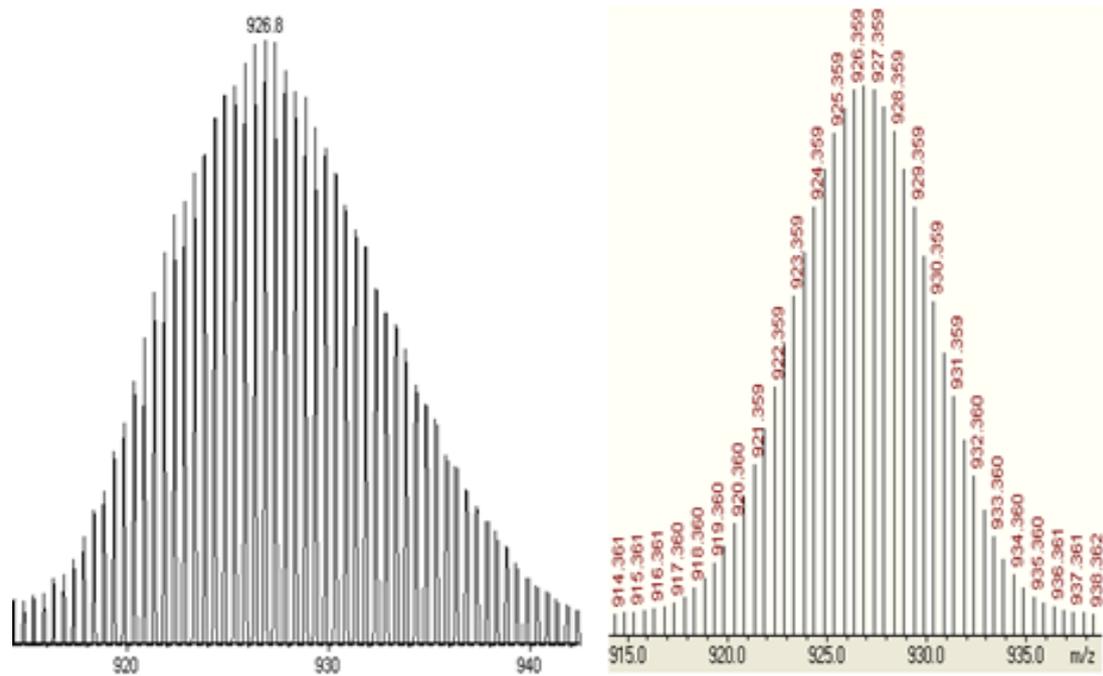
**Fig. S3** (a) XPS spectra of **1** for Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub>. (b) XPS spectra of **1** for Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub>. (c) XPS spectra of **1** for As 3d<sub>5/2</sub> and As 3d<sub>3/2</sub>



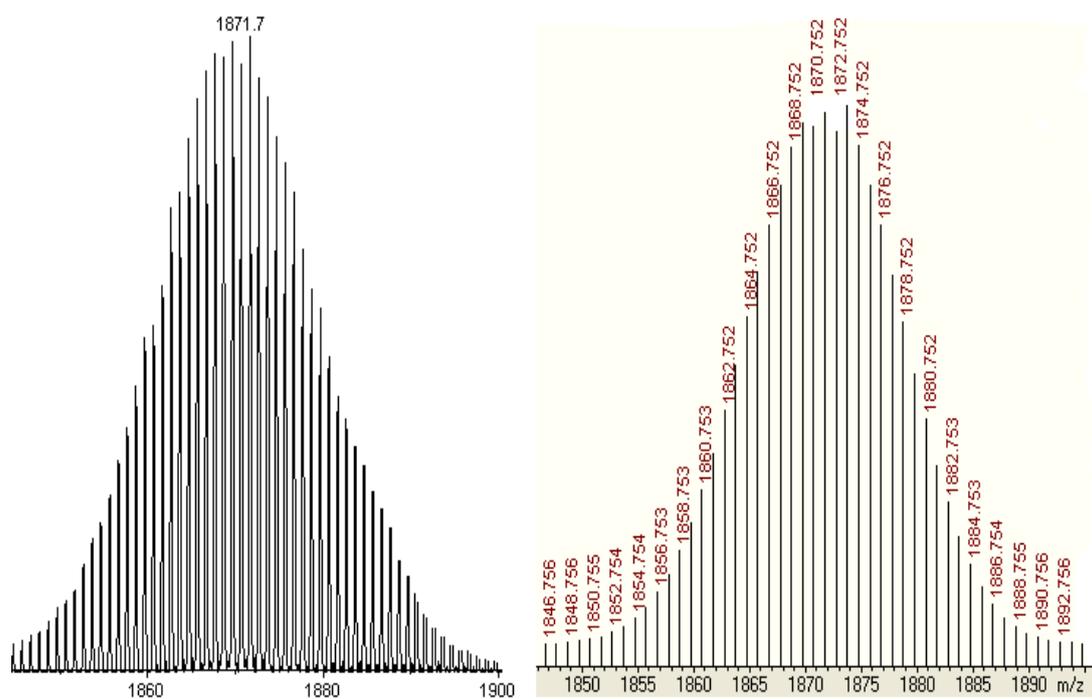
**Fig. S4 (a)** TG-DSC curves of compound **1a**



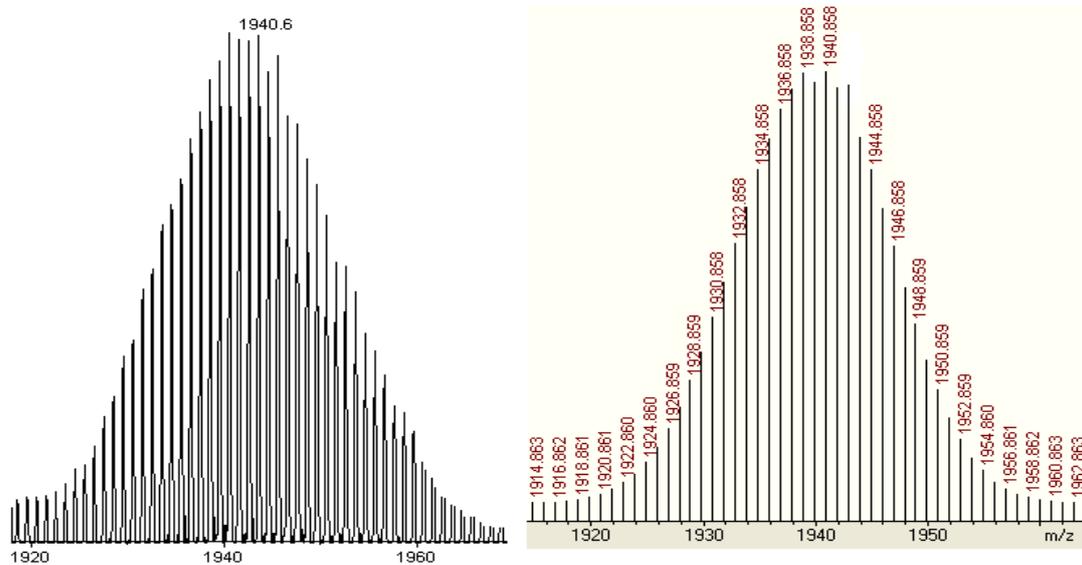
**Fig. S4 (b)** TG-DSC curves of compound **1b**



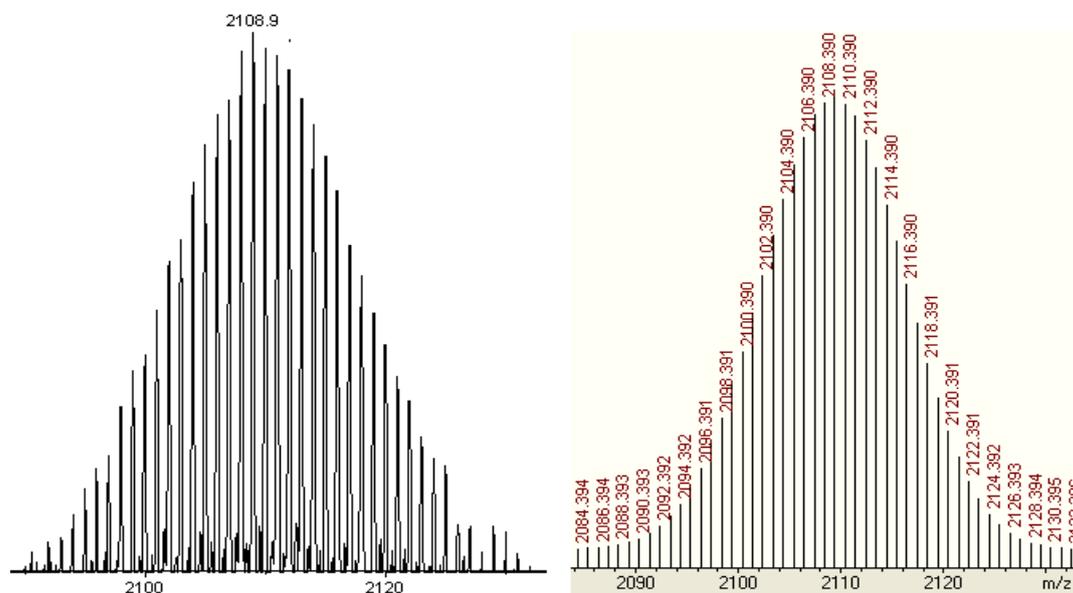
(a)  $[\text{H}_7\text{K}_3(\text{As}_2\text{Mo}_4\text{O}_{18}(\text{OH})_2)_2]^{2-} \cdot \text{H}_2\text{O}$   $m/z = 926.8$



(b)  $[\text{H}_7\text{K}_3\text{NH}_4(\text{As}_2\text{Mo}_4\text{O}_{18}(\text{OH})_2)_2]^- \cdot \text{H}_2\text{O}$   $m/z = 1871.7$



(c)  $[\text{H}_3\text{K}_3(\text{NH}_4)_5(\text{As}_2\text{Mo}_4\text{O}_{18}(\text{OH})_2)_2] \cdot \text{H}_2\text{O}$   $m/z = 1940.6$



(d)  $[\text{K}_3\text{NaAgAs}^{\text{III}}_4\text{As}^{\text{V}}_2\text{Mo}_8\text{O}_{36}(\text{OH})_4]^-$   $m/z = 2108.9$

**Fig. S5** Comparison of the experimental (left) and simulated isotopic envelope (right) for the peak at (a)  $m/z = 926.8$ ; (b)  $m/z = 1871.7$ ; (c)  $m/z = 1940.6$  and (d)  $m/z = 2108.9$ .