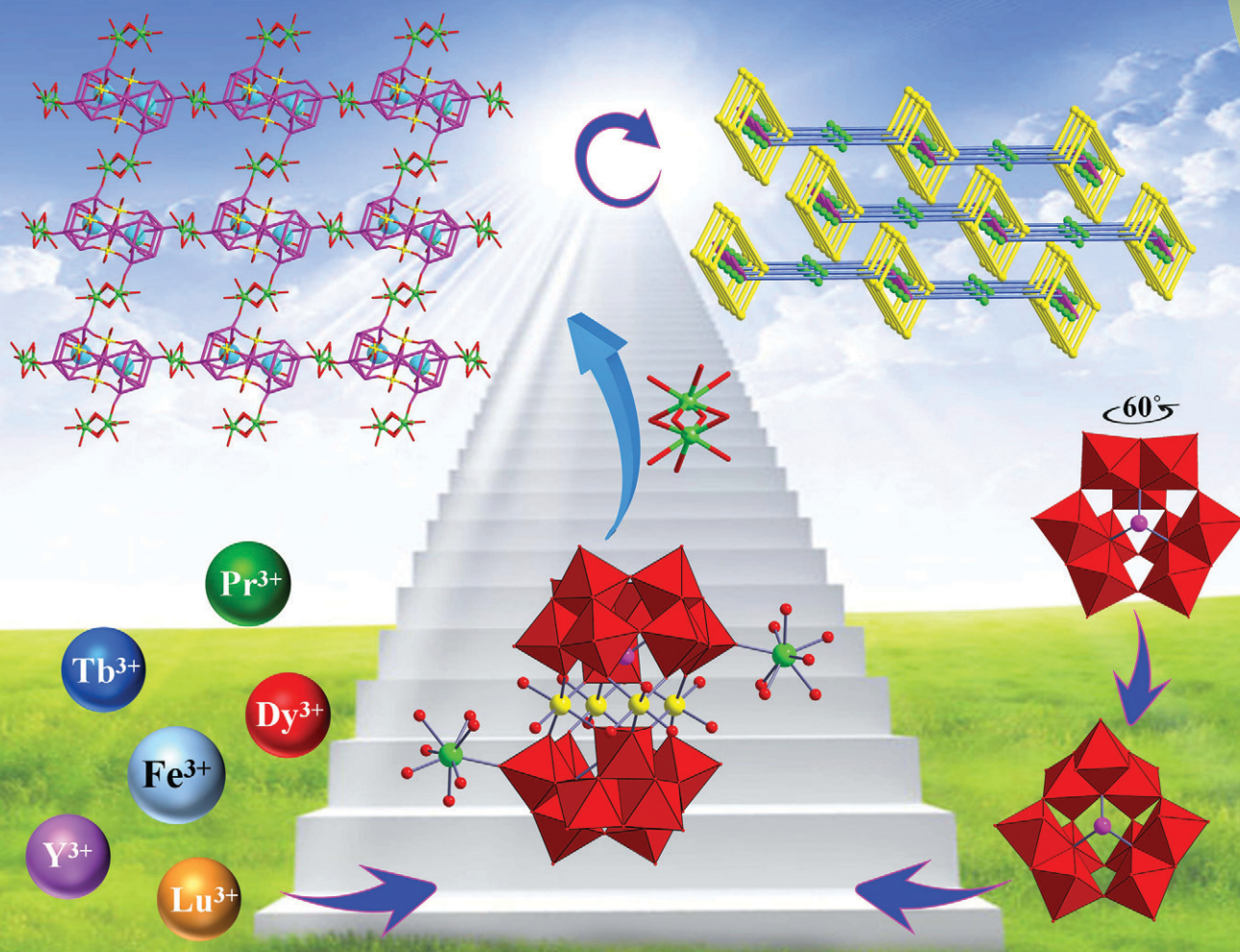


# CrystEngComm

www.rsc.org/crystengcomm



PAPER

Jie Luo, Junwei Zhao *et al.*

The first purely inorganic polyoxotungstates constructed from dimeric tungstoantimonate-based iron–rare-earth heterometallic fragments


 CrossMark  
click for updates

 Cite this: *CrystEngComm*, 2015, 17, 5002

# The first purely inorganic polyoxotungstates constructed from dimeric tungstoantimonate-based iron-rare-earth heterometallic fragments†

Lijuan Chen, Jing Cao, Xinghua Li, Xing Ma, Jie Luo\* and Junwei Zhao\*

The rational self-assembly of a trilacunary Keggin precursor with Fe<sup>3+</sup> and RE<sup>3+</sup> (rare-earth) ions via a conventional aqueous solution method has led to a series of novel tungstoantimonate-based Fe-RE heterometallic derivatives [Pr(H<sub>2</sub>O)<sub>8</sub>][Pr(H<sub>2</sub>O)<sub>6</sub>][Fe<sub>4</sub>(H<sub>2</sub>O)<sub>10</sub>(B-β-SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>·16H<sub>2</sub>O (1) and [RE(H<sub>2</sub>O)<sub>7</sub>]<sub>2</sub>[Fe<sub>4</sub>(H<sub>2</sub>O)<sub>10</sub>(B-β-SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>·22H<sub>2</sub>O [RE = Tb<sup>III</sup> (2), Dy<sup>III</sup> (3), Lu<sup>III</sup> (4), Y<sup>III</sup> (5)], which have been further structurally characterized by elemental analysis, IR spectroscopy, powder X-ray diffraction (PXRD), single-crystal X-ray diffraction and thermogravimetric (TG) analysis. To the best of our knowledge, 1–5 represent the first purely inorganic Fe-RE heterometallic tungstoantimonates based on the trilacunary Keggin [B-β-SbW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> unit. In 1, the tetra-Fe<sup>III</sup> substituted sandwich-type unit [Fe<sub>4</sub>(H<sub>2</sub>O)<sub>10</sub>(B-β-SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]<sup>6-</sup> is built up of two trilacunary Keggin subunits [B-β-SbW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> sandwiching a rhomb-like {Fe<sup>III</sup><sub>4</sub>} cluster, and then the disordered Pr<sup>III</sup> cations work as bridges that link adjacent sandwich-type units [Fe<sub>4</sub>(H<sub>2</sub>O)<sub>10</sub>(B-β-SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]<sup>6-</sup>, giving rise to the first 2-D extended sheet based on tungstoantimonate fragments and Fe-RE heterometallic cations. 2–5 are isomorphic and exhibit a discrete structure composed of a tetra-Fe<sup>III</sup> substituted sandwich-type unit [Fe<sub>4</sub>(H<sub>2</sub>O)<sub>10</sub>(B-β-SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]<sup>6-</sup> and two supporting [RE(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup> cations. The electrochemical and electrocatalytic properties of 1 and 2 have been investigated in detail in a 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> supporting electrolyte, and both 1 and 2 illustrate obvious electrocatalytic activity toward the reduction of NO<sub>2</sub><sup>-</sup> and BrO<sub>3</sub><sup>-</sup>.

 Received 31st March 2015,  
Accepted 12th May 2015

DOI: 10.1039/c5ce00633c

[www.rsc.org/crystengcomm](http://www.rsc.org/crystengcomm)

## Introduction

It is well known that the featured oxygen-enriched surfaces, high negative charges and controllable sizes of lacunary polyoxometalate (POM) precursors derived from several classic polyoxoanions (POAs), such as the Keggin type {XM<sub>12</sub>O<sub>40</sub>}, Dawson type {X<sub>2</sub>M<sub>18</sub>O<sub>62</sub>}, and Lindqvist type {M<sub>6</sub>O<sub>19</sub>}, are the reasons why they are often recommended as excellent multidentate inorganic ligands that link various transition-metal (TM) or rare-earth (RE) cations into novel polynuclear functional aggregates with diverse metal nuclearities, beautiful structural topologies and unique properties.<sup>1</sup> Among the well-known class of TM or RE containing POM aggregates, the sandwich-type POM-based derivatives have been widely explored. Within the class of those species, the sandwich-type species constructed from two trivalent Keggin [α-XW<sub>9</sub>O<sub>34</sub>]<sup>9/10-</sup> (X = Si<sup>IV</sup>, Ge<sup>IV</sup>, P<sup>V</sup>, As<sup>V</sup>) or Dawson [α-X<sub>2</sub>W<sub>15</sub>O<sub>56</sub>]<sup>12-</sup> (X = P<sup>V</sup>,

As<sup>V</sup>) fragments and a TM core probably represent the best known and most studied subfamily since the first rhomb-like tetra-Co<sup>II</sup> substituted sandwich-type species [Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(B-α-PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]<sup>10-</sup> was reported by Weakley *et al.* in 1973.<sup>2</sup> The existence of Sb<sup>III</sup>-containing POMs has been known for a long time,<sup>3</sup> and most of the published findings are based on the trivalent Keggin [SbW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> fragment. Among these tungstoantimonates (TAs), a majority of them are dimeric sandwich-type structures constructed from two trivalent Keggin [SbW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> fragments encapsulating a metal cluster. In 1997, Krebs *et al.* firstly reported the synthesis approaches of the [B-α-SbW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> POA and the dimeric Krebs-type sandwich [Sb<sub>2</sub>W<sub>22</sub>O<sub>74</sub>(OH)<sub>2</sub>]<sup>12-</sup> POA,<sup>4</sup> where the [Sb<sub>2</sub>W<sub>22</sub>O<sub>74</sub>(OH)<sub>2</sub>]<sup>12-</sup> POA is composed of two trivalent Keggin-type segments [B-β-SbW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> joined *via* a sandwich belt of two interior {WO<sub>2</sub>}<sup>2+</sup> and two exterior {WO(OH)<sub>2</sub>}<sup>2+</sup> groups. Subsequently, Krebs and co-workers showed that two exterior {WO(OH)<sub>2</sub>}<sup>2+</sup> moieties can be substituted by extraneous {M(H<sub>2</sub>O)<sub>3</sub>}<sup>2+/3+</sup> fragments, leading to the TM-substituted [Sb<sub>2</sub>W<sub>20</sub>M<sub>2</sub>O<sub>70</sub>(H<sub>2</sub>O)<sub>6</sub>]<sup>n-</sup> POAs (M = Fe<sup>III</sup>, Co<sup>II</sup>, Mn<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>).<sup>5,6</sup> From then on, the continuous interest in exploring TM-substituted Krebs-type TAs has persisted and the rate of discovering novel derivatives has been steadily growing. As we know, the groups of Proust, Kortz, Bi and Wang all

Henan Key Laboratory of Polyoxometalate Chemistry, Institute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, PR China. E-mail: luojie@henu.edu.cn, zhaojunwei@henu.edu.cn

† Electronic supplementary information (ESI) available: Additional data. CSD 429364–429368 for 1–5. See DOI: 10.1039/c5ce00633c

demonstrated that two exterior  $\{\text{WO}(\text{OH})_2\}^{2+}$  moieties of this structure-type can be easily replaced by organometallic groups forming novel organometallic derivatives such as  $[\text{Sb}_2\text{W}_{20}\text{O}_{70}(\text{Ru}(p\text{-cymene}))_2]^{10-}$ ,<sup>7</sup>  $[\text{Sb}_2\text{W}_{20}\text{O}_{70}(\text{RuC}_6\text{H}_6)_2]^{10-}$ ,<sup>8</sup>  $[\text{Sb}_2\text{W}_{20}\text{O}_{70}(\text{RuC}_{10}\text{H}_{14})_2]^{10-}$ ,<sup>8</sup>  $[\text{Sb}_2\text{W}_{20}\text{Ru}_2(\text{H}_2\text{O})_2(\text{dmsO})_6\text{O}_{68}]^{4-}$ ,<sup>9</sup> and  $[\{\text{Sn}(\text{C}_4\text{H}_6\text{O}_2)(\text{H}_2\text{O})\}_2(\text{WO}_2)_2(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2]^{10-}$ .<sup>10</sup> On the other hand, Kortz *et al.* also showed that adamantane-like  $\{\text{Ru}_4\text{O}_6(\text{H}_2\text{O})_9\}^{4+}$  cluster units were able to take the place of two terminal  $\{\text{WO}(\text{OH})_2\}^{2+}$  groups.<sup>11</sup> Furthermore, Hill's group prepared two Krebs-type metal carbonyl complexes  $\text{Na}_{11}\text{H}[\text{Sb}_2\text{W}_{20}\text{O}_{70}(\text{Re}(\text{CO})_3)_2]\cdot 34\text{H}_2\text{O}$  and  $\text{K}_9\text{Na}_3[\text{Sb}_2\text{W}_{20}\text{O}_{70}(\text{Mn}(\text{CO})_3)_2]\cdot 32\text{H}_2\text{O}$ ,<sup>12</sup> in which two tricarbonyl  $\{\text{M}(\text{CO})_3\}^+$  cations substitute two  $\{\text{WO}(\text{OH})_2\}^{2+}$  moieties on the Krebs-type POM skeleton. Later, Kortz evidenced that two inner and two outer W centers in the Krebs-type TA can be substituted by TM cations, resulting in  $[\text{M}_4(\text{H}_2\text{O})_{10}(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  ( $\text{M} = \text{Fe}^{\text{III}}$ ,  $\text{Al}^{\text{III}}$ ).<sup>13,14</sup> Very recently, Reinoso *et al.* also obtained a series of organic functionalization derivatives of TM-substituted Krebs-type POMs  $[\{\text{M}(\text{imc})(\text{H}_2\text{O})\}_2(\text{WO}_2)_2(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2]^{12-}$  ( $\text{M} = \text{Mn}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ) and  $[\{(2,3\text{-pyzdc})_2(\text{NaNi}_2(\text{H}_2\text{O})_4\text{Sb}_2\text{W}_{20}\text{O}_{70})_2\}]^{22-}$ .<sup>15</sup> Meanwhile, the other structure types of TM-substituted derivatives based on trilacunary  $[\text{SbW}_9\text{O}_{33}]^{9-}$  fragments have also been reported. Some representative examples are listed here: Cronin *et al.* isolated a monotitanium embedded POA  $[\text{Na}_5\text{TiO}(\text{B-}\alpha\text{-SbW}_9\text{O}_{33})_2]^{11-}$ , which is composed of two  $[\text{B-}\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$  fragments linked by five sodium ions and a unique square pyramidal  $\text{Ti}(\text{O})\text{O}_4$  group.<sup>16</sup> Pope *et al.* synthesized a di- $\text{UO}_2^{2+}$  sandwiched TA  $[(\text{UO}_2)_2(\text{H}_2\text{O})_2(\text{SbW}_9\text{O}_{33})_2]^{14-}$ .<sup>17</sup> A number of Hervé-type trinuclear substituted sandwich-type TAs were also discovered by several groups with various metal nuclearities ( $\text{Cu}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Mn}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Pd}^{\text{II}}$ ).<sup>18</sup> And a unique hexanuclear substituted sandwich-type TA  $[(\text{MnCl})_6(\text{B-}\alpha\text{-SbW}_9\text{O}_{33})_2]^{12-}$  was communicated by Yamase and co-workers.<sup>19a</sup> Moreover, Hill's group reported a molecular highly unusual feature tetramer  $[\{\text{Na}(\mu\text{-OH}_2)(\text{OH}_2)_2\}_6\{\text{Sn}_6(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2\}]^{16-}$ .<sup>19b</sup> In contrast to TM-substituted TAs, there are few reports on RE-substituted TAs including an unprecedented  $\text{Ce}^{\text{III}}$ -containing derivative  $[(\text{SbW}_9\text{O}_{33})_4(\text{WO}_2(\text{H}_2\text{O}))_2\text{Ce}_3(\text{H}_2\text{O})_8(\text{Sb}_4\text{O}_4)]^{19-}$ ,<sup>20</sup> a  $\text{Y}^{\text{III}}$ -containing trimer  $[\{\text{Y}(\alpha\text{-SbW}_9\text{O}_{31}(\text{OH})_2)(\text{CH}_3\text{COO})(\text{H}_2\text{O})\}_3(\text{WO}_4)]^{17-}$  that is composed of three  $[\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$  segments linked by three  $\text{Y}^{\text{III}}$  ions and a capping, tetrahedral  $\text{WO}_4^{2-}$  group,<sup>21</sup> and two inorganic sandwich-type dimers  $[\text{RE}(\text{H}_2\text{O})_4\text{Sb}_2\text{W}_{21}\text{O}_{72}(\text{OH})]^{10-}$  ( $\text{RE} = \text{Yb}^{\text{III}}$ ,  $\text{Lu}^{\text{III}}$ ) and  $[\text{RE}_2(\text{H}_2\text{O})_8(\text{Sb}_2\text{W}_{20}\text{O}_{70})]^{8-}$  ( $\text{RE} = \text{Yb}^{\text{III}}$ ,  $\text{Lu}^{\text{III}}$ ,  $\text{Y}^{\text{III}}$ ).<sup>22</sup> However, to our knowledge, the research on TM-RE heterometallic TAs containing the trilacunary  $[\text{SbW}_9\text{O}_{33}]^{9-}$  fragments remains largely undeveloped. Under this background, we have isolated a family of organic-inorganic hybrid TM-RE heterometallic TAs with amino acid ligands  $[\text{RE}(\text{H}_2\text{O})_8]_2[\text{Fe}_4(\text{H}_2\text{O})_8(\text{thr})_2][\text{B-}\beta\text{-SbW}_9\text{O}_{33}]_2\cdot 22\text{H}_2\text{O}$  ( $\text{RE} = \text{Pr}^{\text{III}}$ ,  $\text{Nd}^{\text{III}}$ ,  $\text{Sm}^{\text{III}}$ ,  $\text{Eu}^{\text{III}}$ ,  $\text{Gd}^{\text{III}}$ ,  $\text{Dy}^{\text{III}}$ ,  $\text{Lu}^{\text{III}}$ ).<sup>23</sup> As a part of our continuous work, herein, we report a series of  $[\text{B-}\beta\text{-SbW}_9\text{O}_{33}]^{9-}$ -based 3d-4f heterometallic purely inorganic POMs  $[\text{Pr}(\text{H}_2\text{O})_8][\text{Pr}(\text{H}_2\text{O})_6][\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2]\cdot 16\text{H}_2\text{O}$  (1) and  $[\text{RE}(\text{H}_2\text{O})_2]_2[\text{Fe}_4(\text{H}_2\text{O})_{10}][\text{B-}\beta\text{-SbW}_9\text{O}_{33}]_2\cdot 22\text{H}_2\text{O}$  ( $\text{RE} = \text{Tb}^{\text{III}}$  (2),

$\text{Dy}^{\text{III}}$  (3),  $\text{Lu}^{\text{III}}$  (4),  $\text{Y}^{\text{III}}$  (5)). Their common characteristic is that they comprise a tetra- $\text{Fe}^{\text{III}}$  substituted sandwich-type unit  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  with the bonding RE ingredients on their surface. 1 displays the 2-D extended sheet constructed from the tetra- $\text{Fe}^{\text{III}}$  substituted sandwich-type units  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  through  $\text{Pr}^{\text{III}}$  linkers, whereas the molecular structures of 2-5 consist of a tetra- $\text{Fe}^{\text{III}}$  substituted sandwich-type unit  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  and two supporting  $[\text{RE}(\text{H}_2\text{O})_8]^{3+}$  cations. As far as we know, 1-5 stand for the first purely inorganic TM-RE heterometallic TAs. The electrochemical and electrocatalytic properties of 1 and 2 have been investigated in detail.

## Experimental

### Materials and physical measurements

The trilacunary precursor  $\text{Na}_9[\text{B-}\alpha\text{-SbW}_9\text{O}_{33}]\cdot 19.5\text{H}_2\text{O}$  was synthesized as previously described<sup>4</sup> and further identified by IR spectroscopy. All other reagents were used as purchased without further purification. Hydrogen elemental analysis was performed on a Perkin-Elmer 2400-II CHNS/O analyzer. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed using a Perkin-Elmer Optima 2000 ICP-AES spectrometer. IR spectra were recorded with a Nicolet FT-IR 360 spectrometer using KBr pellets in the range of  $4000\text{--}400\text{ cm}^{-1}$ . Powder X-ray diffraction (PXRD) patterns were collected using a Bruker D8 ADVANCE instrument with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056\text{ \AA}$ ). Cyclic voltammograms were recorded on a CS electrochemical workstation (Wuhan CorrTest Instrument Co. Ltd) at room temperature. Twice-distilled water was used throughout the experiments. A conventional three-electrode system was used. The working electrode was a glassy carbon, a platinum gauze was used as a counter electrode and an  $\text{Ag}/\text{AgCl}$  electrode was referenced. The supporting electrolyte of 1 and 2 was  $0.5\text{ mol L}^{-1}\text{ Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$  aqueous solution. TG analyses were carried out under a  $\text{N}_2$  atmosphere using a Mettler-Toledo TGA/SDTA 851e instrument with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  from 25 to  $750\text{ }^\circ\text{C}$ .

### Preparations of 1-7

$[\text{Pr}(\text{H}_2\text{O})_8][\text{Pr}(\text{H}_2\text{O})_6][\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2]\cdot 16\text{H}_2\text{O}$  (1).  $\text{Na}_9[\text{B-}\alpha\text{-SbW}_9\text{O}_{33}]\cdot 19.5\text{H}_2\text{O}$  (0.200 g, 0.070 mmol),  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  (0.032 g, 0.118 mmol), and  $\text{PrCl}_3\cdot 6\text{H}_2\text{O}$  (0.070 g, 0.197 mmol) were dissolved in 15 mL of water with stirring and the pH value of the solution was carefully adjusted to 0.5 using a dilute HCl solution ( $4\text{ mol L}^{-1}$ ). The solution was stirred for 2 h, heated at  $80\text{ }^\circ\text{C}$  for 2 h and then filtered when it cooled to room temperature. Slow evaporation of the filtrate at room temperature led to green yellow cubic block crystals of 1 for several days. Yield: ca. 33% (based on  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ ). Anal. calcd. (found %) for  $\text{H}_{80}\text{Fe}_4\text{O}_{106}\text{Pr}_2\text{Sb}_2\text{W}_{18}$  (1): H 1.38 (1.57), Fe 3.83 (3.71), Pr 4.83 (4.66), Sb 4.17 (4.38), W 56.72 (56.59). IR (KBr pellets,  $\text{cm}^{-1}$ ): 3393(vs), 1634(s), 957(m), 889(w), 777(vs), 662(m), 472(w), 418(w).



[Tb(H<sub>2</sub>O)<sub>7</sub>]<sub>2</sub>[Fe<sub>4</sub>(H<sub>2</sub>O)<sub>10</sub>][B-β-SbW<sub>9</sub>O<sub>33</sub>]<sub>2</sub>·22H<sub>2</sub>O (2). The synthesis process of 2 is similar to 1, except that TbCl<sub>3</sub>·6H<sub>2</sub>O (0.070 g, 0.187 mmol) replaced PrCl<sub>3</sub>·6H<sub>2</sub>O. Yield: ca. 30% (based on FeCl<sub>3</sub>·6H<sub>2</sub>O). Anal. calcd. (found %) for H<sub>92</sub>Fe<sub>4</sub>O<sub>112</sub>Sb<sub>2</sub>W<sub>18</sub>Tb<sub>2</sub> (2): H 1.55 (1.64), Fe 3.74 (3.64), Tb 5.32 (5.40), Sb 4.07 (4.00), W 55.35 (55.45). IR (KBr pellets, cm<sup>-1</sup>): 3397(vs), 1643(s), 953(m), 883(w), 783(vs), 649(m), 474(w), 421(w).

[Dy(H<sub>2</sub>O)<sub>7</sub>]<sub>2</sub>[Fe<sub>4</sub>(H<sub>2</sub>O)<sub>10</sub>][B-β-SbW<sub>9</sub>O<sub>33</sub>]<sub>2</sub>·22H<sub>2</sub>O (3). The synthesis process of 3 is similar to 1, except that DyCl<sub>3</sub>·6H<sub>2</sub>O (0.100 g, 0.265 mmol) replaced PrCl<sub>3</sub>·6H<sub>2</sub>O. Yield: ca. 35% (based on FeCl<sub>3</sub>·6H<sub>2</sub>O). Anal. calcd. (found %) for H<sub>92</sub>Fe<sub>4</sub>O<sub>112</sub>Sb<sub>2</sub>W<sub>18</sub>Tb<sub>2</sub> (3): H 1.55 (1.64), Fe 3.74 (3.64), Dy 5.32 (5.40), Sb 4.07 (4.00), W 55.35 (55.45). IR (KBr pellets, cm<sup>-1</sup>): 3413(vs), 1632(s), 952(m), 878(w), 788(vs), 660(m), 469(w), 421(w).

[Lu(H<sub>2</sub>O)<sub>7</sub>]<sub>2</sub>[Fe<sub>4</sub>(H<sub>2</sub>O)<sub>10</sub>][B-β-SbW<sub>9</sub>O<sub>33</sub>]<sub>2</sub>·22H<sub>2</sub>O (4). The synthesis process of 4 is similar to 1, except that LuCl<sub>3</sub>·6H<sub>2</sub>O (0.070 g, 0.180 mmol) replaced PrCl<sub>3</sub>·6H<sub>2</sub>O. Yield: ca. 38% (based on FeCl<sub>3</sub>·6H<sub>2</sub>O). Anal. calcd. (found %) for H<sub>92</sub>Fe<sub>4</sub>O<sub>112</sub>Sb<sub>2</sub>W<sub>18</sub>Lu<sub>2</sub> (4): H 1.54 (1.65), Fe 3.72 (3.60), Lu 5.82 (5.71), Sb 4.05 (3.94), W 55.05 (55.17). IR (KBr pellets, cm<sup>-1</sup>): 3407(vs), 1638(s), 952(m), 889(w), 782(vs), 655(m), 474(w), 421(w).

[Y(H<sub>2</sub>O)<sub>7</sub>]<sub>2</sub>[Fe<sub>4</sub>(H<sub>2</sub>O)<sub>10</sub>][B-β-SbW<sub>9</sub>O<sub>33</sub>]<sub>2</sub>·22H<sub>2</sub>O (5). The synthesis process of 5 is similar to 1, except that YCl<sub>3</sub>·6H<sub>2</sub>O (0.100 g, 0.330 mmol) replaced PrCl<sub>3</sub>·6H<sub>2</sub>O. Yield: ca. 36% (based on FeCl<sub>3</sub>·6H<sub>2</sub>O). Anal. calcd. (found %) for H<sub>92</sub>Fe<sub>4</sub>O<sub>112</sub>Sb<sub>2</sub>W<sub>18</sub>Y<sub>2</sub> (5): H 1.59 (1.67), Fe 3.83 (3.74), Y 3.05 (3.16), Sb 4.17 (4.29), W 56.68 (56.59). IR (KBr pellets, cm<sup>-1</sup>): 3392(vs), 1633(s), 953(m), 883(w), 776(vs), 660(m), 474(w), 415(w).

## X-ray crystallography

Intensity data for 1–5 were collected on a Bruker APEX-II CCD diffractometer using graphite monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 296(2) K. Direct methods were used to solve their structures and locate the heavy atoms using the SHELXTL-97 program package.<sup>24</sup> The remaining atoms were found from successive full-matrix least-squares refinements on  $F^2$  and Fourier syntheses. Routine Lorentz polarization and empirical absorption corrections were applied. No hydrogen atoms associated with water molecules were located from the difference Fourier map. All non-hydrogen atoms were refined anisotropically except for some oxygen atoms and water molecules. It should be pointed out that the Pr1 and Pr2 cations are disordered over two positions with the site occupancy of 50% for each position. Similar disordered phenomenon has been observed in the previous document.<sup>25a</sup> Crystal data and structure refinements for 1–5 were summarized in Table 1. The CCDC reference numbers for 1–5 are 429364–429368, respectively. These data can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz-karlsruhe.de).

## Results and discussion

### Synthesis

Over the past several decades, a number of POM-based TM-RE heterometallic derivatives (PTRHDs) have been successfully synthesized, leading to a growing family of PTRHDs with an intriguing variety of architectures and topologies, since the first series of PTRHDs [RE(H<sub>2</sub>O)<sub>5</sub>{Ni(H<sub>2</sub>O)}<sub>2</sub>As<sub>4</sub>W<sub>40</sub>O<sub>140</sub>]<sup>21–</sup> (RE = Y<sup>III</sup>, Ce<sup>III</sup>, Pr<sup>III</sup>, Nd<sup>III</sup>, Sm<sup>III</sup>, Eu<sup>III</sup>, Gd<sup>III</sup>)

Table 1 Crystallographic data and structural refinements for 1–5

	1	2	3	4	5
Formula	H <sub>80</sub> Fe <sub>4</sub> O <sub>106</sub> Sb <sub>2</sub> W <sub>18</sub> Pr <sub>2</sub>	H <sub>92</sub> Fe <sub>4</sub> O <sub>112</sub> Sb <sub>2</sub> W <sub>18</sub> Tb <sub>2</sub>	H <sub>92</sub> Fe <sub>4</sub> O <sub>112</sub> Sb <sub>2</sub> W <sub>18</sub> Dy <sub>2</sub>	H <sub>92</sub> Fe <sub>4</sub> O <sub>112</sub> Sb <sub>2</sub> W <sub>18</sub> Lu <sub>2</sub>	H <sub>92</sub> Fe <sub>4</sub> O <sub>112</sub> Sb <sub>2</sub> W <sub>18</sub> Y <sub>2</sub>
$M_r$ (g mol <sup>-1</sup> )	5834.66	5978.78	5985.94	6010.88	5838.60
$T$ (K)	296(2)	296(2)	296(2)	296(2)	296(2)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a$ (Å)	12.7448(10)	12.7304(5)	12.7569(12)	12.7131(16)	12.7178(5)
$b$ (Å)	12.7563(9)	13.0108(5)	13.0680(12)	12.9743(17)	13.0050(5)
$c$ (Å)	16.1414(12)	15.9909(6)	16.0200(15)	15.960(2)	15.9829(6)
$\alpha$ (deg)	78.1290(10)	75.3150(10)	75.2730(10)	75.090(2)	75.2040(10)
$\beta$ (deg)	74.3740(10)	74.3990(10)	74.4050(10)	75.892(6)	74.3750(10)
$\gamma$ (deg)	83.6220(10)	76.0750(10)	75.9710(10)	75.818(2)	75.9460(10)
$V$ (Å <sup>3</sup> )	2468.9(3)	2425.05(16)	2444.0(4)	2405.1(5)	2418.00(16)
$Z$	1	1	1	1	1
$D_c$ (g cm <sup>-3</sup> )	3.924	4.094	4.067	4.150	4.010
$\mu$ (mm <sup>-1</sup> )	23.059	23.938	23.834	24.718	23.751
No. of reflections collected	12 495	12 450	12 172	12 121	12 372
No. of independent reflections	8478	8447	8355	8369	8416
$R_{int}$	0.0389	0.0358	0.0455	0.0339	0.0495
Limiting indices	$-15 \leq h \leq 14$ $-15 \leq k \leq 11$ $-19 \leq l \leq 18$	$-15 \leq h \leq 15$ $-10 \leq k \leq 15$ $-19 \leq l \leq 18$	$-13 \leq h \leq 15$ $-15 \leq k \leq 15$ $-18 \leq l \leq 18$	$-14 \leq h \leq 15$ $-10 \leq k \leq 15$ $-18 \leq l \leq 18$	$-9 \leq h \leq 15$ $-15 \leq k \leq 15$ $-19 \leq l \leq 18$
GOF on $F^2$	1.007	1.043	1.013	1.017	1.029
$R_1, wR_2$ [ $I > 2\sigma(I)$ ]	0.0522, 0.1337	0.0365, 0.0923	0.0503, 0.1271	0.0432, 0.1106	0.0549, 0.1450
$R_1, wR_2$ [all data]	0.0613, 0.1393	0.0399, 0.0942	0.0566, 0.1312	0.0522, 0.1157	0.0599, 0.1493

were published by Xue *et al.* in 2004.<sup>25b</sup> However, the preparation of novel PTRHDs has been a great challenge because the pH stability region for TM cations in aqueous solutions is different from that of RE cations; furthermore, there are unavoidable competitive reactions among highly negative POM precursors, strongly oxyphilic RE ions and less active TM ions in the same reaction system.<sup>26</sup> Consequently, it is comparatively difficult to seek suitable reaction conditions that would capacitate the acquisition of novel PTRHD aggregates. In order to further explore novel extended aggregates in this domain with the “property-adding” feature, an effective strategy was developed to utilize the lacunary POAs as inorganic polydentate building units to capture TM and RE ions for constructing the extended PTRHD multifunctional hybrid materials. Highly lacunary POM precursors are selected as the ideal candidates because of their nucleophilic oxygen-enriched surfaces and high negative charges, which allow incorporation of more metal centers.<sup>27</sup> It should be pointed out that the choice of diverse “connectors” such as TM cations or RE cations is important since they can effectively link lacunary POM precursors. As far as we know, since the first extended inorganic PTRHD was discovered by Wang’s group in 2007,<sup>28</sup> hitherto, more than twenty extended PTRHDs have been obtained by means of various TM or RE linkers (Table 2).<sup>29</sup> In Table 2, it was evident that only seven examples of extended PTRHDs with RE linkers have been reported. In 2007, Wang *et al.* reported the first 1-D chiral ladder-like chain based on tetra-Mn<sup>III</sup> substituted  $[\text{Mn}_4\text{Si}_2\text{W}_{18}\text{O}_{68}(\text{H}_2\text{O})_2]^{12-}$  units and  $\text{Ce}^{3+}$  linkers.<sup>27</sup> Subsequently, the first 2-D inorganic aggregate

$\text{K}_3\text{Na}_3\{\text{Nd}_2(\text{H}_2\text{O})_{12}\text{Cu}_4(\text{H}_2\text{O})_2(\text{SiW}_9\text{O}_{34})_2\}-21\text{H}_2\text{O}$  built by tetra-Cu<sup>II</sup> sandwiched  $[\text{Cu}_4(\text{H}_2\text{O})_2(\text{SiW}_9\text{O}_{34})_2]^{12-}$  units and  $\text{Nd}^{3+}$  linkers was also obtained by them.<sup>29b</sup> In 2010, Mailane *et al.* reported a 1-D double-chain system  $\text{Cs}_4[(\gamma\text{-SiW}_{10}\text{O}_{36})_2(\text{Cr}(\text{OH})(\text{H}_2\text{O}))_3(\text{La}(\text{H}_2\text{O})_7)_2]_3\cdot 19\text{H}_2\text{O}$ , in which sandwich-type  $[(\gamma\text{-SiW}_{10}\text{O}_{36})_2(\text{Cr}(\text{OH})(\text{H}_2\text{O}))_3]^{10-}$  moieties were connected by  $\text{La}^{3+}$  cations.<sup>29g</sup> In 2012, Niu’s group obtained a 1-D helical chain formed by  $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$  POAs and  $\text{RE}^{3+}$  cations, which was further extended to a 3-D framework through  $\text{Cu}^{2+}$  cations. Recently, Yang and coworkers discovered the first 3-D Mn–Ce heterometallic organic–inorganic hybrid framework  $\text{K}_4\text{Na}_4[\text{Ce}_2(\text{ox})_3(\text{H}_2\text{O})_2]_2\{[\text{Mn}(\text{H}_2\text{O})_3]_2[\text{Mn}_4(\text{GeW}_9\text{O}_{34})_2(\text{H}_2\text{O})_2]\}-14\text{H}_2\text{O}$  constructed by sandwich-type TM-substituted POAs and mixed 3d and 4f metal linkers.<sup>29p</sup> They also synthesized two 3-D frameworks  $\text{KNa}_7\{[\text{Sm}_6\text{Mn}(\mu\text{-H}_2\text{O})_2(\text{OCH}_2\text{COO})_7(\text{H}_2\text{O})_{18}]\{\text{Na}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}\}\}-22\text{H}_2\text{O}$  and  $\text{K}_4\{[\text{Sm}_4\text{Cu}_2(\text{gly})_2(\text{ox})(\text{H}_2\text{O})_{24}]\{\text{NaP}_5\text{W}_{30}\text{O}_{110}\}\text{Cl}_2\cdot 25\text{H}_2\text{O}$  that contain  $\{\text{P}_5\text{W}_{30}\}$  units and TM/RE–carboxylate–RE connectors.<sup>29q</sup> It is obvious that only three examples of extended purely inorganic PTRHDs have been reported. On the other hand, the exploration on purely inorganic TM–RE heterometallic TAs remains largely undeveloped. This background provides us with an excellent opportunity to exploit the TA–TM–RE system. Eventually, we have successfully obtained a novel 2-D purely inorganic TM–RE heterometallic TA  $[\text{Pr}(\text{H}_2\text{O})_8][\text{Pr}(\text{H}_2\text{O})_6][\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2]\cdot 16\text{H}_2\text{O}$  (1) and four 0-D purely inorganic TM–RE heterometallic TAs  $[\text{RE}(\text{H}_2\text{O})_7]_2[\text{Fe}_4(\text{H}_2\text{O})_{10}][\text{B-}\beta\text{-SbW}_9\text{O}_{33}]_2\cdot 22\text{H}_2\text{O}$  [RE = Tb<sup>III</sup> (2), Dy<sup>III</sup> (3), Lu<sup>III</sup> (4), Y<sup>III</sup> (5)]. In the beginning, 1 was first obtained by reaction of  $\text{Na}_9[\text{B-}\alpha\text{-SbW}_9\text{O}_{33}]\cdot 19.5\text{H}_2\text{O}$ ,  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  and  $\text{PrCl}_3\cdot 6\text{H}_2\text{O}$  in an aqueous solution, pH = 0.5, at 80 °C. And then the

**Table 2** The summary of extended POM-based TM–RE heterometallic materials

Year	Dimension	Linkers	Phase
2007	1-D	$\text{Ce}^{3+}$	$\text{K}_4\text{Na}_2\{[\text{Ce}(\text{H}_2\text{O})_7]_2\text{Mn}_4\text{Si}_2\text{W}_{18}\text{O}_{68}(\text{H}_2\text{O})_2\}\cdot 21.5\text{H}_2\text{O}^{27}$
2008	1-D	$\text{Cu}^{2+}$	$\text{K}_2\text{H}_7\{[\text{RE}(\text{PW}_{11}\text{O}_{39})_2]\text{Cu}_2(\text{bpy})_2(\mu\text{-ox})\}\cdot x\text{H}_2\text{O}^{29a}$
	2-D	$\text{Nd}^{3+}$	$\text{K}_3\text{Na}_3\{\text{Nd}_2(\text{H}_2\text{O})_{12}\text{Cu}_4(\text{H}_2\text{O})_2(\text{SiW}_9\text{O}_{34})_2\}\cdot 21\text{H}_2\text{O}^{29b}$
2009	1-D	$\text{Cu}^{2+}$	$[\text{H}_9\{\text{Ce}(\alpha\text{-PW}_{11}\text{O}_{39})_2\}\text{Cu}(\text{en})_2] 6\text{H}_2\text{O}^{29c}$
	2-D	$\text{Cu}^{2+}$	$[\text{Cu}(\text{en})_2][\text{Cu}(\text{en})(\text{OH})_3\text{La}(\text{SiW}_{11}\text{O}_{39})]\cdot 20\text{H}_2\text{O}^{29d}$
2010	1-D	$\text{Cu}^{2+}$	$\text{H}_2[\text{Cu}(\text{en})_2\text{H}_2\text{O}]_8[\text{Cu}(\text{en})_2]_3\{[(\alpha\text{-SiW}_{11}\text{O}_{39})\text{Ce}(\text{H}_2\text{O})(\eta^2, \mu\text{-}1, 1)\text{CH}_3\text{COO}]_4\}\cdot 22\text{H}_2\text{O}^{29e}$
	1-D	$\text{Cu}^{2+}$	$\text{H}_8[\text{Cu}(\text{en})_2\text{H}_2\text{O}]_4[\text{Cu}(\text{en})_2]_4\{[\text{Cu}(\text{en})_2][\text{La}(\text{PW}_{11}\text{O}_{39})_2]\}_2\cdot 18\text{H}_2\text{O}^{29f}$
	1-D	$\text{La}^{3+}$	$\text{Cs}_4[(\gamma\text{-SiW}_{10}\text{O}_{36})_2(\text{Cr}(\text{OH})(\text{H}_2\text{O}))_3(\text{La}(\text{H}_2\text{O})_7)_2]_3\cdot 19\text{H}_2\text{O}^{29g}$
2011	1-D	$\text{Cu}^{2+}$	$\{[\text{Cu}(\text{en})_2]_{1.5}[\text{Cu}(\text{en})(2,2'\text{-bipy})(\text{H}_2\text{O})_n]\text{RE}[(\alpha\text{-PW}_{11}\text{O}_{39})_2]\}_6$ (RE = Ce, Pr) <sup>29h</sup>
	2-D	$\text{Cu}^{2+}$	$\{[\text{Cu}(\text{en})_2]_2(\text{H}_2\text{O})[\text{Cu}(\text{en})(2,2'\text{-bipy})]\text{RE}[(\alpha\text{-HPW}_{11}\text{O}_{39})_2]\}_4$ (RE = Gd, Tb, Er) <sup>29h</sup>
	3-D	$\text{Cu}^{2+}$	$\{[\text{Cu}(\text{en})_2]_{1.5}[\text{Cu}(\text{en})(2,2'\text{-bipy})]\text{Nd}[(\alpha\text{-H}_5\text{PW}_{11}\text{O}_{39})_2]\}_3$ <sup>29h</sup>
	2-D	$\text{Cu}^{2+}$	$[\text{Cu}(\text{en})_2]_2\text{H}_6[\text{Ce}(\alpha\text{-PW}_{11}\text{O}_{39})_2]\cdot 8\text{H}_2\text{O}^{29i}$
	2-D	$\text{Cu}^{2+}$	$[\text{Cu}(\text{dap})_2(\text{H}_2\text{O})][\text{Cu}(\text{dap})_2]_{4.5}[\text{Dy}(\alpha\text{-PW}_{11}\text{O}_{39})_2]\cdot 4\text{H}_2\text{O}^{29i}$
	2-D	$\text{Cu}^{2+}$	$[\text{Cu}(\text{dap})(\text{H}_2\text{O})_2]_{0.5}[\text{Cu}(\text{dap})_2]_4\text{H}_2[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]\cdot 3\text{H}_2\text{O}^{29j}$
2012	3-D	$\text{Fe}^{3+}$	$[\text{e-PMo}^{\text{VI}}_8\text{Mo}^{\text{VI}}_4\text{O}_{37}(\text{OH})_3\{\text{La}(\text{H}_2\text{O})_5(\text{Fe}(\text{CN})_6)_{0.25}\}_4]\cdot 12\text{H}_2\text{O}^{29k}$
	1-D	$\text{K}^+$	$\text{K}(\text{enH}_2)_4[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]_2\{[\text{Cu}(\text{en})_2]_{1.5}\text{Gd}[(\alpha\text{-H}_{1.75}\text{SiW}_{11}\text{O}_{39})_2]\}_2\sim 15\text{H}_2\text{O}^{29l}$
	3-D	$\text{RE}^{3+}, \text{Cu}^{2+}$	$(\text{enH}_2)_{0.5}\{[\text{Cu}(\text{en})_2]_{1.5}\text{RE}[(\alpha\text{-HSiW}_{11}\text{O}_{39})]\}_3\cdot 3\text{H}_2\text{O}$ (RE = La, Ce) <sup>29l</sup>
	3-D	$\text{Cu}^{2+}$	$(\text{enH}_2)_2\{[\text{Cu}(\text{en})_2(\text{H}_2\text{O})][\text{Cu}(\text{en})_2]\text{RE}[(\alpha\text{-H}_{1.5}\text{SiW}_{11}\text{O}_{39})_2]\}_6\cdot 6\text{H}_2\text{O}$ (RE = Pr, Sm) <sup>29l</sup>
	1-D	$\text{Cu}^{2+}$	$[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]_2\{[\text{Cu}(\text{en})_2]_2[\text{Cu}(\text{pzda})_2][(\alpha\text{-H}_2\text{SiW}_{11}\text{O}_{39})\text{Ce}(\text{H}_2\text{O})_2]\}_n\cdot n\text{H}_2\text{O}^{29m}$
	1-D	$\text{Cu}^{2+}$	$[\text{Cu}(\text{dap})(\text{H}_2\text{O})_2]_{0.5}[\text{Cu}(\text{dap})_2(\text{H}_2\text{O})]_3[\text{Cu}(\text{dap})_2]_3[\text{RE}(\alpha\text{-AsW}_{11}\text{O}_{39})_2]\cdot x\text{H}_2\text{O}$ (RE = Pr, Eu) <sup>29n</sup>
	2-D	$\text{Cu}^{2+}$	$[\text{Cu}(\text{dap})_2]_{5.5}[\text{RE}(\alpha\text{-AsW}_{11}\text{O}_{39})_2]\cdot x\text{H}_2\text{O}$ (RE = Tb, Dy) <sup>29n</sup>
	2-D	$\text{Cu}^{2+}$	$\text{Na}[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]_4[\text{Cu}(\text{en})_2]_2[\text{Cu}(\text{H}_2\text{O})_4]_{0.5}\{[\text{Cu}(\text{en})_2]_2\text{H}_2\text{Ce}^{\text{IV}}(\alpha\text{-AsW}_{11}\text{O}_{39})_2]\}_2\cdot 10\text{H}_2\text{O}^{29n}$
	2-D	$\text{Cu}^{2+}$	$\text{Na}_3[\text{Cu}(\text{en})_2(\text{H}_2\text{O})][\text{Cu}(\text{en})_2]_{1.5}[\text{H}_3\text{RE}(\alpha\text{-AsW}_{11}\text{O}_{39})_2]\cdot x\text{H}_2\text{O}$ (RE = Pr, Nd, Sm, Eu, Tb) <sup>29n</sup>
2013	3-D	$\text{Mn}^{2+}, \text{Ce}^{3+}$	$\text{K}_4\text{Na}_4[\text{Ce}_2(\text{ox})_3(\text{H}_2\text{O})_2]_2\{[\text{Mn}(\text{H}_2\text{O})_3]_2[\text{Mn}_4(\text{GeW}_9\text{O}_{34})_2(\text{H}_2\text{O})_2]\}\cdot 14\text{H}_2\text{O}^{29o}$
	1-D	$\text{Cu}^{2+}$	$[\text{Cu}(\text{en})_2(\text{H}_2\text{O})][\text{Cu}(\text{en})_2][\text{Tb}(\alpha\text{-PW}_{11}\text{O}_{39})(\text{H}_2\text{O})_2(\text{ox})\text{Cu}(\text{en})]\cdot 6\text{H}_2\text{O}^{29p}$
2014	3-D	$\text{Mn}^{2+}, \text{Sm}^{3+}$	$\text{KNa}_7\{[\text{Sm}_6\text{Mn}(\mu\text{-H}_2\text{O})_2(\text{OCH}_2\text{COO})_7(\text{H}_2\text{O})_{18}]\{\text{Na}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}\}\}-22\text{H}_2\text{O}^{29q}$
	3-D	$\text{Mn}^{2+}, \text{Sm}^{3+}$	$\text{K}_4\{[\text{Sm}_4\text{Cu}_2(\text{gly})_2(\text{ox})(\text{H}_2\text{O})_{24}]\{\text{NaP}_5\text{W}_{30}\text{O}_{110}\}\text{Cl}_2\cdot 25\text{H}_2\text{O}^{29q}$

replacement of the  $\text{Pr}^{\text{III}}$  cation by  $\text{Tb}^{\text{III}}$ ,  $\text{Dy}^{\text{III}}$ ,  $\text{Lu}^{\text{III}}$ ,  $\text{Y}^{\text{III}}$  cations led to the formation of 2–5. **1** exhibited a 2-D sheet architecture while 2–5 are isolated structures. These results imply that the nature of RE cations may influence the structural diversity of the products. Moreover, investigations on other RE cations in this system are in the avenue. To further study the effect of different TM cations on structural diversity, when the  $\text{Fe}^{3+}$  cations were replaced by  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  cations under the same conditions, however, only some amorphous precipitates were isolated. Therefore, TM ions also play an important role in the construction of products. Next, the step by step assembly strategy will be employed in this system. That is, prefabricated TM substituted TA precursors will be used to react with RE cations or prefabricated RE substituted TA precursors will be used to react with TM cations to construct our desired TA-based TM–RE heterometallic derivatives. Certainly, the pH of the solution is a key factor; when the pH was approximately adjusted to 0.5, the products were obtained. However, the systemic development on TA-based TM–RE heterometallic derivatives still remains a great difficulty for us. In the future, we will continuously explore and discover novel extended PTRHDs by changing different synthetic conditions including pH, temperature and reactants.

### Structural descriptions

1–5 were all prepared *via* a similar conventional aqueous solution method and the common structural characteristic of 1–5 is that they include a tetra- $\text{Fe}^{\text{III}}$  substituted Krebs-type sandwich  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  unit, which is constructed from two trilacunary Keggin subunits  $[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  encapsulating a rhomb-like  $\{\text{Fe}^{\text{III}}_4\}$  cluster. In the  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  unit, the Fe and W atoms can be unambiguously determined by checking their anisotropic thermal displacement parameters and the Fe–O or W–O distances. This unambiguous determination of the 3d-metal and W atom in tetra-TM substituted Krebs-type sandwich POMs is very common.<sup>5,6,13</sup> In addition, the phase purity of 1–5 is determined by the consistency of the experimental PXRD patterns of the as-prepared samples with the XRD patterns obtained from the single-crystal X-ray diffraction (Fig. 1).

**1** crystallizes in the triclinic space group  $P\bar{1}$  and its structural unit consists of a sandwich-type  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  POA and two crystallographically independent  $\text{Pr}^{3+}$  cations (Fig. 2a). The sandwich-type  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  POA can be simplified into two cages encapsulating a  $\{\text{Fe}^{\text{III}}_4\}$  belt (Fig. 2b). The well-known sandwich-type  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  POA is composed of two trivacant Keggin  $[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  building blocks in a staggered fashion sandwiching a central symmetric rhomb-like  $\{\text{Fe}^{\text{III}}_4\}$  group, in which the four  $\text{Fe}^{\text{III}}$  cations lie at the corners of a rhombus with adjacent two edges of 5.656 and 5.664 Å; meanwhile, adjacent  $\text{Fe}^{\text{III}}$  cations are bridged by the Fe–O–W–O–Fe bonds, and the distance of two inner Fe $\cdots$ Fe is 5.408 Å while the distance of two external Fe $\cdots$ Fe is 9.945 Å (Fig. 3). This connection mode is somewhat distinct from that in the

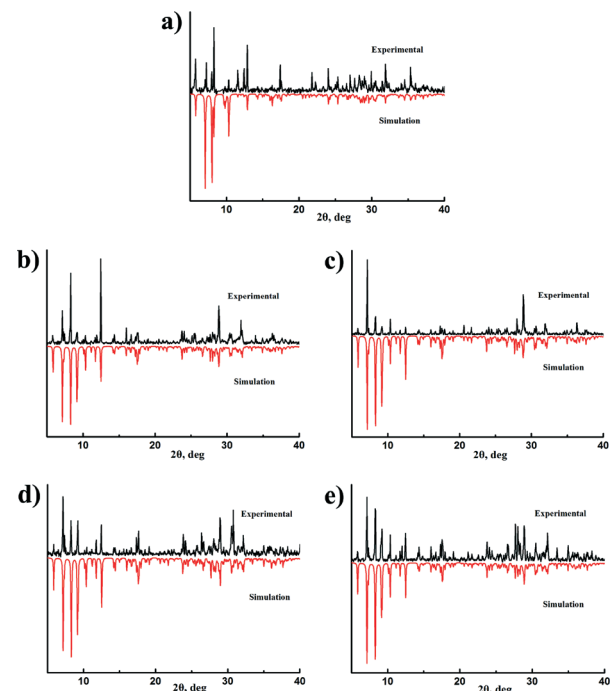


Fig. 1 (a) The experimental PXRD and simulated XRD patterns of the as-prepared **1**. (b) The experimental PXRD and simulated XRD patterns of the as-prepared **2**. (c) The experimental PXRD and simulated XRD patterns of the as-prepared **3**. (d) The experimental PXRD and simulated XRD patterns of the as-prepared **4**. (e) The experimental PXRD and simulated XRD patterns of the as-prepared **5**.

tetra- $\text{Fe}^{\text{III}}$  sandwiched unit  $[\text{Fe}_4(\text{en})(\text{B}-\alpha\text{-GeW}_9\text{O}_{34})_2]^{8-}$  reported by our group recently,<sup>30</sup> in which four  $\text{Fe}^{\text{III}}$  centers are connected by Fe–O–Fe bonds. Nevertheless, the sandwich belt of the POA in **1** is defined by two types of inequivalent  $\text{Fe}^{\text{III}}$  cations, which contain two interior  $\text{Fe}^{\text{III}}$  ions (Fe2 and Fe2A) and two exterior  $\text{Fe}^{\text{III}}$  cations (Fe1 and Fe1A). Albeit two types of  $\text{Fe}^{\text{III}}$  cations display the octahedral geometries, their coordination surroundings are somewhat different. The octahedral Fe2<sup>III</sup> cation is defined by two O atoms from one  $[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  fragment [Fe–O: 1.956(10)–1.971(11) Å], two

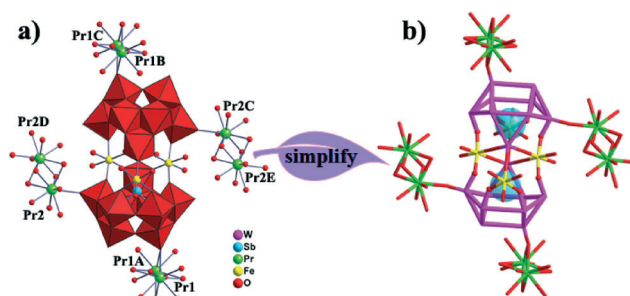


Fig. 2 (a) Polyhedral/ball-and-stick representation of the structural unit of **1**. Lattice water molecules are omitted for clarity. The atoms with the suffix A, B, C, D, and E are generated by the symmetry operation: A:  $-x, 1-y, 2-z$ ; B:  $1+x, 1+y, -1+z$ ; C:  $1-x, 2-y, 1-z$ ; D:  $-x, 3-y, 1-z$ ; E:  $1+x, -1+y, z$ . (b) The simplified view of the structural unit of **1**.



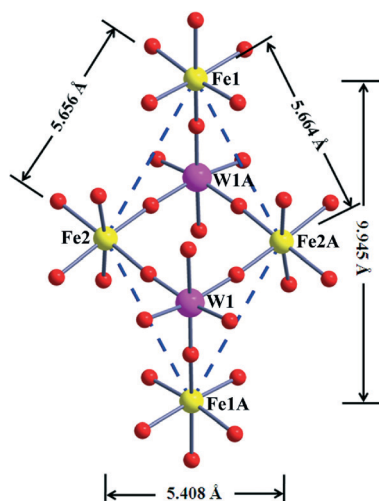


Fig. 3 The central symmetric rhomb-like  $\{\text{Fe}^{\text{III}}_4\}$  group in **1** showing the  $\text{Fe}\cdots\text{Fe}$  distances. The atoms with the suffix A are generated by the symmetry operation: A:  $1 - x, 2 - y, 1 - z$ .

O atoms from the other  $[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  fragment [ $\text{Fe}-\text{O}$ : 1.918(11)–1.963(10) Å] and two O atoms from two terminal  $\text{H}_2\text{O}$  ligands [ $\text{Fe}-\text{O}$ : 2.087(11)–2.089(13) Å], whereas the octahedral  $\text{Fe}^{\text{III}}$  cation is built by two O atoms from one  $[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  fragment [ $\text{Fe}-\text{O}$ : 1.906(11)–1.941(11) Å], one O atom from the other  $[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  fragment [ $\text{Fe}-\text{O}$ : 1.972(10) Å] and three O atoms from three terminal  $\text{H}_2\text{O}$  ligands [ $\text{Fe}-\text{O}$ : 2.034(11)–2.098(14) Å]. It is interesting that each sandwich-type dimeric  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  POA is combined with the four adjacent same ones alternatively by O–Pr–O bonds resulting in a unique 2-D sheet architecture (Fig. 4a). However, the linkers are defined by two types of inequivalent  $\text{Pr}^{\text{III}}$  (Pr1 and Pr2) ions. The  $\text{Pr}^{\text{III}}$  cation coordinates directly to the terminal atom that is away from the sandwich belt of the  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  POA; what's more, the  $\text{Pr}^{\text{III}}$  cation is disordered over two positions (Pr1 and Pr1A) with a site occupancy of 50% for each position and the  $\text{Pr}\cdots\text{Pr}$  distance is 1.842(4) Å. The  $\text{Pr}^{\text{III}}$  cation exhibits an eight-coordinate severely distorted square antiprismatic configuration [ $\text{Pr}-\text{O}$ : 2.518(11)–2.72(4) Å]. The  $\text{Pr}^{\text{III}}$  cations can be viewed as connectors that link the sandwich-type POAs into an infinite 1-D chain. The  $\text{Pr}^{\text{II}}$  cation links to the terminal O atom near the sandwich belt of the  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  POA, and it is also disordered over two positions (Pr2 and Pr2D) with the site occupancy of 50% for each position and the  $\text{Pr}\cdots\text{Pr}$  distance is 3.102(6) Å. Nevertheless, the  $\text{Pr}^{\text{II}}$  cation displays a nine-coordinate monocapped square antiprism configuration [ $\text{Pr}-\text{O}$ : 2.36(2)–2.62(5) Å], and the  $\text{Pr}^{\text{II}}$  cations function as connectors to join neighboring 1-D chains further into a 2-D sheet construction (Fig. 4a, b). As illustrated in Fig. 4c, adjacent 2-D sheets are regularly aligned in a staggered pattern to reduce the steric hindrance. As far as we know, **1** represents the first 2-D extended sheet constructed from the tetra- $\text{Fe}^{\text{III}}$  substituted sandwich-type units  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  through  $\text{Pr}^{\text{III}}$  linkers. From a topology viewpoint, supposing

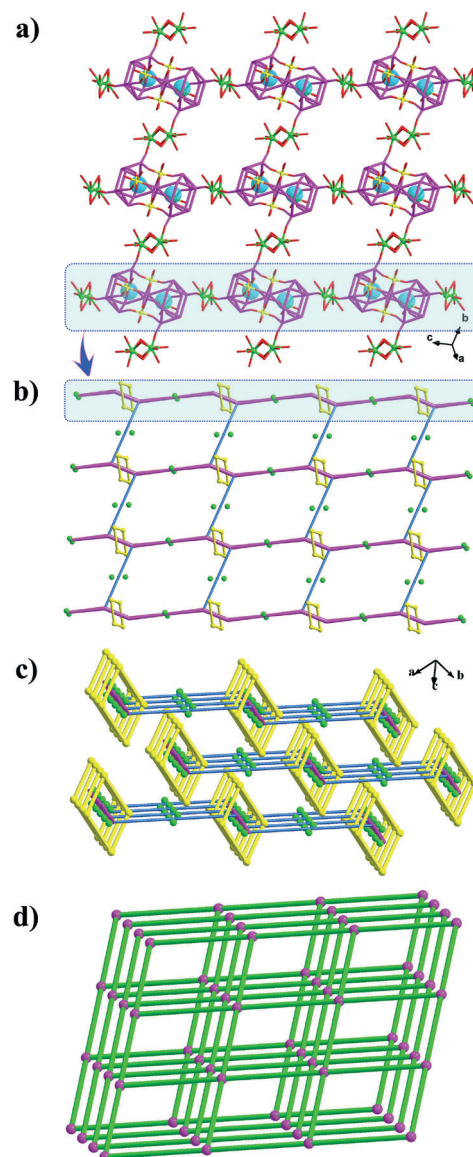


Fig. 4 (a) The 2-D sheet architecture constructed from  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  POAs and  $\text{Pr}^{\text{III}}$  linkers in **1**. Lattice water molecules are omitted for clarity. (b) The simplified schematic view of the 2-D sheet, in which yellow rhombs represent  $\{\text{Fe}^{\text{III}}_4\}$  groups and green balls stand for disordered  $\text{Pr}^{\text{III}}$  cations. (c) The packing of schematic 2-D sheets exhibiting a staggered pattern to reduce the steric hindrance. (d) The 2-D (4,4) topological sheet.

that the structural unit of  $[\text{Pr}(\text{H}_2\text{O})_8][\text{Pr}(\text{H}_2\text{O})_6][\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]$  is considered as a four-connected node, the 2-D sheet of **1** facilitates a 2-D (4,4)-network topology (Fig. 4d). As a result, the discovery of **1** offers us a useful guidance for the development of the complicated inorganic or organic–inorganic coordination networks of TA-based TM–RE heterometallic derivatives.

To our knowledge, the well-known highly charged trivalent species  $[\text{SbW}_9\text{O}_{33}]^{9-}$  is obtained by removal of three edge-sharing  $\text{WO}_6$  octahedra of a hypothetical parent Keggin anion, which can be depicted as the combination of three  $\{\text{W}_3\text{O}_{13}\}$  groups around the  $\{\text{SbO}_3\}$  central pyramid and

possesses two isomers B- $\alpha$  and B- $\beta$ . Formally, the  $[\text{B-}\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  anion can be envisioned as an isomer of the  $[\text{B-}\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$  anion; that is, the  $60^\circ$  rotation of one edge-shared  $\{\text{W}_3\text{O}_{13}\}$  group in the  $[\text{B-}\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$  anion generates the  $[\text{B-}\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  anion. It should be noted that the sandwich-type  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  POA presented in **1** contains two  $[\text{B-}\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  building blocks. However, the  $[\text{B-}\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  fragment was not used as the starting material during the preparation of **1**; therefore, the isomerization of B- $\alpha \rightarrow$  B- $\beta$  of the  $[\text{SbW}_9\text{O}_{33}]^{9-}$  unit must have occurred. The conceivable reaction process is similar to that reported by Krebs.<sup>4</sup> The precursor  $[\text{B-}\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$  is obtained in a basic medium; when the reaction medium is changed to be acidic, the precursor  $[\text{B-}\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$  has a higher tendency to isomerize to the  $[\text{B-}\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  fragment.<sup>4,31</sup> This is in good accordance with the synthetic conditions for **1**, which was obtained at pH 0.5. Such isomerization phenomenon has been reported in previous research on TAs, as listed in Table S1.<sup>†</sup><sup>32</sup> 2–5 are isostructural and belong to the triclinic space group  $P\bar{1}$ ; therefore, only **2** is discussed in detail herein. Although they were obtained in the same system as **1**, their structural constructions are somewhat different. On one hand, the common characteristic of the sandwich-type  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  POAs in **1** and **2** is that they can be described as two trivalent Keggin  $[\text{B-}\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  units sandwiching a central symmetric  $\{\text{Fe}^{\text{III}}_4\}$  segment, resulting in the classic sandwich-type assembly. On the other hand, four striking differences between them can be found: (a) there are two crystallographically unique  $\text{Pr}^{\text{III}}$  cations in **1**; in contrast, only one crystallographically independent  $\text{Tb}^{\text{III}}$  cation is observed in **2**; (b) the coordination positions of RE cations on the surfaces of  $[\text{B-}\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  units are differentiated: in **1**, two types of  $\text{Pr}^{\text{III}}$  cations are simultaneously combined with the terminal O atoms that are away from and near the sandwich belt of the  $[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_{10}(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  POA; on the contrary, in **2**, the  $\text{Tb}^{\text{III}}$  cations link to terminal O atoms that are adjacent to the sandwich belt of POA (Fig. 5a); (c) each  $\text{Pr}^{\text{III}}$  cation in **1** is disordered over two positions with a site occupancy of 50% for each position while the  $\text{Tb}^{\text{III}}$  cation in **2** is completely localized with a site occupancy of 100%; (d) **1** shows a 2-D sheet architecture, whereas **2** employs a discrete structure. In addition, the  $[\text{Tb}(\text{H}_2\text{O})_7]_2[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2]$  entities in **2** are regularly arranged in the  $-\text{AAA}-$  motif along the  $b$  or  $c$  axis (Fig. 5b).

It is obvious that **1**–**5** all consist of tetra- $\text{Fe}^{\text{III}}$  substituted dimeric sandwich-type  $[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_{10}(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  POAs as the fundamental building blocks. This tetra- $\text{Fe}^{\text{III}}$  substituted Krebs-type sandwich POA  $[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_{10}(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  (**A**) is comparable to the tetra- $\text{Fe}^{\text{III}}$  substituted Weakley's sandwich-type POA  $[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-Fe}^{\text{III}}\text{W}_9\text{O}_{34})_2]^{10-}$  (**B**) that was reported by Niu's group in 2013 (Fig. 6).<sup>33</sup> The common feature of **A** and **B** is that they were prepared by making use of  $\text{Na}_9[\text{B-}\alpha\text{-SbW}_9\text{O}_{33}]\cdot 19.5\text{H}_2\text{O}$  and can be viewed as two trivalent Keggin-type fragments anchoring a tetra- $\text{Fe}^{\text{III}}$  core illustrating the classic sandwich-type subfamily. Although **A** is somewhat similar to the **B**, the main

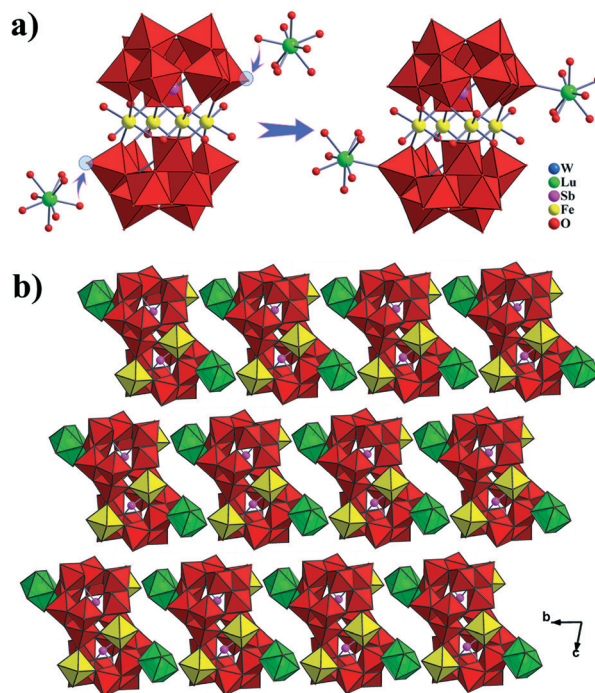


Fig. 5 (a) Polyhedral/ball-and-stick representation of the structural unit of **2**. (b) The packing view of **2** in the  $bc$  plane. Lattice water molecules are omitted for clarity.

discrepancies between **A** and **B** rest on three aspects: (1) the synthetic methods are discrepant: **A** was synthesized under the conventional aqueous solution while **B** was separated under the hydrothermal conditions; (2) the differences of the trivalent Keggin-type fragments give rise to the imparities of their structures: **A** contains two  $[\text{B-}\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  fragments with the presence of a lone pair of electrons on the tri-coordinate  $\text{Sb}^{\text{III}}$  heteroatom, whereas **B** includes two  $[\text{B-}\alpha\text{-FeW}_9\text{O}_{34}]^{11-}$  fragments with the four-coordinate  $\text{Fe}^{\text{III}}$  heteroatom; (3) the greatest differences between them are that **A** contains a rhomb-like tetra- $\text{Fe}^{\text{III}}$  group, in which adjacent  $\text{Fe}^{\text{III}}$  cations are bridged by the  $\text{Fe-O-W-O-Fe}$  bonds; however, adjacent  $\text{Fe}^{\text{III}}$  cations are

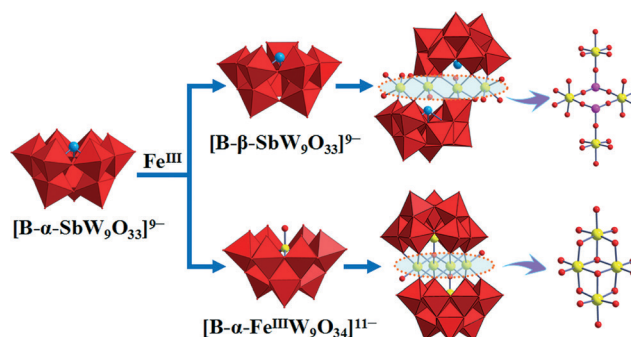


Fig. 6 The comparison of the tetra- $\text{Fe}^{\text{III}}$  substituted Krebs' sandwich-type  $[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_{10}(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  in **1**–**5** and the previously reported tetra- $\text{Fe}^{\text{III}}$  substituted Weakley's sandwich-type POA  $[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-Fe}^{\text{III}}\text{W}_9\text{O}_{34})_2]^{10-}$ .



joined by the Fe–O–Fe bonds in **B**. Moreover, comparing 1–5 with  $[\text{RE}(\text{H}_2\text{O})_8]_2[\text{Fe}_4(\text{H}_2\text{O})_8(\text{thr})_2](\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2 \cdot 22\text{H}_2\text{O}$  ( $\text{RE} = \text{Pr}^{\text{III}}, \text{Nd}^{\text{III}}, \text{Sm}^{\text{III}}, \text{Eu}^{\text{III}}, \text{Gd}^{\text{III}}, \text{Dy}^{\text{III}}, \text{Lu}^{\text{III}}$ ) reported by us in 2014, two obvious differences in synthetic methods and structures can be observed: (1) the pH of the reaction system of 1–5 is controlled at *ca.* 0.5, whereas the pH of the reaction solution of  $[\text{RE}(\text{H}_2\text{O})_8]_2[\text{Fe}_4(\text{H}_2\text{O})_8(\text{thr})_2](\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2 \cdot 22\text{H}_2\text{O}$  is adjusted to *ca.* 1.2; (2) **1** displays the inorganic 2-D extended sheet built by tetra- $\text{Fe}^{\text{III}}$  sandwich-type units  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  *via*  $\text{Pr}^{3+}$  linkers, 2–5 exhibit the inorganic isolated structure based on  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  with two supporting  $[\text{RE}(\text{H}_2\text{O})_7]^{3+}$  cations on the top and bottom sides, while  $[\text{RE}(\text{H}_2\text{O})_8]_2[\text{Fe}_4(\text{H}_2\text{O})_8(\text{thr})_2](\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2 \cdot 22\text{H}_2\text{O}$  adopt the isolated organic–inorganic hybrid architecture functionalized by amino acid ligands, in which two thr ligands substitute for two water ligands of the classic  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  POA leading to the  $[\text{Fe}_4(\text{H}_2\text{O})_8(\text{thr})_2(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  hybrid unit.

Furthermore, to the best of our knowledge, tetranuclear TM substituted sandwich-type POMs mainly comprise other seven kinds of structural types as well as the above-mentioned Weakley- and Krebs-type structures (Fig. 7). In 2006, Kortz's group published an asymmetric dimeric species  $[\text{Zr}_4\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_4(\beta\text{-SiW}_{10}\text{O}_{37})_2]^{10-}$  consisting of  $\beta_{22-}$  and  $\beta_{12-}$   $\text{SiW}_{10}\text{O}_{37}$  segments sandwiching a  $[\text{Zr}_4\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_4]^{10+}$  cluster (Fig. 7a).<sup>34</sup> In the same year, Mizuno *et al.* synthesized an unexpected cyclic tetra- $\text{Ti}^{\text{IV}}$  substituted silicotungstate  $[\{\gamma\text{-SiTi}_2\text{W}_{10}\text{O}_{36}(\text{OH})_2\}_2(\mu\text{-O})_2]^{8-}$  (Fig. 7b).<sup>35</sup> Subsequently, Hill and co-workers prepared a highly active tetraruthenium homogeneous catalyst for water oxidation  $[\{\text{Ru}^{\text{IV}}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$ , in which two staggered  $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$  fragments incorporate an adamantane-like  $[\text{Ru}^{\text{IV}}_4(\mu\text{-O})_4(\mu\text{-OH})_2(\text{H}_2\text{O})_4]^{6+}$  core (Fig. 7c).<sup>36</sup> Meanwhile, Dolbecq's group obtained a unique

phosphotungstate  $[(\text{PW}_{11}\text{O}_{39})_2\text{Fe}_4^{\text{III}}\text{O}_2(\text{dmbpy})_4]^{6-}$  with a butterfly-like tetra- $\text{Fe}^{\text{III}}$   $[\text{Fe}_4^{\text{III}}\text{O}_2(\text{dmbpy})_4]^{8+}$  hybrid cluster encapsulated between two monolacunary  $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$  segments (Fig. 7d).<sup>37</sup> In 2010, Liu's group reported an acetate-functionalized tetra-Zr sandwiched POM  $[\text{Zr}_4(\text{OH})_6(\text{CH}_3\text{COO})_2(\alpha\text{-PW}_{10}\text{O}_{37})_2]^{10-}$  built by two dilacunary  $[\alpha\text{-PW}_{10}\text{O}_{37}]^{8-}$  subunits linked *via* a  $[\text{Zr}_4(\text{OH})_6(\text{CH}_3\text{COO})_2]^{8+}$  central cluster (Fig. 7e).<sup>38</sup> Recently, Mizuno *et al.* isolated two novel Zinc-containing sandwich-type silicotungstates  $[\{\text{Zn}_2\text{W}(\text{O})\text{O}_3\}_2\text{H}_4\{\alpha\text{-SiW}_9\text{O}_{33}\}_2]^{8-}$  (Fig. 7f) and  $[\{\text{Zn}_2\text{W}(\text{O})\text{O}_3\}_2\text{H}_4\{\beta\text{-SiW}_9\text{O}_{33}\}_2]^{8-}$  (Fig. 7g), which consist of two  $[\text{SiW}_9\text{O}_{33}]^{8-}$  subunits sandwiching the unprecedented distorted hexaprismane core  $[\{\text{Zn}_2\text{W}(\text{O})\text{O}_3\}_2]^{4+}$ .<sup>39</sup> Simultaneously, they also communicated a tetra-silver substituted sandwich-type silicotungstate  $[\text{Ag}_4(\gamma\text{-H}_2\text{SiW}_{10}\text{O}_{36})_2]^{8-}$  constructed from two  $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$  subunits encapsulating a diamond-shaped  $[\text{Ag}_4]^{4+}$  cluster (Fig. 7h).<sup>40</sup>

### IR spectra

IR spectra for 1–5 were recorded in the range of 4000 and 400  $\text{cm}^{-1}$  with KBr pellets (Fig. S1†). In the low-wavenumber region ( $\nu < 1000 \text{ cm}^{-1}$ ), IR spectra of 1–5 display four similar characteristic vibration patterns derived from the Keggin-type framework observed at 649–662, 952–957, 878–889 and 776–788  $\text{cm}^{-1}$ , which are ascribed to  $\nu(\text{Sb}-\text{O}_a)$ , terminal  $\nu(\text{W}-\text{O}_t)$ , corner-sharing  $\nu(\text{W}-\text{O}_b)$  and edge-sharing  $\nu(\text{W}-\text{O}_c)$ , respectively. The similarity of IR spectra of 1–5 in the low-wavenumber domain suggests that all of them contain the tetra- $\text{Fe}^{\text{III}}$  substituted sandwich-type  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  units in their skeletons. Compared with the IR spectrum of  $\text{Na}_{10}[\text{B}-\alpha\text{-SbW}_9\text{O}_{34}]\cdot 19.5\text{H}_2\text{O}$  [767, 920, 890 and 715  $\text{cm}^{-1}$  for  $\nu(\text{Sb}-\text{O}_a)$ ,  $\nu(\text{W}-\text{O}_t)$ ,  $\nu(\text{W}-\text{O}_b)$ , and  $\nu(\text{W}-\text{O}_c)$  asymmetry stretching vibrations],<sup>4</sup> four characteristic asymmetry vibration peaks for 1–5 have different shifts, which may be assigned to the configuration transformation of  $[\text{B}-\alpha\text{-SbW}_9\text{O}_{33}]^{9-} \rightarrow [\text{B}-\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  and the implanting of the rhomb-like  $\{\text{Fe}^{\text{III}}_4\}$  cluster to the vacant sites of two  $[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  fragments. Furthermore, these IR data are comparable to those of the dimeric Krebs' structure  $\text{Na}_6[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]\cdot 32\text{H}_2\text{O}$  [678, 948, 883 and 773  $\text{cm}^{-1}$  for  $\nu(\text{Sb}-\text{O}_a)$ ,  $\nu(\text{W}-\text{O}_t)$ ,  $\nu(\text{W}-\text{O}_b)$  and  $\nu(\text{W}-\text{O}_c)$  asymmetry stretching vibrations];<sup>13</sup> four characteristic asymmetry vibration bands for 1–5 only have little shifts, indicating that RE cations have certain effect on  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  POAs.

### Electrochemical and electrocatalytic properties

To survey their electrochemical and electrocatalytic properties, the cyclic voltammetry (CV) measurements of **1** and **2** were carried out in 0.5 mol  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$  aqueous solution. Both compounds display similar electrochemical (Fig. 8, S2, and S3†) and electrocatalytic properties, which may result from the same POA building unit  $[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  in their structures of **1** and **2**. The reproducibility of cyclic voltammograms is indicative of the stability of **1** and **2** in this medium (Fig. S4†).

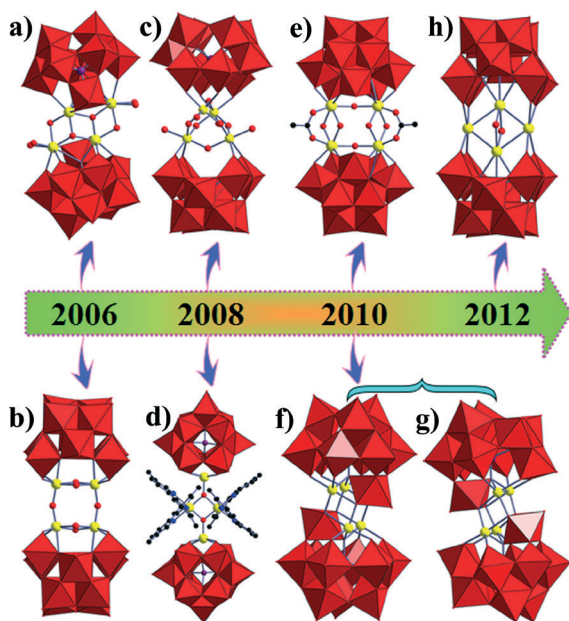


Fig. 7 Illustrations of some representative tetranuclear (a–h) sandwich-type compounds previously reported.

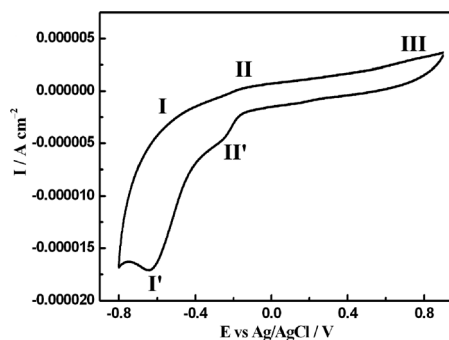


Fig. 8 Cyclic voltammogram of **1** (concentration:  $1.73 \times 10^{-4}$  mol L<sup>-1</sup>) in 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> aqueous solution (pH = 1.44). Scan rate: 30 mV s<sup>-1</sup>.

Fig. 8 demonstrates the typical cyclic voltammogram for **1** (at a concentration of  $1.73 \times 10^{-4}$  mol L<sup>-1</sup>) dissolved in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> + Na<sub>2</sub>SO<sub>4</sub> aqueous solution, pH = 1.44, at a scan rate of 30 mV s<sup>-1</sup>. The typical cyclic voltammogram for **2** is illustrated in Fig. S3a.† In the negative potential direction, the cyclic voltammogram exhibits two pairs of redox waves with the corresponding  $E_{1/2}$  peak potentials located at -0.566 V (I/I') and -0.197 V (II/II') for **1** and -0.550 V (I/I') and -0.185 V (II/II') for **2** [ $E_{1/2} = (E_{pa} + E_{pc})/2$ ], respectively. In the positive potential direction, there is only an ill-defined oxidation peak appearing at +0.749 V (III) for **1** and +0.734 V (III) for **2**, and the corresponding reduction peak is not readily visible. As expected, the W<sup>VI</sup>-based waves are seen at the more negative potential than the Fe<sup>III</sup>-based wave. The  $\Delta E_p$  values of two couples of redox waves (I-I' and II-II') in the cyclic voltammograms are 178 mV and 100 mV for **1** and 223 mV and 107 mV for **2**, respectively (Tables S2, S3†), which suggest the quasi-reversible redox processes of W<sup>VI</sup> centers in the POA frameworks (the theoretical value of the  $\Delta E_p$  value for a reversible one-electron transfer process is about 59 mV). These results are in accordance with the previous documents.<sup>41</sup> The appearance of a single oxidation peak potential at +0.749 V (III) for **1** and +0.734 V (III) for **2** confirms the irreversible process of the Fe<sup>III</sup> centers.<sup>42</sup> The related discussion on the influences of the scan rate and the pH on the electrochemical behaviors of **1** and **2** are shown in the ESI† (Fig. S2, S3, S5, S6, and S7; Tables S2 and S3).

As is well known, electrocatalytic properties of POMs have been widely explored on account of their capability of delivering the electrons to other species and experiencing rapid multi-electron transfer redox processes.<sup>43</sup> Some groups have been working on the exploration of the electrocatalytic reductions of POMs (such as Mialane, Dolbecq, Kortz and Wang and so on).<sup>43,44</sup> Inspired by the previous excellent work, we have also done some research on electrocatalytic properties. Recently, our group reported that two novel Cu<sup>II</sup>-RE<sup>III</sup> heterometallic germanotungstate hybrids had obvious electrocatalytic activities toward nitrite and bromate and a Fe<sup>III</sup>-Pr<sup>III</sup> heterometallic TA hybrid was effective in the electrocatalytic reduction of nitrite, bromate and hydrogen peroxide.<sup>45</sup> Here, **1** and **2** were employed to probe their electrocatalytic

activities toward the reduction of nitrite (NO<sub>2</sub><sup>-</sup>) and bromate (BrO<sub>3</sub><sup>-</sup>) in 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> aqueous solution, pH 1.44 (Fig. 9 and S8†). As illustrated in Fig. 9a, it can be clearly seen that with the addition of nitrite, the Fe<sup>III</sup>-based peak current intensity remains almost unvaried, and the cathodic reduction current intensities of two couples of W<sup>VI</sup>-based waves gradually increase, meanwhile the corresponding anodic oxidation current intensities decrease gradually. Moreover, compared with the first redox couple (I-I'), the second redox couple (II-II') shows a weak evolution trend. These results indicate that the reduction process of nitrite is mainly controlled by the reduced species of tungsten-oxo clusters in **1**. This phenomenon is in good agreement with the previous reports.<sup>46</sup> Furthermore, the electrocatalytic activity of **1** toward the reduction of bromate was also measured (Fig. 9b), and the electrocatalytic procedure occurs on the first (I-I') and second (II-II') redox couples. With the addition of BrO<sub>3</sub><sup>-</sup>, the cathodic peak current intensities of two redox couples gradually enhance and the opposite anodic peak current intensities decrease, whereas the Fe<sup>III</sup>-based wave is almost unaffected by the addition of BrO<sub>3</sub><sup>-</sup>. The results indicate that the reduction of bromate is also mainly mediated by the reduced species of tungsten-oxo clusters in **1**. It is apparent that **2** exhibits a similar electrocatalytic behavior toward the reduction of NO<sub>2</sub><sup>-</sup> and BrO<sub>3</sub><sup>-</sup> (Fig. S8†). In addition, the electrocatalytic activities of Na<sub>9</sub>[B- $\alpha$ -SbW<sub>9</sub>O<sub>33</sub>]-19.5H<sub>2</sub>O, FeCl<sub>3</sub>

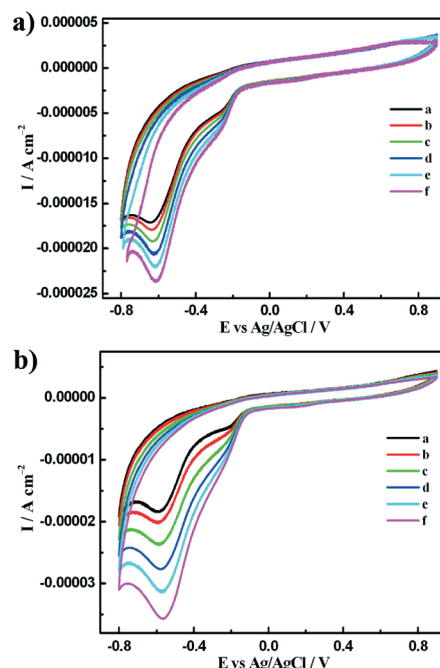


Fig. 9 (a) Cyclic voltammograms of **1** (concentration:  $1.73 \times 10^{-4}$  mol L<sup>-1</sup>) in 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> aqueous solution, pH = 1.44, with the addition of various concentrations of NaNO<sub>2</sub> (a: 0, b:  $1 \times 10^{-5}$ , c:  $3 \times 10^{-5}$ , d:  $7 \times 10^{-5}$ , e:  $1 \times 10^{-4}$ , f:  $1.5 \times 10^{-4}$  mol L<sup>-1</sup>). (b) Cyclic voltammograms of **1** (concentration:  $1.73 \times 10^{-4}$  mol L<sup>-1</sup>) in 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> aqueous solution, pH = 1.44, with the addition of various concentrations of NaBrO<sub>3</sub> (a: 0, b:  $1 \times 10^{-5}$ , c:  $3 \times 10^{-5}$ , d:  $5 \times 10^{-5}$ , e:  $7 \times 10^{-5}$ , f:  $9 \times 10^{-5}$  mol L<sup>-1</sup>).

$\cdot 6\text{H}_2\text{O}$ ,  $\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  toward the reduction of  $\text{NO}_2^-$  and  $\text{BrO}_3^-$  were also performed under similar conditions (Fig. S9–S12<sup>†</sup>). The results show that  $\text{Na}_9[\text{B}-\alpha\text{-SbW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$  exhibits very weak electrocatalytic activities toward the reduction of  $\text{NO}_2^-$  and  $\text{BrO}_3^-$  under similar conditions (Fig. S9<sup>†</sup>). As shown in Fig. S10,<sup>†</sup>  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  has almost no electrocatalytic activity toward the reduction of  $\text{NO}_2^-$ , whereas it illustrates weak electrocatalytic activity toward the reduction of  $\text{BrO}_3^-$ . As expected, both  $\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  have no electrocatalytic activities toward the reduction of  $\text{NO}_2^-$  and  $\text{BrO}_3^-$  (Fig. S11 and S12<sup>†</sup>). These comparative experiments further confirm that the electrocatalytic activities of 1 and 2 toward the reduction of nitrite and bromate are mainly controlled by tungsten-oxo cluster fragments in their structures. However, the electrocatalytic activities of 1 and 2 that are better than  $\text{Na}_9[\text{B}-\alpha\text{-SbW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$  may be derived from the synergistic contribution of  $[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]^{9-}$  and  $\{\text{Fe}^{\text{III}}_4\}$  segments, which suggests that the incorporation of TM cations into lacunary polyoxotungstate matrices can improve the electrocatalytic activities. According to the method introduced by Keita, we can estimate and compare the catalytic efficiency (CAT) of 1 and 2 for the reduction of nitrite and bromate. Take  $\text{NaNO}_2$  for example, the CAT of 1' is defined by:  $\text{CAT} = 100 \times \{I_p(\text{POM}, \text{NaNO}_2) - I_p(\text{POM})\} / I_p(\text{POM})$  where  $I_p(\text{POM})$  and  $I_p(\text{POM}, \text{NaNO}_2)$  are the cathodic peak current intensities in the absence and in the presence of  $\text{NaNO}_2$ , respectively.<sup>47</sup> In Table S4,<sup>†</sup> the CAT values of the first W reduction peak (I') for 1 and 2 (catalyst,  $1.47 \times 10^{-4} \text{ mol L}^{-1}$ ) with regard to  $1 \times 10^{-5} \text{ mol L}^{-1} \text{ NaNO}_2$  are calculated to be 4.78% and 4.55%; with regard to  $3 \times 10^{-5} \text{ mol L}^{-1} \text{ NaNO}_2$ , the values are calculated to be 12.07% and 9.89%; with regard to  $1.5 \times 10^{-4} \text{ mol L}^{-1} \text{ NaNO}_2$ , the values are calculated to be 38.08% and 29.31%, respectively. Obviously, the results demonstrate that the CAT of 1 is slightly higher than 2 in the electrocatalytic reduction of nitrite. Table S5<sup>†</sup> displays the CAT values of 1 and 2 for the bromate reduction; it is evident that the CAT of 1 is also slightly higher than 2 in the electrocatalytic reduction of  $\text{BrO}_3^-$ . However, under the same conditions, the catalytic activities of 1 and 2 in the reduction of  $\text{BrO}_3^-$  are higher than that of  $\text{NO}_2^-$  (Fig. 9 and S8<sup>†</sup>).

### TG analyses

The thermal stability of 1–5 has been investigated on crystalline samples under a nitrogen atmosphere from 25 to 750 °C. The TG curves indicate that 1–5 undergo a slow one-step weight loss process (Fig. 10). For 1, the weight loss of 13.26% involves the loss of 16 lattice water molecules and 24 coordination water molecules (calcd. 12.34%). The weight loss of 14.18%, 14.46%, 14.37% and 14.82% for 2, 3, 4 and 5 corresponds to the loss of 22 lattice water molecules and 24 coordination water molecules (calcd. 13.85%, 13.83%, 13.78%, and 14.18%, respectively).

## Conclusions

Two types of novel purely inorganic TA-based Fe–RE heterometallic derivatives have been successfully separated under

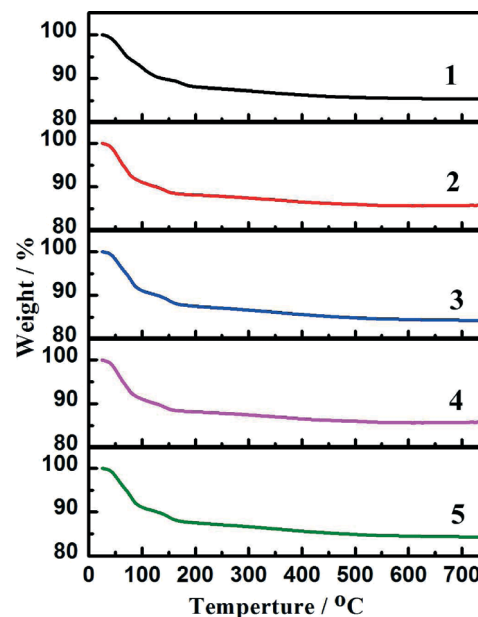


Fig. 10 The TG curves of 1–5.

the conventional aqueous solution method and structurally characterized by elemental analysis, IR spectroscopy, PXRD, single-crystal X-ray diffraction and TG analysis. 1–5 represent the first purely inorganic Fe–RE heterometallic TAs based on tetra- $\text{Fe}^{\text{III}}$  substituted sandwich-type  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  POAs. Furthermore, other types of tetra-TM sandwiched POMs have been summarized and compared. In addition, the electrochemical and electrocatalytic properties of 1 and 2 have been evaluated in aqueous media. Both 1 and 2 manifest obvious electrocatalytic activity toward the reduction of  $\text{NO}_2^-$  and  $\text{BrO}_3^-$ . The successful syntheses of these heterometallic compounds will provide us with a new opportunity for further searching and finding novel purely inorganic TA-based TM–RE heterometallic derivatives. In the next work, we will utilize prefabricated TM substituted TA precursors to react with RE cations or prefabricated RE substituted TA precursors to react with TM cations to design and prepare desired TA-based TM–RE heterometallic derivatives with interesting structures and unique properties by making use of different TM and RE pairs and different synthetic strategies. We believe that many more TA-based TM–RE heterometallic derivatives will be discovered by means of the step by step assembly strategy. Moreover, implanting polycarboxylic ligands to TM or RE centers in this reaction system to construct organic–inorganic hybrid TA-based TM–RE heterometallic derivatives is also our other goal during the course of our PTRHD exploration.

## Acknowledgements

The authors acknowledge the support from the Natural Science Foundation of China (21301049, U1304208), the 2014 Special Foundation for Scientific Research Project of Henan University, the Natural Science Foundation of Henan Province



(122300410106), the Foundation of State Key Laboratory of Structural Chemistry (20120013), the 2012 Young Backbone Teachers Foundation from Henan Province (2012GGJS-027) and the 2013, 2014 Students Innovative Pilot Plans of Henan University.

## References

- (a) X. Fang, P. Kögerler, Y. Furukawa, M. Speldrich and M. Luban, *Angew. Chem., Int. Ed.*, 2011, **50**, 5212; (b) M. V. Vasylyev and R. Neumann, *J. Am. Chem. Soc.*, 2004, **126**, 884; (c) U. Kortz, A. Müller, J. van Slageren, J. Schnack, N. S. Dalal and M. Dressel, *Coord. Chem. Rev.*, 2009, **253**, 2315; (d) J. D. Compain, P. Mialane, A. Dolbecq, I. M. Mbomekallé, J. Marrot, F. Sécheresse, E. Rivière, G. Rogez and W. Wernsdorfer, *Angew. Chem., Int. Ed.*, 2009, **48**, 3077; (e) S. G. Mitchell, C. Streb, H. N. Miras, T. Boyd, D. L. Long and L. Cronin, *Nat. Chem.*, 2010, **2**, 308; (f) A. Müller and S. Roy, *Coord. Chem. Rev.*, 2003, **245**, 153; (g) D. L. Long, R. Tsunashima and L. Cronin, *Angew. Chem., Int. Ed.*, 2010, **49**, 1736.
- T. J. R. Weakley, H. T. J. Evans, J. S. Showell, G. F. Tourné and C. M. Tourné, *J. Chem. Soc., Chem. Commun.*, 1973, 139.
- J. Fischer, L. Richard and R. Weiss, *J. Am. Chem. Soc.*, 1976, **98**, 3050.
- M. Bösing, I. Loose, H. Pohlmann and B. Krebs, *Chem. – Eur. J.*, 1997, **3**, 1232.
- I. Loose, E. Droste, M. Bösing, H. Pohlmann, M. H. Dickman, C. Rosu, M. T. Pope and B. Krebs, *Inorg. Chem.*, 1999, **38**, 2688.
- M. Piepenbrink, E. M. Limanski and B. Krebs, *Z. Anorg. Allg. Chem.*, 2002, **628**, 1187.
- D. Laurencin, R. Villanneau, P. Herson, R. Thouvenot, Y. Jeannin and A. Proust, *Chem. Commun.*, 2005, 5524.
- L. H. Bi, G. Al-Kadamany, E. V. Chubarova, M. H. Dickman, L. F. Chen, D. S. Gopala, R. M. Richards, B. Keita, L. Nadjo, H. Jaensch, G. Mathys and U. Kortz, *Inorg. Chem.*, 2009, **48**, 10068.
- L. H. Bi, B. Li, S. Bi and L. X. Wu, *J. Solid State Chem.*, 2009, **182**, 1401.
- L. C. Zhang, H. Xue, Z. M. Zhu, Q. X. Wang, W. S. You, Y. G. Li and E. B. Wang, *Inorg. Chem. Commun.*, 2010, **13**, 609.
- I. V. Kalinina, N. V. Izarova and U. Kortz, *Inorg. Chem.*, 2012, **51**, 7442.
- C. C. Zhao, C. S. Kambara, Y. Yang, A. L. Kaledin, D. G. Musaev, T. Q. Lian and C. L. Hill, *Inorg. Chem.*, 2013, **52**, 671.
- U. Kortz, M. G. Savelieff, B. S. Bassil, B. Keita and L. Nadjo, *Inorg. Chem.*, 2002, **41**, 783.
- M. Carraro, B. S. Bassil, A. Sorarù, S. Berardi, A. Suchopar, U. Kortz and M. Bonchio, *Chem. Commun.*, 2013, **49**, 7914.
- (a) B. Artetxe, S. Reinoso, L. S. Felices, P. Vitoria, A. Pache, J. Martín-Caballero and J. M. Gutierrez-Zorrilla, *Inorg. Chem.*, 2015, **54**, 241; (b) B. Artetxe, S. Reinoso, L. S. Felices, L. Lezama, A. Pache, C. Vicent and J. M. Gutierrez-Zorrilla, *Inorg. Chem.*, 2015, **54**, 409.
- T. McGlone, L. Vilà-Nadal, H. N. Miras, D.-L. Long, J. M. Poblet and L. Cronin, *Dalton Trans.*, 2010, **39**, 11599.
- A. J. Gaunt, I. May, R. Copping, A. I. Bhatt, D. Collison, O. D. Fox, K. T. Holman and M. T. Pope, *Dalton Trans.*, 2003, 3009.
- (a) P. Mialane, J. Marrot, E. Rivière, J. Nebout and G. Herve, *Inorg. Chem.*, 2001, **40**, 44; (b) U. Kortz, N. K. Al-Kassem, M. G. Savelieff, N. A. Al Kadi and M. Sadakane, *Inorg. Chem.*, 2001, **40**, 4742; (c) D. Volkmer, B. Bredenkötter, J. Tellenbröcker, P. Kögerler, D. G. Kurth, P. Lehmann, H. Schnablegger, D. Schwahn, M. Piepenbrink and B. Krebs, *J. Am. Chem. Soc.*, 2002, **124**, 10489; (d) A. C. Stowe, S. Nellutla, N. S. Dalal and U. Kortz, *Eur. J. Inorg. Chem.*, 2004, 3792; (e) L. H. Bi, M. Reicke, U. Kortz, B. Keita, L. Nadjo and R. J. Clark, *Inorg. Chem.*, 2004, **43**, 3915; (f) D. Drewes, M. Piepenbrink and B. Krebs, *J. Cluster Sci.*, 2006, **17**, 361; (g) R. R. Cui, H. L. Wang, X. Y. Yang, S. H. Ren, H. M. Hu, F. Fu, J. W. Wang and G. L. Xue, *Chin. J. Chem.*, 2007, **25**, 176; (h) J. P. Wang, P. T. Ma, J. Li, H. Y. Niu and J. Y. Niu, *Chem. – Asian J.*, 2008, **3**, 822.
- (a) T. Yamase, K. Fukaya, H. Nojiri and Y. Ohshima, *Inorg. Chem.*, 2006, **45**, 7698; (b) C. C. Zhao, E. N. Glass, B. Chica, D. G. Musaev, J. M. Sumliner, R. B. Dyer, T. Q. Lian and C. L. Hill, *J. Am. Chem. Soc.*, 2014, **136**, 12085.
- G. L. Xue, J. Vaissermann and P. Gouzerh, *J. Cluster Sci.*, 2002, **13**, 409.
- M. Ibrahim, S. S. Mal, B. S. Bassil, A. Banerjee and U. Kortz, *Inorg. Chem.*, 2011, **50**, 956.
- A. H. Ismail, B. S. Bassil, I. Römer and U. Kortz, *Z. Anorg. Allg. Chem.*, 2013, **639**, 2510.
- J. W. Zhao, J. Cao, Y. Z. Li, J. Zhang and L. J. Chen, *Cryst. Growth Des.*, 2014, **14**, 6217.
- G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.
- (a) B. Li, J.-W. Zhao, S.-T. Zheng and G.-Y. Yang, *Inorg. Chem.*, 2009, **48**, 8294; (b) G. L. Xue, B. Liu, H. M. Hu, J. H. Yang, J. W. Wang and F. Fu, *J. Mol. Struct.*, 2004, **690**, 95.
- (a) R. C. Howell, F. G. Perez, S. Jain, W. D. Horrocks, A. L. Rheingold and L. C. Francesconi, *Angew. Chem., Int. Ed.*, 2001, **40**, 4031; (b) B. S. Bassil, M. H. Dickman, I. Römer, B. Kammer and U. Kortz, *Angew. Chem., Int. Ed.*, 2007, **46**, 6192; (c) S. Yao, Z. M. Zhang, Y. G. Li, Y. Lu, E. B. Wang and Z. M. Su, *Cryst. Growth Des.*, 2010, **10**, 135.
- S. T. Zheng, M. H. Wang and G. Y. Yang, *Chem. – Asian J.*, 2007, **2**, 1380.
- W. L. Chen, Y. G. Li, Y. H. Wang and E. B. Wang, *Eur. J. Inorg. Chem.*, 2007, 2216.
- (a) J. F. Cao, S. X. Liu, R. G. Cao, L. H. Xie, Y. H. Ren, C. Y. Gao and L. Xu, *Dalton Trans.*, 2008, 115; (b) Z. M. Zhang, Y. G. Li, W. L. Chen, E. B. Wang and X. L. Wang, *Inorg. Chem. Commun.*, 2008, **11**, 879; (c) B. Li, J. W. Zhao, S. T. Zheng and G. Y. Yang, *J. Cluster Sci.*, 2009, **20**, 503; (d) B. Nohra, P. Mialane, A. Dolbecq, E. Rivière, J. Marrot and F. Sécheresse, *Chem. Commun.*, 2009, 2703; (e) D. Y. Du, J. S. Qin, S. L. Li, Y. Q. Lan, X. L. Wang and Z. M. Su, *Aust. J.*

- Chem.*, 2010, **63**, 1389; (f) D. Y. Du, J. S. Qin, S. L. Li, X. L. Wang, G. S. Yang, Y. G. Li, K. Z. Shao and Z. M. Su, *Inorg. Chim. Acta*, 2010, **363**, 3823; (g) J. D. Compain, P. Mialane, A. Dolbecq, I. M. Mbomekallé, J. Marrot, F. Sécheresse, C. Duboc and E. Rivière, *Inorg. Chem.*, 2010, **49**, 2851; (h) J. Y. Niu, S. W. Zhang, H. N. Chen, J. W. Zhao, P. T. Ma and J. P. Wang, *Cryst. Growth Des.*, 2011, **11**, 3769; (i) D. Y. Shi, L. J. Chen, J. W. Zhao, Y. Wang, P. T. Ma and J. Y. Niu, *Inorg. Chem. Commun.*, 2011, **14**, 324; (j) L. J. Chen, D. Y. Shi, Y. Wang, H. L. Chen, Z. D. Geng, J. W. Zhao, P. T. Ma and J. Y. Niu, *J. Coord. Chem.*, 2011, **64**, 400; (k) J. D. Compain, K. Nakabayashi and S. Ohkoshi, *Inorg. Chem.*, 2012, **51**, 4897; (l) S. W. Zhang, J. W. Zhao, P. T. Ma, H. N. Chen, J. Y. Niu and J. P. Wang, *Cryst. Growth Des.*, 2012, **12**, 1263; (m) S. W. Zhang, J. W. Zhao, P. T. Ma, J. Y. Niu and J. P. Wang, *Chem. – Asian J.*, 2012, **7**, 966; (n) D. Y. Shi, J. W. Zhao, L. J. Chen, P. T. Ma, J. P. Wang and J. Y. Niu, *CrystEngComm*, 2012, **14**, 3108; (o) H. Y. Zhao, J. W. Zhao, B. F. Yang, H. He and G. Y. Yang, *Cryst. Growth Des.*, 2013, **13**, 5169; (p) H. Y. Zhao, J. W. Zhao, B. F. Yang, H. He and G. Y. Yang, *CrystEngComm*, 2013, **15**, 5209; (q) Y. Y. Li, J. W. Zhao, Q. Wei, B. F. Yang, H. He and G. Y. Yang, *Chem. – Asian J.*, 2014, **9**, 858.
- 30 S. B. Tian, Y. Z. Li, J. W. Zhao, P. T. Ma and L. J. Chen, *Inorg. Chem. Commun.*, 2013, **33**, 99.
- 31 R. X. Tan, X. H. Pang, Y. L. Ren, X. H. Wang and R. Li, *Z. Anorg. Allg. Chem.*, 2011, **637**, 1178.
- 32 (a) A. Dolbecq, J. D. Compain, P. Mialane, J. Marrot, E. Riviere and F. Sécheresse, *Inorg. Chem.*, 2008, **47**, 3371; (b) F. Hussain, M. Reicke and U. Kortz, *Eur. J. Inorg. Chem.*, 2004, 2733; (c) B. W. Chen, W. L. Chen, Y. G. Li and E. B. Wang, *J. Cluster Sci.*, 2011, **22**, 73.
- 33 D. D. Zhang, C. Z. Wang, S. Z. Li, J. P. Liu, P. T. Ma, J. P. Wang and J. Y. Niu, *J. Solid State Chem.*, 2013, **198**, 18.
- 34 B. S. Bassil, M. H. Dickman and U. Kortz, *Inorg. Chem.*, 2006, **45**, 2394.
- 35 Y. Goto, K. Kamata, K. Yamaguchi, K. Uehara, S. Hikichi and N. Mizuno, *Inorg. Chem.*, 2006, **45**, 2347.
- 36 Y. V. Geletii, B. Botar, P. Kögerler, D. A. Hillesheim, D. G. Musaev and C. L. Hill, *Angew. Chem., Int. Ed.*, 2008, **47**, 3896.
- 37 C. Pichon, A. Dolbecq, P. Mialane, J. Marrot, E. Rivière, M. Goral, M. Zynek, T. McCormac, S. A. Borshch, E. Zueva and F. Sécheresse, *Chem. – Eur. J.*, 2008, **14**, 3189.
- 38 W. Zhang, S. X. Liu, C. D. Zhang, R. K. Tan, F. J. Ma, S. J. Li and Y. Y. Zhang, *Eur. J. Inorg. Chem.*, 2010, 3473.
- 39 Y. Kikukawa, K. Yamaguchi and N. Mizuno, *Inorg. Chem.*, 2010, **49**, 8194.
- 40 Y. Kikukawa, Y. Kuroda, K. Yamaguchi and N. Mizuno, *Angew. Chem., Int. Ed.*, 2012, **51**, 2434.
- 41 (a) B. S. Bassil, S. Nellutla, U. Kortz, A. C. Stowe, J. van Tol, N. S. Dalal, B. Keita and L. Nadjo, *Inorg. Chem.*, 2005, **44**, 2659; (b) F. Hussain, U. Kortz, B. Keita, L. Nadjo and M. T. Pope, *Inorg. Chem.*, 2006, **45**, 761.
- 42 (a) M. Sadakane and E. Steckhan, *Chem. Rev.*, 1998, **98**, 219; (b) U. Kortz, M. G. Savelieff, B. S. Bassil, B. Keita and L. Nadjo, *Inorg. Chem.*, 2002, **41**, 783; (c) N. Anwar, M. Vagin, F. Laffir, G. Armstrong, C. Dickinson and T. McCormac, *Analyst*, 2012, **137**, 624.
- 43 (a) Z. G. Han, Y. L. Zhao, J. Peng, Y. H. Feng, J. N. Yin and Q. Liu, *Electroanalysis*, 2005, **17**, 1097; (b) B. Nohra, H. E. Moll, L. M. R. Albelo, P. Mialane, J. Marrot, C. Mellot-Draznieks, M. O'Keeffe, R. N. Biboum, J. Lemaire, B. Keita, L. Nadjo and A. Dolbecq, *J. Am. Chem. Soc.*, 2011, **133**, 13363.
- 44 (a) L. H. Bi, U. Kortz, S. Nellutla, A. C. Stowe, J. V. Tol, N. S. Dalal, B. Keita and L. Nadjo, *Inorg. Chem.*, 2005, **44**, 896; (b) Z. M. Zhang, Y. F. Qi, C. Qin, Y. G. Li, E. B. Wang, X. L. Wang, Z. M. Su and L. Xu, *Inorg. Chem.*, 2007, **46**, 8162; (c) I. M. Mbomekalle, P. Mialane, A. Dolbecq, J. Marrot, F. Sécheresse, P. Berthet, B. Keita and L. Nadjo, *Eur. J. Inorg. Chem.*, 2009, 5194; (d) M. Ammam, I. M. Mbomekalle, B. Keita, L. Nadjo, T. M. Anderson, X. Zhang, K. I. Hardcastle, C. L. Hill and J. Fransaer, *J. Electroanal. Chem.*, 2010, **647**, 97.
- 45 (a) J. W. Zhao, D. Y. Shi, L. J. Chen, P. T. Ma, J. P. Wang, J. Zhang and J. Y. Niu, *Cryst. Growth Des.*, 2013, **13**, 4368; (b) J. W. Zhao, Y. Z. Li, F. Ji, J. Yuan, L. J. Chen and G. Y. Yang, *Dalton Trans.*, 2014, **43**, 5694.
- 46 (a) B. Keita, P. de Oliveira, L. Nadjo and U. Kortz, *Chem. – Eur. J.*, 2007, **13**, 5480; (b) X. Wang, H. Hu, A. Tian, H. Lin and J. Li, *Inorg. Chem.*, 2010, **49**, 10299.
- 47 (a) B. Keita, A. Belhouaria, L. Nadjo and R. Contant, *J. Electroanal. Chem.*, 1995, **381**, 243; (b) F. M. Zonoz, I. M. Zonoz, A. Jamshidi and M. H. Alizadeh, *Solid State Sci.*, 2014, **32**, 13.