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1. Introduction

Polyoxometalates (POMs) are the discrete anionic clusters that can be condensed by oxo-bridged early transition metal atoms in their high oxidation states (usually Mo$^{VI}$, W$^{VI}$, V$^{5+}$, Nb$^{5+}$ or Ta$^{5+}$). These metal atoms are coordinated by six oxygen ligands giving rise to [MO$_6$] octahedral geometries and then the resulting [MO$_6$] units are further joined together by corner-, edge- (rarely face-) sharing oxygen atoms (formally O$^2-$ or occasionally HO$^-$ ions). With regard to polyoxoanions (POAs), several classical types have been reported: Keggin, Well-Dawson, Lindqvist, Anderson-Evans, Weakley, Silverton, Stranberg, etc. After Pope and Müller published a review article that comprehensively elucidated the fascinating structural characteristics and important potentials in several disciplines of POMs in 1991, a myriad of unexpected POM structures came to constantly emerging. Then a special thematic issue on POMs organized by Hill in 1998 not only rapidly accelerated the discovery of peculiar POM species, but also provoked the emerge of some new research areas in POM chemistry. The flexible and diversiform structures endow POM-based materials many versatile performances in various areas such as catalysis, medicine, materials science, nanotechnology, molecular magnetism and photochemistry. Historically, the first TM substituted POM (TMSP) was communicated in 1837 by Berzelius as early as 183 years ago and even the first structural determination of the phosphotungstic acid H$_3$[PW$_5$O$_{12}$]·29H$_2$O was accomplished until 1936 by Keggin by virtue of the powder X-ray diffraction study.

Based on their nucleophilic oxygen-enriched surfaces, POM units can act as excellent inorganic multidentate candidates to integrate transition-metal (TM), rare-earth (RE) or both into their structures. Thereby, a vast array of novel TM, RE or TM–RE-containing POMs have being dug out gradually. For example, the first RE-containing POM (RECP) (NH$_4$)$_2$[H$_2$CeMo$_{12}$O$_{40}$]·nH$_2$O was discovered by Barbieri in 1914. Then in 1971, Peacock and Weakley successfully separated a family of 1.2 series RECPs [RE(W$_{6}$O$_{39}$)$_2$]$^{3+}$, [RE(SiW$_{12}$O$_{39}$)$_2$]$^{13+}$ and [RE(RE$_3$W$_{15}$O$_{61}$)$_2$]$^{15+}$, which are a milestone in the history of RECP chemistry. Historically, the first TM substituted POM (TMSP) was communicated by Simmons. 

Xing Ma was born in Anhui, China in 1995 and now she is pursuing her BS degree in chemistry at Henan University. In 2013, she as a student began to conduct scientific research in the group of Prof. Junwei Zhao in Henan Key Laboratory of Polyoxometalate Chemistry. Her current research interest is focused on the designed synthesis and luminescent properties of organic–inorganic hybrid rare-earth-containing polyoxometalate materials.

Wen Yang was born in Henan Province, China. Currently, she is majoring in materials chemistry to receive the BS degree at Henan University and works as a student in Henan Key Laboratory of Polyoxometalate Chemistry under the supervision of Prof. Junwei Zhao. Her current research is concentrated on the preparation and electrochemical properties of novel rare-earth substituted...
Scheme 1 Schematic representation of the assembly processes of RECPs. Several typical POAs and three significant properties are highlighted.

at the 1962 (Stockholm) International Conference on Coordination Chemistry (ICCC) and its structure (it is an 11-tungstosilicate wherein one W atom of the Keggin structure was replaced by a Co$^{2+}$ ion) was confirmed by St. Moritz at the 1966 ICCC. Moreover, the composition, size, shape, solubility, redox potential, magnetic and catalytic properties of TMSPs are relatively easy to be fine-tuned by elaborate selection of types and oxidation states of TM ions. Therefore, the development of TMSPs is much faster than that of RECPs. However, RECPs can exhibit special luminescent, Lewis acid catalytic or magnetic functionalities by taking advantage of the electronic and structural features of RE ions (Scheme 1): (i) Depending on the special electronic properties of lanthanide (Ln) cations (the shielding of the 4f orbitals by the filled 5s$^2$5p$^6$ subshells), Ln-containing compounds often have good fluorescence activity and long lifetime, which makes them be used in optical fields such as light-emitting diodes, plasma displays, sensory probes, medicinal analyses, monitoring drug delivery as well as cell imaging; (ii) high coordination numbers and flexible coordination geometries of RE ions

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Junwei Zhao obtained the BS degree in chemistry in 2002 and gained his MS degree under the supervision of Prof. Jingyang Niu in 2005 from Henan University. In 2008, he received his PhD under the supervision of Prof. Guo-Yu Yang at Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences. After then, he joined Henan University, was promoted to a full Professor in chemistry in 2014 and was ranked as an academic leader of Department of Education of Henan Province in 2015. He is mainly engaged in the synthesis and preparative chemistry of polyoxometalate-based functional materials and the relevant optical, electrical, magnetic and medical properties.
endow them with the ability of leaving some residual coordination sites that can act as the effective Lewis acids for the activation of substrates. It has proved that the introduction of some RE ions (Lewis acidic cations) into POM skeletons can form recoverable catalysts with high chemoselectivities. On the other hand, oxyphilic RE ions can easily combine with oxygenic ligands (such as POM fragments herein) that are guided by the Hard and Soft Acids and Bases (HSAB) theory; account of the presence of the large number of unpaired 4f electrons, RE ions are widely utilized to manufacture molecule-based magnetic materials. Hence, RECPs have always been a sparkling and important subclass in the large family of POMs. Moreover, the emergence of some novel high-nuclear RECPs in the past decade has also aroused the worldwide increasing attention on high-nuclear RECP chemistry.

In this highlight article, we will begin to give the intensive accounts on some typical RECPs obtained in the past decade according to the unit of \([\text{Ln}((\text{OH})_2)_2\text{O}]^{18-}\) (Fig. 1). The synthetic strategies, structural characteristics and some important properties will be simultaneously involved in this highlight article. We hope this highlight article to be able to provide some useful highlights for designing and synthesizing novel RECPs with neoteric structures and wonderful properties in the following time.

2. Results and discussion

![Fig. 2](image)

**Fig. 2** (a) The \([\text{a-GeW}_1\text{O}_8\text{Y}((\text{H}_2\text{O})_2)_5]^{18+}\) building block. (b) The 1-D chain formed by \([\text{a-GeW}_1\text{O}_8\text{Y}((\text{H}_2\text{O})_2)_5]^{18+}\) units. (c) View of \([\text{RE}((\text{H}_2\text{O})_2)_2\text{O}_8\text{O}_3\text{W}_{11}\text{O}_{39}]^{20+}\). (d) View of \([\text{RE}((\text{H}_2\text{O})_2\text{Sb}_2\text{W}_{12}\text{O}_{42}(\text{OH})_2]^{20+}\). (e) Two possible isomers of the structural unit of \([\text{La}((\text{SiW}_6\text{O}_{19})_2]^{16+}\) (Copied from ref. 25). (f) View of enantiopure \(\text{K}_{1\alpha}\text{Na}_{1\alpha}\text{H}_2\text{O}((\text{Pr}((\text{PW})_{11}\text{O}_{39})_2]^{8.3\text{L-proline}}21.5\text{H}_2\text{O} and \(\text{K}_{1\alpha}\text{Na}_{1\alpha}\text{H}_2\text{O}((\text{Pr}((\text{PW})_{11}\text{O}_{39})_2]^{8.3\text{D-proline}}17\text{H}_2\text{O} (Copied from ref. 26). (WO_3 yellow, XO_3 bright green, RE: light purple, O: red)

2.1 Mononuclear RECPs

2.1.1 Mononuclear Keggin-type RECPs (MKRECPs)

It is generally known that the removal of a \([\text{M}=\text{O}]\) group can make the Keggin-type \([\text{XM}_2\text{O}_{39}]^{18+}\) skeleton transform to a \([\text{XM}_2\text{O}_{39}]^{20+}\) fragment with a larger “bite angle” defect site, which can clenach a metal ion into the defect site. Meanwhile, the high coordination RE ion inserted into the vacant site of the monovacant \([\text{XM}_2\text{O}_{39}]^{20+}\) moiety can provide several (usually 2–4) additional available coordination sites and further are used as linkers to combine one or more other lacunary POM units together. Since Peacock and Weakley first isolated the sandwich-type \([\text{RE}((\text{SiW}_{11}\text{O}_{39})_2]^{15+}\) POAs, a large number of mononuclear RECPs have been unremittingly reported. For the long period, Peacock–Weakley type MKRECPs (1-2-type) with discrete structures have dominated the mainstream status in the realm of MKRECPs. Until 2001, Pope et al. for the first time communicated two 1-D zigzag chains based on 1:1-type \([\text{RE}((\text{SiW}_{11}\text{O}_{39})_2]^{15+}\) MKRECP units. After that, several kinds of special MKRECPs with extended structures have been obtained. By virtue of the nature of different RE cations, Milane and coworkers not only synthesized a 1-D zigzag chainlike MKRECP \([\text{Eu}((\text{SiW}_{11}\text{O}_{39})_2]^{15+}\) but also isolated a 1-D linear MKRECP \([\text{Yb}((\text{SiW}_{11}\text{O}_{39})_2]^{15+}\) Inspired by the previous innovative work, Niu’s group addressed a novel 1-D chain MKRECP built by \([\text{a-SiW}_{10}\text{O}_{39}]\beta\text{Pr}((\text{H}_2\text{O})_2]^{17+}\) units via \([\text{NaPr}((\text{H}_2\text{O})_2]^{7+}\) bridges. With the further exploration, they reported a novel 1-D zigzag chain architecture based on \([\text{a-GeW}_{11}\text{O}_{39}]\gamma\text{H}_2\text{O}]^{15+}\) in 2006 (Fig. 2a, 2b) which is different from Pope’s work. Besides, in the past decade, some other discrete MKRECPs have also been synthesized. As more \([\text{M}=\text{O}]\) groups can lose from the Keggin POA, the negative charge of the resulting vacant POA can increase, which renders the vacant POA to become more nucleophilic and endows them higher reactivity to bind with RE ions. In 2013, by reaction of divacant precursor TBA\(\text{H}_4\text{[c-SiW}_{10}\text{O}_{39}] with \)[RE(acac)]\(2+\) \(\text{RE} = \text{Dy}^{III}, \text{Gd}^{III}, \text{La}^{III}\) (acac = acetylacetonate) in a mixed acetone–water solvent system, Mizuno et al. synthesized a new type of sandwich-type MKRECP with vacant sites \([\text{RE}((\text{H}_2\text{O})_2]^{15+}\) (Fig. 2c), in which the vacant sites are surrounded by coordinating \(\text{W}–\text{O}\) and \(\text{Ln}–\text{O}\) oxygen atoms. In the same year, Kortz’s group prepared the mono-RE derivatives of the Krebs-type 22-tungsto-2-antimonate \([\text{RE}((\text{H}_2\text{O})_2\text{Sb}_2\text{W}_{12}\text{O}_{39}(\text{OH})_2]^{16+}\) \(\text{RE} = \text{Yb}^{III}, \text{Lu}^{III}\) (Fig. 2d) by reaction of RE ions with \([\text{Sb}_2\text{W}_{12}\text{O}_{39}((\text{OH})_2]^{12+}\) in aqueous acidic (pH 5) medium. It is rather intriguing that \([\text{RE}((\text{H}_2\text{O})_2\text{Sb}_2\text{W}_{12}\text{O}_{39}(\text{OH})_2]^{16+}\) contains two \([\text{a-SbW}_{11}\text{O}_{39}]^{8+}\) fragments joined by two tungsten ions, leading in the lacunary \([\text{Sb}_2\text{W}_{12}\text{O}_{39}]^{14+}\) unit, which is then coordinated to a RE ion and a tungsten atom, giving rise to an architecture with idealized \(\text{C}_3\) symmetry (Fig. 2d). On the other hand, recently, the exploration and preparation of chiral MKRECPs has become an emerging field in POM chemistry because of the flexible rotation of the \([\text{XM}_2\text{O}_{39}]^{n+}\) moiety and intriguing 4f–4f transitions of RE ions, thus, chiral \([\text{RE}((\text{XM}_2\text{O}_{39})_2]^{15+}\) POAs have attracted increasing interest due to potential applications in asymmetric catalysts, chiral recognition and biological fields. Kortz et al. used the reaction of RE ions with the chiral monovacant Keggin-type \([\beta\text{SiW}_{11}\text{O}_{39}]^{8+}\) precursor in a 1:2 molar ratio in KCl medium at pH 5 and separated a series of chiral MKRECPs \([\text{RE}((\beta\text{SiW}_{11}\text{O}_{39})_2]^{15+}\) \(\text{RE} = \text{La}^{III}, \text{Ce}^{III}, \text{Sm}^{III}, \text{Eu}^{III}, \text{Gd}^{III}, \text{ Tb}^{III}, \text{Yb}^{III}, \text{Lu}^{III}\) (Fig. 2e), which represent the first RECPs based on chiral \([\beta\text{SiW}_{11}\text{O}_{39}]^{8+}\) fragments. Results indicate that large RE ions...
enantiomerically pure polyoxotungstates Na_{0.5}[L(H$_2$O)$_{2n-1}$NH$_3$]$_n$[Na$_n$[Ce$_8$(H$_2$O)$_{20}$]$_2$]-OH, [(H$_2$O)$_{20}$][L(H$_2$O)$_{2n-1}$NH$_3$][Na$_n$[Ce$_8$(H$_2$O)$_{20}$]$_2$]-OH (Fig. 3a) and also investigated their optical activities by the circular dichroism (CD) spectra. Similarly, we also obtained an acenmic phosphotungstate KNa$_3$[HPrO$_4$][Sm(α-PW$_{11}$O$_{39}$)$_3$]·8.3H$_2$O. (b) Views of two enantiomerically pure polyoxotungstates KNa$_3$[HPrO$_4$][Sm(α-PW$_{11}$O$_{39}$)$_3$]·8.3H$_2$O based on Anderson-type [Al(OH)$_6$Mo$_6$O$_{19}$]$_2$– cations and successfully separated a novel 1-D zigzag chain-like MARECP [La(H$_2$O)$_2$Al(OH)$_6$Mo$_6$O$_{19}$]$_2$·4nH$_2$O. (c) The 1-D helical chain of [La(H$_2$O)$_2$Al(OH)$_6$Mo$_6$O$_{19}$]$_2$·4nH$_2$O and L-, D-(+)-cerium tartrate or D-(–)-cerium tartrate by reaction of the trivacant Keggin [n-SiW$_{11}$O$_{39}$]$^{10–}$ and L- (+)-cerium tartrate or D-(–)-cerium tartrate (Fig. 3b). More interestingly, chiral tartrate ligands directly are combined with the unprecedented vacant [SiW$_{11}$O$_{39}$]$^{10–}$ segments. Moreover, Z-scan result illustrates that two enantiomerically pure polyoxotungstates are the first chiral POMs that show two-photon absorption properties typical of the third-order nonlinear optical response.

2.1.3 Mononuclear Anderson-type RECPs (MARECPs)

Due to the low surface charges of Anderson POAs, reports on MARECPs in the past decade are very rare. However, in 2002, Das and co-workers reported a 1-D zigzag chain-like MARECP [La(H$_2$O)$_2$Al(OH)$_6$Mo$_6$O$_{19}$]$_2$·4nH$_2$O based on Anderson-type [Al(OH)$_6$Mo$_6$O$_{19}$]$^{12–}$ units and RE connectors (Fig. 3d). Another series of 1-D chain-like MARECPs [RE(H$_2$O)$_2$Cr(OH)$_6$Mo$_6$O$_{19}$]$_2$·4nH$_2$O (RE = La$^{3+}$, Nd$^{3+}$, Gd$^{3+}$, Tb$^{3+}$) were obtained by their group in 2014. This work fills a vacancy of the Anderson-type species in the field of mononuclear MARECPs.

2.1.4 Mononuclear Lindqvist-type RECPs (MLRECPs)

In the classical Lindqvist POM family, the typical decatungstate [W$_{10}$O$_{42}$]$^{2–}$ isopolyanion can be considered as two monovacant Lindqvist [W$_{10}$O$_{42}$]$^{2–}$ units linked by four corner-sharing oxygen atoms. To date, relevant reports on MLRECPs are very rare. Luo et al. utilized the assembly of decatungstate [W$_{10}$O$_{42}$]$^{2–}$ units and [Ce(H$_2$O)](DMF)$_8$]$^{4+}$ cations and successfully separated a novel 1-D MLRECP [Ce(H$_2$O)($\text{DMF}$)$_8$][W$_{10}$O$_{42}$]·DMF·CH$_2$OH. (d) View of the 1-D zigzag chain of [La(H$_2$O)$_2$Al(OH)$_6$Mo$_6$O$_{19}$]$_2$·4nH$_2$O. (WO, and MoO$_2$ yellow, XQ: bright green, RE: light purple, O: red, C: gray, N: blue)
Meanwhile, the remarkable progress on organic–inorganic hybrid DKRECPs have been made and some novel structures of this subset should be highlighted here. Niu and coworkers not only communicated a class of novel \((\eta^5,\mu_{-1,1})\)-aceto-bridging phosphotungstate-based DKRECP hybrids with discrete structures \([(\alpha-x-PW_{10}O_{39})RE(H_2O)(\eta^5,\mu_{-1,1})-CH_2COO)]^{10-}\) (RE = Y^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}) (Fig. 4d) and \([(\alpha-x-PW_{10}O_{39})Sm_2(\eta^5,\mu_{-1,1})-CH_2COO)]^{10-}\) (Fig. 4c). It should be noted that \([(\alpha-x-PW_{10}O_{39})RE(H_2O)_2(\eta^5,\mu_{-1,1})-CH_2COO)]^{10-}\) shows the discrete structures including two mono-RE substituted Keggin \([RE(\alpha-x-PW_{10}O_{39})_2]^{14-}\) subunits bridged by an oxalate ligand while \([(\alpha-x-PW_{10}O_{39})Sm_2(\eta^5,\mu_{-1,1})-CH_2COO)]^{10-}\) displays the 1-D chain motif formed by the unusual divacant di-Tm-containing \([(\alpha-x-PW_{10}O_{39})_2]^{14-}\) subunits by oxalate linkers (Fig. 4f). Moreover, these interesting 1-D chains are aligned in two different spatial orientations (Fig. 4f). This construction fashion was observed for the first time in POM chemistry. In 2014, Hussain et al reported a series of \((\eta^7,\mu_{-1,1})\)-aceto-bridging silicotungstate-based DKRECP hybrids \([(RE(\alpha-SiW_{10}O_{39})(H_2O))_2(\mu-CH_2COO)]^{12-}\) (RE = Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Sm^{3+}) by a reaction of Na_{10}(\alpha-SiW_{10}O_{39})·16H_2O with \(RE(NO_3)_{12}\cdot n\) H_2O in KAc–HAc buffer at pH 4.5, which are also almost isometric to those phosphotungstate-based DKRECP hybrids made by Niu et al.33 Except for the above discussed oxalate-bridging 1-D chain architecture, Niu et al also discovered another novel 1-D organic–inorganic hybrid DKRECP \([Sm(H_2O)_6]_2[Sm(H_2O)_2]_2(DMSO)(\alpha-SiW_{10}O_{39})]^{14-}\) with mixed \([Sm(H_2O)_6]^{14-}\) and \([Sm(H_2O)_2]_2(DMSO)]^{14-}\) pendants on both sides of the 1-D chain (DMSO = dimethyl sulfoxide) (Fig. 4g, 4h). In addition, Xu et al reported a citrate-decorated Keggin-type di-Dy\(^{3+}\)-containing tungstoarsenate \([Dy(Hcit)_2(AsW_{10}O_{39})]^{11-}\) (Hcit = citric acid) with two non-adjacent substituted sites occupied (Fig. 4j). Notably, the citric acid ligand is first introduced to the RE–POM system and this compound is the first DKRECP with two non-adjacent substituted sites. It is well known that aromatic carboxylic acids are excellent multifunctional ligands in the construction of TMSP hybrids, therefore, they should be also able to be introduced to the system of RECPs. Thus, by reaction of pic (pic = 2-picolinate), \([As_2W_{10}O_{39}(H_2O)]^{14-}\) precursor and TbOAc, in the ratios of 4: 1: 2 at the acidic condition (pH 3.6–3.9), Boskovic et al separated a di-Tb\(^{3+}\)-containing tungstoarsenate with pic ligands \([Tb_2(pic)(H_2O)](\beta-AsW_{10}O_{39})_2WO_4(pic)]^{16-}\) (Fig. 4j), in which two tetra-vacant Keggin \([\beta-AsW_{10}O_{39}]^{9-}\) units oriented at 180° with respect to each other are connected by three \(WO_4(pic)]^{16-}\) moieties and two Tb\(^{3+}\) centers.38 Among the multitude applications of POMs, Lewis acid catalysts are very rare in comparison with the Brønsted acid and oxidation catalysts in most situations. Nevertheless, by virtue of the high coordination numbers and flexible coordination geometries, RE cations can not only leave residual coordination sites but also further act as effective Lewis acids for activation of substrates.40,13c,13e On the base of this feature, Mizuno and collaborators designed and synthesized a series of efficient POM-
based Lewis acid DKRECP catalysts [[RE(H$_2$O)$_3$(acetone))$_2$][γ-SiW$_{10}$O$_{36}$]]$^{10+}$ (RE = Y$^{3+}$, Nd$^{3+}$, Eu$^{3+}$, Gd$^{3+}$, Tb$^{3+}$, Dy$^{3+}$) by reactions of TBA$_4$H$_2$[γ-SiW$_{10}$O$_{36}$] with RE(acac)$_3$ in 2012 (Fig. 4k)$^{41}$ in which two silicotungstate units are pillared by two RE cations. These DKRECP catalysts, nucleophilic oxygen-enriched surfaces of negatively charged POMs and the incorporated RE cations can respectively function as Lewis bases and Lewis acids. The experimental results of cyanoisilylation of carbonyl compounds with trimethylsilyl cyanide indicate DKRECPs with larger RE cations manifest higher catalytic activities for cyanoisilylation due to the higher activation ability of C=O bonds (higher Lewis acidity) and sterically less hindered Lewis acid sites. Amongst these DKRECP catalysts checked, the [[Nd(H$_2$O)$_3$(acetone)][$\gamma$-SiW$_{10}$O$_{36}$]$_2$]$^{10+}$ shows the remarkable catalytic performance for cyanoisilylation of various ketones and aldehydes with producing the corresponding cyanohydrin trimethylsilyl ethers in high yields.$^{43}$

### 2.2.2 Dinuclear Dawson-type RECPs (DDRECPs)

![DDRECPs](image)

**Fig. 5** (a) The centrosymmetric structure of [[α$_2$-La(H$_2$O)$_3$P$_2$W$_{17}$O$_{61}$]]$^{4+}$. (b) View of the structural unit of [[Nd$_2$(H$_2$O)$_6$(α$_2$-P$_2$W$_{17}$O$_{61}$)]$^{12+}$. (c) The 1-D chain motif of [[Nd(H$_2$O)$_3$(α$_2$-P$_2$W$_{17}$O$_{61}$)]$^{10+}$. (d) The 2-D extended layer of [[Nd$_2$(H$_2$O)$_6$(α$_2$-P$_2$W$_{17}$O$_{61}$)]$^{12+}$. (e) View of the structural unit of [[K$_2$P$_2$W$_{17}$O$_{61}$](H$_2$O)$_{16}$]RE$_2$(H$_2$O)$_{25}$. (f) The 3-D framework of [[K$_2$P$_2$W$_{17}$O$_{61}$](H$_2$O)$_{16}$]RE$_2$(H$_2$O)$_{25}$. (Copied from ref. 42). (WO$_2$: yellow and blue, XO$_2$: bright green, RE: light purple, O: red)

Compared with DKRECPs, the research developments of DDRECPs are laggardly and few examples have been reported during the past decade. In 2006, Hasenkopf et al separated a centrosymmetric DDRECP [[α$_2$-La(H$_2$O)$_3$P$_2$W$_{17}$O$_{61}$]]$^{4+}$ in aqueous solution (Fig. 5a).$^{42}$ Such phenomenon that a RECP is composed of two mononuclear Dawson phosphotungstate subunits with the α$_1$ configuration is very uncommon in the field of POMs. Meanwhile, by controlling the ratio of Nd$^{3+}$/[α$_2$-P$_2$W$_{17}$O$_{61}$]$^{10+}$, Wang et al obtained the first 2-D extended structure based on [[Nd$_2$(H$_2$O)$_6$(α$_2$-P$_2$W$_{17}$O$_{61}$)]$^{14+}$ DDRECP units (Fig. 5b) connected via trivalent Nd$^{3+}$ ions under hydrothermal conditions (Fig. 5b,5c,5d).$^{43}$ In this compound, the Nd$^{3+}$ ions located in the vacant sites of the [[α$_2$-P$_2$W$_{17}$O$_{61}$]]$^{10+}$-fragments firstly connect adjacent [[α$_2$-P$_2$W$_{17}$O$_{61}$]]$^{10+}$-fragments to form a 1-D chain [[Nd(H$_2$O)$_3$(α$_2$-P$_2$W$_{17}$O$_{61}$)]$^{12+}$ (Fig. 5c), and then these 1-D [[Nd(H$_2$O)$_3$(α$_2$-P$_2$W$_{17}$O$_{61}$)]$^{12+}$ chains further are combined with adjacent chains to create a 2-D extended layer by means of all Nd$^{3+}$ ions. It should be pointed out that the most evident difference between [[α$_2$-La(H$_2$O)$_3$P$_2$W$_{17}$O$_{61}$]]$^{12+}$ and [[Nd(H$_2$O)$_3$(α$_2$-P$_2$W$_{17}$O$_{61}$)]$^{12+}$ is that the former comprises the mononuclear [[α$_2$-P$_2$W$_{17}$O$_{61}$]]$^{10+}$-fragments whereas the latter consists of mononuclear [[α$_2$-P$_2$W$_{17}$O$_{61}$]]$^{10+}$-fragments. As we know, the corona [P$_2$W$_{17}$O$_{61}$]$^{14-}$ is one important derivative of Dawson POMs and can be viewed as a combination of four hexavanadate P$_2$W$_{17}$O$_{61}$$^{14-}$ entities via eight W–O–W linkers. By reaction of coronary precursor [P$_2$W$_{17}$O$_{61}$]$^{14-}$ and early RE cations, Pope et al obtained novel 3-D frameworks constructed from [[K$_2$P$_2$W$_{17}$O$_{61}$](H$_2$O)$_{16}$]RE$_2$(H$_2$O)$_{25}$. (RE = La$^{3+}$, Ce$^{3+}$, Pr$^{3+}$, Nd$^{3+}$) DDRECP units (Fig. 5e, 5f)$^{44}$ which opens up the study on the RE chemistry of the [P$_2$W$_{17}$O$_{61}$]$^{14-}$ anion.

### 2.2.3 Dinuclear Anderson-type RECPs (DARECPs)

![DARECPs](image)

**Fig. 6** (a) View of the structural unit of [[(CH$_3$NO$_2$)$_3$RE(H$_2$O)$_4$] [IMo$_{2}$O$_{3}$N] [NO$_3$]-4H$_2$O. (b) The 2-D extended network of [[(CH$_3$NO$_2$)$_3$RE(H$_2$O)$_4$] [IMo$_{2}$O$_{3}$N] [NO$_3$]-4H$_2$O. (WO$_2$: yellow, XO$_2$: bright green, RE: light purple, O: red, C: gray, N: blue)

During the course of probing dinuclear RECPs, the research on DARECPs remains largely unexplored because of the low surface charge of Anderson POAs. In 2004, Krebs et al obtained a family of 1-D infinite chain-like polyoxomolybdates based on DARECP building blocks [[La(H$_2$O)$_{16}$][TeMo$_{2}$O$_{32}$]$_{6}$·6nH$_2$O, [[Ce(H$_2$O)$_{16}$][TeMo$_{2}$O$_{32}$]$_{6}$·7nH$_2$O, [[Pr(H$_2$O)$_{16}$][TeMo$_{2}$O$_{32}$]$_{6}$·8nH$_2$O and [[Nd(H$_2$O)$_{16}$][TeMo$_{2}$O$_{32}$]$_{6}$·8nH$_2$O by reaction of telluric acid, potassium molybdate and rare earth salts in the pH 5.5 aqueous solution, however, their 1-D chain construction modes are somewhat different. In the construction of 1-D chains, the [TeMo$_{2}$O$_{32}$]$^{17-}$ POA acts as a hexadentate ligand for La$^{3+}$ ions and as a tetradentate ligand for Ce$^{3+}$, Pr$^{3+}$ and Nd$^{3+}$ ions.$^{45}$ As an extension of their work, in 2005, they found two di-RE bisupporting DARECPs [[RE(H$_2$O)$_{16}$][TeMo$_{2}$O$_{32}$]$·$10H$_2$O (RE = Ho$^{3+}$, Y$_1$I$_{10}$)$^{45b}$ These results show that the lanthanide contraction has a remarkable influence on their structural construction modes. In 2006, two unusual 2-D extended network DARECPs [[(CH$_3$NO$_2$)$_3$RE(H$_2$O)$_4$] [IMo$_{2}$O$_{3}$N] [NO$_3$]-4H$_2$O (RE = La$^{3+}$, Ce$^{3+}$, C$_2$H$_5$NO$_2$ = pyridine-4-carboxylic acid) (Fig. 6a) were synthesized by Wang’s group.$^{46}$ Interestingly, this 2-D extended network is constituted by RE coordination polymer chains.
linked together by [Mo₆O₃₄]⁵⁻ POAs (Fig. 6b) and is on behalf of the first example of 2-D inorganic–organic hybrid polyoxometalates based on A-type Anderson POAs.

2.2.4 Other dinuclear RECPs

Apart from the above mentioned dinuclear RECPs, several interesting isopolymetallates stabilized by dinuclear RE cations have been also discovered in the past decade. In the field of isopolymolybdates, Evans’ group reported a class of novel dinuclear RECPs based on octamolybdate units: highly hydrated [Dy₄₂(H₂O)₇₂][Mo₆O₃₄]·7H₂O and its partially dehydrated product [Dy₂₂(H₂O)₃₄][Mo₆O₃₄]·3H₂O, and highly hydrated [Nd₂(H₂O)₃₄][Mo₆O₃₄]·3H₂O and its partially dehydrated product [Nd₂(H₂O)₂₈][Mo₆O₃₄]·3H₂O and they found that the partial dehydration of both highly hydrated RE octamolybdates topotactically condenses the isolated RE₂MoO₇ chains into the 3-D framework structures, leading to channels along the [Mo₆O₃₄]⁺ chain direction in the obtained products.

In the domain of isopolynitrogens, many building blocks have been separated such as [W₁₂O₃₆]⁷⁻, [H₂W₁₂O₃₆]⁶⁻, [W₁₁O₃₆]⁵⁻, [H₂W₁₀O₃₀]¹⁰⁻, [H₂W₁₂O₃₈]¹₂⁻, and [H₂W₆O₈]¹⁰⁻. In 2006, Jiang et al synthesized a class of rare 3-D frameworks built by dinuclear RECPs [{RE(H₂O)₇₂}²⁺ (H₂M₆O₁₈O₅)]⁻ (RE = LaIII, SmIII, EuIII, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Yb³⁺, Lu³⁺, M = W or W/Mo), which are assembled from the arrangement of paradocecataugate [H₂M₆O₁₈O₅]⁻ POAs and [RE(H₂O)₇₂]⁺ links. In 2008, Cao and collaborators isolated a novel dinuclear cerium(III)-containing pentadecatungstate [H₂Ce₂(H₂O)₆Cl(W₆O₁₈O₉)]⁻ with an approximate C₁ symmetry by reaction of Na₂WO₄·2H₂O and Ce(NO₃)₃·6 H₂O in aqueous acidic medium (optimal pH = 5.0) (Fig. 7a). The most remarkable structural characteristics of this compound is that there are [W₁₀O₃₆]⁷⁻ units are connected with each other to give rise to a 15-member ring by corner-sharing WO₆ octahedra and this asymmetrical 15-member ring was stabilized by two Ce³⁺ ions, in which the Cl⁻ ion plays a role of terminal ligand for one of the Ce³⁺ ions. Thereafter, Kortz et al synthesized the V-shaped [RE₂(H₂O)₆₆][W₆O₁₈(OH)]⁷⁻ POA (RE = SmIII, EuIII) by reaction of RE and WO₄²⁻ ions in aqueous acidic medium (pH = 3.2) (Fig. 7b), in which the [W₁₂] cluster is made up of two undecatungstate [W₁₁] subunits and a hexatungstate [W₁₂] subunit and one other RE ion bridges two [W₁₂] subunits together by four μ-oxo bridges while the other RE ion simultaneously coordinates to two [W₁₁] subunits and a [W₁₂] subunit by three μ-oxo bridges. In the same year, they also reported a family of S-shaped dinuclear RE-containing isopolynitrogens [RE₂(H₂O)₆₆][W₆O₁₈(OH)]⁷⁻ (RE = LaIII, CeIII, TbIII, DyIII, HoIII, ErIII, TmIII, YbIII, LuIII) (Fig. 7c) and this S-shaped dinuclear RE-containing 22-isopolynitrogens can be polymerized to the 1-D chain structure by the bridging role of RE ions (Fig. 7d). Subsequently, Su’s group also separated a novel S-shaped di-cerium(III) 22-isopolynitrogens [Ce₂(H₂O)₆₆Cl(W₆O₁₈(OH))]¹⁶⁻ by reaction of Na₂WO₄·2 H₂O, Na₂SO₄ and Ce(NO₃)₃·6 H₂O (pH = 5.5), which is constructed from two discrete [W₁₂] subunits linked through two nine-coordinate Ce³⁺ ions (Fig. 7e). The obvious distinction between the above mentioned two S-shaped dinuclear RE-containing 22-isopolynitrogens is as follows: two [HW₁₇O₃₈]⁻ subunits are directly connected with each other by sharing two oxygen atoms in [RE₂(H₂O)₆₆][W₆O₁₈(OH)]⁷⁻ whereas two [H₂W₁₁O₃₆]⁻ subunits are bridged together by two Ce³⁺ links in [Ce₂(H₂O)₆₆Cl(W₆O₁₈(OH))]¹⁶⁻. In addition, utilizing the linking propensity of the sulfite encapsulated polyoxovanadate precursor [As₅V₈O₃₄(SO₃)]⁶⁻ with RE cations, Das and co-workers obtained a group of novel RE-containing polyoxovanadates [{RE(H₂O)₇₂}₆As₈V₁₄ O₂₅(SO₃)]·8H₂O (RE = LaIII, SmIII, CeIII, TbIII) with 2-D extended structures. In the structural unit, fourteen distorted [VO₃] square pyramids combines with each other in the edge-sharing mode to form a [V₁₄] cluster with a disordered SO₃⁻ unit in the centre, and then four handle-like [As₅O₅] units graft to the equatorial position of the [V₁₄] cluster to construct the basic skeleton of the [As₅V₈O₃₄(SO₃)]⁶⁻ cluster anion (Fig. 7f). Finally, two [RE(H₂O)₇₂]⁺ ions are symmetrically attached to the cluster anion by a terminal oxygen from the cluster anion. In the 2-D extended structure, each [As₅V₈O₃₄(SO₃)]⁶⁻ cluster anion is surrounded by six [RE(H₂O)₇₂]⁺ ions whereas each [RE(H₂O)₇₂]⁺ ion connects with three [As₅V₈O₃₄(SO₃)]⁶⁻ cluster anions (Fig. 7g).

2.3 Trinuclear RECPs

2.3.1 Trinuclear Keggin-type RECPs (TKRECPs)
Kortz’s group successfully synthesized a special trinuclear YIII-containing tungstoiminate \([YO_3(OH)](CH_3COO)(H_2O)\) by a simple one-pot reaction of YIII ions with [α-SbWO_4]_2– and WO_4^2– ions in a 3:3:1 molar ratio in LiOAc/ AcOH buffer at pH 5.3 (Fig. 8a). In this POA, a tetrahedral WO_4^2– capping unit is in the encirclement of three [α-SbWO_4]_2– units linked by three YIII ions. Although AsIII, SbIII and BiIII heteroatoms all own the lone pair electrons, the ionic radius of BiIII (1.17 Å) is bigger than AsIII (0.72 Å) and SbIII (0.90 Å), which renders it to exhibit a significant difference in inducing the structural diversity of RECPs. In addition, with the appearance of underlying applications in catalytic activity, ferroelectric, piezoelectric and non-linear dielectric susceptibility, tungstoantimonates are regarded as one of potential solid functional materials. In 2012, Xu and coworkers isolated three unprecedented giant TKRECPs [[BiW_13O_34](WO_4)(Bi(μ₃-O)(μ₃-OH))(RE(μ₃-O)(COO)(H_2O))]_22– (RE = PrIII, NdIII, LaIII) by reacting Na[BiW_12O_39](OH)_2]·4H_2O. Na[BiW_14O_41]·16H_2O with LnCl_3 in the participation of Na_2CO_3 in aqueous solution (pH ~7.0) (Fig. 8e). The [[BiW_13O_34](WO_4)(Bi(μ₃-O)(μ₃-OH))(RE(μ₃-O)(COO)(H_2O))]_22– POA can be explained as follows: the [[Pr(μ₃-O)(COO)]_3]_5 cation first joins three trivalent [α-Bi-Wo_4]_2– fragments together forming a trigonal alignment, and then is connected to the fourth [α-Bi-Wo_4]_2– fragment through a [[Bi(μ₃-O)(μ₃-OH)]_3]_5 cation and an additional six-coordinate tungsten atom. This POA represents the largest RE-containing polyoxotungstobismuthate. Furthermore, a suitable ligand selection is the key factor to obtain the desired structural features and properties. By making use of H_2CAM (2,6-dicarboxy-4-hydroxyypyridine), Mirzaei et al made a series of novel inorganic–organic hybrids [Na(H_2CAM)(RE(HCAM)(H_2O))]_2 ][SiW_12O_40]·nH_2O (RE = LaIII, CeIII, EuIII), in which a polynuclear cation [Na(H_2CAM)(RE(HCAM)(H_2O))]_26 coordinates to the [SiW_12O_40]_6 POA (Fig. 8f). Moreover, unprecedented anion–π interactions in inorganic–organic Keggin-type POM frameworks were described and analyzed for the first time.

Because of the existence of the lone pair electrons located on the top of trigonal pyramids of AsIII, SbIII and BiIII heteroatoms, the stereochemistry effect of the lone pair electrons may act in the structural formation of POMs. Thus, AsIII, SbIII and BiIII containing RECPs always exhibit unique spatial structures. Specifically speaking, the stereo-directing lone pair electrons of these heteroatoms greatly influence the further condensation of the POAs such as preventing the formation of plenary structures. Nevertheless, these lone pair electrons are beneficial to the formation of more open architectures through introducing bridging electrophiles. In the past decade, many interesting trinuclear RECPs have emerged by continuous attempts of chemists. Using the adaptable precursors and the bench-top reaction condition in acidic (pH < 2) aqueous media, the 1-D chain tungstoarsenate [Nd₃As₃W₁₄O₄₄OH(H₂O)]₁₀– was synthesized by Boskovic et al in 2010. The [Nd₃As₃W₁₄O₄₄OH(H₂O)]₁₀– POA consists of three [β-as-AsIII₃W₁₃O₃₃]_6 and one [β-β-AsIII₃W₁₂O₃₉]_6 fragments (Fig. 8a), in which the [β-β-AsIII₃W₁₂O₃₉]_6 fragment was firstly observed. There are three crystallographically unique square antiprismatic NdIII ions in [Nd₃As₃W₁₄O₄₄OH(H₂O)]₁₀– POA, moreover, a NdIII ion acts as a template for the assembly of POA and two NdIII ions work as linkers to construct the 1-D chain (Fig. 8b).

Then, Xu et al reported a carbonate and trinuclear dysprosium sandwiched tungstoarsenate K₃[H₃Dy₂(H₂O)CH₃COO]₂[α-α-As₃W₁₄O₄₆][α-β-As₃W₁₄O₄₆]·22H₂O in 2012, in which three DyIII ions create an equatorial belt formed by two isomeric trivacant Keggin fragments [α-α-As₃W₁₄O₄₆]_6 and [α-β-As₃W₁₄O₄₆]_6, and the CO₃²– is encapsulated in the triangle plane (Fig. 8c), giving rise to a stable dysprosium carbonate-containing sandwich-type POM. During the exploration of novel tungstoarsenate-based TKRECPs, tungstoiminate-based TKRECPs have also attracted increasing interest due to some similar reaction behaviors of SbIII and AsIII elements. In 2011,
In addition to the above discussed neoteric TKRECPs, several interesting TDRECPs with infinite extended architectures were discovered. In 2006, Wang’s group separated the first 1-D chain TDRECP built by monovacant Dawson anions and tri-Na[O] cations [Nd₂(H₂O)₉(µ₂-P₂W₁₉O₆₆)]⁺ (Fig. 9a, 9b). In 2011, four open Wells–Dawson silicotungstates with similar 2-D extended structures Na₂Cs₅H₂[Tb₂(H₂O)₉Si₇W₁₉O₆₆]·17H₂O, Na₃Cs₅Dy[H₂O]₉C₁₅H₂O₆₆Cl·17H₂O, Na₃Cs₅Ho[H₂O]₉Si₇W₁₉O₆₆]·18H₂O (Fig. 9c, 9d) and Na₃Cs₅Gd[H₂O]₉C₁₅H₂O₆₆Cl·17H₂O were isolated by Patzke et al from the one-step reaction of Na₃[SiW₁₉O₆₆]n H₂O with RE(NO₃)₃·nH₂O in a sodium acetate buffer, which are the first open Wells–Dawson RE encapsulated silicotungstates containing [α-SiW₁₉O₆₆]⁻ POAs.

2.4 Quadrnuclear RECPs

2.4.1 Quadrnuclear Keggin-type RECPs (QKRECPs)

In the preparations of QKRECPs, the divacant [AsW₁₀O₃₄](H₂O)₄⁻ precursor has aroused considerable interest and stimulated the production of a class of novel [AsW₁₀O₃₄]-based QKRECPs because of the following reasons: (i) the stereo-directing influence of the lone pair on the As[O] atom allows the formation of lacunary Keggin fragments and endows the distinctive reactivity compared with those defect POM moieties anchoring tetrahedral heteromorph groups; (ii) the [WO(H₂O)]⁻ ligand between two [B₂-AsW₁₀O₃₄]⁻ fragments could serve as a starting point for rotation and dissociation, which may facilitate the generation of various building blocks in solution at different pH values; (iii) this precursor is easier to be prepared in good yield. In the following discussion, the statements will be expanded according to the number of [AsW₁₀O₃₄]⁻ subunits per compound. Utilizing the preformed precursor and disassembly and reassembly processes, Boskovik et al obtained a novel QKRECP [Dy₂As₂W₂O₈(H₂O)₂(H₂C₂NO₂)₂]⁻ (C₂H₆NO₂ = glycerine) involving two glycidic ligands (Fig. 10a). This skeleton of the [Dy₂As₂W₂O₈(H₂O)₂(H₂C₂NO₂)₂]⁻ POA is assembled from two [B₂-AsW₁₀O₃₄]⁻ fragments connected via two unprecedented [W₂O₆(glycerine)] groups accompanying each glycidic ligand coordinating to two W₆VI centers in a bidentate fashion. Moreover, in this compound, the Dy³⁺ cations act as linkers to form the novel 1-D chain architecture (Fig. 10b). Very recently, Niu et al obtained six tritrate-bridging tetra-RE substituted QKRECP dimers [RE₂(C₆H₄O₇)(C₆H₄O₇)(AsW₁₅O₅₀)]tí⁻ (RE = Ho²⁺, Er³⁺, Tm³⁺, Yb³⁺, Lu⁵⁺, Y³⁺) (Fig. 10c), which consists of two [B₂-AsW₁₀O₃₄]⁻ fragments in a stagger fashion, sandwiching a unique cage-like RE-organic cluster formed by four RE cations and four tartaric acid segments. Three more kinds of novel QKRECPs containing four [AsW₁₀O₃₄]⁻ fragments have been synthesized by the precursor [As₂W₁₀O₄₅(H₂O)]⁴⁻ in the past decade. For example, in 2011, Boskovik and collaborators synthesized and characterized a new family of QKRECPs with gly ligands [RE₂As₁₃W₁₉O₇₀(glycine)]⁻ (RE = Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Y³⁺), in which two [As₂W₁₀O₃₄]⁻ subunits are bridged together by four RE cations and two tungsten centers (Fig. 10d). In the formation of this series of compounds, the [As₂W₁₀O₄₅(H₂O)]⁴⁻ POA experiences a structural rearrangement so as to accommodate inclusion of the RE ions, with transformation into the [As₂W₁₀O₃₄]⁻ subunits. This process occurs via loss of the terminal aqua ligand from the [W₃O₆(H₂O)]⁻ linker, with the subsequent change in the respective orientation of two trivacant [B₂-AsW₁₀O₃₄]⁻ fragments. The current magnetic susceptibility data have indicated the onset of slow magnetic relaxation for [Dy₂As₂W₂O₈(H₂O)₂(H₂C₂NO₂)₂]⁻ with the energy barrier to magnetization reversal determined to be 3.9(1) K. Furthermore, its X-band EPR spectrum further shows the presence of a non-negligible fourth order transverse component of the anisotropy, which is responsible for the small effective energy barrier observed for [Dy₂As₂W₂O₈(H₂O)₂(H₂C₂NO₂)₂]⁻. To date, it represents the first POM-supported polynuclear lanthanoid-based SMM. In 2014, Boskovik’s group first afforded a novel QKRECP [As₄d(YW₁₉O₄dY₂O₄dGly)]⁶⁻ (H₂O)₄]⁶⁻ (Fig. 10e) by incorporation of glycine (Gly) ligands into an yttrium-tungstostenenate structural backbone and then utilized the site-selective incorporation of Mo and replacement of glycine with eanantiopure L- or D-norleucine (L- or D-Nle) giving rise to two enantiomorphous compounds [As₄d[Mo(V)₂Mo(V)₂W₂]₄₋₄₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋_-...
(pydc)$_2$H$_2$O)$_{38}$ (H$_2$pydc = pyridine-2,3-dicarboxylic acid) containing six [B-α-As$_3$W$_{12}$O$_{40}$]$^{6–}$ subsets by the bridging role of two pydc ligands (Fig. 10). It shouldn’t be neglected that the trivacant precursor [B-α-As$_3$W$_{12}$O$_{40}$]$^{6–}$ can also construct some novel QKRECPs due to the excellent coordination ability of the vacant sites. Thereby, Wang et al successfully synthesized three large Ce-containing tungstoarsenate aggregates [[Ce$_2$O$_2$(H$_2$O)$_4$]$_2$[WO(H$_2$O)$_3$]$_{12}$$^{3–}$, [Ce$_2$As$_4$W$_{14}$O$_{37}$]$^{34–}$ and [Ce$_3$As$_5$W$_{24}$O$_{75}$]$^{12–}$ (ala = L-α-alanine) by the precursor [B-α-As$_3$W$_{12}$O$_{40}$]$^{6–}$ using via a step-by-step assembly process. The tetrameric POA [[Ce$_2$O$_2$(H$_2$O)$_4$]$_2$[WO(H$_2$O)$_3$]$_{12}$$^{3–}$ is constructed from two sandwich-type [[Ce$_2$O$_2$(H$_2$O)$_4$] [WO(H$_2$O)$_3$]$_{12}$$^{3–}$ moieties bridged by two Ce$^{4+}$ ions (Fig. 11a). In the POA [Ce$_3$As$_5$W$_{24}$O$_{75}$]$^{12–}$, four Ce$^{4+}$ ions function as linkers to link four [B-α-As$_3$W$_{12}$O$_{40}$]$^{6–}$ units, generating a new type of cryptand cluster (Fig. 11b). In contrast to the classical cryptate POA [As$_3$W$_{12}$O$_{40}$]$^{12–}$, [Ce$_3$As$_5$W$_{24}$O$_{75}$]$^{12–}$ can be considered that the positions of four W linkers are replaced by four Ce$^{4+}$ centers. The unusual alamine-decorated cryptand-type POA [Ce$_3$As$_5$W$_{24}$O$_{75}$]$^{12–}$ is assembled from four [B-α-As$_3$W$_{12}$O$_{40}$]$^{6–}$ subunits connected by two WO$_2$, two WO$_2$, two Ce$_2$(H$_2$O)$_3$(ala) and a linear W$_6$(OH)$_2$(O$_2$) group (Fig. 11c), in which four organic α-alanine ligands are coordinated directly on the surface of the aggregate. Apart from [As$_3$W$_{12}$O$_{40}$]-based QKRECPs, other QKRECPs were also discovered. For instance, two QKRECPs [RE$_2$($\alpha$-1,4)-Ge$_6$W$_{18}$O$_{66}$]$_{12–}$ (RE = Dy$^{III}$, Er$^{III}$) containing two [($\alpha$-1,4)-Ge$_6$W$_{18}$O$_{66}$]$^{12–}$ subunits were made by Xu et al based on the [$\gamma$-Ge$_6$W$_{18}$O$_{66}$]$^{6–}$ precursor, which represent the first RECP with two dicumulant Keggin-type POA units sandwiching four RE ions (Fig. 12a). Different from the Xu’s method, Reinoso et al utilized GeO$_2$, Na$_2$WO$_4$ and RE cations in NaOAc buffer to obtain a series of QKRECPs [RE$_2$(H$_2$O)$_6$($\beta$-Ge$_6$W$_{18}$O$_{66}$)]$_{12–}$ (RE = Gd$^{III}$, Tb$^{III}$, Dy$^{III}$, Ho$^{III}$, Er$^{III}$, Tm$^{III}$, Yb$^{III}$, Lu$^{III}$). In addition, Niu and coworkers reported an interesting double-parallel chain germanotungstate based on QKRECP subunits [[Sm$_2$(Ge$_6$W$_{18}$O$_{66}$)(DMSO)$_2$(H$_2$O)$_3$]$_{12–}$ (Fig. 12b), in which the two parallel chains [[Sm$_2$(Ge$_6$W$_{18}$O$_{66}$)(DMSO)$_2$(H$_2$O)$_3$]$_{12–}$ are joined together through [Sm(DMSO)$_2$(H$_2$O)$_3$]$^{12–}$ moieties (Fig. 12c). Other side, Liu et al reported a tri-Nb$^{V}$ substituted germanotungstate-based QKRECP [[Ge$_6$W$_{24}$O$_{90}$$_6$]$_{12–}$ (Fig. 12d), which is made up of four tri-Nb$^{V}$ substituted Keggin [Ge$_6$W$_{24}$O$_{90}$$_6$]$^{7–}$ segments bond by four Eu$^{III}$ cations. In addition, Wang et al communicated a tungstomolybdate-based QKRECP [[(Y$_2$H$_4$O)$_{14}$Sb$_2$W$_{22}$O$_{72}$]$^{14–}$ in which a Krebs-type [Sb$_2$W$_{22}$O$_{72}$]$^{14–}$ subunit was supported by four Y$^{III}$ ions.

**Fig. 12** (a) View of [RE$_2$(\$\alpha$-1,4)-Ge$_6$W$_{18}$O$_{66}$](H$_2$O)$_3$]$^{12–}$; (b) View of the structural unit of [[Sm$_2$(Ge$_6$W$_{18}$O$_{66}$)(DMSO)$_2$(H$_2$O)$_3$]$_{12–}$; (c) View of the 1-D chain of [[Sm$_2$(Ge$_6$W$_{18}$O$_{66}$)(DMSO)$_2$(H$_2$O)$_3$]$_{12–}$; (d) View of [[Ge$_6$W$_{24}$O$_{90}$$_6$]$_{12–}$ (WO$_6$ yellow, NbO$_6$ orange, XO$_6$ bright green, RE: light purple, O: red, S: turquoise, C: cray, N: blue)

**2.4.2 Quadrinuclear Dawson-type RECPs (QDRECPs)**

Through the one-step reaction of Na$_{10}$[Si$_6$W$_{18}$O$_{66}$]·12H$_2$O with Gd(NO$_3$)$_3$·nH$_2$O in a sodium acetate buffer, Patzke et al synthesized a novel QDRECP ([Gd$_2$(H$_2$O)$_6$][Gd$_2$(H$_2$O)$_6$Si$_2$W$_{18}$O$_{66}$]$^{12–}$ (Fig. 13a), in which two Gd$^{III}$ cations are located in the peripheral pocket of the [Si$_6$W$_{18}$O$_{66}$]$^{16–}$ anion whereas two Gd$^{III}$ cations are bound to the terminal oxygen atoms of both sides. More intriguingly, adjacent [Gd$_2$(H$_2$O)$_6$]Si$_2$W$_{18}$O$_{66}$]$_{10}$ moieties are combined together through the Gd$^{III}$ cations located on both sides forming the 3-D framework, represents the first 3D inorganic coordination polymer based on Ln-substituted Wells–Dawson POMs. In 2005, Hill et al separated a novel sandwich-type QDRECP

**Fig. 13** (a) View of [Gd$_2$(H$_2$O)$_6$][Gd$_2$(H$_2$O)$_6$Si$_2$W$_{18}$O$_{66}$]$^{12–}$; (b) View of [[Y$_3$(HO)$_2$(H$_2$O)$_3$]$^{12–}$; (c) View of [[Nd$_3$(HO)$_2$(H$_2$O)$_3$]$^{12–}$; (d) View of [[RE$_3$(HO)$_2$(H$_2$O)$_3$]$^{12–}$.
[\{Y(\mu_3-OH)\}_2(H_2O)_6\}(\alpha_2-P_2W_{17}O_{51})]\] consisting of a \{Y(\mu_3-OH)\} cubane cluster encapsulated by two trivacant Dawson [\alpha_2-P_2W_{17}O_{51}] subunits (Fig. 13b).\] In the same year, a fascinating bisupporting DDRECP \{[Nd(H_2O)_6](Nd(H_2O)_6)(\alpha_2-P_2W_{17}O_{51})]\] (Fig. 13c) was found by Wang et al, which is assembled from a dimer \{[Nd(H_2O)_6](\alpha_2-P_2W_{17}O_{51})\][\alpha_4-] and two [Nd(H_2O)_3]^{3+} cations.\] The dimeric \{[Nd(H_2O)_3](\alpha_2-P_2W_{17}O_{51})\][\alpha_4-] anion is made up of two \{P_2W_{17}O_{51}\} Nd(H_2O)_3 subunits connected via two common terminal oxygen atoms. In 2013, Yang et al reported the \{P_2W_{16}\} including DDRECPs \{[RE_2(\mu-OH)](H_2O)_{12}(\alpha_2-P_2W_{16}O_{50})\] (RE = Sm^{3+}, Tb^{3+}) (Fig. 13d),\] in which each Sm^{3+} ion in the cavity is positioned disorderly and has a site occupancy of 0.5.

2.4.3 Quadrinuclear Lindqvist-type RECPs (QLRECPs)

![Fig. 14](image_url) (a) View of [RE(C_2O_4)(H_2O)_4(OH)W_{17}O_{51}]^{10-}. (b) View of [RE(C_2O_4)W_{16}O_{48}]^{20-}. (WO_4: yellow, RE: light purple, O: red, C: gray)

In 2014, our group made a groundbreaking work in the development of QLRECPs and successfully obtained two types of unique oxalate-connector QLRECPs \{RE_2(C_2O_4)(H_2O)_4(OH)W_{16}O_{48}\] (Fig. 14a) and \{RE_2(C_2O_4)W_{16}O_{48}\] (RE = Eu^{3+}, Ho^{3+}, Er^{3+}, Tb^{3+}) (Fig. 14b)\]. It should be pointed out that \{RE_2(C_2O_4)(H_2O)_4(OH)W_{16}O_{48}\] were obtained when only Na\(^+\) ions are present in the reaction, whereas \{RE_2(C_2O_4)W_{16}O_{48}\] were formed when Na\(^+\) and K\(^+\) ions are used in the reaction. \{RE_2(C_2O_4)(H_2O)_4(OH)W_{16}O_{48}\] stand for the first rectangular double-oxalate-bridging tetra-Ln cluster encapsulated divalent Lindqvist isopolyoxotungstate hybrids and \{RE_2(C_2O_4)W_{16}O_{48}\] represent the first square double-oxalate-bridging tetra-Ln cluster anchored isopolyoxotungstate hybrids. This work provides the remarkable feasibility for constructing unprecedented gigantic hybrid poly(isopolyoxotungstate) species with special properties. Moreover, the solid-state luminescent and decay behavior of \{RE_2(C_2O_4)(H_2O)_4(OH)W_{16}O_{48}\] and \{RE_2(C_2O_4)W_{16}O_{48}\] (RE = Eu^{3+}, Tb^{3+}) have been profoundly probed.\] Moreover, Niu and coworkers reported the first class of novel tetranuclear RE-containing peroxopolyoxotungstate \{RE(WO_4)Q(H_2O)_6(W_O_2O_2)\]\] (RE = La^{3+}, Pr^{3+}) with a WO_5\(^2-\) template core (Fig. 15a).\] The central WO_5\(^2-\) core and four tetradentate building blocks \{W_O_2O_2\} are bridged together by four \{REO_3\} linkers with distorted tricapped trigonal prism coordination geometry, moreover, the central WO_5\(^2-\) core exhibits an interesting tetrahedral geometry. Seven W atoms are regularly arranged in the bent 2–3–2 pattern to finish the skeleton of \{W_O_2O_2\}, in which two W atoms in the opposite sides of \{W_3\} hinge exhibit distorted pentagonal bipyramidal coordination environment and the remaining W atoms adopt the common WO_6 octahedral geometry (Fig. 15b). In 2014, Su’s group explored a versatile one-pot strategy to obtain two tetra-Ce\] containing polyoxotungstate nanoclusters \{Ce_6(H_2O)_12W_{14}O_{44}(OH)_{12}\] (Fig. 15c) (pH = 4.5) and \{Ce_6(H_2O)_12W_{16}O_{50}(OH)_{12}\] (pH = 1.5), which represent the largest RE-containing isopolyoxotungstates to date.\] The \{Ce_6\} fragment is constructed from three \{W_3\} bridges, in which the \{W_3\} fragment (Fig. 15d) is derived from the α-Keggin \{H_2W_12O_{40}\] by removal of a (WO_4) octahedron. The latter is a dimeric POA containing two identical \{Ce_6\} subunits related by an inversion center. In \{Ce_6\} subunit, one Ce\] is trapped at the bottom of the central cavity in \{Ce_6\} entity and the other Ce\] attaches to the flanks of the \{Ce_6\} entity. The two \{Ce_6\} entities are combined by two “attacked” Ce\] cations and stabilized by two “trapped” Ce\] cations. The \{Ce_6\} entity is constructed from three \{W_3\} fragments (Fig. 15f) linked by three \{WO_4\} octahedra. it is worthy to mention that the \{W_3\} fragment (Fig. 15i) in the latter is completely distinct from he \{W_3\} fragment (Fig. 15d) in the former.

2.5 Pentanuclear Keggin-type RECPs (PKRECPs)

In the past ten years, only several PKRECPs were reported. In 2006, Krebs et al separated a unique PKRECP \{H_2O(H_2O)_10(H_2O)_12AsW_{64}O_{220}\] (Fig. 16a) consisting of six trivacant Keggin [\alpha_2-AsW_{64}O_{220}] subunits joined by a bridging \{H_2O(H_2O)_10(H_2O)_12AsW_{64}O_{220}\} group, which exhibits an neoteric arrangement fashion of six trilucrany Keggin [\alpha_2-AsW_{64}O_{220}] subunits. In 2010–2012, An and coworkers discovered several 3-D extended inorganic frameworks based on PKRECP units \{RE(H_2O)_12[RE(H_2O)_12(H_2O)_10(REB_W_11O_23)_2](H_2O)\] (RE = Ce^{3+}, Eu^{3+}, Tb^{3+}, Er^{3+}, Yb^{3+}).

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Nd^{III} (Fig. 16b), \{RE[(H_{2}O)_{6}]RE[(H_{2}O)_{6}]RESiW_{12}O_{40}^{2−}\} (RE = La^{III}, Ce^{IV}) and \{|[(H_{2}O)Nd]^{3+}[(H_{2}O)Nd][NdSiW_{12}O_{40}][(H_{2}O)NdSiW_{12}O_{40}]\}^{76}. Notably, \{RE[(OH)_{2}]RE[(H_{2}O)_{6}]REBW_{12}O_{40}H_{2}O\} 20 H_{2}O is made up of RE-substituted double Keggin-type POMAs \{|[(H_{2}O)_{4}] RE[(BW)_{12}O_{40}]\}^{10} linked by Ln cations to generate a 3-D open framework with 1-D channels (Fig. 16c). \{RE[(H_{2}O)_{6}]RE[(H_{2}O)_{6}] RESiW_{12}O_{40}^{2−}\} demonstrates the similar 3-D open framework with 1-D channels to \{RE[(H_{2}O)_{6}]RE[(H_{2}O)_{6}]REBW_{12}O_{40}H_{2}O\} 20 H_{2}O and \{|[(H_{2}O)Nd]^{3+}[(H_{2}O)Nd][NdSiW_{12}O_{40}][(H_{2}O)NdSiW_{12}O_{40}]\}^{−}\) reveals the other 3-D open framework constructed from two kinds of building blocks \{|[(H_{2}O)NdSiW_{12}O_{40}]\}^{10} and \{|[(H_{2}O)NdSiW_{12}O_{40}]\}^{10} that are concatenated together by Nd^{III} cations. In 2012, a neoteric W/Nb mixed-addendum quadrangular PKRECP \{Cs[Ge_{2}W_{9}O_{34}]SO_{4}Eu_{2}(H_{2}O)_{8}\}^{1+} (Fig. 16d) was isolated by Liu’s group, which is composed of two telephone-receiver-like \{[Ge_{2}W_{9}O_{34}Eu_{2}]^{2+}\} (Fig. 16e) building units linked by two Eu^{3+} cations via O–Eu–O bridges. It should be pointed out that one of the Eu^{3+} cations in a telephone-receiver-like building unit is substituted by an eleven-coordinate Cs^{+} cation and a sulfate ion bridges the Cs^{+} ion and an adjacent Eu^{3+} ion leading to the symmetry of the quadrangle decreasing from D_{6h} to C_{2h}. In addition, Niu et al prepared a novel 1-D chain-like [La_{4}] containing peroxoxyxopoloxomolybdate \{H_{2}La(12O_{27})(MoO_{3}O_{22}O_{2})_{4}\}^{6−} (Fig. 17b), in which adjacent tetra-La^{III} including peroxoxyxopoloxomolybdate [La_{4}(MoO_{3}O_{3})(H_{2}O)_{6}(MoO_{3}O_{22}O_{2})_{4}]^{6+} (Fig. 17a) units are connected by additional La^{III} cations to create the 1-D structure. \n
2.6 Hexanuclear RECPs

![Fig. 17](image-url) View of the tetra-Ln including peroxoxyxopoloxomolybdate \{RE_{2}(MoO_{3}O_{3})(H_{2}O)_{3}O_{22}O_{2}O\}^{6+}. (b) The 1-D chainlike structure of \{H_{2}La(12O_{27})(MoO_{3}O_{22}O_{2})_{4}\}^{6+:} (c) The 2-D extended architecture \{HRE_{2}(MoO_{3}O_{22}O_{2}O)\}^{6+:} (W0, yellow, bright green, RE: light purple, O: red).

In 2008, Boskovic and collaborators communicated a [Gd_{4}] incorporated hexanuclear Keggin RECP (HKRECP) with additional acetate ligands \{Gd_{4}As_{4}WO_{42}OH_{2}(H_{2}O)_{3}OAc\}^{76} (Fig. 18a) that comprises four \{B-α-As_{4}WO_{42}OH_{2}\}^{6−} and two \{B-β-As_{4}WO_{42}OH_{2}\}^{6−} trivanadic Keggin subunits that are connected together through corner sharing with an edge-shared \{W_{6}O_{16}\} group, two edge-shared \{W_{6}O_{16}\} groups and four \{W_{6}O_{16}\} octahedrals, which represents the highest nuclearity POM-encapsulated GeI_{3} complex. Its variable temperature magnetic susceptibility investigation reveals spin-only magnetism with a near perfect Curie-type temperature dependence of the susceptibility. Furthermore, some extended architectures including HKRECP building units were also discovered. For instance, Li et al obtained a series of 1-D chain-like QKRECPs \{RE_{2}(H_{2}O)\}^{1+}[As_{4}W_{46}OH_{2}(proline)O_{151}]^{6−} (Fig. 18b) (RE = Tb^{III}, Dy^{III}, x = 22; RE = Nd^{III}, x = 26) in 2013, and adjacent \{RE_{2}(H_{2}O)\}^{1+}[As_{4}W_{46}OH_{2}(proline)O_{151}]^{6−} clusters are linked together by double eight-coordinate RE cations producing 1-D chain motif (Fig. 18c). It is worth mentioning that the \{RE_{2}(H_{2}O)\}^{1+}[As_{4}W_{46}OH_{2}(proline)O_{151}]^{6−} cluster consists of four \{B-α-As_{4}WO_{42}OH_{2}\} fragments, two \{W_{6}O_{16}\} fragments, two unfamiliar \{W_{6}O_{16}\} moieties, one \{W_{6}O_{16}\} dimer and four hydrated \{RE_{2}(H_{2}O)\}^{1+} (n = 2 or 3) ions. Niu and coworkers also reported a type of novel 3-D extended architecture with hybrid HKRECP units \{RE[(H_{2}O)_{6}]La(12O_{27})(MoO_{3}O_{22}O_{2})_{4}\}^{6−} (α-PW_{12}O_{40}H)RE(H_{2}O)_{4}\}^{6−} (RE = La^{III}, Ce^{IV}, H_{2}L = 2,5-pyridinedicarboxylic acid) (Fig. 18d, 18e) and examined their photocatalytic properties for degradation of rhodamine-B (RhB) upon 500 W Hg lamp irradiation. Liu’s group reported a 1-D NbW mixed-addendum HKRECP \{[Ge_{2}Nb_{2}O_{6}W_{9}O_{34}]Eu_{2}(H_{2}O)_{8}\}^{11−} (Fig. 18f, 18g) assembled from telephone receiver-like \{[Ge_{2}Nb_{2}O_{6}W_{9}O_{34}]Eu_{2}\} building units by sharing water ligands from adjacent Eu^{3+} cations, and two isostructural hexanuclear Dawson-type RECPs (HDRECPs) with formula unit of \{RE_{2}(H_{2}O)_{6}[PW_{12}O_{40}]\}^{6−} (RE = Eu^{III}, Ce^{IV}) (Fig. 18h) and its 1-D chain alignment is constructed from sandwich-type tri-Nb^{V} substituted Dawson \{RE_{2}(P_{9}W_{32}O_{90})\}^{6−} fragments linked by alternative RE-O–W bridges (Fig. 18i). Reviewing the history, in 2005 Hill et al synthesized a sandwich POM-supported hydroxoxy/oxo cluster \{[Yb_{2}(μ-O)(μ-OH)_{2}(H_{2}O)_{10}](α-PW_{12}O_{40})\}^{14−} anchoring a trigonal antiprismatic hexa-Yb^{III} cluster around a μ-Oxo atom, which was obtained from the carbonate-assisted hydrolysis of Yb^{3+} cations in the participation of the trivanadic Dawson \{α-PW_{12}O_{40}\}^{3−} precursor (Fig. 18j).
of the giant molybdenum blue wheel RECP \(\text{Mo}_6\text{O}_{20}\text{H}_2\text{La}((\text{H}_2\text{O})_3)_6\) \((\text{Fig. 18k})\) established by two trimeric \((\text{Mo}_2\text{P}_2\text{W}_7\text{O}_{19}\text{H}_2)\text{La}((\text{H}_2\text{O})_3)_6\) subunits linked by twelve Na\(^+\) cations.\(^{13}\) Other else, Cronin et al prepared a giant \([\text{CeO}_8]\) molybdenum blue wheel \([\text{Mo}_{90}\text{Mo}_{20}]_{\text{Ce}_6}\text{O}_{39}\text{H}_9((\text{H}_2\text{O})_7)^{14}\) \((\text{Fig. 18i})\) by the building block rearrangement of the tetradecameric \([\text{Mo}_{144}]\) archetype and the control of the architecture’s curvature in solution from the addition of the Ce\(^{3+}\) cation. The wheel RECP includes 10 \([\text{Mo}_9]\), 4 \([\text{Mo}_2]\), 10 \([\text{Mo}_3]\), 2 \([\text{Mo}_4]\), 4 \([\text{CeO}_2]\) and 2 \([\text{CeO}_3]\) groups.\(^{15}\) Furthermore, the 2-D extended architecture \([\text{H}_2\text{Re}(\text{H}_2\text{O})_{36}\text{Mo}_4\text{O}_7\text{O}_2\text{Mo}_2\text{O}_2\text{O}_2]\) \((\text{RE} = \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Nd}^{3+}\) \((\text{Fig. 17c})\) constructed from hexa-RE containing polyoxomolybdate units were also reported.\(^{17}\)

**2.7 Octanuclear RECPs**

Historically, the first octa-\(\text{Gd}^{3+}\) bridging polytungstoarsenate nanocluster \([\text{Gd}_{6}\text{As}_{40}\text{W}_{125}\text{O}_{368}(\text{H}_2\text{O})_{22}]^{18}\) \((\text{Fig. 19a})\) was reported by Hussain et al in 2009 by a one-pot reaction starting from a 1:2 ratio of the divacant POM \(\text{K}_{14}\text{As}_{2}\text{W}_{16}\text{O}_{37}(\text{H}_2\text{O})\) and \(\text{Gd(NO}_3)_3\) \(6\text{H}_2\text{O}\) in NaOAc/CH\(_3\)COOH buffer at pH 4.7.\(^{19}\) This nanocluster is formed by two equivalent \([\text{Gd}_{6}\text{As}_{40}\text{W}_{125}\text{O}_{368}(\text{H}_2\text{O})_{22}]^{18}\) units are related by an inversion center and the \([\text{Gd}_{6}\text{As}_{40}\text{W}_{125}\text{O}_{368}(\text{H}_2\text{O})_{22}]^{18}\) unit can be visualized as a fusion of two equally charged trimeric units \([\text{Gd}_{3}\text{As}_{20}\text{W}_{60}\text{O}_{150}(\text{H}_2\text{O})_{10}]^{18}\) connected via \(\text{W}–\text{O}–\text{W}\) and \(\text{Gd}–\text{O}–\text{W}\) linkers. Another octanuclear RE-containing polytungstoarsenate hybrid \([\text{Ts}(\text{pic})\text{H}_2\text{O}]_{2}(\text{B}-\text{AsW}_{60}\text{O}_{180}(\text{WO}_4)_{22}\text{pic})\) \((\text{Fig. 19c})\) was also reported by Boskovic and collaborators through the reaction of preformed precursor \([\text{As}_{2}\text{W}_{16}\text{O}_{40}(\text{H}_2\text{O})]\) \(^{15,20}\). Its photophysical measurements demonstrate the importance of the smaller Tb–O–W angles provided by edge- rather than corner-sharing in limiting the quenching of the organic-ligand-sensitized terbium luminescence by the POM ligands.\(^{21}\) In 2013, by the precise control of the one-pot reaction, the first Ce\(^{3+}\)-stabilized RECP with Se\(^{3+}\) or Te\(^{3+}\) heteroatoms \([\text{XO}_3\text{W}_{12}\text{O}_{34}\text{O}_3\text{Ce}((\text{H}_2\text{O})_5\text{WO}_4)_{22}(\text{X} = \text{Se}^{3+} \text{or Te}^{3+}\))\) \((\text{Fig. 19d})\) was successfully separated by Wang et al, which is an octameric aggregate constructed from eight \([\text{XO}_3\text{W}_{12}\text{O}_{34}\text{O}_3\text{Ce}]\) units, four \([\text{WO}_8]\) octahedra and a \([\text{W}_4]\) unit.\(^{15}\) Alternatively, this octameric aggregate can be reckoned as the fusion of two half-units \([\text{XO}_3\text{W}_{12}\text{O}_{34}\text{O}_3\text{Ce}((\text{H}_2\text{O})_5\text{WO}_4)_{22}]^{24}\) \((\text{RE} = \text{Ho}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}, \text{Yb}^{3+}, \text{Lu}^{3+}\) \((\text{Fig. 19f, 19g})\) can be assembled by the chiral \([\text{XO}_3\text{W}_{12}\text{O}_{34}(\text{B}-\text{AsW}_{60}\text{O}_{180})]\) \(^{22}\) dimers when the Cs\(^+\) cation is present.\(^{23}\) More interestingly, two types of tetramers \(\{\beta\}([\text{XO}_3\text{W}_{12}\text{O}_{34}(\text{B}-\text{AsW}_{60}\text{O}_{180})])^{22}\)
coexist in the solid state. Moreover, electronic spray ion (ESI) mass spectrometry and $^{195}$W NMR spectroscopy exhibit that [[RE$_6$(H$_2$O)$_3$(GeW$_6$O$_{18}$)$_2$]]$^{32-}$ tetramers can disassemble into [RE$_6$(H$_2$O)$_3$(GeW$_6$O$_{18}$)]$^{25-}$ dimers upon dissolution.  

In the same year, Hussain et al isolated a series of tetra-RE substituted tetrameric tungstophosphates [[RE$_2$PW$_5$O$_{18}$]$_2$(W$_6$O$_{18}$)(OH$_2$)(H$_2$O)$_2$]$^{26-}$ [RE = Y$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Gd$^{3+}$, Tb$^{3+}$, Dy$^{3+}$, Ho$^{3+}$, Er$^{3+}$, Tm$^{3+}$, Yb$^{3+}$] (Fig. 19b) by reaction of the divacant [P$_2$W$_{10}$O$_{40}$(H$_2$O)$_2$]$^{19+}$ polyanion with Ln(NO$_3$)$_3$·nH$_2$O salts in potassium chloride solution. 

The backbone of [[RE$_2$PW$_5$O$_{18}$]$_2$(W$_6$O$_{18}$)(OH$_2$)(H$_2$O)$_2$]$^{26-}$ is built by four [A-α-PW$_5$O$_{18}$]$^{24-}$ fragments, eight RE cations and seven additional tungsten atoms in a [[RE$_2$W$_6$O$_{18}$]]$^{6+}$ group and can be also viewed as two packman-shaped asymmetric entities (Fig. 19i) that are symmetry-related by a $C_2$ axis through a central tungsten atom.

2.8 Decanuclear RECPs

In 2009, Boskovic’s group utilized the one-pot reactions of divacant precursor Na$_2$[B-α-AsW$_6$O$_{18}$] and YbCl$_3$·6H$_2$O in a 1 : 3 mole ratio in NaAc–HAc buffer at pH 4.7 and obtained a decanuclear RECP [Yb$_{10}$As$_4$W$_{30}$O$_{90}$(OH)$_2$(H$_2$O)$_{20}$(OAc)$_{12}$]$_{100-17a}$. The giant decanuclear RECP cluster is composed of eight [B-α-AsW$_6$O$_{18}$]$^{4+}$ subunits, two pyramidal As$_4$O$_9$ groups, twelve WO$_6$ octahedra, two edge-shared and acetate-bridged W$_6$O$_{18}$ groups and ten Yb$^{3+}$ cations (Fig. 20a). 

Its structural novelty partly arises from the incorporation of additional bridging acetate ligands that can bridge both Yb and W centers. Variable temperature magnetic susceptibility study indicates that the intramolecular magnetic exchange interactions within Yb$^{3+}$ cations via the Yb–O–W–O–Yb pathways are negligible.  

2.9 Dodecanuclear RECPs

In the past decade, only two dodeca-Ce$^{3+}$ containing POMs appeared. In 2013, Wang et al separated an unprecedented dodeca-Ce$^{3+}$ substituted selenotungstate aggregate [[(SeO)$_3$W$_4$O$_{20}$]$_2$(Ce$_6$(H$_2$O)$_{20}$)(W$_4$O$_{16}$)Ce$_4$W$_4$(H$_2$O)$_2$](SeO$_3$)$_2$(NO$_3$)$_2$]$_{14-}$ (Fig. 20b) by the one-pot reaction of Na$_2$WO$_4$·2H$_2$O, Na$_2$SeO$_3$ and Ce(NO$_3$)$_3$·6H$_2$O. 

This polyxoanionic skeleton consist of eight Keggin-type [(SeO)$_3$W$_4$Ce] derivative segments, four {WO$_4$} octahedra, a folded-planar-like {W$_4$} group and two {Ce$_2$(NO$_3$)$_2$(SeO$_3$)$_2$} segments. Moreover, four Ce$^{3+}$ cations in {Ce$_2$(NO$_3$)$_2$(SeO$_3$)$_2$} segments are well connected with the folded-planar-like {W$_4$} group by SeO$_3$$_{2+}$ and NO$_3^-$ linkers. Transmission electron microscopy (TEM) study indicates that its single POA assemble into the intact uniform sized inorganic hollow spheres in dilute water/acetone solution. In 2014, Cronin et al reported an gigantic Ce$_{12}$ doped decameric molybdenum blue wheel {Mo$_{50}$VO$_{19}$Ce$_{12}$O$_{46}$H$_2$(H$_2$O)$_{71}$}$_{5-}$ (simplified as {Mo$_{20}$Ce$_{21}$}) (Fig. 20c), which comprises two interconnected {Mo$_{50}$VO$_{19}$Ce$_{12}$O$_{46}$H$_2$(H$_2$O)$_{71}$}$_{5-}$ [{Mo$_{10}$Ce$_6$}] clusters through two Ce$^{3+}$ cations. Intriguingly, the dimeric cluster {Mo$_{20}$Ce$_{21}$} can be transformed directly to the monomeric species {Mo$_{10}$Ce$_6$} upon...
addition of a potassium salt. This controllable strategy to synthesize gigantic POMs incorporating “active sites” in their anionic scaffolds allows their availability as “molecular synthons” for higher-order assembly.

2.10 Hexadecanuclear RECPs

Based on a self-assembly process of the precursor $\text{[As}_3\text{W}_{12}\text{O}_{40}\text{(H}_2\text{O})]^{4-}$ and oxophilic RE cations, a neoteric class of hexadecanuclear RE substituted arsenotungstate $\text{[RE}_{16}\text{As}_{16}\text{W}_{26}\text{O}_{85}\text{(OH)}_4\text{(H}_2\text{O})_{12}]^{80-}$ ($\text{RE} = \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Th}^{4+}, \text{Dy}^{3+}, \text{Ho}^{3+}$) were isolated in alkali salt solutions (Fig. 20d). This POA can be looked on as the combination of two identical $\text{[RE}_{8}\text{As}_{8}\text{W}_{26}\text{O}_{85}\text{(OH)}_{4}\text{(H}_2\text{O})_{12}]^{80-}$ asymmetric subunits by an inversion centre. Different from the reported $\text{[Ce}_{12}\text{H}_2\text{O}_{18}\text{W}_{16}\text{O}_{32}]^{86-}$ POA, two kinds of building blocks type-1-$\text{[As}_3\text{W}_{12}\text{O}_{40}\text{(H}_2\text{O})_{2}]^{16-}$ and type-2-$\text{[As}_8\text{W}_{26}\text{O}_{85}\text{(OH)}_{4}\text{(H}_2\text{O})_{12}]^{80-}$ with the arrangement mode of type-1-type-2-type1-type2.

2.11 Icosanuclear RECPs

In 2007, Kortz’s group obtained the 20-cerium(III)-containing 100-tungsto-10-germanate $\text{[Ce}_{20}\text{Ge}_{10}\text{W}_{100}\text{O}_{36}\text{(H}_2\text{O})_{26}]^{56-}$ by the conventional reaction of the trivalent precursor $\text{Na}_{10}[-\text{GeW}_{6}\text{O}_{34}]$ and $\text{CeCl}_{3}-7\text{H}_2\text{O}$ in a 1:1 ratio in water ($p$H = 5.0) (Fig. 20e). This POA can be described as a dimeric entity composed of two half units of $\text{[Ce}_{10}\text{Ge}_{4}\text{W}_{16}\text{O}_{36}\text{(OH)}_{4}\text{(H}_2\text{O})_{12}]^{56-}$ bridged by two Ce-O(W) bonds. Each half unit contains five unprecedented dilacunary Keggin $\text{[8k(11)-GeW}_{6}\text{O}_{28}]$ subunits connected asymmetrically by ten Ce$^{3+}$ ions, leading to an asymmetric assembly with $C_1$ symmetry. Notably, this work demonstrates that the large RE cations are excellent linkers for integrating lacunary POM building blocks together to construct specific giant assemblies.

2.12 Icositetranuclear RECPs

Inspired by indication of the icosanuclear RECP based on trivacant $[-\text{GeW}_{6}\text{O}_{34}]^{18-}$ building block, Reimoso and collaborators utilized the simple one-pot reaction of $\text{Na}_{10}[-\text{W}_{100}\text{O}_{36}\text{(H}_2\text{O})_{26}]$ and $\text{Ce}_{10}\text{Ge}_{10}\text{W}_{100}\text{O}_{36}\text{(H}_2\text{O})_{26}$ and isolated the first giant crown-shaped ring icositetranuclear RECP $\text{[K}_{2}\text{Ce}_{2}\text{Ge}_{2}\text{W}_{12}\text{O}_{36}\text{(OH)}_{2}\text{(H}_2\text{O})_{12}]^{52-}$ (Fig. 20f, 17f) which can be regarded as the product of the K$^+$-directed self-assembly of twelve di- $\text{Ce}^{3+}$ substituted Keggin $\text{[Ce}_{2}\text{Ge}_{2}\text{W}_{12}\text{O}_{36}]^{52-}$ subunits. This crown-shaped POA not only comprises a unique $\text{Ce}_{6}\text{O}_{12}$ central ring showing Ce$^{3+}$-Ce$^{3+}$ antiferromagnetic interactions in which a K$^+$ ion is captured by internal H$_2$O molecules, but also demonstrates a central cavity available for ion encapsulation in an inorganic analog of the crown ethers. In addition, adjacent $\text{[K}_{2}\text{Ce}_{2}\text{Ge}_{2}\text{W}_{12}\text{O}_{36}\text{(OH)}_{2}\text{(H}_2\text{O})_{12}]^{52-}$ units can be combined together by Ce-O-W bridges to propagate the 1-D alignment (Fig. 20g).

3. Applications

It is well known that orbitally degenerate ground states of almost all the RE ions, apart from Gd$^{3+}$ and Eu$^{3+}$ ions with the $f$ electron configuration, are split by the spin–orbit coupling and the crystal field effect. However, due to the internal nature of 4f orbitals of RE ions, the contribution of the spin–orbit coupling is larger than the crystal-field effect to some extent, which not only greatly influences the magnetic properties of RE ions, but also provides a significant reason why RE-containing compounds hold an important position in the magnetism field. In the past decade, the magnetic investigations on RECPs have been also performed by some researchers. The related summary is listed in Table 1. and several selected examples are discussed as below.

In 2013, Mizuno et al. synthesized a class of heterodinuclear RECPs $\text{[TBA}_{6}\text{H}_{4}([\text{Dy}_{2}\text{-(OH)}_{3}\text{Eu}](\gamma\text{-SiW}_{10}\text{O}_{38})_2])$ (DyEu) and $\text{[TBA}_{6}\text{H}_{4}([\text{Dy}_{2}\text{-(OH)}_{3}\text{Lu}](\gamma\text{-SiW}_{10}\text{O}_{38})_2])$ (DyLu) exhibit the temperature- and frequency-dependent $\chi^\prime$ and $\chi^\prime\prime$ signals, explicitly revealing the SMM behavior. However, weak ac signals for $\text{[TBA}_{6}\text{H}_{4}([\text{Dy}_{2}\text{-(OH)}_{3}\text{Yb}](\gamma\text{-SiW}_{10}\text{O}_{38})_2])$ (DyYb) were seen under zero external field, may be derived from the strong quantum tunneling of magnetization that was caused by the adjacent Yb$^{3+}$ ion. Thus, in order to inhibit the quantum tunneling of magnetization, the ac magnetic-susceptibilities of DyYb were measured under an external field of 1800 Oe, at this time, the temperature- and frequency-dependent $\chi^\prime$ and $\chi^\prime\prime$ signals were observed. Furthermore, their relaxation times $(\tau)$ of were obtained by the frequency dependence of the $\chi^\prime\prime$ signals. Using the Arrhenius law $(\tau = \tau_0 \exp(\Delta E/RT))$ to fit the plots of $\ln\tau$ versus $1/RT$ afford the energy barriers for magnetization reversal $(\Delta E/kT)$ of $1.8 \times 10^{-3}$ s for DyEu, $8.2 \times 10^{-7}$ s for DyYb, and $1.9 \times 10^{-6}$ s for DyLu. The energy barriers increase in the order of DyLu < DyYb < DyEu with an increase in the ionic radii of Ln$^{3+}$ ions, which suggest that their energy barriers for magnetization reversal can be tuned by adjusting the coordination geometry and anisotropy of the Dy$^{3+}$ ion and by tuning the adjacent Ln$^{3+}$ ion in the heterodinuclear $\text{[Dy}_{2}\text{-(OH)}_{3}\text{Ln}](\gamma\text{-SiW}_{10}\text{O}_{38})_2]$ cores. The structure of hexadecanuclear RECP $\text{[Gd}_{16}\text{As}_{16}\text{W}_{100}\text{O}_{36}\text{(H}_2\text{O})_{26}]^{5+}$ (Fig. 21). As it is a paramagnetic system without orbital contribution, the curve of magnetic susceptibility can be fitted by using the follow equation:

$$\chi = [N(\beta/\gamma)^2(S + 1)/3kT] + \chi_{dia}$$

Here, $g$ is defined as 2.0, the resulting $\chi_{dia}$ value is 0.0034emu·mol$^{-1}$ ($\chi_{dia}$ denotes the diamagnetic correction) and the resulting spin value $S$ is 3.468. The $\chi_{dia}$ value is in good agreement with the value for diamagnetic...
susceptibility calculated from Pascal constants. The spin value corresponds to the spin of non-interacting Gd\(^{3+}\) ions (\(S = 7/2\)), and is in consistence with the large Gd–Gd distances from 5.9 to 6.3 Å because of the indirect linking through O–W–O bridges.

On the other hand, RE-doped materials are of great interest for a wide range of potential applications in light-emitting diodes, tunable lasers, sensory probes, fluorescent tubes, plasma displays, etc.\(^{7,8}\) These unique application functionalities can be ascribed to the narrow emission and high color purity generated from the RE ions.\(^{9}\) Additionally, RE ions are often subjected to weak light absorption owing to the forbidden f–f transitions, entailing the direct excitation of RE ions to be very inefficient if high-power laser excitation isn’t used. This difficulty can be surmounted by the luminescence sensitization or antenna effect.\(^{9a,9b}\)

Thus, the photoluminescence properties of some RECPs have been also investigated at room temperature (Table 1).\(^{21,30,44,51,59,61,64,68,69,73,77,78,80}\) For example, Zhao and co-workers probed the solid-state photoluminescence behavior of Na\(_{10}\)\([\text{ Tb}_{2}(\text{OC}_\text{H}_\text{3})_\text{4})(\text{OH})\text{W}_\text{18Nb}_\text{6O}_{\text{43}}]\cdot\text{30H}_{\text{2}}\text{O} at room temperature.\(^{21}\) The emission spectrum upon excitation at 369 nm exhibits four groups of bands at 490, 495 nm; 543, 545 nm; 584, 588 nm; and 621 nm, which can be respectively assigned to \(5\text{D}_\text{4} \rightarrow 5\text{F}_\text{3}, \ 5\text{D}_\text{4} \rightarrow 5\text{F}_\text{4} , \ 5\text{D}_\text{4} \rightarrow 5\text{F}_\text{5} \) and \(5\text{D}_\text{4} \rightarrow 5\text{F}_\text{6}\) transitions of Tb\(^{3+}\) ions (Fig. 22a). Monitoring Tb\(^{3+}\) \(5\text{D}_\text{4} \rightarrow 5\text{F}_\text{5}\) emission at 543 nm, its excitation spectrum displays a broadband between 250 and 350 nm that is originated from the absorption of [W\(_{18}\)O\(_{43}\)]\(^{−}\) segment, indicating that the luminescence emission partly comes from the contribution of POM-centered ligand-to-metal charge-transfer (LMCT) process. This phenomenon somewhat differs from the observation in \([\text{ Tb}(\text{pic})(\text{H}_\text{2}\text{O})\text{B}·\text{B}·\text{AsW}_\text{18O}_{\text{43}}]\cdot\text{WO}_\text{2} (\text{pic})_\text{6}\) and the result reported by Yamase\(^{3a}\). Moreover, its decay behavior conforms to a biexponential function as \(I = A_1 \exp(−t/\tau_1) + A_2 \exp(−t/\tau_2)\), affording lifetimes of \(\tau_1 = 0.43\) ms and \(\tau_2 = 1.25\) ms (Fig. 22b). This behavior is analogous to that of hydrated Tb\(^{3+}\) complexes,\(^{38,39}\) which also coincides with the case that each Tb\(^{3+}\) cation is coordinated by two water ligands based on the single-crystal structural analysis of Na\(_{10}\)\([\text{ Tb}_{2}(\text{OC}_\text{H}_\text{3})_\text{4})(\text{OH})\text{W}_\text{18Nb}_\text{6O}_{\text{43}}]\cdot\text{30H}_{\text{2}}\text{O}. Liu’s group investigated the solid-state photoluminescence behavior of Cs\(_2\)K\(_2\)[Ge\(_{18}\)W\(_{18}\)Nb\(_{6}\)O\(_{43}\)](H\(_2\)O\(_{3}\))\(_{23}\)H\(_2\)O at room temperature.\(^{69}\) Five characteristic emission bands located at 579, 592, 614, 651 and 699 nm are seen and correspond to the \(5\text{D}_{\text{0}} \rightarrow 5\text{F}_{\text{2}}, \ 5\text{D}_{\text{0}} \rightarrow 5\text{F}_{\text{3}}, \ 5\text{D}_{\text{0}} \rightarrow 5\text{F}_{\text{4}}, \ 5\text{D}_{\text{0}} \rightarrow 5\text{F}_{\text{5}}\) and \(5\text{D}_{\text{0}} \rightarrow 5\text{F}_{\text{6}}\) transitions of Eu\(^{3+}\) ions, respectively (Fig. 22c). In general, the \(5\text{D}_{\text{0}} \rightarrow 5\text{F}_{\text{0}}\) transition is symmetry-forbidden in a field of symmetry. But the \(5\text{D}_{\text{0}} \rightarrow 5\text{F}_{\text{0}} \) transition is seen here, revealing that the site symmetry of the Eu\(^{3+}\) is low in Cs\(_2\)K\(_2\)[Ge\(_{18}\)W\(_{18}\)Nb\(_{6}\)O\(_{43}\)](H\(_2\)O\(_{3}\))\(_{23}\)H\(_2\)O. Furthermore, the \(I(5\text{D}_{\text{0}} \rightarrow 5\text{F}_{\text{2}})/I(5\text{D}_{\text{0}} \rightarrow 5\text{F}_{\text{1}})\) ratio is 7.25, which also supports this point. Moreover, its solution photoluminescence behavior was also probed and the solution emission spectrum manifests the uniform manner to the solid-state emission spectrum, suggesting the uniform coordination environments of Eu\(^{3+}\) ions in the solid and solution states. The luminescence response experiments to various carboxylic acids such as acetate, oxalic, malonic and succinic acids have been performed. The results illustrate that the emission intensity significantly rises upon the addition of malonic acid while the introduction of other three carboxylic acids does not lead to obvious changes to the emission spectra (Fig. 22d).

This luminescent response may be interpreted by the substitution of coordinated water molecules by the polarizable C–O donors of the malonic acid in solution state.\(^{69,94}\)

Apart from above-mentioned magnetic and luminescence properties of RECPs, other application explorations such as Lewis acid–base catalysis, photocaltalysis, electrocatalysis, photochromism, ferroelectric properties etc have been also involved in this field (Table 1).\(^{62,79,80,61,21c}\) These properties are not discussed here.

4. Summary and outlook

In the past decade, a large number of inorganic or organic–inorganic hybrid RECPs with diverse structures and interesting properties have been prepared and excavated due to the driving force originating from their intriguing applications ranging from catalysis to magnetism. These systematic and profound researches on RECPs not only gradually highlight and underline an important place of the RECP branch in the frontier area of POM chemistry, but also can provide the great valuable guidance to the ongoing and continuous developments of exploring and discovering novel functional RECPs. Obviously, during the course of preparing RECPs, the conventional solution approach is the most useful and efficient method, however, the hydrothermal technique very little involves. In the conventional solution system, initial reactants, pH value, reaction time, temperature and the selection of solvent are often considered as the important reaction parameters in controlling the possibility of reaction and affecting the formation and crystal growth of the product phases. In addition to these various parameters, the judicious option of synthetic strategies is a crucial factor. Hence, some effective synthetic strategies such as the one-pot reaction strategy of simple starting materials, the adaptive POM precursors as the starting building blocks, the mixed solvent method, the buffer solution control with appropriate pH range, the alkali metal-directed self-assembly, and the
Table 1 Summary of applications of some RECPs.

<table>
<thead>
<tr>
<th>Formula</th>
<th>RE</th>
<th>Properties</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$<em>{5.68}$Ce$</em>{0.32}$H$<em>4$(Yb$</em>{0.323}$As$<em>{0.68}$W$</em>{0.36}$O$_{6.86}$OH)$<em>2$(H$<em>2$O)$</em>{26}$(OAc)$</em>{11}$·84H$_2$O</td>
<td>Yb$^{3+}$</td>
<td>the decrease of $\gamma\alpha T$ with decreasing temperature is due to the thermal depopulation of higher multiplet states</td>
<td>17a</td>
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<td>K$_2$Na$_6$[Se$<em>2$O$<em>6$]$</em>{1.5}$(Ce$</em>{0.50}$H$<em>2$O$</em>{3.00}$)[(WO$_4$)$_2$(W$_2$O$_7$)$_2$]·81H$_2$O</td>
<td>Ce$^{3+}$</td>
<td>the dominant antiferromagnetic interactions</td>
<td>17b</td>
</tr>
<tr>
<td>Na$<em>{20}$K$<em>4$C$<em>3$$</em>{10}$(Ga$</em>{0.9}$As$</em>{0.1}$W$<em>{0.36}$O$</em>{6.86}$OH)$_2$(H$<em>2$O)$</em>{24}$H$_2$O (n=220)</td>
<td>Gd$^{3+}$</td>
<td>the single ion behavior</td>
<td>17d</td>
</tr>
<tr>
<td>Na$<em>{20}$K$<em>4$Ni(H$<em>2$O)$</em>{2}$(K$<em>3$-K$</em>{2}$Ce$</em>{20}$C$<em>6$</em>{2}$(W$</em>{0.36}$O$_{6.86}$OH)$_2$(H$<em>2$O)$</em>{23}$·nH$_2$O (n=178)</td>
<td>Ce$^{3+}$</td>
<td>the antiferromagnetic interactions</td>
<td>17f</td>
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<tr>
<td>[Sm(H$<em>2$O)$</em>{3}$<em>{12}][Sm(H$<em>2$O)$</em>{2}$(Sm(H$<em>2$O)$</em>{2}$)<a href="DMSO">Sm(H$<em>2$O)$</em>{2}$</a>(α-SiW$</em>{12}$O$_{40}$)]·4.5H$_2$O</td>
<td>Sm$^{3+}$</td>
<td>the coexistence of strong spin-orbital coupling interactions and very weak ferromagnetic responses</td>
<td>19e</td>
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<tr>
<td>TBA$_2$H$<em>2$[RE{μ$<em>2$-OH}RE']{γ-SiW$</em>{12}$O$</em>{40}$}]</td>
<td>RE = Dy$^{3+}$; RE' = Eu$^{3+}$; Yb$^{3+}$; Lu$^{3+}$</td>
<td>the single molecule magnet behavior</td>
<td>22</td>
</tr>
<tr>
<td>[((CH$_3$)$_2$N)$<em>2$]$</em>{(α-PW$<em>1$O$</em>{13}$H)Nd(H$_2$O)$<em>2$]}$</em>{12}$·8H$_2$O</td>
<td>Nd$^{3+}$; Sm$^{3+}$</td>
<td>the coexistence of the spin-orbital coupling interactions and weak antiferromagnetic exchange interactions</td>
<td>33</td>
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<tr>
<td>[(CH$_3$)$<em>2$N]$</em>{2}[(α-PW$<em>1$O$</em>{13}$Sm(H$_2$O)$_2$)(H$<em>2$O)]$</em>{2}$[(μ$_2$-1,1)-CH$_2$COO]$_3$]$_3$·6H$_2$O</td>
<td>[C(NH$_3$)$<em>2$]$</em>{2}$[Dy$<em>2$(Hcit)$<em>2$(AsW$</em>{12}$O$</em>{40}$)]·9H$_2$O</td>
<td>Dy$^{3+}$</td>
<td>the weak antiferromagnetic coupling interactions and the thermal depopulation of the Dy$^{3+}$ excited states</td>
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<td>Na$<em>{20}$[Bi$<em>2$(W$</em>{0.36}$O$</em>{6.86}$OH)$<em>2$]$</em>{12}$(Bi$<em>6$$</em>{15}$(μ$_2$-OH)$_3$) (Pr$_2$(H$_2$O)$<em>3$O)]$</em>{9}$H$_2$O</td>
<td>Pr$^{3+}$</td>
<td>the progressive depopulation of excited Stark sublevels of the Pr$^{3+}$ ions at low temperature and the weak antiferromagnetic interactions</td>
<td>59</td>
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<td>K$_3$H$_2$Li[HO$<em>3$(C$</em>{2}$H$<em>4$O)$</em>{3}$(C$<em>2$H$<em>4$O)$</em>{(8W_3}O</em>{18})]$·28H$_2$O</td>
<td>Ho$^{3+}$</td>
<td>the progressive depopulation of excited Stark sublevels of the Ho$^{3+}$ ions at low temperature and the weak antiferromagnetic interactions</td>
<td>62</td>
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<td>(HDABCO)$<em>3$H$<em>3$LiT$1$(Tb$</em>{0.323}$AsW$</em>{0.36}$O$_{6.86}$OH)$_2$[(gly$_2$)$<em>2$]$</em>{2}$·25H$_2$O</td>
<td>Tb$^{3+}$</td>
<td>the single molecule magnet behavior</td>
<td>63</td>
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<td>Na$_{20}$[D$_2$(H$<em>2$O)$<em>2$(β-GeW$</em>{12}$O$</em>{40}$)]·44H$_2$O</td>
<td>Dy$^{3+}$</td>
<td>the single molecule magnet behavior</td>
<td>68</td>
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<tr>
<td>Na$<em>{20}$<a href="H$_2$O">Eu$_2$(C$_2$O$_4$(H$_2$O)$_2$O)</a>$</em>{2}$_{12}$H$_2$O</td>
<td>Eu$^{3+}$</td>
<td>the declining of $\gamma\alpha T$ upon cooling prevalingly originates from the progressive depopulation of the excited state of Eu$^{3+}$ cations</td>
<td>73</td>
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<tr>
<td>K$_3$Na$_2$[Ho$_2$(C$_2$O$_4$(H$_2$O)$<em>2$O)]$</em>{6}$.H$_2$O</td>
<td>Ho$^{3+}$</td>
<td>the antiferromagnetic coupling interactions within HoIII centers and thermal depopulation of the Stark sublevels of the Ho$^{3+}$ cation</td>
<td>73</td>
</tr>
<tr>
<td><a href="Ce$_2$(H$_2$O)$_3$%5BCe(H$_2$O)$_2$O%5DCe$_%7B17%7D$W$_%7B15%7D$O$_%7B39%7D$">CeK$_2$(H$_2$O)$_3$</a>]·20H$_2$O</td>
<td>Ce$^{3+}$</td>
<td>the declining of $\gamma\alpha T$ upon cooling is due to the depopulation of the higher Stark levels of the Ce$^{3+}$ ions</td>
<td>76a</td>
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<tr>
<td>KCe$_2$(H$<em>2$O)$<em>3$[Ce$(H$<em>2$O)$<em>2$]$</em>{2}$[SiW$</em>{12}$O$</em>{40}$]$</em>{2}$·40H$_2$O</td>
<td>Ce$^{3+}$</td>
<td>the declining of $\gamma\alpha T$ upon cooling is due to the depopulation of the higher Stark levels of the Ce$^{3+}$ ions</td>
<td>76b</td>
</tr>
<tr>
<td>[Ce(HL)$_3$(H$_2$O)$_3$][Ce(H$<em>2$O)$<em>2$O]$<em>2$[(n-PW$<em>1$O$</em>{13}$H)Ce$</em>{17}$W$</em>{15}$O$</em>{39}$(H$_2$O)]·2H$_2$O</td>
<td>Ce$^{3+}$</td>
<td>the antiferromagnetism coupling interactions</td>
<td>79</td>
</tr>
<tr>
<td>K$_2$(H$_2$O)$_2$[Eu(W$_2$O$_7$)$_2$]·xH$_2$O</td>
<td>Eu$^{3+}$</td>
<td>red photoluminescence excitement peak: 460 nm emission peaks: ¼D$<em>{4p}$→F$</em>{5/2}$ (582 nm), ¾D$<em>{4p}$→F$</em>{5/2}$ (596 nm), ¾D$<em>{4p}$→F$</em>{2}$ (616 nm), ¾D$<em>{4p}$→F$</em>{1}$ (652 nm) and ¾D$<em>{4p}$→F$</em>{1}$ (704 nm)</td>
<td>21a</td>
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<tr>
<td>Na$<em>{20}$K$<em>4$[(α-SiW$</em>{12}$O$</em>{40}$)(H$_2$O)]·2(μ$_2$-CH$_2$COO)·22H$_2$O</td>
<td>Tb$^{3+}$</td>
<td>green photoluminescence excitement peak: 330 nm emission peaks: 1/4D$<em>{4p}$→F$</em>{5/2}$ (546 nm), 3/4D$<em>{4p}$→F$</em>{1}$ (584 nm) and 3/4D$<em>{4p}$→F$</em>{3}$ (623 nm)</td>
<td>21b</td>
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<tr>
<td>KNa$<em>3$[HPro]·[Sm(α-PW$<em>1$O$</em>{13}$)$</em>{2}$]·Pro·18H$_2$O</td>
<td>Sm$^{3+}$</td>
<td>excitation peak: 410 nm emission peaks: ¼G$<em>{52}$→H$</em>{52}$ (555 nm), ¾G$<em>{52}$→H$</em>{52}$ (595 nm) and ¾G$<em>{52}$→H$</em>{52}$ (620 nm)</td>
<td>21c</td>
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<tr>
<td>K$_3$L$_i$Li[H$_2$B$_2$(pic)$<em>3$]$</em>{12}$(H$<em>2$O)$<em>2$(β-AsW$</em>{12}$O$</em>{40}$)(WO$_3$(pic)$_3$)]·5H$_2$O</td>
<td>Tb$^{3+}$</td>
<td>green photoluminescence excitement peak: 275 nm emission peaks: 1/4D$<em>{4p}$→F$</em>{5/2}$ (492 nm), 3/4D$<em>{4p}$→F$</em>{1}$ (544 nm), 3/4D$<em>{4p}$→F$</em>{4}$ (583 nm) and 3/4D$<em>{4p}$→F$</em>{1}$ (623 nm)</td>
<td>39</td>
</tr>
<tr>
<td>(H$_2$py)$_2$[Eu$_2$(H$_2$O)$_2$]$_2$(α$<em>2$-F$<em>2$W$</em>{17}$O$</em>{39}$)]·5H$_2$O</td>
<td>Eu$^{3+}$</td>
<td>excitation peak: 398 nm emission peaks: 1/4D$<em>{4p}$→F$</em>{5/2}$ (578 nm), ¾D$<em>{4p}$→F$</em>{5/2}$ (591 nm), ¾D$<em>{4p}$→F$</em>{2}$ (648 nm) and ¾D$<em>{4p}$→F$</em>{1}$ (696 nm)</td>
<td>44</td>
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</table>
inducing reaction strategy of the lone electron pair stereochemical effect of some heteroatoms have been constantly and intensively utilized and attempted in the preparations of RECPs. These synthetic strategies have been involved in the above-mentioned discussion. Above all, this review primarily concentrates on the elaborate statements about novel structures from mononuclear RECPs to icositetranuclear RECPs. We put emphasis on illuminating structural characterstics, the linking or assembly modes of different compositions and structural types of different building blocks in some representative examples. Certainly, some interesting or important properties are also concerned at the same time.

<table>
<thead>
<tr>
<th>Formula</th>
<th>RE Properties</th>
<th>Ref</th>
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<tbody>
<tr>
<td>$\text{[Na}_2\text{(H}_2\text{O})_6\text{La(H}_2\text{O})_2\text{][H}_2\text{Ce}_2\text{(H}_2\text{O})_2\text{ClW}_6\text{Si}<em>6\text{O}</em>{29}]·6\text{H}_2\text{O}$</td>
<td>Ce$^{3+}$ blue photoluminescence excitation peak: 264 nm emission peaks: 5d→$^9$F$_{2g}$ (488 nm)</td>
<td>51</td>
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<td>$\text{Na}_2\text{[BiW}<em>6\text{O}</em>{19}\text{][(WO}_4\text{)]}_2{\text{Ba}_2\text{(μ}_2\text{O}(\mu}_2\text{OH})}_2}$</td>
<td>Pr$^{3+}$ excitation peak: 230 nm emission peaks: $^1$S$_0→^1$I$_6$ (411 nm), $^1$H$_4→^1$D$_2$ (464 nm), f-f transitions of $^3$P$_0→^1$H$_4$ (480 nm, 492 nm)</td>
<td>59</td>
</tr>
<tr>
<td>$\text{Pr}_2\text{(H}_2\text{O})_8\text{CO}_3$</td>
<td>95H$_2$O</td>
<td>61</td>
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<tr>
<td>$\text{Na}_2\text{Cs}_3\text{Dy[H}_2\text{Si}_2\text{O}_5\text{]⊂[Ce}_2\text{H}_2\text{O}_6\text{]Cl}_3\text{·17H}_2\text{O}}$</td>
<td>Dy$^{3+}$ excitation peak: 357 nm emission peaks: $^3$F$<em>{2g}→^3$H$</em>{11/2}$ (479 nm) and $^3$F$<em>{2g}→^3$H$</em>{13/2}$ (574 nm) yellow photoluminescence excitation peak: 325 nm emission peaks: $^3$F$<em>{2g}→^3$H$</em>{11/2}$ (485 nm), $^3$F$<em>{2g}→^3$H$</em>{13/2}$ (573 nm) and $^3$F$<em>{2g}→^3$H$</em>{15/2}$ (663 nm).</td>
<td>68</td>
</tr>
<tr>
<td>$\text{Cs}_2\text{K}_2{\text{Ge}_2\text{W}_6\text{Nb}<em>6\text{O}</em>{29}}\text{Eu[H}_2\text{O}}_3}$</td>
<td>23H$_2$O</td>
<td>Eu$^{3+}$ excitation peak: 394 nm emission peaks: $^5$D$<em>{0}→^5$F$<em>5$ (579 nm), $^5$D$</em>{0}→^5$F$</em>{1}$ (592 nm), $^5$D$<em>{0}→^5$F$<em>2$ (614 nm), $^5$D$</em>{0}→^5$F$</em>{1}$ (651 nm) and $^5$D$<em>{0}→^5$F$</em>{1}$ (699 nm)</td>
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<td>$\text{Na}_2\text{[Ta}_2\text{C}_2\text{O}_7\text{][H}<em>2\text{O})</em>{10}\text{OH}\text{W}<em>6\text{O}</em>{19}]·3\text{H}_2\text{O}$</td>
<td>Tb$^{3+}$ excitation peak: 369 nm emission peaks: $^5$D$<em>{0}→^5$F$</em>{1}$ (490 nm, 495 nm), $^5$D$<em>{0}→^5$F$</em>{5}$ (543 nm, 545 nm), $^5$D$<em>{0}→^5$F$</em>{1}$ (584 nm, 588 nm) and $^5$D$<em>{0}→^5$F$</em>{1}$ (621 nm)</td>
<td>73</td>
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<tr>
<td>$\text{Na}_2\text{[Ni(H}_3\text{Sm})\text{[H}_2\text{Sm}_2\text{O}_3\text{]Mo}_3\text{O}_4\text{[Mo}_2\text{O}_4\text{]_2}_4\·24\text{H}_2\text{O}$</td>
<td>Sm$^{3+}$ excitation peak: 435 nm emission peaks: $^5$G$<em>{5/2}→^5$H$</em>{15/2}$ (551 nm), $^5$G$<em>{3/2}→^5$H$</em>{13/2}$ (570 nm), and $^5$G$<em>{5/2}→^5$H$</em>{11/2}$ (653 nm)</td>
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<td>$\text{Na}_2\text{[Ta}_2\text{H}_2\text{O}_4\text{][As}_2\text{W}<em>6\text{O}</em>{18}\text{]⊂[proline]<em>2\text{O}</em>{13}]·22\text{H}_2\text{O}$</td>
<td>Tb$^{3+}$ excitation peak: 338 nm emission peaks: $^5$D$<em>{0}→^5$F$</em>{1}$ (490 nm), $^5$D$<em>{0}→^5$F$</em>{1}$ (544 nm), $^5$D$<em>{0}→^5$F$</em>{1}$ (586 nm) and $^5$D$<em>{0}→^5$F$</em>{1}$ (621 nm)</td>
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<td>$\text{K}_2\text{Na}_2\text{H}_2\text{[Eu}_2\text{H}_2\text{O}_4\text{][P}<em>2\text{W}</em>{15}\text{Nb}<em>2\text{O}</em>{43}]·45\text{H}_2\text{O}$</td>
<td>Eu$^{3+}$ excitation peak: 394 nm emission peaks: $^5$D$<em>{0}→^5$F$</em>{1}$ (579 nm), $^5$D$<em>{0}→^5$F$</em>{1}$ (591 nm), $^5$D$<em>{0}→^5$F$</em>{1}$ (613 nm), $^5$D$<em>{0}→^5$F$</em>{1}$ (651 nm) and $^5$D$<em>{0}→^5$F$</em>{1}$ (699 nm)</td>
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<td>$\text{K}_2\text{Na}_2\text{H}_2\text{[H}_2\text{O}_4\text{][P}<em>2\text{W}</em>{15}\text{Nb}<em>2\text{O}</em>{43}]·25\text{H}_2\text{O}$</td>
<td>Eu$^{3+}$ excitation peak: 394 nm emission peaks: $^5$D$<em>{0}→^5$F$</em>{1}$ (579 nm), $^5$D$<em>{0}→^5$F$</em>{1}$ (591 nm), $^5$D$<em>{0}→^5$F$</em>{1}$ (613 nm), $^5$D$<em>{0}→^5$F$</em>{1}$ (651 nm) and $^5$D$<em>{0}→^5$F$</em>{1}$ (699 nm)</td>
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The area of POMs is currently entering into a new phase whereby it is possible to design and control both the structures and functionalities of the systems. On base of the previous results and our critical comprehensions, several personal insights or viewpoints are presented here to help researchers that are engaged in this domain to understand the frontiers of RECP science and grasp the future development direction of neoteric RECPs. Meanwhile, we hope to motivate others to step into this area bringing in new ideas and perspectives.

(i) From the viewpoint of synthetic chemistry, in view of the fact that the hydrothermal reaction is seldom used to prepare RECPs, as a result, the extension of the synthetic approach from the conventional solution...
system to the hydrothermal reaction system will favor to the discovery of novel RECP hybrids accompanying the introduction of some functional components and can also result in the formation of unseen non-equilibrium POM fragments and unexpected functionalities that are not accessible from the near equilibrium environments under the conventional solution conditions.

(ii) As a hotspot research field of inorganic chemistry, the chiral POM-based materials have attracted extensive interest while relevant reports about chiral RECPs are sparse, which suggests that introducing appropriate chiral ligands (including inorganic and organic) to the RECP system to produce chiral RECPs will be an emerging area that bears potential applications in asymmetric catalysis, nonlinear optic, gas separation and molecular recognition.

(iii) The exploration and discovery of much higher nuclear RE incorporated POM aggregations or nanoclusters remains a great and severe challenge albeit an icositetranuclear RECP has been isolated because the encapsulation of much more RE cations to the POM matrices can enhance and tune the magnetic, luminescent or bifunctional catalytic performances of high-nuclear RECPs.

(iv) To date, the majority of reported RECPs are purely inorganic, which inevitably entails the synthesis and study of organic–inorganic hybrid RECPs to become a new research topic. Whereby, multifunctional organic ligands (e.g., polycarboxylic ligands, amino acids, etc.) will be brought in the reaction system to construct organic–inorganic hybrid RECP clusters or high-dimensional frameworks. In addition, by virtue of the antenna effect of functional organic ligands in some degree overcome or improve the low absorptivity of RE cations in the ultraviolet-visible region and sensitize the emission of RE cations, thus enhance the luminous efficiency of RE cations.

Acknowledgements

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Abbreviations

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<tr>
<th>POM</th>
<th>Polyoxometalate</th>
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<tr>
<td>POA</td>
<td>Polyoxoanion</td>
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<td>RE</td>
<td>Rare earth</td>
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<td>TM</td>
<td>Transition metal</td>
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<td>Ln</td>
<td>Lanthanide</td>
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<td>TMS</td>
<td>Transition metal substituted polyoxometalate</td>
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<td>RECP</td>
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<td>TEM</td>
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Notes and references

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Graphic Abstract

Significant developments on rare-earth-containing polyoxometalate chemistry: synthetic strategies, structural diversities and correlative properties

Xing Ma, Wen Yang, Lijuan Chen* and Junwei Zhao*