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### Controllable Synthesis and Catalytic Performance of Nanocrystals of **Rare-Earth-Polyoxometalates**

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**S** Supporting Information

ABSTRACT: Large-scale isolation of nanocrystals of rare-earth-polyoxometalates (RE-POMs) catalysts is important in fundamental research and applications. Here, we synthesized a family of monomeric RE-POMs by the self-assembly of Ta/W mixed-addendum POM {P<sub>2</sub>W<sub>15</sub>Ta<sub>3</sub>O<sub>62</sub>} and rare-earth (RE) ions. These RE-POMs with molecular formulas of  $[RE(H_2O)_7]_3$ - $P_2W_{15}Ta_3O_{62} \cdot nH_2O$  (RE = Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) are all electroneutral molecular clusters, insoluble in water and common organic solvents. The electronic structures, electrochemical properties, and catalytic activities of them have been investigated by experimental and computational



methods. In particular, based on a mild and controllable synthetic process, a convenient and controllable approach to prepare nanocrystals and self-organized aggregates of these monomers has been developed. They exhibit remarkable heterogeneous catalytic activity for cyanosilylation. Both the increased Lewis acid strength of RE in the title compounds, as indicated by theoretical calculations, and the decreased particle size contribute to their high catalytic performances.

#### INTRODUCTION

Rare-earth-polyoxometalates (RE-POMs) have been attracting ever-growing interest owing to their peculiar physicochemical properties and applications in the fields of luminescence,<sup>1-3</sup> magnetochemistry,<sup>4–6</sup> electrochemistry,<sup>7,8</sup> and particularly catalysis.9,10 Due to the Lewis acid nature of RE ions, RE-POMs have shown remarkable performance in catalyzing various organic reactions, such as Diels-Alder, Mukaiyamaaldol, Mannich, and protein hydrolysis.<sup>11-13</sup> With the coexistence of both a Lewis acid (RE ions) and a Lewis base (POM), RE-POMs have been found to show great potential in catalyzing cyanosilylation, from which cyanohydrins-important and otherwise hard to obtain intermediates in the synthesis of  $\alpha$ -hydroxy acids,  $\beta$ -aminoalcohols, and other biological compounds—can be facilely produced.<sup>14–18</sup>

The above-mentioned RE-POMs catalytic systems reported in the literature are mainly homogeneous, which are applicative for the organic phase soluble and stable RE-POMs (generally tetrabutylammonium salts of POMs), for example, monometalsubstituted POMs  $\left[\alpha - \text{RE}(H_2O)_4 P_2 W_{17}O_{61}\right]^{6-}$  and  $\left[\alpha - \text{RE}\right]^{6-}$  $(H_2O)PW_{11}O_{39}]^{4-}$  (RE = Y, La, Eu, Sm or Yb),<sup>10,11</sup> and silicotungstate dimers [{RE(H<sub>2</sub>O)<sub>2</sub>(acetone)}<sub>2</sub>( $\gamma$ - $SiW_{10}O_{36}O_{2}^{-10-}$  (RE = Y, Nd, Eu, Gd, Tb, or Dy).<sup>14,15</sup> But most RE-POMs with novelty structures can only exist as inorganic salts.<sup>19,20</sup> They cannot be dissolved in organic solvent and usually show a very small surface area. On the other hand,

the structures of these compounds cannot be maintained in aqueous solutions. Therefore, they can serve as valid catalysts in neither homogeneous nor heterogeneous systems. It is highly desirable to prepare the nanocrystals of RE-POMs and develop heterogeneous catalytic systems with a high surface area and therefore enhanced catalytic activities.<sup>9,21,22</sup>

However, it is very difficult to isolate RE-POMs catalysts in the nanocrystal form utilizing the reaction of RE and lacunary polyoxotungstates (POTs), which is the main synthetic strategy to prepare RE-POMs currently.<sup>23-27</sup> Owing to the high alkalinity of lacunary POTs and the high oxophilicity of RE ions, the reactions between them and the crystallization course of the producing RE-POMs are difficult to control. In most cases, therefore, these RE-POMs can only be isolated as single crystals in low yields.

In this work, in considering its moderate reactivity (discussed in "Synthesis and Reactivity"), Ta/W mixed-addendum POM  $[P_2W_{15}Ta_3O_{62}]^{9-29}$  was selected to react with various RE salts (Y and the full range of lanthanide except for the radioactive Pm) to construct nanostructured novel RE-POMs. Consequently, a convenient and controllable approach was developed to generate 15 RE-POMs (listed Table 1). Ten of these obtained RE-POMs with the general formula of  $[RE(H_2O)_7]_3$ -

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Table 1. Labeling of the Title Compounds and the Average RE-O(Ta) Bond Lengths, and Relevant Ionic Radii for the RE

compounds			
monomer	chain	RE-O(Ta) bond lengths (Å)	RE ionic radii (Å) <sup>32</sup>
Y-POM		2.252	Y (0.0893)
	La-POM <sup>30</sup>	2.421	La (0.1061)
	Ce-POM <sup>30</sup>	2.385	Ce (0.1034)
	Pr-POM <sup>30</sup>	2.353	Pr (0.1013)
	Nd-POM <sup>30</sup>	2.362	Nd (0.0995)
	Sm-POM	2.305	Sm (0.0964)
Eu-POM		2.289	Eu (0.0950)
Gd-POM		2.306	Gd (0.0938)
ТЬ-РОМ		2.253	Tb (0.0923)
Dy-POM		2.244	Dy (0.0908)
Ho-POM		$2.198^{31}$	Ho (0.0894)
Er-POM		2.229	Er (0.0881)
Tm-POM		2.201	Tm (0.0869)
Yb-POM		2.195	Yb (0.0858)
Lu-POM		2.133 <sup>30</sup>	Lu (0.0848)

 $P_2W_{15}Ta_3O_{62} \cdot nH_2O$  [RE = Y (*n* = 27), Eu (*n* = 26), Gd (*n* = 25), Tb (*n* = 26), Dy (*n* = 25), Ho (*n* = 25), Er (*n* = 26), Tm (*n* = 26), Yb (*n* = 26), Lu (*n* = 25)] (Figure 1 and Table 1)



**Figure 1.** Combined polyhedral/ball-and-stick representation of the monomers (a, RE = Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) and chain compound (b, Sm-C-2). Color scheme for polyhedra: WO<sub>6</sub> (teal), PO<sub>4</sub> (pink), TaO<sub>6</sub> (lime); for spheres: RE (yellow), Sm (dark yellow), O (red).

show discrete monomeric structures. The synthetic approach of these monomers, as the title compounds, was further optimized for rapid preparation of nanocrystals and aggregates with different morphologies in large scale. They have been shown to effectively catalyze the cyanosilylation of a number of aldehydes and ketones with trimethylsilyl cyanide (TMSCN).

#### EXPERIMENTAL SECTION

Synthesis of the Single Crystals of  $[Y(H_2O)_7]_3[P_2W_{15}Ta_3O_{62}]$ 27H<sub>2</sub>O (Y-POM). A sample of  $K_5Na_4[P_2W_{15}O_{59}(TaO_2)_3]$ ·17H<sub>2</sub>O<sup>28</sup> (0.20 g, 0.04 mmol) was dissolved in 25 mL of deionized water at 75 °C. Solid NaHSO<sub>3</sub> (0.04 g, 0.38 mmol) was added with stirring until the yellow solution became colorless, and then solid  $Y(NO_3)_3$ ·6H<sub>2</sub>O (0.05 g, 0.13 mmol) was added. The resulting clear solution was acidified with 1.0 mL of HCl (aq. 1 M) or 2.0 mL of glacial acetic acid, and further stirred at 75 °C for 30 min and then cooled to room temperature. The reaction solution was kept in an open beaker for crystallization at room temperature. Colorless sheet single crystals began to appear within 3 days. Final yield: 0.18 g (82% based on  $K_5Na_4[P_2W_{15}O_{59}(TaO_2)_3]$ ·17H<sub>2</sub>O). Anal. Calcd (%) for  $[Y(H_2O)_7]_3$ - $[P_2W_{15}Ta_3O_{62}]$ ·27H<sub>2</sub>O: P 1.13, Y 4.86, Ta 9.90, W 50.27; found P 1.23, Y 4.75, Ta 10.06, W 49.85. IR (KBr disks): 1622(w), 1090(m), 951(s), 908(s), 777(vs), 519(s) cm<sup>-1</sup>. Synthesis of the Single Crystals of Eu-POM–Lu-POM. Eu-POM–Lu-POM were prepared following the procedure descried for Y-POM, but using respectively  $EuCl_3 \cdot 6H_2O$ ,  $GdCl_3 \cdot 6H_2O$ ,  $TbCl_3 \cdot 6H_2O$ ,  $DyCl_3 \cdot 6H_2O$ ,  $HoCl_3 \cdot 6H_2O$ ,  $ErCl_3 \cdot 6H_2O$ ,  $TmCl_3 \cdot 6H_2O$ ,  $YbCl_3 \cdot 6H_2O$ , and  $LuCl_3 \cdot 6H_2O$  as the starting lanthanide salt. The final products of sheet crystals were obtained with yields of 85%, 86%, 88%, 89%, 87%, 85%, 85%, 86%, 88%, and 84% respectively.

Synthesis of the Single Crystals of Sm-POM.  $[Sm_3(H_2O)_{19}]-[P_2W_{15}Ta_3O_{62}] \cdot 18H_2O$  (Sm-POM) was prepared following the procedure descried for La-POM,<sup>30</sup> but using Sm(NO<sub>3</sub>)<sub>3</sub> as rareearth reagent. The final yield for Sm-POM (tufted crystals) was 56%.

**Preparation of the Aggregate of Y-POM. Step I**: A sample of  $K_5Na_4[P_2W_{15}O_{59}(TaO_2)_3]\cdot 17H_2O$  (0.20 g, 0.04 mmol) was dissolved in 25 mL of deionized water at 75 °C. Solid NaHSO<sub>3</sub> (0.04 g, 0.38 mmol) was added with stirring until the yellow solution became colorless. Solid Y(NO\_3)\_3·6H\_2O (0.1 g, 0.26 mmol) was added, resulting in a colorless solution. The clear solution was acidified with of HCl (aq. 1 M) and further stirred at 75 °C for 30 min.

Step II was performed in the following three different ways:

**Step IIa:** The clear solution was cooled to room temperature under vigorous stirred for 6 h. The resulting suspension was collected on a membrane filter and washed with 10 mL of deionized water and airdried (**Y-POM-H<sub>2</sub>O-6h** isolated yield 33%).

**Step IIb**: After being cooled to room temperature, 2.1 mL of ethanol (ethanol/ $H_2O = 1:12$ ) was added under stirring. The resulting suspension was stirred at 850 rpm for 4 h, and then collected on a membrane filter and washed with 10 mL of deionized water and airdried (**Y-POM-1:12–4h** isolated yield 54%).

**Step IIc:** After being cooled to room temperature, 25 mL of ethanol (ethanol/H<sub>2</sub>O = 1:1) was added in 5 min under stirring to from a turbid mixture (**Y-POM-1:1–0h**). Then the resulting turbid solution was vigorous stirred for half an hour (**Y-POM-1:1–0.5h**), 1 h (**Y-POM-1:1–1h**), 2 h (**Y-POM-1:1–2h**), and 4 h (**Y-POM-1:1–4h**, isolated yield 91%) respectively. The final products were respectively collected on a membrane filter and washed with deionized water and ethanol and air-dried.

Large-scale synthesis of the aggregates of **Y-POM-1:1–0.5h** was readily achieved by simply increasing all reactant by a factor of 10. The product was obtained in about 80% yield.

The aggregates of other compounds (Eu-POM–Lu-POM) were prepared by adopting the same procedures as that of **Y-POM** with the use of the respective starting rare-earth salts.

Cyanosilylation Reaction. A typical cyanosilylation reaction was performed as follows: 0.5 mmol aldehyde/ketone, 0.75 mmol TMSCN, and 1 mol % catalyst was added to a 10 mL Schlenk vase. The reaction mixture was stirred (600 rpm) at 25 °C under nitrogen. The reactions progresses of aldehydes with TMSCN were monitored by <sup>1</sup>H NMR by tracing the decrease of the <sup>1</sup>H resonance of CHO hydrogen and the increase of the characteristic hydrogen in the products. The reactions of ketones with TMSCN were monitored by GC analysis. Conversions were determined by GC analysis using naphthalene as internal standard. The products were confirmed by comparison their GC retention times and <sup>1</sup>H NMR spectra with those of authentic samples. Conversions were determined by GC analysis using naphthalene as the internal standard. After the reaction was completed, the catalyst was recovered by centrifugation and purified by washing with acetone and deionized water and then air-dried for the next cycle. Before the catalytic test, the title catalysts were activated at 120 °C under a vacuum for 2 h.

#### RESULTS AND DISCUSSION

**Structures and Properties.** As shown in Table 1, the selfassembly of  $\{P_2W_{15}Ta_3\}$  with RE (Y<sup>III</sup> and the entire series of lanthanide ions La<sup>III</sup>–Lu<sup>III</sup> except for the radioactive *Pm*), can produce 15 compounds, which include two structural types: monomers (Figure 1a) and one-dimensional chain compounds (Figure 1b). Four of the five chain compounds (La-POM, Ce-POM, Pr-POM, and Nd-POM) have been reported in our previous work.<sup>30</sup> Eleven compounds, including the 10 monomers (Y-POM, Eu-POM, Gd-POM, Tb-POM, Dy-POM, Ho-POM, Er-POM, Tm-POM, Yb-POM, and Lu-POM) and one chain compound (Sm-POM) are reported here for the first time. Single crystal X-ray diffraction analysis and TG curves (Figures S2-S4) revealed that the 10 monomers,  $[RE(H_2O)_7]_3P_2W_{15}Ta_3O_{62} nH_2O$   $[RE = Y (n = 27), Eu (n = 27)]_3P_2W_{15}Ta_3O_{62} nH_2O$ 26), Gd (n = 25), Tb (n = 26), Dy (n = 25), Ho (n = 25), Er (n = 25), = 26), Tm (n = 26), Yb (n = 26), and Lu (n = 25)], possess similar structures with only slight differences in bond lengths and angles and the numbers of lattice water molecules. The structure of Y-POM is described below as an example. As shown in Figure 1a, each  $\{P_2W_{15}Ta_3\}$  moiety in Y-POM is connected with three Y through three Ta-O-Y bridges. Every Y links to a  $\{P_2W_{15}Ta_3\}$  unit and seven aqua ligands, resulting in a square-antiprismatic geometry with a total coordination number of eight. The structure of Sm-POM  $Sm_3(H_2O)_{21}$ ]- $[P_2W_{15}Ta_3O_{62}]$ ·18H<sub>2</sub>O (Figure 1b) is similar to that of the previously reported chain compounds (Re<sub>3</sub>(H<sub>2</sub>O)<sub>22</sub>- $P_2W_{15}Ta_3O_{62} \cdot nH_2O$  [Re = La (n = 16), Ce (n = 16), Pr (n = 16), Nd (n = 17)].<sup>30</sup>

Notably, the formation of the RE-POMs in this manuscript is controlled by the ionic radii of RE. As shown in Table 1, the final structures are all monomers for RE ionic radii less than 0.095 Å, as for Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y. RE ions with ionic radii greater than 0.0964 Å (as for La, Ce, Pr, Nd, and Sm) can link adjacent  $\{La_3(H_2O)_{22}P_2W_{15}Ta_3O_{62}\}$  units to form chain complexes. However, analogous compounds could not be obtained if RE<sup>III</sup> ion was replaced by a smaller cation, such as Sc<sup>III</sup>, Zr<sup>IV</sup>, and Hf<sup>IV</sup>. The average RE–O bond lengths of the 15 compounds listed in Table 1 decrease with atomic number, which is consistent with the trend in the ionic radii of the lanthanide ions and follows the lanthanide contraction principle.<sup>32</sup>

Bond valence sums (BVS)<sup>33</sup> analyses of the title compounds indicated the following oxidation states: W(VI), Ta(V), P(V), and RE(III). The BVS values for O atoms in the POMs skeleton are -2. The values for all the terminal O atoms of the RE ions are less than 0.43, indicating their aqua ligand nature.<sup>34</sup> These title compounds are electroneutral molecular clusters with no discrete countercations (for example alkali metal ions) in the lattice, which is unusual in RE-POMs. For this reason, all of these compounds are almost insoluble in water and common organic solvents, such as methanol, ethanol, acetone, chloroform, and acetonitrile. This property is beneficial for their use in heterogeneous catalysis. The solid photoluminescence behaviors of Sm-POM, Eu-POM, and Tb-POM were investigated at room temperature (Figures S11-S14). They exhibit the characteristic emissions of Sm, Eu, and Tb, respectively.

Electronic Structure and Electrochemical Properties. Cyclic voltammograms (CVs, Figure 2a) of Y-POM and  $K_5Na_4[P_2W_{15}O_{59}(TaO_2)_3]$ ·17H<sub>2</sub>O ({ $P_2W_{15}(TaO_2)_3$ }) both showed three redox processes, while  $K_6[P_2W_{18}O_{62}]$  ({ $P_2W_{18}$ }) showed two redox processes at the same condition. It is worth noting that Y-POMs and { $P_2W_{15}(TaO_2)_3$ } possess similar redox potential but obviously lower than that of { $P_2W_{18}$ }. For instance, the first cathodic peak potentials of Y-POM and { $P_2W_{15}(TaO_2)_3$ } appeared at -0.97 and -0.93 V respectively, which are obviously lower than that of { $P_2W_{18}$ } at -0.49 V. It can be concluded through the CVs comparisons that the substitution of  $Ta^V$  for W<sup>VI</sup> has remarkable influences on the potentials, but the incorporating of the RE ions does not cause obvious changes in the redox potential between Y-POM



Figure 2. (a) CVs of  $\{P_2W_{18}\}$ ,  $\{P_2W_{15}(TaO_2)_3\}$ , and Y-POM on modified carbon paste electrodes, in 1 M Hac/NaAc buffer solution, scan rate: 20 mV·s<sup>-1</sup> the reference electrode was SCE. (b) LUMO compositions of  $\{P_2W_{18}\}$ ,  $\{P_2W_{15}(TaO_2)_3\}$ , and Y-POM.

and  $\{P_2W_{15}(TaO_2)_3\}$ . Relatively, the lowest unoccupied orbital (LUMO, Figure 2b) of the one-electron reduction species of **Y-POM**,  $\{P_2W_{15}(TaO_2)_3\}$  and  $\{P_2W_{18}\}$  are all localized at the equatorial W centers, which clearly shows that the redox centers of these species are at equatorial W positions.<sup>35,36</sup> Under the same conditions, Eu-POM and Yb-POM showed similar CVs curves with that of Y-POM. While an addition irreversible anode peak appears at +0.48 eV in the CVs curve of Ce-POM (Figure S23) corresponds to the redox process of Ce<sup>III</sup>/Ce<sup>IV</sup>.<sup>37</sup>

**Synthesis and Reactivity.** The moderate reactivity of Ta/ W POM  $[P_2W_{15}Ta_3O_{62}]^{9-}$  is crucial for the controllable synthesis of the title compounds and their nanocrystals and aggregates. First, the substitution of Ta<sup>V</sup> for W<sup>VI</sup> can not only increase the negative charge of the polyanion but also lead to polarized charge distribution on  $[P_2W_{15}Ta_3O_{62}]^{9-}$  (Figure 3). The {Ta<sub>3</sub>} section becomes a nucleophilic center of the



**Figure 3.** Ball-and-stick representation of  $[P_2W_{15}Ta_3O_{62}]^{9-}$  fragment (a) and molecular electrostatic potentials (MEPs) of the 3D surface (b). The color of the electronic density isosurface (r 1/4 0.022 e/ua) is a function of the MEP value. Red regions represent nucleophilic areas where the electrostatic potential is negative, and blue regions represent electrophilic areas where the electrostatic potential is less negative.

polyanion toward RE coordination; consequently, the reactivity of  $[P_2W_{15}Ta_3O_{62}]^{9-}$  is superior to that of plenary POMs (for example,  $[P_2W_{18}O_{62}]^{6-}$ ), which are generally inert toward RE, because their terminal oxo ligands are coordinated to the metal atoms with a considerable degree of  $\pi$ -bonding.<sup>20</sup> Second, the more moderate reactivity of  $[P_2W_{15}Ta_3O_{62}]^{9-}$  toward RE than lacunary POTs leads to the reaction more controllable. The direct addition of RE salts into the solution of  $[P_2W_{15}Ta_3O_{62}]^{9-}$ does not cause any precipitation, which is unlike the high alkalinity lacunary POTs. As a result, all the title compounds can be synthesized through a simple reaction procedure under undemanding conditions in the temperature range of 50–90 °C and in the pH range of 2.0–6.5. The controllable synthesis conditions of the title compounds provide favorable conditions for the isolation of nanoscale RE-POMs.

Preparation of the Single Crystals, Nanoparticles, and Aggregates. As shown in Scheme 1, the reaction of

Scheme 1. Synthetic Route of the Single Crystals and Aggregates of Y-POM under Different Conditions and the Corresponding Photograph of the Single Crystals of Y-POM (a) and the Scanning Electron Microscope Images of Y-POM-H<sub>2</sub>O-6h (b), Y-POM-1:12-4h (c), and Y-POM-1:1-4h (d)



 $[P_2W_{15}O_{59}(TaO_2)_3]^{9-}$ , NaHSO<sub>3</sub>, and Y<sup>3+</sup> in acidic solution resulted in a clear solution. Sheet single crystals of the title compounds grew from the reaction solution after standing for 3 days (Y-POM, Scheme 1a), with isolated yields of more than 80%. If the resulting solution was vigorously stirred for 6 h at room temperature, an amorphous solid was obtained with low isolated yield (33%) (Y-POM-H<sub>2</sub>O-6h Scheme 1b). Micronsized irregular sheets could be observed (Y-POM-1:12-4h, Scheme 1c), after adding a small quantity of ethanol to the reaction solutions (ethanol/water = 1:12) and stirring for 4 h. Increasing the ethanol/water ratio to 1:1, rhombic plate aggregates formed after stirring for 4 h (Y-POM-1:1-4h, Scheme 1d and Figures S15). Therefore, amorphous Y-POM can form in water slowly, but this process is uncontrollable. The addition of ethanol to the reaction solution could accelerate the precipitation, increase the yield, and also greatly influence the morphological structures of Y-POM. The assemble mechanism and the effect of ethanol for the state of aggregation are not clear now, but there are two possible factors.<sup>38</sup> First, the some weak interactions, maybe coordination, may exist between ethanol and the RE in RE-POM. Second, different ratios of ethanol/water can adjust the polarity of the mixed solution, which results in different aggregation speeds and different morphologies.

Time-dependent morphology changes were studied by separating and examining the products at different time (0, 0.5, 1, 2, and 4 h) after the addition of ethanol (1:1). The newly formed suspension particles after the addition of ethanol were fine nanocrystals of **Y-POM** (**Y-POM-1:1–0h**, Figures 4a and



Figure 4. SEM images of the nanoparticles Y-POM-1:1–0h (a) and aggregates: Y-POM-1:1–0.5h (b), Y-POM-1:1–1h (c), and Y-POM-1:1–2h (d).

S17). When the suspension solution was further stirred for half an hour, these nanoparticles assemble into cauliflower-like spherical aggregates with an average particle size of 159 nm (Y-POM-1:1-0.5h, Figures 4b and S16). If the stirring time was prolonged to 1 h, the micron-scale clusters aggregates were observed (Y-POM-1:1-1h, Figure 4c). Plate aggregates were observed after 2 h (Y-POM-1:1-2h, Figure 4d), which further evolved into rhombic plate aggregates Y-POM-1:1-4h (Scheme 1d) 4 h later. The purity of these microcrystal and nanocrystal particles were all confirmed by powder X-ray diffraction (PXRD) patterns (Figure S8) and inductively coupled plasma analysis.

Catalytic Activities. The cyanosilylations of carbonyl compounds with trialkylsilyl cyanide (TMSCN) are important C-C bond-forming reactions in organic synthesis for producing cyanohydrin derivatives, which are useful starting materials for the synthesis of several biological active compounds due to the presence of hydroxyl and nitrile functionalities.<sup>18</sup> Many Lewis acid catalysts, that can electrophilically activate carbanyl groups, and nucleophilic catalysts, that can activate TMSCN, have been reported that can effectively promote cyanosilylation.<sup>39-45</sup> It has been also demonstrated that cyanosilylation can be catalyzed by some RE-POMs that combine Lewis acid and Lewis base active sites on the same POM molecules.<sup>13-16,46</sup> The coordinated water molecules of the title compounds were gradually lost from room temperature to about 300 °C (Figures S2 and S4) resulting in open coordination sites of RE, which could behave as Lewis acid sites. Simultaneously, the  $\{P_2W_{15}Ta_3O_{62}\}$ skeletons possessing electronegative surfaces could act as

Lewis base sites. Thus, the title compounds are expected to be effective Lewis acid—base catalysts.

The cyanosilylation reactions of benzaldehyde with TMSCN catalyzed by different RE-POMs (Table 2) and the reactions of

OTMS

## Table 2. Cyanosilylation of Benzaldehyde and TMSCN Catalyzed by Different RE-POMs $^a$



<sup>*a*</sup>Reaction conditions: TMS(CN) 0.75 mmol, benzaldehyde 0.5 mmol, catalysts (1 mol %), under N<sub>2</sub>, 25 °C. <sup>*b*</sup>Yields were determined by GC analysis using naphthalene as the internal standard. <sup>*c*</sup>TOF = converted substrate (mol)/catalyst (mol)/time (h). <sup>*d*</sup>The catalysts in Entries 8–17 were ground samples of the as-prepared single crystal products.

different aldehydes/ketones with TMSCN catalyzed by Y-POM-1:1–0.5h were examined (Table 3). As shown in Table 2, the catalytic activities of the aggregates of the title compounds (Entries 1-7) were apparently higher than that of the single crystal products (Entries 8–11), probably because of the increased surface areas (Table S2). As shown in Table 2 and Figure 5, it needs 3.5, 4, and 5 h to finish the reactions catalyzed by Y-POM-1:1-0h (Entry 1), Y-POM-1:1-0.5h (Entry 2), and Y-POM-1:1-4h (Entry 4), respectively. And it took about 9 h for the single crystal products of Y-POM. However, the catalytic activity of Y-POM-1:1-0h was markedly decreased after the first cycle (Figure S18). IR spectra (Figure S21) of Y-POM-1:1-0h before and after the catalytic reaction remained unchanged indicating the decrease of the catalytic activity is not owing to the decomposition of compounds. SEM images (Figure S22) showed that the small particles aggregated into bulk sample after the catalytic reaction, while the recovered catalyst of Y-POM-1:1-0.5h and Y-POM-1:1-4h could be reused for at least three cycles of the cyanosilylation without an appreciable loss of catalytic performance (Figures S19 and S20). And their morphology did not change significantly (Figure S22). The TOF of Y-POM-1:1-0.5h (24.8) is higher than that of crystal products of Y-POM (12.5) and the reported heterogeneous  $[Nd(H_2O)_5]_2MoV_2O_{26}$ (14) and  $[Sm(H_2O)_5][Sm(H_2O)_7]$  (10),<sup>47</sup> but obviously lower than the homogeneous RE-POMs reported by the Mizuno group (Table S3).<sup>14,15</sup>

Table 3. Cyanosilylation of TMSCN and Aldehydes/Ketones Catalyzed by Y-POM-1:1-0.5h

0			отмз
R'	R	R'	R
Entry	Aldehyde/ Ketone <sup>a</sup>	Yield (%) <sup>b</sup>	Time (h)
1	С <sup>С</sup> н	99	4
2	Г	98	4
3	O C H	92	4
4	Г. I.	98	4
5	F' CH	91	4
6	XU <sup>I</sup> H	70	4
7	()°	90	4
8	$\bigcirc^{\circ}$	90	4
9	$\chi O^{\circ}$	25	4
10	Ů	51	4
11	a Cl	46	4

<sup>*a*</sup>Reaction conditions: TMSCN 0.75 mmol, benzaldehyde 0.5 mmol, catalysts 1 mol %, 25  $^{\circ}$ C under N<sub>2</sub>. <sup>*b*</sup>Conversions were determined by GC analysis using naphthalene as the internal standard.



Figure 5. Conversion of cyanohydrin trimethylsilyl ether vs reaction time catalyzed by Y-POM and the aggregates.

The title compounds (Entries 8–11) present a much higher catalytic activity than that of the chain compounds previously reported (Entries 12–14).<sup>30</sup> This can be explained because the title compounds feature a more open coordination space and less steric hindrance around the RE ions. On the other hand, there were no notable differences in the catalytic activity among the title compounds with different RE (Entries 3–11), although the RE ionic radii showed a wide variation. This may be because the ionic radius has a negligible influence compared with the open coordination sites around RE Lewis acid centers.

The catalytic efficiency of the title compounds **Y-POM** and **Yd-POM** was remarkable higher than that of  $K_7[Y(\alpha-1-P_2W_{17}O_{61})]$  (YP<sub>2</sub>W<sub>17</sub>, Entry 15) and  $K_7[Yb(\alpha-1-P_2W_{17}O_{61})]$ 



Figure 6. Energy levels and d orbital contributions of Y-POM and  $YP_2W_{17}$  (green lines represent LUMOs containing d orbitals of Y).

(YbP<sub>2</sub>W<sub>17</sub>, Entry 16), which are composed of the monovacant Dawson POMs and RE.<sup>48,49</sup> In lacunary RE-POMs, the RE ions are deeply embedded in the lacuna of the negatively charged POMs skeleton, which can weaken the electropositivity and Lewis acidity of the RE and also decrease the available coordination space. Conversely, in the title compounds all the RE ions are located in the external polar region of the  $\{P_2W_{15}Ta_3O_{62}\}$  skeleton, and the anion cluster and cations in the title compounds are relatively independent. Such a bonding pattern should decrease the interaction between the RE and  $\{P_2W_{15}Ta_3O_{62}\}$ . Hence, their Lewis acidity or Lewis alkalinity may be enhanced. Furthermore, more coordination space of RE is available for substrate molecules.

To further understand the difference between the title compounds and the monovacant RE-POMs, theoretical calculations were employed to determine their Lewis acid/ base character. The calculated HOMO of Y-POM and YP2W17 are both composed of the p orbitals of O atoms (Figure 6). The HOMO energy level of Y-POM is slightly lower than that of  $YP_{2}W_{17}$ . Thus, the Lewis base character of the POMs section of **Y-POM** may be slightly weaker than that of  $YP_2W_{17}$ . On the other hand, the lowest energy levels of the unoccupied orbitals containing d orbital of Y atom for Y-POM and YP<sub>2</sub>W<sub>17</sub> are very similar. But remarkably, the d orbitals of Y for Y-POM contributed greatly to the LUMOs in the range from 22.3% to 98.1%. The Y atoms in  $YP_2W_{17}$  have only 1.7% d orbital contributions for LUMOs. The electrons accepting ability of Y in **Y-POM** is likely stronger than that of  $YP_2W_{17}$ . Hence, the Lewis acid character of Y in Y-POM may be greater than that in  $YP_2W_{17}$ . Thus, it can be concluded that the higher catalytic activity of the title compounds mainly results from the higher Lewis acid character.

The cyanosilylation reactions of different aldehydes/ketones with TMSCN catalyzed by **Y-POM-1:1–0.5h** were examined as shown in Table 3. The conversion efficiencies of aldehydes (Entries 1-6) are generally higher than that of ketones (Entries 7-11). Different substituents on the aromatic ring of benzaldehyde derivatives had no notable effect on the reaction yields among Entries 1, 2, 3, 4, and 5, which proceeded

smoothly with conversion higher than 90% in 4 h, while under the same conditions, the catalytic performances for 4-*tert*butylbenzaldehyde (Entry 6) were relatively low. Cyclic aliphatic ketones (Entries 7 and 8) can also smoothly react with TMSCN to afford the corresponding products in high yields. One exception is 4-*tert*-butylcyclohexanone (Entry 9), which is similar to 4-*tert*-butylbenzaldehyde (Entry 6) in aldehydes derivatives. Less reactive acetophenone derivatives (Entries 10 and 11) are also converted into the corresponding cyanohydrin trimethylsilyl ethers but in relatively low yields.

No signal was observed in the <sup>31</sup>P NMR spectrum in the catalytic process of Entries 1, 2, 3, and 8 in Table 2, indicating that **Y-POM** was insoluble and no catalyst decomposition occurred. After the cyanosilylation reactions, the catalysts could be easily recovered quantitatively (>99.9%) by centrifugation and purified by washing with acetone and deionized water and could be reused in the next cycles (Figures S19 and 20). The PXRD patterns and the IR spectrum of the recovered samples were unchanged after cyanosilylation (Figures S9 and S21).

#### CONCLUSIONS

By the reaction of Ta/W mixed-addendum POM  $\{P_2W_{15}Ta_3O_{62}\}$  and RE, a convenient and controllable synthetic method for a family of RE-POMs has been discovered and further developed to facilely prepare the nanocrystals and aggregates of these compounds for the first time. The aggregates of five different morphologies were isolated by controlling conditions. The remarkable catalytic activity of the title catalysts for the cyanosilylation were elucidated by the following factors. (i) In the crystal structures of the title compounds, there is open coordination space around the RE cations available for substrate molecules. (ii) The RE cations are located in the external polar region of the  $\{P_2W_{15}Ta_3O_{62}\};$ such a bonding pattern endows the RE with strong Lewis acidity, as indicated by theoretical calculations. (iii) The nanocrystals and aggregates possess increased surface areas and surface atoms. The substitution reaction of the labile terminal aqua ligands on the RE cations by organic ligands and the assembly mechanism of the aggregates are currently under investigation.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b00763.

Characterization methods and X-ray crystallography analysis (crystallographic collection and refinement details), PXRD, FTIR, TG, SEM and TEM images BET surface areas, solid-state emission spectra, additional catalytic experiments and computational details (PDF)

#### **Accession Codes**

CCDC 1507120, 1507123–1507126, 1507128, 1520009, and 1544162–1544163 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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