

Communication

Formation of Artificial Mn_4YO_4 -Cluster Mimicking the Oxygen-Evolving Center in Photosynthesis

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Abstract

The oxygen-evolving center (OEC) in photosynthesis is a unique biological Mn_4CaO_5 -cluster that splits water into electrons, protons, and dioxygen. It is a great challenge for chemists to develop a robust and precise mimic of the OEC in the laboratory. Herein, we report the formation of a rare-earth-element-containing Mn_4YO_4 -cluster that represents an excellent and robust model of the OEC. The key synthetic precursor, the Mn_3YO_2 -cluster, is reported for the first time, which possesses an identical mixed-valence $\text{Mn}^{\text{III}}_2\text{Mn}^{\text{IV}}$ metal core and a hydrogen-bonding network coordination sphere. This precursor is very reactive and can convert into various compounds in solution. Importantly, it has been found that the presence of organic bases significantly influences the distribution of intermediates and promotes the formation of the Mn_4YO_4 -cluster. Meanwhile, two Mn_4YO_4 -clusters are described, which closely mimic the main metal-oxide core and peripheral ligands, as well as the oxidation states of the four Mn ions in the OEC, revealing that both the terminal ligands and a bridging carboxylate are variable. This new Mn_4YO_4 -cluster displays a remarkable stability in the presence of water in acetonitrile solution. These findings shed new light on the synthesis of rare-earth-element-containing clusters and the rational design of robust artificial water-splitting catalysts, and provide chemical insights into the dynamic structural changes of both biological and artificial clusters.

Keywords: photosynthesis; oxygen-evolving center; biological Mn_4CaO_5 -cluster; artificial Mn_4YO_4 -cluster; artificial Mn_3YO_2 -cluster; formation mechanism



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1. Introduction

The oxygen-evolving center (OEC) in photosystem II (PSII) of oxygenic photosynthetic organisms is a unique biological Mn_4CaO_5 -cluster that splits water into electrons, protons, and dioxygen, producing nearly all the dioxygen in Earth's atmosphere and playing a central role in energy and material transformation for sustaining the biosphere [1–4]. This biological catalyst serves as a blueprint to develop water-splitting catalysts in artificial photosynthesis [5–7]. The catalytic cycle of the OEC involves five S-states (S_n , $n = 0\sim 4$) (Figure 1) [8–11]. Recently, the detailed structures of the OEC in different S-states have been reported [12–18], providing a benchmark to investigate the catalytic mechanism for the oxygen-evolving reaction in photosynthesis [19–27]. However, the detailed structure changes and the formation of an O-O bond during the catalytic cycle of the OEC remain

elusive due to the complexity of protein environments in PSII and the lack of chemical clusters that precisely mimic the OEC [23,28–30].

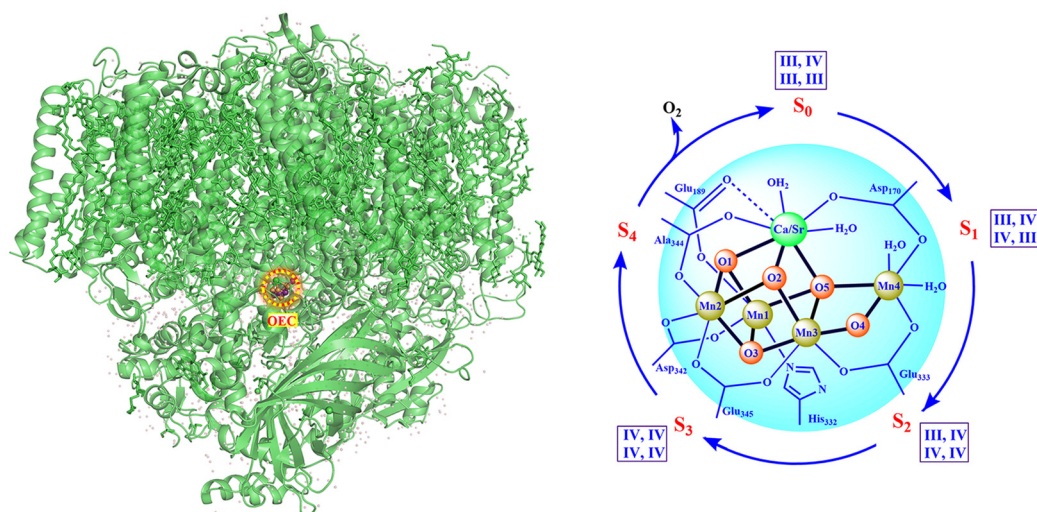


Figure 1. The location of the OEC in PSII [1] (**left**) and the catalytic cycle of the OEC [9] (**right**). The oxidation states of the four Mn ions in each state are given in squares.

Previously, numerous artificial clusters have been synthesized [31–45], in which the artificial Mn_4CaO_4 -cluster and Mn_4SrO_4 -cluster [46–48] closely mimic the main metal-oxide core and peripheral ligands of the OEC. However, these alkaline-earth-element-containing clusters are unstable in aqueous solution due to the dissociation of the redox-inactive Ca^{2+} or Sr^{2+} ions [49], which precludes in-depth investigation. To improve the stability of OEC mimics, a rare-earth-element-containing Mn_4YO_4 -cluster has been synthesized [50], which exhibits remarkable stability, offering a valuable structural and functional model for the OEC. However, compared to the alkaline-earth-element-containing clusters, the efficient synthesis of this rare-earth-element-containing cluster has been a long-standing challenge for chemists, and its formation mechanism remains fully unknown. It is urgently needed to reveal the synthesis mechanism of the rare-earth-element-containing cluster and to develop new robust and precise mimics of the OEC.

Herein, the formation mechanism of the Mn_4YO_4 -cluster is investigated. The key synthetic precursor, the Mn_3YO_2 -cluster, and its conversion are reported for the first time. Meanwhile, two Mn_4YO_4 -clusters that closely mimic the geometric and electronic structures of the OEC are described, revealing that both the terminal ligands and a bridging carboxylate ligand are flexible. These findings shed new light on the synthesis of robust OEC mimics and provide chemical insights into the dynamic structural changes in both natural and artificial clusters.

2. Results and Discussion

Previously, a Mn_4YO_4 -cluster was synthesized through a two-step protocol as shown in Figure 2. A precursor was generated by a reaction of $\text{Y}(\text{CF}_3\text{SO}_3)_3$, $\text{Mn}(\text{Acac})_2$ (Acac = acetylacetonate), ${}^n\text{Bu}_4\text{NMnO}_4$ (${}^n\text{Bu}$ = n-butyl), and pivalic acid in boiling acetonitrile in the first step. The precursor was then treated with 1,8-naphthyridine (Napy) in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ solution, leading to the formation of the Mn_4YO_4 -cluster in the second step [50]. Extensive efforts were made to purify and characterize the precursor. Eventually, the precursor was successfully crystallized and isolated from the CH_3CN reaction solution at low temperature.

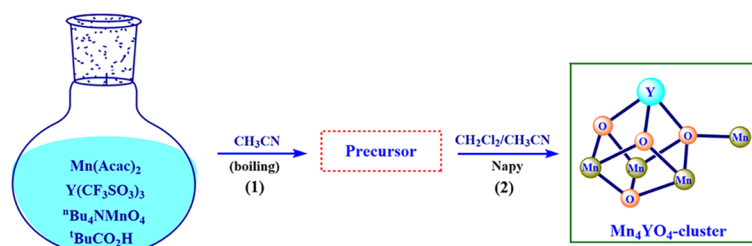


Figure 2. Synthesis procedure for artificial Mn_4YO_4 -cluster.

The crystal structure of the precursor, $\text{Mn}_3\text{YO}_2(\text{tBuCO}_2)_9(\text{tBuCO}_2\text{H})_3$ (**1**), is shown in Figure 3A. It contains a Mn_3YO_2 core, in which Mn2, Mn3 and two μ_3 -oxygen (O1, O2) form a Mn_2O_2 rhombic plane. Both Mn1 and the Y ion are located above this plane, resulting in a cis-conformation for the Mn_3YO_2 core. All three Mn ions are six-coordinate. The oxidation states of three Mn ions in **1** are III, IV, and III, respectively, as confirmed by bond valence sum (BVS) calculations [51–53] (Table S3). The peripheral ligands are provided by nine pivalate (Piv) anions and three pivalic acid molecules. These terminal pivalic acid molecules and pivalate anions form strong intramolecular hydrogen bonds with their nearby ligands, contributing to stabilizing the whole structural framework of the Mn_3YO_2 -cluster in **1**. Notably, the structure of this precursor to the Mn_4YO_4 -cluster is in sharp contrast to that of the Mn_4CaO_4 -cluster, where a Mn_3CaO_4 cubane and one mono-Mn(III) center were found to be two key intermediates in the formation of the Mn_4CaO_4 -cluster [54]. Furthermore, to the best of our knowledge, the Mn_3YO_2 -cluster in **1** with a mixed-valence $\text{Mn}^{\text{III}}_2\text{Mn}^{\text{IV}}$ core and a hydrogen-bonding network coordination sphere represents a highly specific class of heterometallic rare-earth manganese-oxide clusters.

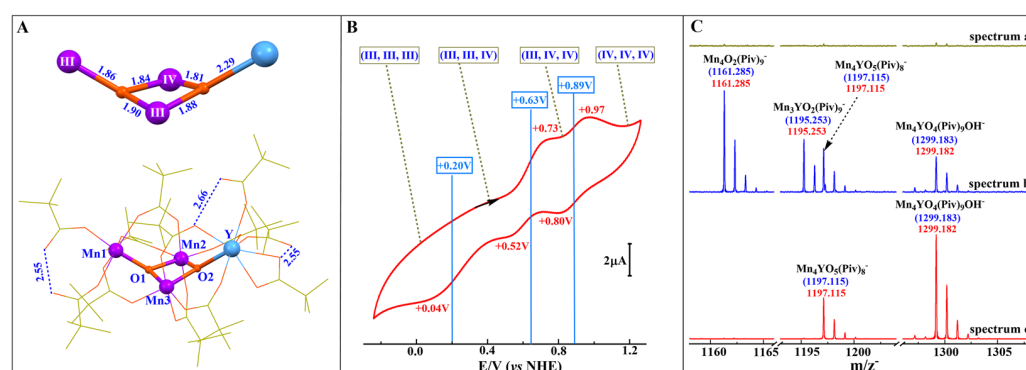


Figure 3. The structure, redox properties, and conversion of **1**. (A) The structure for the Mn_3YO_2 core and peripheral ligands of **1**. Mn, Y, O, and C atoms are shown in purple, sky blue, orange, and yellow, respectively. Distances are given in Å. The oxidation states of Mn ions are shown in Roman numerals. Dashed lines indicate the hydrogen-bond interaction. For clarity, all hydrogen atoms are omitted. (B) CV measurement of **1** in 1,2-dichloroethane. All potentials are referenced to NHE. The scan direction is indicated by the arrow. The possible oxidation states of the three Mn ions in different redox states are given in rectangles. (C) HR-ESI mass spectroscopic measurements for the conversion of **1** in the $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ solution with different equivalents of Napy. Spectrum a, without organic base; Spectrum b, with half an equivalent of Napy; Spectrum c, with one equivalent of Napy. Experimental and calculated m/z^- values are given in red and blue, respectively.

Figure 3B shows the cyclic voltammetry (CV) measurement of **1** in 1,2-dichloroethane. Two redox potentials of +0.63 V and +0.89 V versus normal hydrogen electrode (NHE) are resolved for $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{IV}}]/[\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_2]$ and $[\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_2]/[\text{Mn}^{\text{IV}}_3]$ redox couples, respectively. Interestingly, these values are significantly lower than those for the oxidation of Mn^{III} ions in the Mn_4XO_4 -cluster ($\text{X} = \text{Ca}/\text{Sr}/\text{Y}$) [46,48,50] reported previously. This

difference is likely due to the hydrogen-bond network in **1**, which contributes to stabilizing the high oxidation state of the Mn ions in the cluster.

To investigate the conversion process of the Mn_3YO_2 -cluster (**1**) into the Mn_4YO_4 -cluster (**2**), we performed high-resolution electrospray ionization (HR-ESI) mass spectrometry measurements on the reaction solution in the second step in Figure 2.

Figure 3C shows the mass spectra recorded on the $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ reaction solution of **1** in the presence of different equivalents of organic base (i.e., Napy). In the absence of organic base (Spectrum a), almost no fragments corresponding to the Mn_3YO_2 -cluster or Mn_4YO_4 -cluster can be distinguished. In the presence of half an equivalent of Napy (Spectrum b), four fragments with m/z^- values of 1161.285, 1195.253, 1197.115, and 1299.182 are observed, which are assigned to $[\text{Mn}_4\text{O}_2(\text{tBuCO}_2)_9]^-$, $[\text{Mn}_3\text{YO}_2(\text{tBuCO}_2)_9]^-$, $[\text{Mn}_4\text{YO}_5(\text{tBuCO}_2)_8]^-$, and $[\text{Mn}_4\text{YO}_4(\text{tBuCO}_2)_9(\text{OH})]^-$, respectively, with corresponding calculated m/z^- values of 1161.285, 1195.253, 1197.115, and 1299.183 (Figure S4). In the presence of one equivalent of Napy (Spectrum c), fragments corresponding to $[\text{Mn}_4\text{YO}_4(\text{tBuCO}_2)_9(\text{OH})]^-$ and $[\text{Mn}_4\text{YO}_5(\text{tBuCO}_2)_8]^-$ with m/z^- values of 1299.182 and 1197.115 become dominant, whereas the $[\text{Mn}_4\text{O}_2(\text{tBuCO}_2)_9]^-$ and $[\text{Mn}_3\text{YO}_2(\text{tBuCO}_2)_9]^-$ fragments disappear. These observations clearly demonstrate that the presence of an organic base significantly influences the distribution of intermediates and promotes the formation of the Mn_4YO_4 -cluster. Notably, the product derived from the $[\text{Mn}_4\text{O}_2]$ fragment was successfully isolated and structurally characterized as $\text{Mn}_4\text{O}_2(\text{tBuCO}_2)_8(\text{Napy})(\text{tBuCO}_2\text{H})$ (**5**), while another additional by-product, $\text{Mn}_2\text{Y}_2\text{O}_2(\text{tBuCO}_2)_8(\text{tBuCO}_2\text{H})_2(\text{DMF})_2$ (**4**), was also obtained after recrystallization of the precipitate formed in the second step in Figure 2.

To examine whether other organic bases could support the conversion of the Mn_3YO_2 -cluster to the Mn_4YO_4 -cluster, Napy was replaced by isoquinoline (Isoq), and $\text{Mn}_4\text{YO}_4(\text{tBuCO}_2)_9(\text{Isoq})$ (**3**) was successfully isolated and structurally characterized. As shown in Figure 4E,F, it is composed of a Mn_3YO_4 cubane attached to one dangling Mn ion via a μ_4 -oxide bridge, forming an asymmetric Mn_4YO_4 -cluster. The peripheral ligands are provided by nine pivalate anions and a neutral Isoq molecule. All four Mn ions are six-coordinate, and their oxidation states are (III, IV, IV, III) as confirmed by BVS calculations (Table S4).

Compared with the structure of **2** obtained after the treatment of the Mn_3YO_2 -cluster with one equivalent of Napy in CH_2Cl_2 and CH_3CN solution (Figure 4C,D), three differences are observed in **3**: (i) One chelating pivalate anion is coordinated to the yttrium instead of to the dangling manganese. (ii) The neutral organic base (i.e., Isoq or Napy) is coordinated to the dangling manganese instead of to the yttrium. (iii) One pivalate anion switches its coordination mode from bridging Mn1 and Y in **2** to bridging Mn1 and Mn4 in **3**. Previously, it has been found that the neutral terminal ligands on $\text{Ca}^{2+}/\text{Sr}^{2+}$ and the dangling Mn ion are exchangeable, while all bridging ligands are rigid and unchangeable [47,48]. Herein, for the first time, we provide clear evidence that not only the terminal ligands on the dangling manganese and the redox-inactive metal ion (Y^{3+}) but also the coordination mode of a bridging carboxylate ligand is variable in these OEC mimics.

Notably, the overall structures of **2** and **3** hold a striking resemblance to the OEC, particularly in terms of the main metal-oxide core architecture and the carboxylate-rich peripheral coordination sphere. The oxidation states of the four Mn ions in both **2** and **3** are (III, IV, IV, III) (Table S4), which are the same as those in the S_1 state of the OEC in PSII [8,9]. Thus, the observed ligand flexibility may mirror the dynamic structural changes of the biological OEC during its catalytic cycle, where carboxylate ligand motions are thought to facilitate substrate water binding and O–O bond formation [14]. It should be noted, however, that these structural variations are observed in the crystalline state and their relevance to solution-phase dynamics remains to be established.

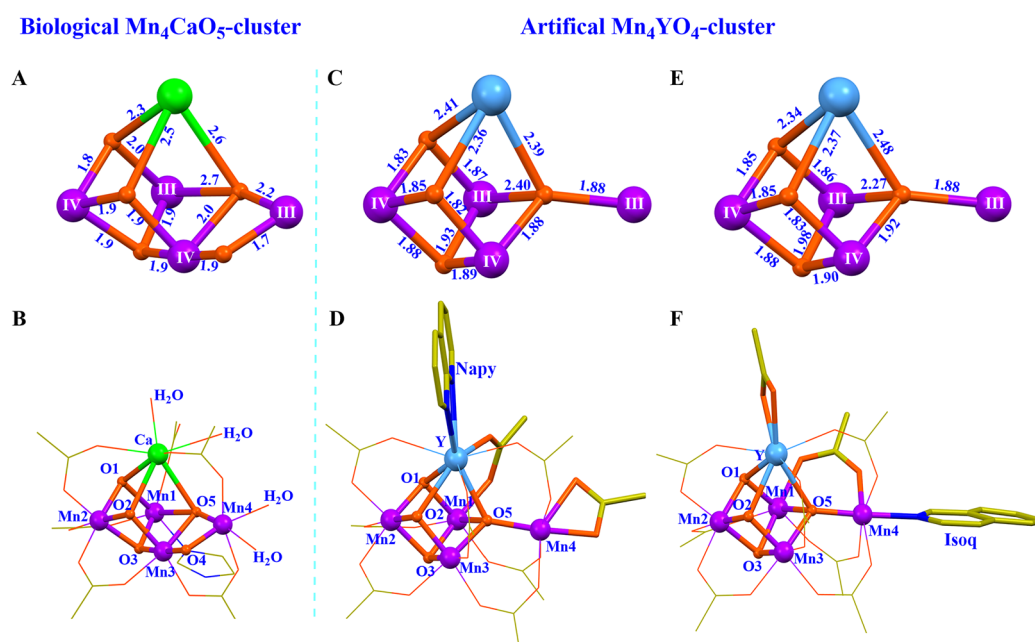


Figure 4. The whole and core structures of the biological Mn_4CaO_5 -cluster [13] and the artificial Mn_4YO_4 -cluster in $\text{Mn}_4\text{YO}_4(^t\text{BuCO}_2)_9(\text{Napy})$ (**2**) and $\text{Mn}_4\text{YO}_4(^t\text{BuCO}_2)_9(\text{Isoq})$ (**3**). (A) The Mn_4CaO_5 core of the OEC. (B) The whole structure of the OEC. (C) The Mn_4YO_4 core of **2**. (D) The whole structure of **2**. (E) The Mn_4YO_4 core of **3**. (F) The whole structure of **3**. Mn, Y, Ca, O, N, and C atoms are shown in purple, sky blue, green, orange, blue, and yellow, respectively. Distances are given in Å. The oxidation states of Mn ions are shown in Roman numerals. For clarity, all hydrogen atoms and methyl groups of tert-butyl are omitted.

Interestingly, in sharp contrast to the high water-sensitivity of the alkaline-earth-element-containing Mn_4CaO_4 -cluster and Mn_4SrO_4 -cluster, complex **3** displays a remarkable stability in acetonitrile solution in the presence of water. As shown in Figure S6A, upon gradual addition of varying amounts of water (0–1000 equivalents) to the acetonitrile solution of **3**, no significant changes were observed in the UV-Vis absorption spectra. Furthermore, time-dependent UV-Vis measurements over 4 h in acetonitrile containing 1000 equivalents of water revealed no notable spectral evolution (Figure S6B). These results confirm that the Mn_4YO_4 -cluster remains stable in the presence of a 1000-fold excess of water in acetonitrile solution. This feature will be crucial for the functional study of this type of artificial cluster in the future.

Therefore, these synthetic Mn_4YO_4 -clusters not only closely mimic the structure of the S_1 -state OEC, but also offer a robust and tunable platform to investigate the dynamic structural changes during the catalytic cycle of the OEC.

3. Materials and Methods

3.1. General Considerations

All synthesis manipulations were carried out under aerobic conditions. All organic solvents were dried by using an A4 molecular sieve. Acetonitrile was further purified by distillation over CaH_2 . All other chemicals were used as received without further purification. $^n\text{Bu}_4\text{NMnO}_4$ was prepared according to the procedure described in the literature [46].

3.2. Preparation of $\text{Mn}_3\text{YO}_2(^t\text{BuCO}_2)_9(^t\text{BuCO}_2\text{H})_3$ (**1**)

$\text{Mn}(\text{Acac})_2$ (0.253 g, 1 mmol) and $\text{Y}(\text{CF}_3\text{SO}_3)_3$ (0.536 g, 1 mmol) were dissolved in 25 mL of boiling acetonitrile. After stirring for 5 min, $^t\text{BuCO}_2\text{H}$ (4.085 g, 40 mmol) (^tBu = t-butyl)

and ${}^n\text{Bu}_4\text{NMnO}_4$ (1.446 g, 4 mmol) were added, and the mixture was stirred continuously for an additional 25 min. The precipitate was removed while the mixture was still hot. After that, the solution was concentrated and dark crystals of **1** formed after several days at 0 °C. The product was washed repeatedly with acetonitrile and dried under vacuum in a yield of ~55% (based on Y). Elemental analysis (%) calculated for **1** ($\text{C}_{60}\text{H}_{111}\text{O}_{26}\text{Mn}_3\text{Y}$): C, 47.97; H, 7.45; and found C, 47.91; H, 7.43.

3.3. Preparation of $\text{Mn}_4\text{YO}_4(\text{}^t\text{BuCO}_2)_9(\text{Napy})$ (**2**)

$\text{Mn}_4\text{YO}_4(\text{}^t\text{BuCO}_2)_9(\text{Napy})$ (**2**) was synthesized via a reaction between **1** and one equivalent of Napy in a $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN} = 2:1$ (vol/vol) solution. After sonication at 50 °C for 5 min, the precipitate was removed, and the solution was kept at 20 °C. Brown crystals of **2** were formed in a few days. The product of **2** was washed with hexane and dried under vacuum in a yield of ~20% (based on Y). Elemental analysis (%) calculated for **2** ($\text{C}_{53}\text{H}_{87}\text{N}_2\text{O}_{22}\text{Mn}_4\text{Y}$): C, 45.05; H, 6.21; N, 1.98; and found C, 45.03; H, 6.21; N, 1.77.

3.4. Preparation of $\text{Mn}_4\text{YO}_4(\text{}^t\text{BuCO}_2)_9(\text{Isoq})$ (**3**)

$\text{Mn}_4\text{YO}_4(\text{}^t\text{BuCO}_2)_9(\text{Isoq})$ (**3**) was synthesized via a reaction between **1** and one equivalent of Isoq in a $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN} = 2:1$ (vol/vol) solution. After sonication at 50 °C for 5 min, the precipitate was removed, and the solution was kept at 20 °C. After several days, reddish-brown single crystals formed. The product of **3** was washed repeatedly with hexane and dried under vacuum in a yield of ~25% (based on Y). Elemental analysis (%) calculated for **3** ($\text{C}_{54}\text{H}_{88}\text{NO}_{22}\text{Mn}_4\text{Y}$): C, 45.94; H, 6.28; N, 0.99; and found C, 46.19; H, 6.27; N, 1.11.

3.5. Isolation of $\text{Mn}_2\text{Y}_2\text{O}_2(\text{}^t\text{BuCO}_2)_8(\text{}^t\text{BuCO}_2\text{H})_2(\text{DMF})_2$ (**4**)

$\text{Mn}_2\text{Y}_2\text{O}_2(\text{}^t\text{BuCO}_2)_8(\text{}^t\text{BuCO}_2\text{H})_2(\text{DMF})_2$ (**4**) was isolated from a reaction between **1** and one equivalent of isoquinoline (Isoq) in a mixture of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN} = 2:1$ (vol/vol). After sonication at 50 °C for 5 min, the precipitate was collected. The precipitate was then recrystallized in CH_2Cl_2 in the presence of N, N-dimethyl formamide (DMF). After several days, crystals of **4** formed at 20 °C. The crystal structure of **4** was shown in Figures S1D and S2A.

3.6. Isolation of $\text{Mn}_4\text{O}_2(\text{}^t\text{BuCO}_2)_8(\text{Napy})(\text{}^t\text{BuCO}_2\text{H})$ (**5**)

$\text{Mn}_4\text{O}_2(\text{}^t\text{BuCO}_2)_8(\text{Napy})(\text{}^t\text{BuCO}_2\text{H})$ (**5**) was isolated from a reaction between **1** and one equivalent of 1,8-naphthyridine (Napy) in a $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN} = 2:1$ (vol/vol) solution. After sonication at 50 °C for 5 min, the precipitate was removed, and the solution was kept at 20 °C. Black crystals of **5** formed within a few days. The crystal structure of **5** was shown in Figures S1E and S2B.

3.7. Stability of Mn_4YO_4 -Cluster in the Presence of Water

The stability of $\text{Mn}_4\text{YO}_4(\text{}^t\text{BuCO}_2)_9(\text{Isoq})$ (**3**) in the presence of water was evaluated by UV-Vis absorption spectroscopy upon the gradual addition of various equivalents of water to the acetonitrile solution (Figure S6A). Time-dependent UV-Vis measurements were also carried out in the acetonitrile solution of **3** containing 1000 equivalents of water (Figure S6B). Both results demonstrate that **3** remains stable even in the presence of a 1000-fold excess of water in acetonitrile.

3.8. X-Ray Crystallography Measurements

Suitable crystals of different samples were selected and mounted on a loop, and then placed on the diffractometer under a nitrogen stream. The diffraction data of **1–5** were collected on a Rigaku XtaLAB AFC10 (RCD3; Tokyo, Japan) diffractometer equipped with a confocal monochromatic Mo-K α radiation source. The diffraction data were processed

by using the Olex2 program [55], and the structure was solved with the ShelXT structure solution program [56] via intrinsic phasing and refined with the ShelXL refinement package using least squares minimization [57].

3.9. Mass Spectroscopic Measurements

High-resolution electrospray ionization mass spectrometry (HR-ESI-MS) measurements were performed using a Bruker Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer Solarix 9.4T (Billerica, MA, USA). Data were processed using DataAnalysis 4.0 (Bruker Daltonics). Before starting the experiments, the syringe and sampling tube were thoroughly washed with dried acetonitrile.

3.10. CV Measurements

Cyclic voltammogram (CV) measurements were performed by using a three-electrode system connected to an electrochemical workstation PGSTAT302N, (Metrohm, Herisau, Switzerland). The working electrode was a glassy carbon disk (diameter of 3 mm, freshly polished), the counter electrode was a platinum disk (diameter of 3 mm, freshly polished) and the reference electrode was an Ag/AgNO₃ electrode (10 mM AgNO₃, 100 mM ⁿBu₄NPF₆ in acetonitrile). The electrolyte solution was 1,2-dichloroethane with 100 mM ⁿBu₄NPF₆. During the measurement, the solution of **1** (2 mM) was kept under an argon atmosphere. Reported potentials of CVs were referenced to normal hydrogen electrode (NHE) calibrated by the potential of ferrocene/ferrocenium measured under the same conditions.

4. Conclusions

In summary, we have investigated the formation mechanism of the artificial Mn₄YO₄-cluster. The key synthetic precursor (Mn₃YO₂-cluster) and its conversion are reported for the first time, demonstrating that the presence of organic bases significantly influences the distribution of intermediates and promotes the formation of the Mn₄YO₄-cluster. Two Mn₄YO₄-clusters have been synthesized with different organic bases, and both closely mimic the main metal-oxide core, peripheral coordination sphere, and the oxidation states of the four Mn ions found in the OEC. Structural comparison reveals that not only the terminal ligands but also the binding mode of a bridging carboxylate can be altered. Furthermore, the new Mn₄YO₄-cluster holds a remarkable stability in the presence of water in acetonitrile solution. These findings shed new light on the synthesis of rare-earth-element-containing artificial clusters and the rational design of robust artificial water-splitting catalysts, and provide chemical insights into the dynamic structural changes of both biological and artificial clusters.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/inorganics14080195/s1>, Figure S1: ORTEP view of the structures of **1** (A), **2** (B), **3** (C), **4** (D), and **5** (E) with 50% probability displacement ellipsoids; Figure S2: Crystal structures of **4**, Mn₂Y₂O₂(^tBuCO₂)₈(^tBuCO₂H)₂(DMF)₂ (A) and **5**, Mn₄O₂(^tBuCO₂)₈(Napy)(^tBuCO₂H) (B); Figure S3: CV measurement of **1** (red) and the blank (blue) in 1,2-dichloroethane; Figure S4: Experimental (red) and calculated (blue) mass spectra for fragments of [Mn₄O₂(^tBuCO₂)₉][−] (A), [Mn₃YO₂(^tBuCO₂)₉][−] (B), [Mn₄YO₅(^tBuCO₂)₈][−] (C), and [Mn₄YO₄(^tBuCO₂)₉(OH)][−] (D); Figure S5: UV-Vis absorption spectra of **1** (blue), **2** (yellow), and **3** (red) in 1,2-dichloroethane; Figure S6: Stability of **3** in acetonitrile solution with different amount of water; Figure S7: FTIR spectra of solid samples of **1** (A), **2** (B), and **3** (C). Table S1: Crystal data and structure refinement for **1–3**; Table S2: Crystal data and structure refinement for **4** and **5**; Table S3: Bond-valence sum (BVS) calculations for Mn ions and oxygen bridges in **1**; Table S4: Bond-valence sum (BVS) calculations for Mn ions and oxygen bridges in **2** and **3**. Table S5: Bond-valence sum (BVS) calculations for Mn ions and oxygen bridges in **4** and **5**.

Author Contributions: Conceptualization, C.Z. and C.C.; methodology, C.Z. and C.C.; investigation, Y.W., Z.W., C.C. and J.H.; writing—original draft, Y.W., Z.W. and C.C.; writing—review and editing, C.Z. and C.C.; supervision, C.Z.; funding acquisition, C.Z. and C.C. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Crystallographic data for 1–3 have been deposited with the joint Cambridge Crystallographic Data Centre and can be obtained using the respective CCDC deposition numbers: 2540561 (1), 2098699 (2), 1913760 (3), 2540560 (4), and 2540563 (5). Supplementary Data accompanying this article is available online.

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Conflicts of Interest: The authors declare no conflicts of interest.

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