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The first artificial Mn_4Ca-cluster mimicking the oxygen-evolving center in photosystem II

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The oxygen-evolving center (OEC) in photosystem II (PSII) of plants, algae and cyanobacteria, is a unique catalyst in nature to split water into O_2, protons and electrons by using sun light. Because of broad fundamental interests and potential applications in artificial photosynthesis, the structure and properties of this unique catalyst have attracted extensive attention during the last two decades. Recent X-ray crystallographic studies of PSII have revealed that the biological OEC is comprised of a unique asymmetric Mn_4Ca-cluster bound to protein groups [1,2] (Figure 1, left). This biological catalyst serves as a blueprint for the development of efficient and cheap artificial catalysts for water-splitting reaction to overcome the bottleneck of entire field of artificial photosynthesis. However, it is a great challenge for chemists to synthesize the whole structure of the OEC in laboratory mainly due to the following reasons: (i) It is very difficult to incorporate Ca^{2+} into Mn_4-cluster through μ-O^{2-} bridges. In principle, the affinity of Ca^{2+} to μ-O^{2-} is significantly weaker than that of Mn ion, thus, in most cases, only multi-manganese cluster instead of MnCa heterometallic cluster can be formed and isolated. (ii) The whole structure of the biological OEC is an asymmetric Mn_4Ca-cluster, which has been thought to be impossible to be synthesized in laboratory. (iii) The ligands of the biological OEC are mainly provided by carboxylate groups and water molecules. In general, it is difficult to introduce these biological ligands to artificial Mn complexes in higher oxidation states. (iv) The redox potential of the Mn_4Ca-cluster is very high (+0.8 ~ +1.0 V vs. NHE) due to the presence of high oxidation state (+4 and +3) of the Mn ions. It is uncertain whether this type of MnCa complexes can be prepared and isolated in a chemical system.

Recently, many artificial Mn complexes have been prepared to mimic the biological OEC in literatures, and some of them contain the Mn_3CaO_4 cluster resembling closely the cubane part of the biological OEC [3,4]. However, it is still a great challenge to mimic the whole asymmetric Mn_4Ca-cluster with similar ligands as observed in PSII.

The author has been devoting to work on the structure and the reaction mechanism of the biological OEC in PSII since the late 1990s, and succeeded in predicting the binding mode of calcium—one of key cofactors of the OEC in 1999 [5]. After more than 15 years of investigation on the biological OEC [6,7], the author entered the field of the artificial photosynthesis. With the help of the knowledge on the biological OEC, we have succeeded in preparing a series of artificial MnCa and MnSr heterometallic complexes to mimic the biological OEC recently [8,9].

In 2015, a new significant progress [10] has been made: the first asymmetric Mn_4Ca-cluster (Figure 1, right) has been synthesized through a two-step procedure with a high yield (~50%) by using inexpensive commercial chemicals ($Bu^n{}_4NMnO_4$, $Mn(CH_3CO_2)_2 \cdot (H_2O)_4$, $Ca(CH_3CO_2)_2 \cdot H_2O$, and pivalic acid). The new artificial Mn_4Ca-cluster displays remarkable structural similarity to that of the OEC in nature in respects of the asymmetric Mn_4Ca core structure and peripheral ligands. The whole complex only has 85 nonhydrogen atoms and a molecular weight (MW) of

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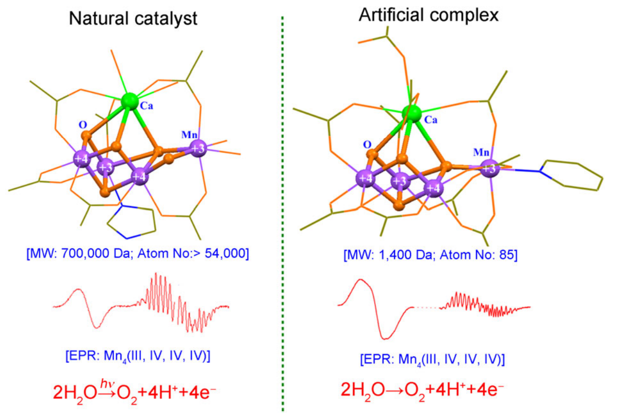

Figure 1 Structural and functional comparisons of the Mn_4Ca-cluster in natural photosynthesis (left) and in artificial photosynthesis (right).

~1,400 Da, compared to the values of ~54,000 non-hydrogen atoms and the molecular weight of 700,000 Da observed for its biological paragon. Like the biological OEC, the artificial Mn_4Ca-cluster can undergo four redox transitions and display two low-temperature electron paramagnetic resonance (EPR) signals (g=2.0 and g=4.9) arising from two distinct ground states. Furthermore, it should be pointed out that there are two potential water-binding sites on Ca and dangler Mn ion in the artificial Mn_4Ca-cluster, which are essentially the same as those observed in the biological OEC. Similar to the biological OEC, the artificial Mn_4Ca-cluster can serve as a catalyst for water-splitting reaction as demonstrated by the cyclic voltammogram (CV) measurements (Figure S9 of reference [10]).

The artificial Mn_4Ca-cluster and its future variants may provide new insights into structural determinants of the biological OEC and the mechanism of the water-splitting reaction, and open new avenues to develop new generations of artificial catalysts for photo water-splitting reaction from earth-abundant and non-toxic chemical elements in future.

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