Polyoxometalates

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Synthesis and Disassembly/Reassembly of Giant Ring-Shaped Polyoxotungstate Oligomers

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Abstract: *The disassembly and reassembly of giant molecules are essential processes in controlling the structure and function of biological and artificial systems. In this work, the disassembly and reassembly of a giant ring-shaped polyoxometalate (POM) without isomerization of the monomeric units is reported. The reaction of a hexavacant lacunary POM that is soluble in organic solvents,* $[P_2W_{12}O_{48}]^{14-}$*, with manganese cations gave the giant ring-shaped POM* $[\{\gamma\text{-}P_2W_{12}O_{48}Mn_4(C_5H_7O_2)_2(CH_3CO_2)\}_6]^{42-}$*. This POM is a hexamer of manganese-substituted* $\{P_2W_{12}O_{48}Mn_4\}$ *units, and its inner cavity was larger than any of those previously reported for ring-shaped polyoxotungstates. It was disassembled into monomeric units in acetonitrile, and the removal of the capping organic ligands on the manganese cations led to reassembly into a tetrameric ring-shaped POM,* $[\{\gamma\text{-}P_2W_{12}O_{48}Mn_4(H_2O)_6\}_4(H_2O)_4]^{24-}$*.*

Disassembly and reassembly processes of self-assembled giant molecules play important roles in controlling structure and function in various biological systems, such as protein folding, translation, and transport by molecular chaperones and proteases.[1] These processes have recently been utilized in the rearrangement of structurally defined self-assembled giant artificial molecules;[2] these reports have prompted considerable research interest because of the potential use of such molecules as artificial enzymes, molecular machines, and drug-delivery systems.[3] Although biological systems utilize multiple types of interaction sites to control disassembly/reassembly processes, most artificial molecules possess only one type of interaction site because of the difficulty in controlling the reassembly of structures that use multiple types of interaction sites.[2,4]

Polyoxometalates (POMs) are anionic metal oxide clusters. By exploiting these robust and structurally well-defined anionic metal frameworks, the direction, number, and type of interaction sites can be precisely controlled at an atomic level.[5] To date, various POM oligomers comprising lacunary and/or metal-substituted POMs have been synthesized, and they show unique catalytic, magnetic, and redox properties depending on the types of lacunary POMs and/or the introduced metal cations.[6] The disassembly/reassembly of POM oligomers would lead not only to new synthetic methods for the preparation of giant POMs but also enable drastic changes in the chemical and physical properties. Although several POM oligomers have been reported to undergo structural transformations,[7] the disassembly/reassembly of POM oligomers is still difficult because 1) the monomeric units often decompose and/or isomerize in aqueous media, 2) stable POM oligomers hardly undergo any transformation, 3) reassembly processes frequently lead to infinite structures, and/or 4) the use of multiple types of interaction sites is quite challenging.[8]

We recently found that lacunary POMs that are soluble in organic solvents are useful for introducing metal cations[9] and that structural transformations are possible without undesired decomposition and isomerization.[10] We considered that the aforementioned difficulties associated with the disassembly/reassembly of POM oligomers could be overcome by using a hexavacant lacunary Dawson-type POM that is soluble in organic solvents. Hexavacant lacunary Dawson-type POMs possess two types of vacant sites, namely edge and middle sites, whereas mono-, di-, and trivacant lacunary POMs possess one type of vacant sites (Figure 1 a). Therefore, metal substitution into a hexavacant lacunary POM and introduction/removal of the capping organic ligands on the substituted metal cations should enable the control of multiple types of interaction sites for use in the disassembly/reassembly of giant POM oligomers.

Herein, we report the synthesis of a giant hexameric ring-shaped POM, $[\{\gamma\text{-}P_2W_{12}O_{48}Mn_4(acac)_2(OAc)\}_6]^{42-}$ (**II**, acac = acetylacetonate, OAc = acetate), by the reaction of hexavacant lacunary $[P_2W_{12}O_{48}]^{14-}$ (**I**) with $Mn(acac)_3$. POM **II** consists of six manganese-substituted monomeric $\{P_2W_{12}O_{48}Mn_4\}$ units, and the inner cavity (19.6 Å × 14.4 Å) is larger than those of any previously reported polyoxotungstates. Each $\{P_2W_{12}O_{48}Mn_4\}$ unit in **II** contains two types of manganese cations with acac and acetate capping ligands, respectively, affording two types of interaction sites. We also describe the disassembly/reassembly of a POM oligomer without isomerization; the disassembly/reassembly of **II** into the tetrameric ring-shaped POM $[\{\gamma\text{-}P_2W_{12}O_{48}Mn_4(H_2O)_6\}_4(H_2O)_4]^{24-}$ (**III**) can be achieved by removing the capping organic ligands coordinated to the manganese cations in **II** (Figure 1 b).

Initially, a tetra-*n*-butylammonium (TBA) salt of the hexavacant lacunary Dawson-type phosphotungstate **I** was synthesized by mixing $K_{12}H_2[\alpha\text{-}P_2W_{12}O_{48}]$[11] and TBABr in aqueous nitric acid (see the Supporting Information for details). The ^{31}P NMR spectrum of **I** in a mixture of [D$_6$]acetone and [D$_4$]methanol (1:1 v/v) showed a single resonance at $\delta = -7.91$ ppm, confirming the presence of a single phosphorus-containing species (see the Supporting Information, Figure S1).[12] The reaction of **I** with four equivalents of $Mn(acac)_3$ in dichloromethane resulted in the

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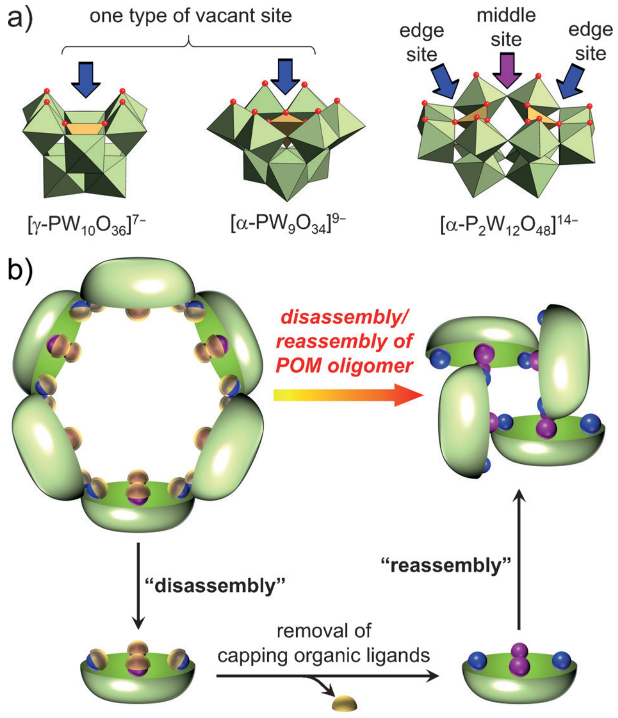

Figure 1. a) Lacunary POMs and the types of possible lacunary sites. b) Disassembly/reassembly of POM oligomers. The atoms are represented by polyhedra and spheres. Mn (edge site) blue, Mn (middle site) purple, O (vacant site) red, P orange, W green. The monomeric hexavacant lacunary Dawson-type POM units and organic capping ligands (acac and acetate) are represented by green and yellow hemispheres, respectively.

formation of green single crystals from the synthesis solution (Figure S2). X-ray crystallographic analysis revealed that the product was the giant, ring-shaped, manganese-substituted phosphotungstate **II** (Figure 2a; see also Figure S3 and Table S1). The anionic part of **II** is an elliptical ring structure comprising a hexamer of monomeric manganese-containing $\{P_2W_{12}O_{48}Mn_4\}$ units, and is slightly distorted from ideal D_{3d} symmetry. The inner cavity of **II** was 19.6 Å long (longer axis) and 14.4 Å wide (shorter axis), and is thus, to the best of our knowledge, larger than those of any previously reported ring-shaped polyoxotungstates (Table S2).[13] The $\{P_2W_{12}O_{48}Mn_4\}$ unit comprises the hexavacant lacunary γ-Dawson-type phosphotungstate, which represents the first report of a new family of lacunary POMs (Figure S4).

Each monomeric $\{P_2W_{12}O_{48}Mn_4\}$ unit contains four manganese cations, and their bond valence sum (BVS) values of two edge (2.99–3.20) and two middle manganese atoms (1.91–2.09) indicate that the respective valences were +3 and +2 (Table S3). Measuring the direct current magnetic susceptibility of a polycrystalline sample of **II** under 0.1 T gave a χT value of 89.41 $cm^3\,K\,mol^{-1}$ at 300 K (Figure S5). This value is close to the sum of the spin-only value (88.50 $cm^3\,K\,mol^{-1}$) for 12 high-spin Mn^{3+} atoms (3.00 $cm^3\,K\,mol^{-1}$; $S=2$, $g=2.00$) and 12 high-spin Mn^{2+} atoms (4.38 $cm^3\,K\,mol^{-1}$; $S=5/2$, $g=2.00$), which also supports the hypothesis that the manganese cations in **II** indeed have these valences.

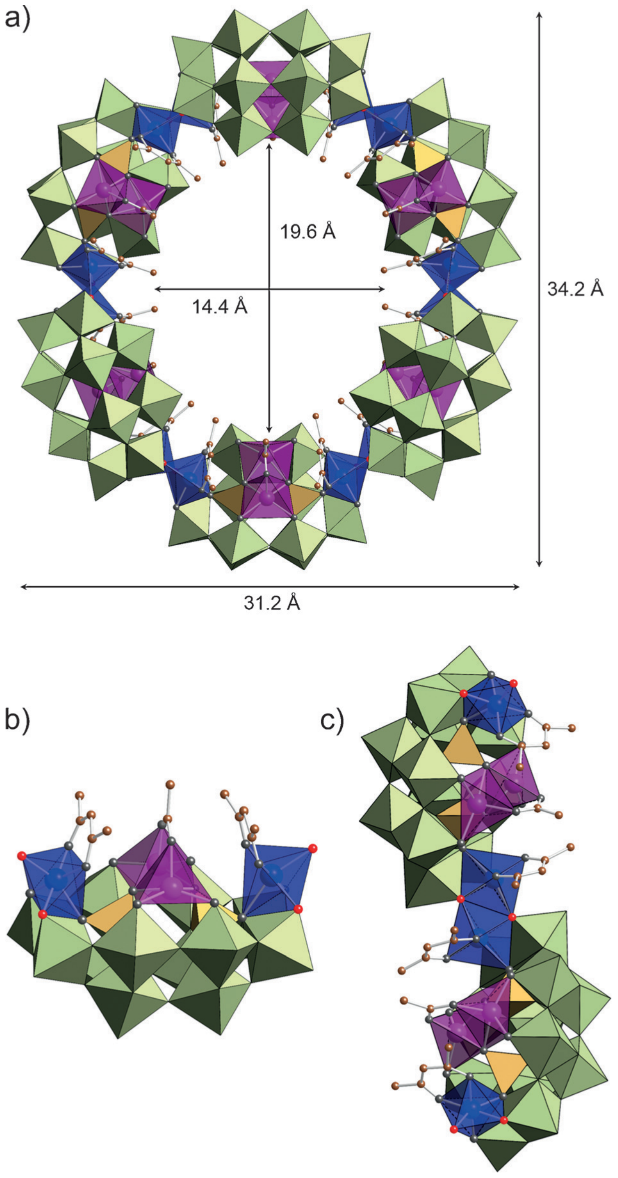

Figure 2. Polyhedral and ball-and-stick representation of a) the anionic part of **II**, b) the monomeric unit of **II**, and c) the connection site of two monomeric units in **II**. The atoms are represented by polyhedra and spheres. C brown, Mn^{3+} (edge site) blue, Mn^{2+} (middle site) purple, O gray (for connecting monomeric units: red), P orange, W green.

Importantly, these manganese cations afforded two types of coordination sites: The two edge Mn^{3+} cations were used for connecting monomeric $\{P_2W_{12}O_{48}Mn_4\}$ units through Mn–O bonds while the two middle Mn^{2+} cations were protected by acetate ligands (Figures 2b,c). GC-MS analysis of the synthesis solution of **II** confirmed the presence of acetic acid and methylglyoxal, which indicates that the Mn^{3+} cations had been partially reduced to Mn^{2+} (middle sites) through oxidative C–C bond cleavage of acetylacetone.[14,15] Based on these results, the formula for the anionic component of **II** is $[\{\gamma\text{-}P_2W_{12}O_{48}Mn^{3+}{}_2Mn^{2+}{}_2(acac)_2(OAc)\}_6]^{42-}$. Most of the reported ring-shaped polyoxotungstates contain alkali metal cations in their cavities (Table S2), probably because condensation of the monomeric units was enabled by a template effect, and therefore, the structural design of giant rings has been difficult. It is conceivable that the construction of the large central pore of **II** was successful because condensation proceeded without such templating metal cations and only the edge Mn^{3+} sites contributed to the condensation reaction as the middle interaction sites were protected.

The cold spray ionization (CSI) mass spectrum of **II** in acetonitrile gave a set of signals centered at *m/z* 4728.4 assignable to $[(TBA)_5H_3P_2W_{12}O_{48}Mn_4(acac)_2(OAc)]^+$, which suggests that **II** was disassembled and dissolved into monomers in this solution (Figure S6a). Analytical ultracentrifugation gave the major sedimentation coefficient distribution at 3.52 S (Figure S7b).[16] This value is very close to that of $(TBA)_6[\alpha\text{-}P_2W_{18}O_{62}]$[17] (3.97 S) in acetonitrile (Figure S7a), also supporting the proposed disassembly of **II** into monomers in this solution.[18] The removal of the protecting capping organic ligands was examined to assess whether the compound could be reassembled into another oligomer. Addition of TBAOH (1M in methanol) to an acetonitrile solution of **II** indeed resulted in their removal, as confirmed by CSI mass-spectrometric analysis (Figure S6).[19]

Addition of diethyl ether and chloroform to the mixture of **II** and TBAOH in acetonitrile resulted in the precipitation of yellow single crystals from the synthesis solution (Figure S2). The sedimentation coefficient of the product in acetonitrile (8.40 S) was significantly larger than those of $(TBA)_6[\alpha\text{-}P_2W_{18}O_{62}]$ and **II** (monomers in this solution; Figure S7c), suggesting that the disassembled monomeric $\{P_2W_{12}O_{48}Mn_4\}$ units had been reassembled to yield a larger oligomer. X-ray crystallographic analysis revealed that the product was the ring-shaped manganese-substituted phosphotungstate **III** (Figure 3a; see also Figure S8, Table S1).

In contrast to the hexameric elliptical ring structure of **II**, **III** is a twisted tetramer made from monomeric $\{P_2W_{12}O_{48}Mn_4\}$ units; the anion has S_4 symmetry. Each monomeric unit contains four manganese cations, and the BVS values of these manganese atoms (two edge sites: 2.03–2.08; two middle sites: 1.98–2.24) indicate that their valences were all +2 (Table S4). The manganese cations at the edge sites had thus been reduced from the +3 (in **II**) to the +2 (in **III**) oxidation state, probably through the aforementioned oxidation of the acac ligands.[15] Measuring the direct current magnetic susceptibility of polycrystalline samples of **III** under 0.1 T gave a χT value of 66.15 $cm^3\,K\,mol^{-1}$ at 300 K (Figure S5). This value is close to the sum of the spin-only value (70.00 $cm^3\,K\,mol^{-1}$) for 16 high-spin Mn^{2+} atoms, thus supporting the proposed valence of the manganese cations in **III**. Furthermore, the BVS values of the six oxygen atoms coordinated to the manganese cations at the edge sites (O11A–O13A, O11B–O13B: 0.34–0.40) were low, indicating that these oxygen atoms were, in fact, aqua ligands (Figure S8). As expected, the acac and acetate ligands had been removed, and the manganese cations at the middle sites were connecting neighboring monomeric units (Figures 3b,c). Notably, the structure of each monomeric $\{P_2W_{12}O_{48}Mn_4\}$ unit was maintained even after the disassembly/reassembly of the POM oligomers. The inner diameter of **III** (5.0 Å) was much smaller than that of **II** (19.6 Å × 14.4 Å; Table S2), and the small cavity captured four water molecules in alignment, which were held in place by multiple hydrogen-bonding networks (Table S5, Figure S9). The MALDI-TOF mass spectrum of **III** that was obtained using DCTB[20] as the matrix showed several signal sets, and the signal set centered at *m/z* 16069.16 was assigned to $[(TBA)_{12}H_{13}(P_2W_{12}O_{48}Mn_4)_4(CH_3CN)_3]^+$ (*m/z* 16069.08) with an error of 5 ppm, supporting the reassembly of the monomeric $\{P_2W_{12}O_{48}Mn_4\}$ units to yield **III** (Figure S10).[21] Based on these results, the formula of the anionic component of **III** is $[\{\gamma\text{-}P_2W_{12}O_{48}Mn^{2+}{}_4(H_2O)_6\}_4(H_2O)_4]^{24-}$.

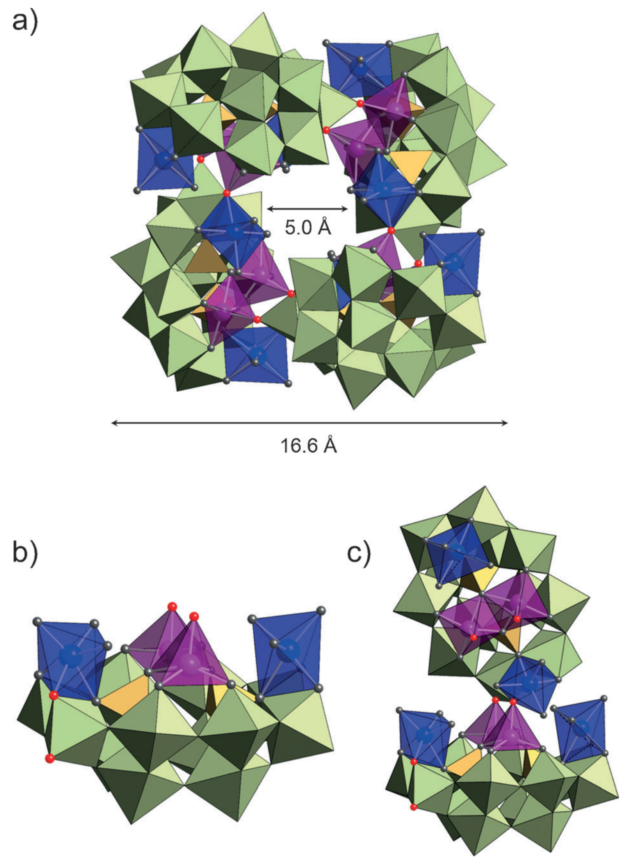

Figure 3. Polyhedral and ball-and-stick representation of a) the anionic part of **III**, b) the monomeric unit of **III**, and c) the connection site of two monomeric units in **III**. The atoms are represented by polyhedra and spheres. C brown, Mn^{2+} (edge site) blue, Mn^{2+} (middle site) purple, O gray (for connecting monomeric units: red), P orange, W green.

In conclusion, by making use of multiple types of interaction sites to imitate the disassembly/reassembly processes in biological systems, the first structural transformation of the anion of a giant ring-shaped POM oligomer has been reported. Based on the two types of vacant sites in **I**, the monomeric manganese-containing $\{P_2W_{12}O_{48}Mn_4\}$ units in **II** contain two types of interaction sites, and the use of these sites was key to the successful reassembly into another oligomer. POMs **II** and **III** display substantially different anion sizes, ring shapes, and magnetic properties.[22] Utilizing multiple interaction sites for disassembly/reassembly therefore leads to complicated structural transformations and expands the methods currently available for the synthesis of giant artificial molecules. We believe that the ability to alter the physical and chemical properties of such compounds could be applied to the development of artificial enzymes, molecular machines, and drug-delivery systems.

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[12] The ^{31}P NMR spectrum of **I** showed a broad resonance ($\Delta_{1/2} =$ 31.5 Hz) owing to rapidly exchanging protons in **I**.

[13] Disordered TBA cations and solvent molecules are probably present in the cavity of **II**.

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[15] In aqueous media, the disproportionation of Mn^{3+} readily proceeds to form Mn^{2+} and Mn^{4+} (MnO_2) species. In contrast, it is well known that $Mn(acac)_3$ is stable against disproportionation in organic media, and that a ligand elimination by single-electron oxidation of an acac ligand in $Mn(acac)_3$ takes place to give $Mn(acac)_2$. During the synthesis of **II**, we observed several products that result from the oxidation of acac, and in addition, no MnO_2 was produced. Therefore, we believe that the formation of Mn^{2+} species is mainly due to the oxidation of acac; see: H. Nishino, *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1922.

[16] The sedimentation coefficient distribution of **II** (Figure S7b) clearly indicates that the major species is the monomer $\{P_2W_{12}O_{48}Mn_4\}$, while an oligomeric species was also present in very small amounts.

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[18] It is known that the sedimentation coefficients of POMs obtained by the analytical ultracentrifugation sedimentation velocity correlate closely with their molecular weights and sizes; see: a) S. Roy, K. L. Planken, R. Kim, D. v. d. Mandele, W. K. Kegel, *Inorg. Chem.* **2007**, *46*, 8469; b) M. Kurasawa, F. Arisaka, T. Ozeki, *Inorg. Chem.* **2015**, *54*, 1650.

[19] We confirmed that the capping organic ligands on **II** were not removed in the absence of base. Therefore, bases are indispensable for the ligand removal. We believe that the role of the base is to abstract protons from **II**. The deprotonation leads to an increase of the anion charge and weakens the interaction between the ligands and manganese cations in **II**, thus possibly facilitating the ligand removal. To confirm this hypothesis, we also carried out the reaction of **II** with the nitrogen base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). In separate experiments, we confirmed that DBU can effectively abstract protons from POMs. The CSI mass spectrum of **II** with DBU (12 equiv) in acetonitrile showed that DBU could promote the ligand removal (Figure S11). These experimental results support our hypothesis of deprotonation-induced ligand removal.

[20] DCTB = *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]; see: L. Ulmer, J. Mattay, G. Torres-Garcia, H. Luftmann, *Eur. J. Mass Spectrom.* **2000**, *6*, 49.

[21] The CSI mass spectrum of **III** showed no peaks, probably owing to the high molecular weight.

[22] The alternating current magnetic susceptibilities of **II** showed temperature- and frequency-dependent χ' and χ'' values under 0.1 T direct current field, indicating the slow relaxation of the magnetization characteristic for single-molecule magnets (Figure S12a, b). On the other hand, the χ' and χ'' values of **III** hardly depended on the frequency (Figure S12c). According to Arrhenius plots, the energy barrier for the magnetization relaxation of **II** is 21.8 K (Figure S12d).

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