

Graduate School of Pure and Applied Sciences

Giant Metal Clusters: Ligand Directed Metal Assembly

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Chapter 1. General Introduction

Chapter 2. Controlled Growth of Iron Oxide within a Confined Organic Cage Space

Chapter 3. Self-Assembly of Mn Ions by Multidentate Bridging Ligands

Chapter 4. General Conclusion

Abstract

Syntheses of nano-sized metal oxide species have been a subject of an intensive study over the past a few decades. There is, however, still little overlap in the size of nanoparticles and molecular metal oxides. To fill the gap is an attractive target for synthetic chemistry. For the preparation of molecular metal oxides, one key to obtaining larger clusters is to learn how we can assemble large numbers of metal ions with precisely controlled size by designing supporting organic ligands. On the other hand, precise control of the growth of the metal oxide particles, which is usually very fast and uncontrollable, is strongly required for the preparation of extremely small metal oxide nanoparticles and is expected to be achieved by using new reaction spaces within organic surfactant ligands. In this thesis, the author developed two new synthetic approaches for the preparation of metal oxide species with sizes lying on the border between conventional metal oxide nanoparticles and molecular metal oxide clusters; 1) the size-controlled synthesis of metal oxide nanoparticles utilizing the precisely controlled nano-space of an organic cage and, 2) the self-assembly of a large number of metal ions into high-nuclearity metal oxide clusters utilizing a highly capable multidentate bridging ligand.

1) Size-controlled synthesis of metal oxide nanoparticles utilizing the precisely controlled nano-space of an organic cage

In chapter 2, a purely covalent organic cage, L_{cage} (Figure 1a), was utilized as a nano-sized reaction container for the growth of ferrihydrite particles and the confined reaction space inside the cage cavity

successfully functioned as a means of directing size-controlled particle formation. Various characterization techniques, including elemental analysis, FT-IR, UV-vis absorption, ^{57}Fe Mössbauer spectroscopy, TEM, AFM and magnetic measurements, revealed the formation of a ferrihydrite core in $\text{Fh}@L_{\text{cage}}$ with a diameter of 2.3 ± 0.5 nm composed of ca. 80 Fe ions (Figure 1b). It was suggested that the formation and growth of the ferrihydrite core is restricted by the cage sphere and the particle diameter is defined by the size of the cage cavity. Owing to the extremely small particle size, $\text{Fh}@L_{\text{cage}}$ also displayed size specific properties. The magnetic measurements showed superparamagnetic behaviour with the blocking temperature of $T_B = 6$ K, while a UV-vis spectrum revealed the significant increase in band gap energy compared to the bulk state due to the quantum confinement effect.

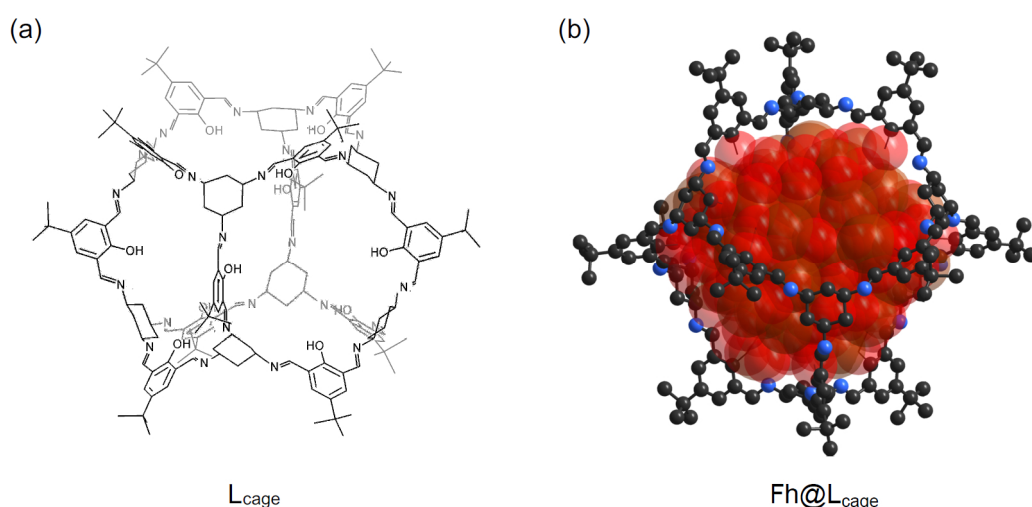


Figure 1 (a) Molecular structure of L_{cage} . (b) Schematic illustration of proposed structure of $\text{Fh}@L_{\text{cage}}$.

2) Self-assembly of a large number of metal ions into high-nuclearity metal oxide clusters utilizing a highly capable multidentate bridging ligand

In chapter 3, reactions of manganese ions with an alkylamine based multidentate ligand, H_5bdp (Figure 2), successfully gave a series of high nuclearity mixed-valence Mn oxide clusters, $[\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}_8\text{O}_5(\text{bdp})_2(\text{O}_2\text{CPh})_{10}(\text{OMe})_2]$ ($[\text{Mn}_{12}]$), $[\text{Mn}^{\text{II}}_8\text{Mn}^{\text{III}}_{10}\text{Mn}^{\text{IV}}\text{O}_{10}(\text{OH})_4(\text{Hbdp})_2(\text{O}_2\text{CPh})_{18}]$ ($[\text{Mn}_{19}]$) and $[\text{Mn}^{\text{II}}_6\text{Mn}^{\text{III}}_{15}\text{O}_{12}(\text{OH})_4(\text{bdp})_2(\text{Hbdp}^*)(\text{H}_2\text{bdp}^*)(\text{O}_2\text{CPh})_{14}]$ ($[\text{Mn}_{21}]$). It was

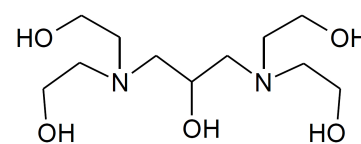


Figure 2 Ligand H_5bdp .

turned out that the deprotonated bdp^{5-} ligands were capable to assemble a large number of Mn ions. Note that $[\text{Mn}_{21}]$ is one of the largest mixed-valence manganese clusters reported to date. All three complexes showed dominant antiferromagnetic interactions between Mn ions and only $[\text{Mn}_{21}]$ exhibited SMM behaviour at low temperature. The different magnetic behaviour in $[\text{Mn}_{19}]$ and $[\text{Mn}_{21}]$, despite their similar oxide core, is likely due to slightly different oxidation states, i.e. the introduction of the Mn^{IV} ions into the centre of the double cubane core of $[\text{Mn}_{21}]$ changed the relative alignment of Jahn-teller axes of Mn^{III} ions, leading to a non-zero molecular magnetic anisotropy.

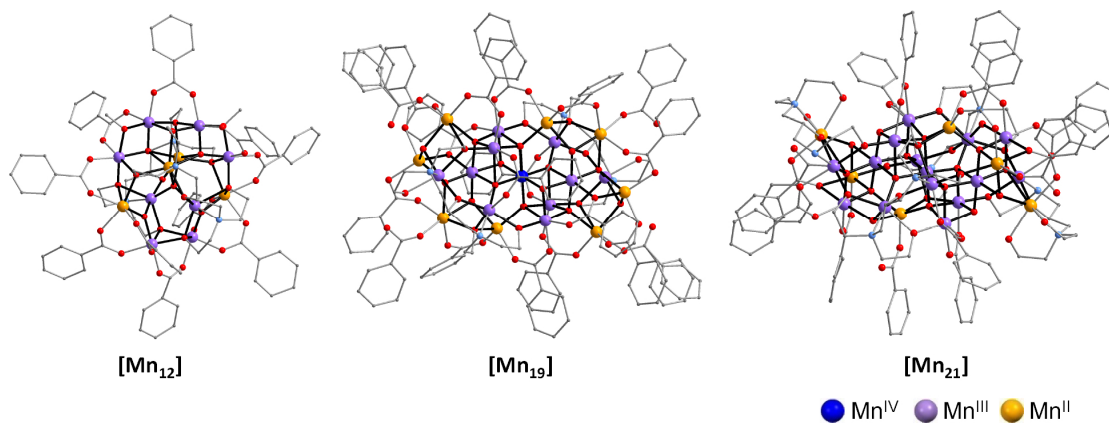


Figure 3 Structures of [Mn₁₂], [Mn₁₉] and [Mn₂₁].

References

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