Macromol. Symp. ***131**, 155–163 (1998)*

An Overview on the Development of Macromolecule-metal Complexes and Brief Sketch on Their Recent Trends

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Abstract:
In early 1970s, there was growing tendency that the macromolecule-metal complexes should have been understood as a molecular science among many international scientists. Y. Y. Jiang, Academia Scinica, firstly proposed an international symposium on this field and the first congress (MMC-1) was held in 1985. From the 4th one, this series has been under the auspices of IUPAC and we have reached MMC-7. The current interests in this field are, for example, photoinduced electron transfer, outer-sphere process, chemical reactions in subnano-geometrical space, multi-electron transfer reaction. They are all linked to the high performances of advanced materials. The role of macromolecules in macromolecule-metal complexes are summarized and recent topics of this area are described.

ROLE OF MACROMOLECULES IN MACROMOLECULE-METAL COMPLEXES

Macromolecular complexes are defined as general term of the complexes participated macromolecules. A representative example is, of course, macromolecule-metal complexes. In addition, intermolecular complexes and molecular assemblies should be included in this category (Ref. 1, 2).

In the macromolecule-metal complexes, role of the macromolecules are construction of specific geometrical space (molecular environment) around the coordination sphere and regulation of the electronic process of the metal complex moiety. The characteristics of the molecular environment made of polymer chains and/or molecular assembly of assemble-philic molecules are steric effect, molecular perturbation, dynamic structural change and long range forces. The direct interactions between the complex site and molecular environment are coordination bond, hydrogen bond and charge-transfer interaction (Fig. 1). In general, these weak interaction

CCC 1022-1360/98/$ 10.00

forces affect multiply and dynamically the electronic process of the metal complex moiety and the total effects are observed as unique aspects of the binding equilibrium, ligand substitution, electron transfer process and catalytic reaction of macromolecule-metal complexes.

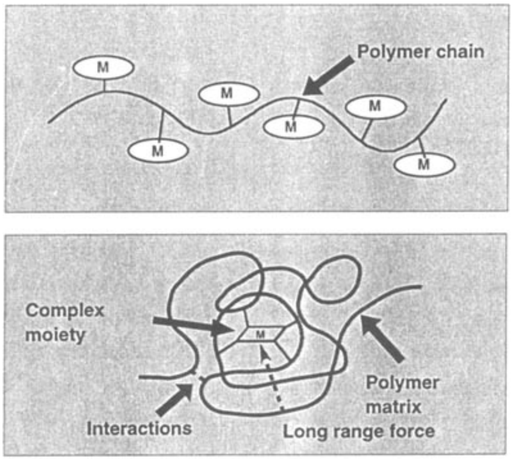


Fig. 1 Schematic illustration of macromolecule-metal complexes.

Allosteric effect on dioxygen binding to the hemoglobin molecule is a well-known example. The small displacement of the structural change by the first dioxygen coordination induces the dynamic conformation change, which is transferred to the neighboring subunits and reduces the activation energy of the second, third and fourth dioxygen binding to the hemes. This is one of the long-range force effect which can be observed as the cooperative binding reaction conjugated to the higher-order structure change of the macromolecules.

Hydrolysis enzyme of polypeptides, namely chymotrypsin, also performs very efficient molecular conversion. The orientation of the residues of serine, hystidine, asparagic acid in the active site play crucial role for the whole relay reactions. Small crevice (11x6x4 Å) made of folded polypeptides acts as binding site for the substrates and accelerates each reaction step. Unfortunately, it is still difficult to realize these reactions by using synthetic macromolecules.

PERFORMANCES OF MACROMOLECULE-METAL COMPLEXES

Development of the advanced materials utilizing the macromolecule-metal complexes is significantly extended. A great deal of attentions have been attracted to the formation of electron-transfer channels, charge-separation process induced by photoexcitation, tunnel effects (outer-sphere electron transfer) and molecular conversion (chemical reaction). Furthermore, the multi-electron transfer systems on molecular assemblies of the complexes and/or mixed-valence complexes will give a clue to the development of new fields of novel molecular conversion as well as artificial photosynthesis. The highly-ordered functions of the macromolecule-metal complexes will also be directly linked to the advanced technologies, such as super conductors, organic ferromagnets and nonlinear optics.

HISTORY OF SYMPOSIUM ON MACROMOLECULE-METAL COMPLEXES (MMC)

In early 1970s, there was growing tendency that the macromolecule-metal complexes should have been understood as a molecular science among many international scientists. Prof. Y. Y. Jiang of Academia Scinica, firstly proposed an international symposium on this field and the first symposium was held in Beijing in 1985. Many scientists participated the symposium internationally and MMC-1 was really successful through his great contribution. At that time, the delegates agreed to open the MMC symposium in every two years (Table 1). From 4th one, this series has been under the auspices of IUPAC. Through Bremen and Guanzhou, we have reached MMC-7 organized by Prof. Reedijik. The numbers of participants have been increasing and it has already decided that MMC-8 Tokyo will be held in 1999.

Table 1 International symposium on Macromolecule-Metal Complexes

	Year	*Place*	*Chairmen*	*Main Theme of Scientific Program*	*Participants*
1	Oct. 1985	Beijing	Y.Y. Jiang	Fundamental aspects of MMC, catalytic behavior, and others	150
2	Oct. 1987	Tokyo	H. Hirai	Electronic process of MMC	300
3	IUPAC July 1989	Princeton	J. Demas J. Sheats	Molecular devices using MMC	160
4	IUPAC Sep. 1991	Siena	R. Barbucci F. Ciardelli	Electro conductivity of MMC-composite, catalytic MMC, and others	150
5	IUPAC Aug. 1993	Bremen	D. Wöhle	MMC for biological, catalytic, electronic and photon induced process	250
6	IUPAC Nov. 1995	Guanzhou	Y.Y. Jiang G.M. Cong	Electro- and ionic-conductivity of MMC, and others	260
7	IUPAC Oct. 1997	Leiden	J. Reedijik	Role of metal ions, complexes, and cluster in MMC system	(150)
8	IUPAC Sep. 1999	Tokyo	E. Tsuchida	Process control of electronic process of MMC for advanced technologies	( )
9	IUPAC 2001	(US)			

CONSTRUCTION OF THE GEOMETRICAL-SPACE BY SELF-ASSEMBLY

It is significant that motive for molecular assembly is considered to assemble-philic properties. In the field of the macromolecule-metal complexes, one of the current interests is process control of the electron transfer reaction by using geometrical space made of self-assembled complexes.

(1) Regulation of the porphyrin-porphyrin distance in the porphyrin fibers

Protoporphyrins derivatives with two amphiphilic alkyl side chains are, for example, easily dispersed in water, to form monomolecular stacked fibers (Ref. 3). The porphyrin-porphyrin distance in the fibers is 3.4 Å and fluorescence is completely quenched, so that construction of the electron transfer pathway through the metal-center will give a nano-sized molecular wire. In addition, dioxygen binding to the porphyrin stacks should lead to effective dioxygen reduction catalysis.

In contrast to these non-fluorescing fibers, some porphyrin stacks fluoresce strongly. For instance, tetraphenylporphyrin with eight alkylphosphochiline side chains, so called *octopusporphyrin*, formed beautiful fibers in water, in which the distance between the porphyrin-porphyrin is 11Å (Ref. 4, 5). Since the porphyrin planes are separated by the steric hindrances of the substituents, the fluorescence intensity and triplet lifetime are almost the same as that of the monomer. The geometrical space between the porphyrin and the neighboring porphyrin can be adjusted by the size of the substituents, and the lifetimes of the excited singlet and triplet states are regulated. These results actually led to photoinduced electron transfers and following redox reactions. The octopusporphyrin fibers act as photochemical catalysis for the long-lived charge separation.

(2) Microscopic observation of the porphyrin arrangement

Octopus-type porphyrins also produce spherical vesicles with diameter of ca. 100 nm (Ref. 6). In cryo-electron micrograph of the red solution, the thickness of the membrane is estimated to be 70 Å, corresponding to monomolecular length of the porphyrin side chains. Interestingly, the white narrow line with the width of 15 Å is clearly seen in the center of the membrane, suggesting relatively low molecular density. Since the cryo-electron microscopy has a great sensitivity to the molecular packing, the white line obviously corresponds to 15 Å space made of porphyrin plane arrays. Cryo-electron microscopy is useful technique for direct observation of molecular environment of Å size.

(3) Reversible O_2-coordination

Using this hydrophobic space constructed by self-assembly of the amphiphilic tetraphenylporphyrins, reversible O_2-coordination has been realized (Ref. 7). For example, tetraphenylheme having four dialkylphosphocholine groups on one side of the rig plane, so called *lipidheme*, produced bilayer vesicles in aqueous solution (Fig. 2). These vesicles can bind and release dioxygen reversibly under physiological conditions, as hemoglobin does. The molecular environment made of the amphiphilic alkyl side chains of the lipidheme prevents the irreversible oxidation of ferrous porphyrin through a proton driven process.

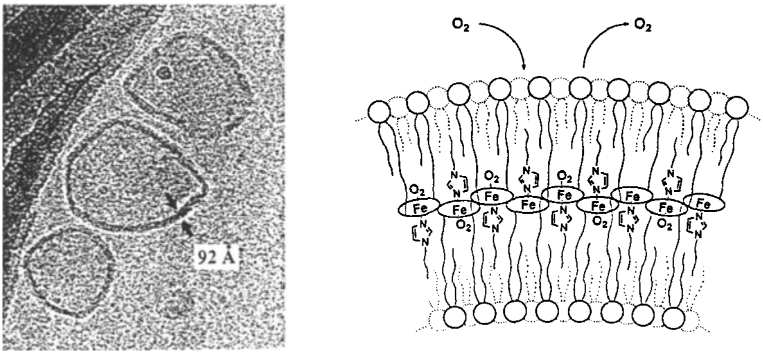


Fig. 2 Electron micrograph of the lipidheme vesicles and their reversible O_2-coordination.

(4) Polymerization of the porphyrin vesicles

The tetraphenylporphyrin with four carotenoids, so called *tetrabixinporphyrin*, are self-organized in pH 9 water to give the monolayered polyene vesicles (Ref. 8). The obtained stiff vesicle are polymerized by irradiation of the visible light. These polymer vesicles remained intact in 95% ethanol and scanning force microscopy images showed perfectly spherical shapes on graphite. This is the first example of the 3D picture of the covalently linked structure of the self-assembled porphyrin. The combination of supramolecular assembly and polymerization is quite useful strategies to prepare rigid and rather stable geometrical space around the active site.

The polyene vesicle membranes with a central porphyrin core can presumably also be used in light induced charge separation processes with external electron acceptors.

MOLECULAR CONVERSION THROUGH MULTI-ELECTRON TRANSFER PROCESS

(1) Synthesis of poly(thioarylene) by oxidative polymerization

Multi-electron transfer reactions are achieved by using multinuclear complexes. For example, mixed valent vanadyl complexes act as multi-electron transfer mediator for the oxidative polymerization of diphenyl disulfide (Ref. 9). The dinuclear complex with mixed valent vanadium(IV, V) can oxidize the disulfide, and the resulting low valent vanadium(III, IV) complex is re-oxidized by dioxygen (Ref. 10). Pure and high molecular weight poly(thiophenylene) can be easily prepared through these reactions (Ref. 11). The obtained polymers show interesting properties such as electronic conductivity, photoreactivity and excellent performances as a processible material. The poly(thiophenylene) with a melting point at 285°C and decomposition temperature above 500°C is obtained as a crystalline powder, fiber and amorphous film. This is a novel molecular conversion through multi-electron transfer process.

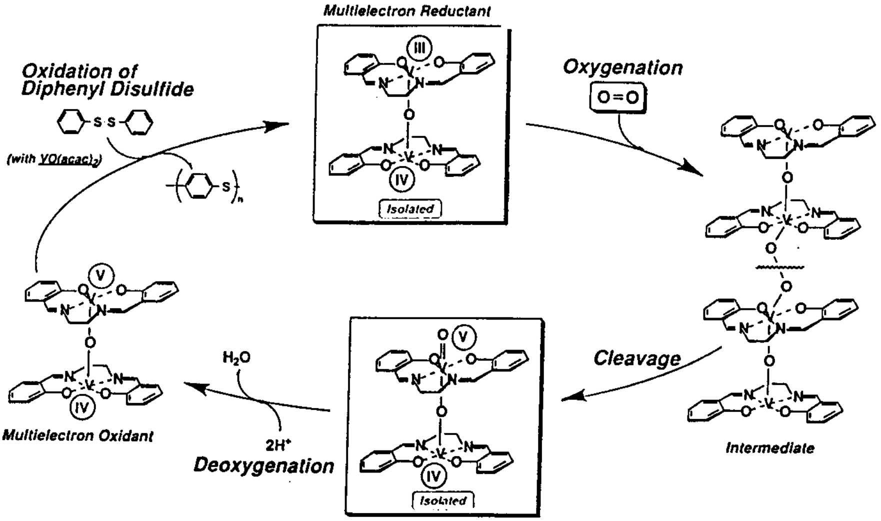
(2) Redox cycle and catalytic mechanism

Diphenyl disulfide is not oxidized directly with only dioxygen because of the high oxidation potential near 1.5 V. In contrast, the multi-electron transfer between the disulfide and dioxygen proceeds efficiently mediated by the multinuclear vanadium complexes (Ref. 12). The redox cycle of the dinuclear vanadyl complex functions to bridge the efficient 2-electron transfer from disulfide to dioxygen. The dinuclear vanadium complex performs as an excellent catalyst for the 4-electron reduction of dioxygen to water. This is an important example in that the complex for the multi-electron transfer process led to a new molecular conversion.

The overall mechanism of the one-step multi-electron transfer is summarized in scheme 1. In this redox cycle, characteristic disproportionation accompanied by the small structural change in the coordination arrangement of the μ-oxo bridged vanadyl complex array was observed. These dynamic change plays an essential role for the efficient electron transfer reactions. This behavior was confirmed by the electrochemical measurements, spectra and X-ray structure determination of the intermediates involved in the mechanism.

(3) Multi-electron transfer process

Single crystal of the oxo-complex as fine black prism can be isolated, and the crystal structure of the complex was solved successfully (Ref. 13). ORTEP drawing of the oxo-complex



Scheme 1 Mechanism of multi-electron transfer reactions of vanadium complex

revealed the molecular structure containing $[V^{IV}OV^{V}{=}O]^{+}$ cation. The vanadium(V) atom is in C_{4v} coordination symmetry.

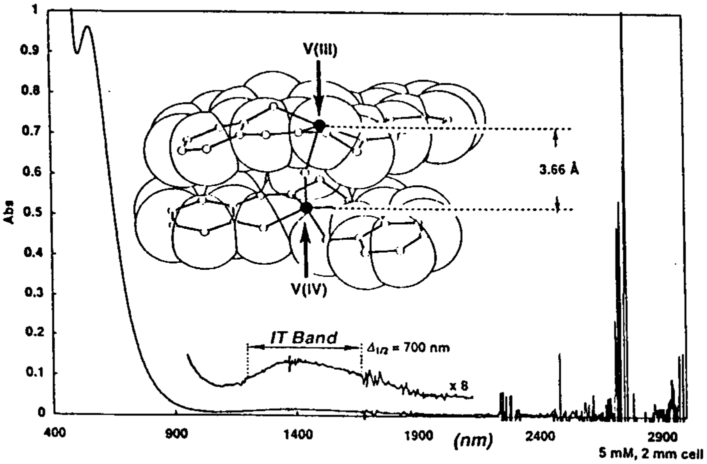


Figure 3 Crystal structure and IT band of the vanadium(III, IV) dinuclear complex.

As to the low-valent vanadium(III, IV) complex, remarkable peak at 1400 nm is observed as an intervalence transfer band in the near-infrared spectra. From the crystal structure, the vanadium-to-vanadium distance is determined to be 3.66 Å. The delocalization parameters of the mixed valence state can be calculated to be 7%. Thus the trivalent state provides an efficient dioxygen coordination site which is in pseudo octahedral coordination arrangement. This is the first example of the regulation of redox reactions by the control of geometrical arrangement of the coordination atoms in the dinuclear complex: $C_{4v} \leftrightarrow O_h$ structural change in coordination symmetry around vanadium is synchronized by the ligation of oxo (O^{2-}) group, which enables the multi-electron transfer process (Ref. 14).

CONCLUSION

In nature, there are a lot of biological reactions which are performed by macromolecule-metal complexes. The polymer matrices, normally polypeptide, affect directly or indirectly to the electronic process of the metal complex moiety, affording extremely efficient reactions. Recent developments of high-resolution spectroscopic techniques are really helpful for determination and understanding the dynamic electronic process on the complex site. Of course, such marvelous reactions observed in metallo-enzymes and metallo-proteins have been established through molecular revolution for long time. However, if one can realize the reactions by using synthetic macromolecules, the strategy of design of the chemical reactions will become widely expanded. This is one of the most significant challenge in the current macromolecular science.

MMC-8 Tokyo will be held in 1999. After two years, many new comers from Asian area will also participate the symposium. The scientific program will be include several basic and applied topics in the field of advanced macromolecule-metal complex. The organizing committee would like to provide forum for the discussions about most recent development of the macromolecule-metal complexes for advanced technologies.

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