

# 論文内容の要旨

論文題目

TEMPO-bound Metalladithiolenes:  
SOMO-HOMO Converted Unique Electronic Structure  
and Their Physical and Chemical Properties.

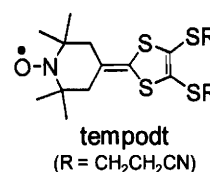
( TEMPO ラジカル—ジチオレン金属錯体 :  
SOMO-HOMO 逆転電子状態の発現と物性及び反応 )

草本 哲郎

## Introduction (Chapter 1)

In recent decades, plenty of functional molecules or molecule-based materials have been developed extensively to realize nano-scale functional devices. Metalladithiolenes are focused on as a promising candidate of such materials due to their interesting physical properties such as electrical (super-)conductivity, magnetism, optical properties, as well as characteristic chemical reactivity such as the binding-release of the ethylene molecule. Since these properties are based on their electronic structures (multi-step redox behavior, delocalized MOs onto  $\pi$ -conjugated skeleton), it is quite important to design and/or control their electronic structures to develop desired properties. On the other hand, TEMPO (= 2,2,6,6-tetramethylpiperidine-1-oxy radical), which is a well known organic radical having  $s = 1/2$  spin on the N-O bond, shows several functions (magnetism, redox property, chemical reactivity) attributable to the unpaired electron. I focused on the fusion of these two molecular systems, metalladithiolenes and TEMPO, to develop a unique electronic structure with the potential for novel physical or chemical properties.

According to this scenario, I designed a new ligand, tempodt. Tempodt is composed of two units, TEMPO moiety and  $\pi$ -conjugated dithiolene moiety with an ability of coordinating to metal ion through sulfur atoms. I developed tempodt-based metal complexes to achieve peculiar electronic structures and novel chemical reactions.



## TEMPO-bound dithiolate ligand, tempodt (Chapter 2)

Tempodt was prepared by phosphonate-mediated coupling reaction. An ESR spectrum of tempodt in  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10^{-4}$  M, r.t.) showed a triplet signal with  $g = 2.007$  and  $A_N = 1.52$  mT, suggesting the existence of an N-O radical (Figure 1). A calculated electronic structure based on DFT method is shown in Figure 2. The SOMO is essentially located at the N-O site in the TEMPO moiety with a minor extension to the dithiolene moiety, and NHOMO is delocalized onto the  $\pi$ -conjugated dithiolene moiety.

These interpretations are in accord with experimental results such as cyclic voltammogram (CV) and UV-Vis spectrum.

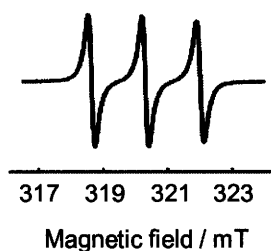
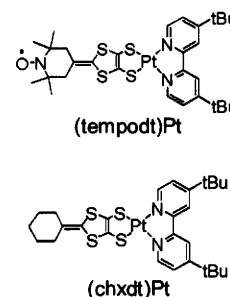


Figure 1. ESR spectrum of tempodt.

## Realization of a unique electronic structure through SOMO-HOMO level conversion based on (tempodt)Pt (Chapter 3)

I then prepared a tempodt-ligated Pt complex, (tempodt)Pt, to investigate a electronic structure of tempodt-based complex having electron-donating ability. It is known that (diimine)(dithiolato)Pt complex has high donating ability, and that the electronic structure around the HOMO and LUMO has been well characterized and simply predicted from CV and UV-Vis spectra. (chxdt)Pt was also prepared as a reference to compare the physical properties.



The UV-Vis spectra of two Pt complexes were almost identical. The CVs of two Pt complexes showed similar oxidation peak potential  $E_{\text{pox}}$  (vs ferrocenium/ferrocene,  $-0.26$  V and  $-0.24$  V for (tempodt)Pt and (chxdt)Pt) attributed to the HOMO level, and reduction potential  $E_{\text{red}}$  ( $-1.80$  V and  $-1.79$  V for (tempodt)Pt and (chxdt)Pt), which is ascribed to the LUMO level. These experimental results suggest the high degree of similarity of the electronic structure around the HOMO and LUMO between the two Pt complexes.

This consideration was reproduced in terms of DFT calculations. In (chxdt)Pt, the HOMO is mainly delocalized on the  $\pi$ -conjugated dithiolene moiety. (tempodt)Pt also has HOMO and LUMO levels similar to those of (chxdt)Pt, while the SOMO is centered on the TEMPO moiety, and the energy level is lower than that of the HOMO (Figure 2).

These electronic structures were confirmed by the  $1e^-$  chemical oxidation reaction of the complexes monitored by UV-Vis spectroscopy (Figure 3). (chxdt)Pt showed new peaks at 820 and 940 nm at the first stage of the oxidation,

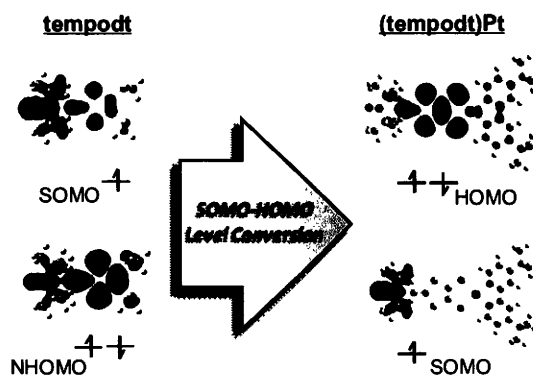


Figure 2. Schematic representation of SOMO-HOMO level conversion with calculated electronic structures of tempodt (uB3LYP/6-31(d)) and (tempodt)Pt (uMPW1PW91/LANL2DZ for Pt, 6-31G(d) for other atoms).

corresponding to the removal of an electron from the HOMO ( $\pi$ -conjugated dithiolate-based orbital). Analogous UV-Vis spectroscopic behavior was observed in the course of the oxidation of (tempodt)Pt, when new peaks at 820 and 940 nm appeared during the first stage of oxidation. This result strongly suggests that the oxidation removed an electron from the HOMO, but not from the SOMO. These UV-Vis results provide a further evidence for the unique electronic structure for (tempodt)Pt shown in Figure 2.

I achieved a drastic electronic structure conversion, namely the SOMO–HOMO level conversion, triggered by the metal coordination. This is the first example in dithiolate complexes to achieve this type of energy level conversion, and as such is an unusual electronic structure.

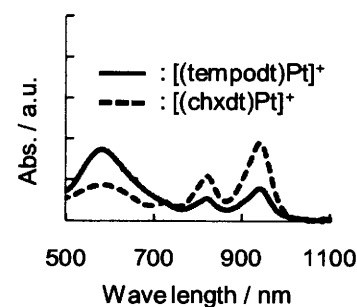
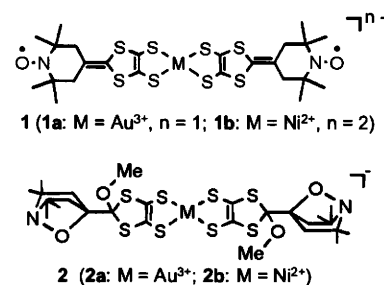


Figure 3. UV-Vis spectra at the first stage of oxidation. Plain line: (tempodt)Pt, dotted line: (chxdt)Pt.

### Novel intramolecular cyclization of TEMPO induced by SOMO-HOMO converted electronic structure for $M(\text{tempodt})_2^{n-}$ ( $M = \text{Au}^{3+}$ , $n = 1$ ; $M = \text{Ni}^{2+}$ , $n = 2$ ) (Chapter 4)

I next focused on the application of above unique electronic structure to develop a new *chemical* phenomena, employing planar metalladithiolenes,  $M(\text{dithiolene})_2^{n-}$  ( $M = \text{Au}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $n = 0, -1, -2$ ). These complexes are known to have characteristic electronic structures in which their HOMOs (SOMOs) delocalized over  $\pi$ -conjugated dithiolene ligands, and that they are easily oxidized to produce ligand-based  $\pi$ -radical species. From this perspective, I



prepared novel planar metalladithiolenes  $M(\text{tempodt})_2^{n-}$  **1** (**1a**:  $M = \text{Au}^{3+}$ ,  $n = 1$ ; **1b**:  $M = \text{Ni}^{2+}$ ,  $n = 2$ ). These complexes showed intramolecular cyclization on TEMPO moiety triggered by the oxidation (generation of  $\pi$ -radical on the HOMO), affording **2a** ( $M = \text{Au}^{3+}$ ) and **2b** ( $M = \text{Ni}^{2+}$ ) respectively.

The two complexes **2a** and **2b** had similar molecular structure, which were revealed by single crystal X-ray diffraction study (Figure 4). In contrast to the similarity of their molecular structures, the spin states were quite different between **2a** and **2b**. **2b** had an unpaired electron delocalized onto  $\pi$ -conjugated dithiolene skeleton, which was evidenced by EPR, whereas **2a** was in a diamagnetic singlet state.

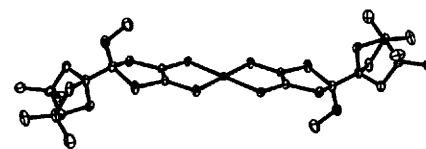


Figure 4. Molecular structure of **2a**.

The proposed formation mechanism of **2** is shown in Figure 5. **1** is oxidized to produce  $\pi$ -radical on the HOMO. The resulting species can be described by several resonance structures, and the structure shown in Figure 5 is the most stable one among all possibilities, due to the quasi-aromatization of the dithiolene rings. Consequently,

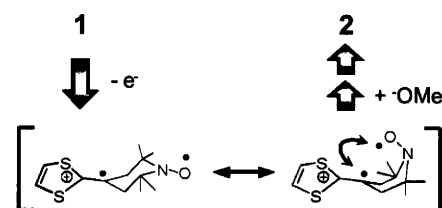


Figure 5. Proposed mechanism for the formation of **2**.

the generated  $\pi$ -radical reacted with the TEMPO radical, resulting in a cyclized structure via C-O bond formation. This is the first example of TEMPO radicals that achieved this type of cyclization through C-O bond formation. This novel reaction is attributable to the SOMO-HOMO converted electronic structure of **1**, in which the electron is removed from HOMO ( $\pi$ -conjugated skeleton), not from SOMO (TEMPO moiety), and to the flexibility of the TEMPO, which realizes the near location between the two  $\pi$ -radicals (reaction centers).

### **Conclusion (Chapter 5)**

I developed tempodt-based complexes exhibiting unique electronic structure through SOMO-HOMO level conversion, in which the energy level of TEMPO-based orbital (SOMO) is lower than  $\pi$ -conjugated dithiolene-based one (HOMO). A novel chemical phenomenon, an intramolecular cyclization reaction of TEMPO, was achieved based on this electronic structure. This study elucidates the controllability of the molecular orbitals for the metalladithiolenes, and provides a new concept to develop novel chemical/physical properties.