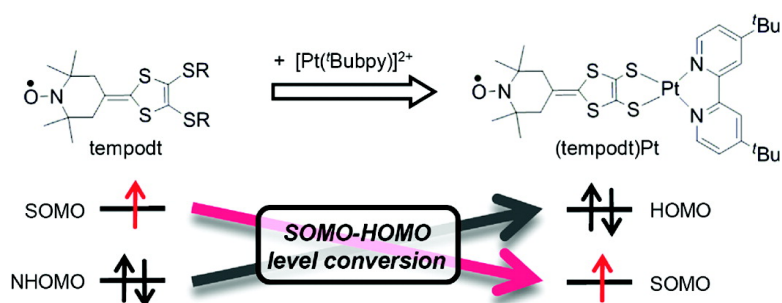


Realization of SOMO#HOMO Level Conversion for a TEMPO-Dithiolate Ligand by Coordination to Platinum(II)

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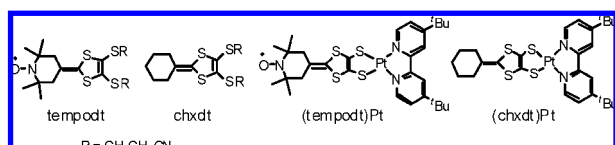
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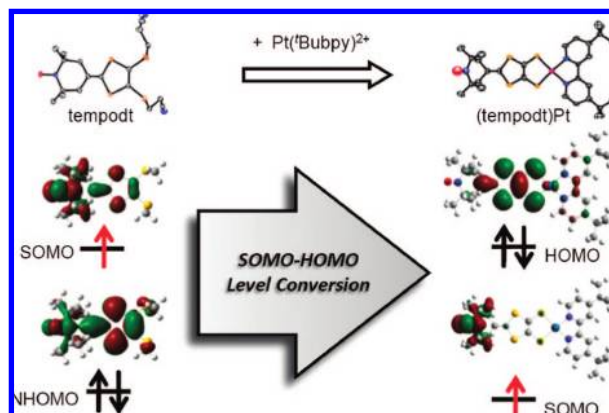
Metalladithiolenes have been extensively studied in recent decades as candidates for molecule-based functional materials. A series of $M(\text{dmit})_2$ compounds ($M = \text{Ni}, \text{Pd}, \text{Pt}$ etc., $\text{dmit} = 2$ -thioxo-1,3-dithiole-4,5-dithiolate) with π -radical electrons bear electrical conductivity, superconductivity, and magnetism,¹ and a series of $\text{Pt}(\text{diimine})(\text{dithiolate})$ complexes show interesting optical properties, including luminescence and nonlinear optics.² In these systems, the characteristic electronic structure of the complexes plays a crucial role in their functionalities. TEMPO (= 2,2,6,6-tetramethylpiperidine-1-oxo radical) shows interesting properties attributable to the unpaired electron, and has been employed in preparing functional materials.³ In the present study, we focused on the fusion of these two molecular systems to realize a unique electronic structure with the potential for stimuli-responsive molecule-based conducting and/or magnetic materials. From this viewpoint, we developed a TEMPO-bound dithiolate ligand (= tempodt) and its Pt complex, (tempodt)Pt. The physical properties and electronic structures of tempodt, (tempodt)Pt, and a one-electron ($1e^-$) oxidized (tempodt)Pt were investigated by comparison with those of TEMPO and related compounds (= chxdt, and (chxdt)Pt), in which a cyclohexane skeleton is attached instead of the TEMPO moiety (Chart 1). We achieved a unique electronic structure for (tempodt)Pt (Scheme 1)⁴ and an intriguing electronic structure change (= SOMO–HOMO conversion) triggered by the coordination of tempodt to $\text{Pt}(\text{Bubpy})^{2+}$.

Chart 1



The ligands tempodt and chxdt were newly synthesized (for details, see Supporting Information). X-ray structure analysis of tempodt (Scheme 1) revealed that the N–O bond length in the TEMPO moiety was 1.293(2) Å, similar to that in other TEMPO derivatives.⁵ An ESR spectrum of tempodt in CH_2Cl_2 (2×10^{-4} M, room temp) showed a triplet signal with $g = 2.007$ and $A_N = 1.52$ mT, suggesting the existence of an N–O radical. Cyclic voltammetry (CV) of tempodt, chxdt, and TEMPO showed that the first oxidation peak potential E_P^{ox} of chxdt and TEMPO were nearly identical, while E_P^{ox} for tempodt was more negative (Supporting Information, Figure S1, Table S1). This finding indicates that the HOMO level of chxdt and the SOMO level of TEMPO are similar, although that of tempodt is higher, probably due to interaction between the TEMPO moiety and the π -conjugated dithiolene moiety (Figure S2c). These experimental results, including UV–vis spectra, were well reproduced by DFT and TD–DFT calculations (Figure S2 and Table S2).⁶ From these results, the

Scheme 1



electronic structure around the HOMO of tempodt is expected to be as shown in Scheme 1, in which the SOMO of tempodt is essentially located at the N–O site in the TEMPO moiety, with a minor extension to the dithiolene moiety.

We then prepared the tempodt-ligated Pt complex using the $\text{Pt}(\text{diimine})(\text{dithiolate})$ skeleton (see Supporting Information). This skeleton is useful in the present research because it is known that the electronic structure around the HOMO and LUMO has been well characterized and simply predicted from CV and UV–vis spectra.²

The molecular structure of (tempodt)Pt was determined by single crystal XRD analysis, as shown in Scheme 1. An ESR spectrum of (tempodt)Pt in CH_2Cl_2 (2×10^{-4} M, room temp) showed a triplet signal with $g = 2.007$ and $A_N = 1.54$ mT, supporting the existence of an N–O radical. UV–vis spectra of both (tempodt)Pt and (chxdt)Pt (Figure 1a,b) showed a broad peak around 650 nm. These peaks shifted to higher energy as the solvent polarity increased,

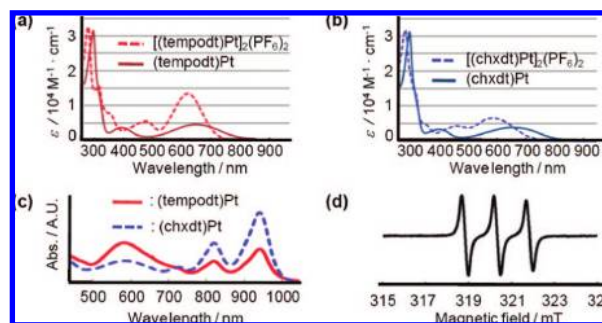


Figure 1. UV–vis spectra of (a) (tempodt)Pt and $[(\text{tempodt})\text{Pt}]_2(\text{PF}_6)_2$, and (b) (chxdt)Pt and $[(\text{chxdt})\text{Pt}]_2(\text{PF}_6)_2$. (c) Observed spectra at the first stage of oxidation: red, (tempodt)Pt; blue, (chxdt)Pt. (d) ESR spectrum of $[(\text{tempodt})\text{Pt}]_2(\text{PF}_6)_2$. All measurements were carried out in CH_2Cl_2 .

indicating that their ground states were more polarized than the excited states. This behavior is characteristic of Pt(diimine)(dithiolate) complexes,² and the peak can be assigned to the intramolecular charge transfer band from a π -conjugated dithiolate-based orbital (= HOMO) to one that is bipyridine-based (= LUMO). The similar UV–vis spectra of the two Pt complexes suggest that their electronic structures (around the HOMO and LUMO) are almost identical. CV was carried out to examine relative HOMO and LUMO levels between the two Pt complexes (Figure S3). The first reduction potentials, E^{red} , of (tempodt)Pt and (chxdt)Pt were -1.80 and -1.79 V (vs Fc/Fc⁺), respectively; this process is ascribed to the bpy moiety (= LUMO). The E_{p}^{ox} values attributed to the HOMO level appeared at -0.24 and -0.26 V for (chxdt)Pt and (tempodt)Pt, respectively. The near-identical E_{p}^{ox} and E^{red} values for the two Pt complexes suggest their almost equal LUMO and HOMO levels (Table S1). The high degree of similarity of the electronic structure around the HOMO and LUMO between the two Pt complexes suggested by the UV–vis and CV results was interpreted in terms of DFT and TD-DFT calculations (Figure S4, and Table S2).⁶ In the case of (chxdt)Pt, the HOMO is widely delocalized on the π -conjugated dithiolate moiety and partially on Pt, while the LUMO is located on the bpy moiety and partially on Pt. This is a typical electronic structure for Pt(diimine)(dithiolate) species.² The compound (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 (Scheme 1 and Figure S4). This peculiar electronic structure is recognized as follows. The π -conjugated dithiolene moiety of tempodt constructs the Pt(diimine)(dithiolate) skeleton by coordination to Pt('Bubpy)²⁺, and forms an extended π -conjugated orbital (= HOMO of (tempodt)Pt). The antibonding interaction between NHOMO of tempodt and HOMO of Pt('Bubpy)²⁺ raises the HOMO of the resulted (tempodt)Pt higher than its SOMO. The large on-site coulomb repulsion on the SOMO and weakness of the interaction between the TEMPO and π -conjugated dithiolate moieties are considered the crucial factors in realizing this electronic structure. As a result, we achieved a drastic electronic structure conversion, namely the SOMO–HOMO level conversion, triggered by the metal coordination. To the best of our knowledge, this is the first example in dithiolate complexes to achieve this type of energy level conversion, and as such is an unusual electronic structure,⁴ which is a possible candidate for stimuli-responsive molecule-based materials such as conducting molecular crystals with gigantic magnetoresistance (GMR), TFT devices with multistimuli responsibility, and so on.

We next focused on the 1e⁻ oxidation of two Pt complexes to further confirm the unique electronic structure of (tempodt)Pt. If the electronic structure of (tempodt)Pt shown in Scheme 1 was to be correct, an electron would be removed from the HOMO under 1e⁻ oxidation. In such a case, the electronic spectrum of the resulting species, (tempodt)Pt⁺, would be similar to that of (chxdt)Pt⁺, which may be obtained by 1e⁻ oxidization of (chxdt)Pt.

The 1e⁻ chemical oxidation reaction of (chxdt)Pt monitored by UV–vis showed new peaks at 820 and 940 nm at the first stage (Figure 1c), corresponding to the removal of an electron from the HOMO (π -conjugated dithiolate-based orbital), while the peaks showed a decrease and a new peak at 580 nm appeared as the reaction proceeded (Figures S5 and S6), suggesting the occurrence of the following chemical reaction. Monitoring of the reaction using ESI-TOF-MS showed a gradual increase in the [(chxdt)Pt]₂⁺ species (Figure S5), implying that the following reaction is dimer formation.

This is reasonable because Pt(diimine)(dithiolate) complexes are known to dimerize by oxidation.^{2c,d} Pap et al. recently reported details of the dimerization process for Pt(diimine)(dithiolate).^{2d} The dimeric nature of the isolated [(chxdt)Pt]₂²⁺ was further characterized by elemental analysis, MALDI- and ESI-TOF-MS (Figures S5b, S7, and S8), and other techniques. An ESR spectrum in CH₂Cl₂ (5×10^{-5} M, room temp) showed no signals, and the temperature dependence of magnetic susceptibility was explained by an $S = 1/2$ dimer model (Figure S9). These results indicate that [(chxdt)Pt]⁺ dimerizes to give [(chxdt)Pt]₂²⁺, in which the generated π -radicals are strongly coupled, resulting in a singlet ground state.

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 (Figures 1c and S15). This result strongly suggests that the oxidation removed an electron from the HOMO, but not from the SOMO. The following spectral change and the UV–vis spectrum of 1e⁻ oxidized (tempodt)Pt (Figures 1a and S6b) were also similar to those of (chxdt)Pt, indicating dimer formation. An ESR spectrum of [(tempodt)Pt]₂(PF₆)₂ shown in Figure 1d presents a triplet signal with $g = 2.007$ and $A_{\text{N}} = 1.53$ mT, with no additional peaks. This result clearly indicates that the N–O radical survives under 1e⁻ oxidation.⁷ These results from the two Pt complexes provide further evidence for the unique electronic structure of (tempodt)Pt (Scheme 1). It is noted that a spin concentration investigation of [(tempodt)Pt]₂(PF₆)₂ revealed that 11% of $S = 1/2$ spin exist per [(tempodt)Pt]⁺ unit as an N–O radical, implying the presence of intradimer antiferromagnetic interaction.

In conclusion, (tempodt)Pt achieved a unique electronic structure via a drastic electronic structure change: the SOMO–HOMO level conversion by means of complex formation.

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Supporting Information Available: Characterization data, and spectral, electrochemical, and calculated data for the present compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- This unusual electronic structure is rarely reported in some organic radicals. For example: Sakurai, H.; Izuoka, A.; Sugawara, T. *J. Am. Chem. Soc.* **2000**, *122*, 9723–9734.
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- Details are described in the Supporting Information.
- The existence of an N–O radical is also confirmed by the IR spectrum (Figure S10).

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