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Communication

Switching of the Electronic Communication between Two {Ru(trpy)(bpy)} (trpy = 2,2′:6′,2″-Terpyridine and bpy = 2,2′-Bipyridine) Centers by Protonation on the Bridging Dimercaptothiadiazolato Ligand

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A stable Ru(II)/Ru(III) mixed-valence state was observed in acetonitrile for the ruthenium binuclear complex bridged by dimercaptothiadiazolate ($\Delta E_{1/2}$ = 220 mV for Ru_2(II,II)/Ru_2(II,III) and Ru_2(II,III)/Ru_2(III,III) processes; $K_{com} = 5.3 \times 10^3$). Upon protonation of the bridging ligand by the addition of equimolar *p*-toluenesulfonic acid, however, the mixed-valence state diminished ($\Delta E_{1/2}$ = 0 mV). The bridging ligand operates as a proton-induced switch of the electronic communication in the dimeric complex.

Molecular systems that respond to external stimuli have received much attention in recent years in connection with, for example, the design of molecular switches and molecular machines.[1] Biological systems exploit a number of chemical and physical signals as stimuli and control their activities in a highly sophisticated fashion.[2] Transfer of protons, which can be regarded as one of the simplest chemical signals, is widely utilized in the biological systems.

In the artificial molecular and supramolecular systems, the protonation/deprotonation processes are utilized for the control of molecular recognition,[3] luminescent properties,[4] redox potential of metal centers,[5] and so on. Among various chemical phenomena, control of the communication between two identical redox centers separated by a bridging ligand[6] is attractive in view of their potential application as switches on molecular wires. Redox communications that have been evaluated by the extent of the separation of the redox waves[7] have not been effectively controlled by an external stimuli like protonation. As far as we know, two previous reports have been found on the control of redox communication by protonation.[8,9] Both studies utilized triazole rings as the coordination and protonation sites. Vos et al. studied the redox interaction of dinuclear ruthenium(II) complexes $[\{Ru(bpy)_2\}(BL)]^{4+}$ in acetonitrile [BL = bis(pyrazinyl)bis(triazole) and bis(pyridyl)bis(triazole)].[8] The splitting of the redox waves, Ru_2(II,II)/(II,III) and Ru_2(II,III)/(III,III), diminished by the successive two-step protonations on the uncoordinated nitrogen atoms of two triazole rings. The single protonation to the π system of the bis(triazole) ligands was not efficient enough to switch off the electronic communication in the complexes. Rocha and Toma have utilized benzotriazole as a bridging ligand.[9] They reported that $[\{Ru^{III}(edta)\}_2(\mu\text{-benzotriazolate})]^{4-}$ in aqueous solution shows stepwise reduction waves at higher pH, but with decreasing pH, the waves gradually coalesce with a negative potential shift due to the protonation of the bridging benzotriazole. However, the complete "switch-off" is not achieved even at pH 2.5 ($\Delta E_{1/2}$ = 75 mV), and the higher acidic conditions caused the decomposition of the complex.

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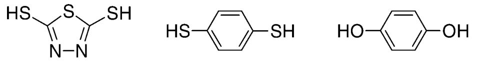
Chart 1. Isoelectronic Bridging Ligands with DMcTH$_2$



We have been interested in the 2,5-dimercapto-1,3,4-thiadiazolate ion (DMcT^{2-}),[10] which can bridge two metal complex units through two external thiolate sulfur atoms.[11] Sulfur donors are expected to have better π-mediating properties and could provide an opportunity to observe characteristic redox interactions. It may be worth pointing out that DMcTH$_2$ is an isoelectronic compound with *p*-benzenedithiol and hydroquinone (Chart 1).

The prevailing π-electron system may give additional merit to utilize DMcT^{2-} as a mediator of the electronic communication. The ligand has Lewis base centers on the thiadiazole ring, which can be utilized as the proton acceptor even in the bridging form. We have now prepared a new dimeric complex, [{Ru(trpy)(bpy)}$_2$(μ-*S,S′*-DMcT)]$^{2+}$ (bpy = 2,2′-bipyridine and trpy = 2,2′:6′,2″-terpyridine) (**1**$^{2+}$). The complex shows the two-step oxidation waves of the ruthenium moieties Ru$_2$(II,II)/(II,III)/(III,III) in acetonitrile. The two-step oxidation processes become a single one upon addition of *p*-toluenesulfonic acid (TsOH), indicating that the protonation of the ligand quenches the electronic communication between two metal centers.

Treatment of [Ru(trpy)(bpy)(H$_2$O)](PF$_6$)$_2$ with K$_2$DMcT in ethanol afforded the binuclear complex [{Ru(trpy)(bpy)}$_2$(μ-DMcT)](PF$_6$)$_2$ [**1**·(PF$_6$)$_2$] in 78% yield.[12] For the single-crystal X-ray structure analysis, we prepared **1**·(SbF$_6$)$_2$ by the crystallization of **1**$^{2+}$ in the presence of NaSbF$_6$.[13] Figure 1 shows the structure of a binuclear complex cation, **1**$^{2+}$. Two {Ru(trpy)(bpy)} units are bridged by a DMcT^{2-} ligand. The crystallographically imposed inversion center reveals the disorder of the DMcT^{2-} ligand over two positions, which disables the detailed discussion of the distances in the DMcT^{2-} ligand. The Ru−N distances are typical for Ru(II) complexes with polypyridyl ligands.[14]

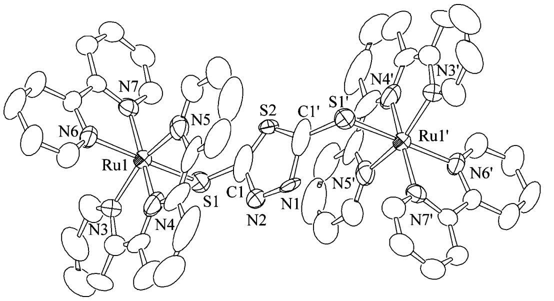


Figure 1. ORTEP plot of the structure of the complex cation **1**$^{2+}$ with 50% probability ellipsoids. Symmetry code: ′, $-x$, $-y$, $-z$.

The UV−vis absorption spectrum of **1**·(PF$_6$)$_2$ in CH$_3$CN showed an intense absorption band at ca. 300 nm and a visible one at 492 nm, being assignable to the ligand-centered $\pi-\pi^*$ and Ru−trpy(π^*) metal-to-ligand charge transfer (MLCT) transitions, respectively.[15] Upon addition of TsOH, the spectrum was changed with the isosbestic point at 384 and 489 nm (Figure S1 of the Supporting Information). The change was completed with the addition of 1 equiv of the acid. The blue shift of the MLCT absorption band to 436 nm is probably related to the decrease of the π-donor charactor of the DMcT^{2-} ligand on the protonation to the endocyclic nitrogen of the thiadiazole ring. The addition of an equimolar amount of triethylamine as a base achieved the complete recovery of the initial spectrum, manifesting the reversible protonation of the binuclear complex **1**$^{2+}$.

The complex **1**·(PF$_6$)$_2$ has one reduction at $E_{1/2} = -1.43$ V and two reversible oxidation waves at $E_{1/2} = 0.54$ and 0.76 V in CH$_3$CN (Figure S2 of the Supporting Information). By comparison with other ruthenium polypyridyl complexes, the reduction wave at −1.43 V is assigned to the reduction of the trpy ligand of two {Ru(trpy)(bpy)}$^{2+}$ units.[15] The stepwise oxidation waves are assigned to the oxidation of the two Ru(II) centers into two Ru(III) centers via mixed-valence state Ru(II)/Ru(III). The separation of 220 mV corresponds to $K_{\mathrm{com}} = 5.3 \times 10^3$. This result reveals that DMcT^{2-} mediates the redox communication of the two metal centers. Upon oxidation of **1**$^{2+}$ from the Ru$_2$(II,II) to Ru$_2$(II,III) state, the area of absorbance between 450 and 650 nm [due to Ru−trpy(π^*) MLCT] showed a blue shift, and a broad intervalence charge transfer (IVCT) transition appeared at about 1822 nm ($\epsilon = 4.0 \times 10^3$ M^{-1} cm^{-1}; Figure 2). Upon further oxidation, the IVCT band disappeared and was replaced by a band at ca. 1000 nm, which can be assigned to

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(12) A methanol solution (30 mL) of K$_2$DMcT (34.7 mg, 0.15 mmol) was added to an ethanol solution (150 mL) of [Ru(trpy)(bpy)(H$_2$O)](PF$_6$)$_2$ (240 mg, 0.30 mmol) at room temperature. The resulting dark purple solution was filtered. The filtrate was kept at room temperature in the dark to afford a black crystalline solid. The solid was collected by filtration and dried under vacuum: 168 mg, 0.117 mmol, 78%; ^{1}H NMR (solvent CD$_3$CN) δ_{H} 6.95 (2H, t), 7.10 (6H, m), 7.48 (4H, d), 7.74 (6H, m), 7.99 (4H, m), 8.32 (12H, m), 8.54 (2H, d), 10.29 (2H, d); UV−vis (CH$_3$CN) λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 492 (1.40×10^4), 313 (6.29×10^4), 293 (7.82×10^4), 282 (6.82×10^4). Anal. Calcd for C$_{52}$H$_{38}$N$_{12}$S$_3$F$_{12}$P$_2$Ru$_2$: C, 44.01; H, 2.70; N, 11.84; S, 6.78. Found: C, 43.48; H, 2.84; N, 11.82; S, 6.64.

(13) Crystal data for [**1**·(SbF$_6$)$_2$]·4CH$_3$COCH$_3$: C$_{64}$H$_{62}$N$_{12}$S$_3$F$_{12}$O$_4$Ru$_2$Sb$_2$, $M = 1833.11$, triclinic, space group $P\bar{1}$, $a = 10.423(3)$ Å, $b = 11.681(3)$ Å, $c = 15.394(4)$ Å, $\alpha = 80.14(1)°$, $\beta = 78.39(1)°$, $\gamma = 77.36(1)°$, $V = 1775.5$ (8) Å^3, $Z = 1$, $T = -120$ °C, 10610 measured reflections and 7187 independent reflections, R1 = 0.0759 and wR2 = 0.1968 for 5284 observed reflections ($I > 2\sigma(I)$) and 460 parameters. The structure was solved with a disordered model in space group $P\bar{1}$. The assumption of the space group as $P1$ did not improve the R values nor fix the disordered model.

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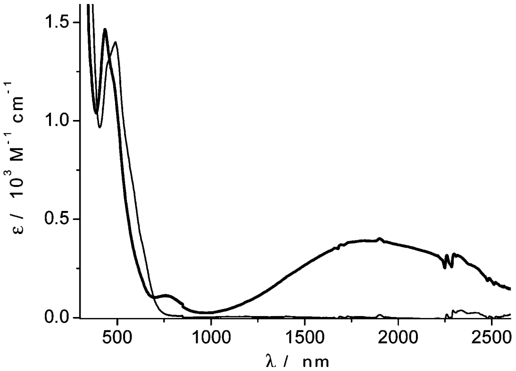


Figure 2. UV−vis−near-IR absorption spectra of a ca. 0.5 mM CH_3CN solution of **1**·$(PF_6)_2$ at rest potential (solid line) and 640 mV vs Ag/AgCl (bold line) with a 1-mm cell length.

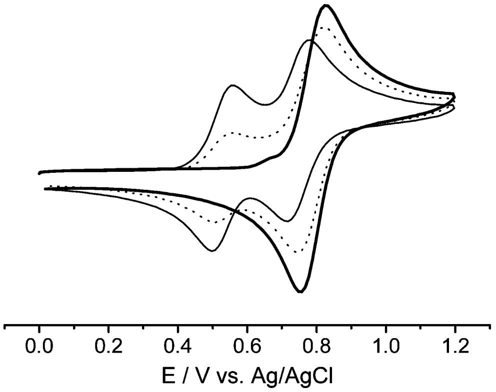


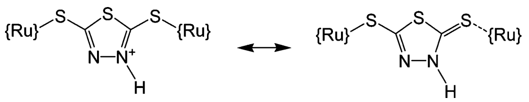
Figure 3. Changes in the cyclic voltammogram of a 0.5 mM solution of **1**·$(PF_6)_2$ upon addition of TsOH in CH_3CN. Solid line: 0.0 equiv of TsOH. Dotted line: 0.5 equiv of TsOH. Bold line: 1.0 equiv of TsOH.

the $DMcT^{2-}$−Ru(III) ligand-to-metal charge transfer band.[16] As a class II mixed-valence system, the electronic coupling element for $\mathbf{1}^{3+}$ is evaluated as 550 cm^{-1} based on the simple Hush theory[17] ($\nu_{max} = 5.5 \times 10^3$ cm^{-1}, $\Delta\nu_{1/2} = 2.2 \times 10^3$ cm^{-1}, $\epsilon = 4.0 \times 10^3$ M^{-1} cm^{-1}, and $r = 8.34$ Å).

Upon addition of TsOH to the solution, stepwise oxidation waves decreased in their current intensities and a new single oxidation wave appeared at 0.81 V (Figure 3). Upon addition of 1 equiv of TsOH, the initial oxidation waves vanished, leaving only the new wave at 0.81 V. The successive addition of triethylamine as a base recovered the initial voltammogram, indicating that the acid−base equilibrium is reversible, as was found in the change of UV−vis absorption spectra. The oxidation wave at 0.81 V should be assigned to the oxidation process of the protonated complex $[\mathbf{1}\cdot H]^{3+}$, where one of the nitrogen atoms of the heteroaromatic ring of the DMcT ligand is protonated. The peak current intensity of the newly appeared redox wave of $[\mathbf{1}\cdot H]^{3+}$ corresponds to that of the sum of two separated waves of the unprotonated complex. Thus, the oxidation of two centers takes place simultaneously, revealing that the protonation on $DMcT^{2-}$ "switched off" the redox communication.

The spectroelectrochemical studies of $\mathbf{1}^{2+}$ were also carried out upon addition of 1 equiv of TsOH. Upon oxidation, the intensity of the MLCT band decreased and the transition at about 900 nm, assignable to the charge transfer from the bridging ligand to Ru(III),[16] appeared (Figure S3 of the Supporting Information). The electronic communication between two {Ru(trpy)(bpy)} units is mediated by the conjugated π-electron system of bridging $DMcT^{2-}$. The mediation can be attributed to the interaction mainly by the hole-transfer mechanism[18] because $DMcT^{2-}$ itself is easily oxidized,[10c,d] showing that the highest occupied molecular orbital level possesses relatively high energy. The π system on $DMcT^{2-}$ is largely perturbed by thiol−thioamide tautomerization on protonation because the protonated $DMcT^{2-}$ can be written in thioamide form where the five-membered ring is not aromatic (Scheme 1).

Scheme 1



The switch of aromaticity based on the thiol−thioamide tautomerization regulates the electronic communication in **1**·$(PF_6)_2$. It may be noted that if the bridging ligand were an oxygen-coordinated one such as uracil, protonation at the ring transforms the coordination site from the enolate form into the keto form, which would weaken the M−O bond to cause the release of a metal atom from the ligand. The stability of the present complex upon protonation should be sustained by the high affinity of sulfur atoms to late-transition-metal ions even in the thioketone form.

In conclusion, we prepared a dinuclear ruthenium complex with dithiolate bridging ligand $DMcT^{2-}$, which shows the switching behavior of the redox communication by protonation of the central ring of the bridging ligand. The dinuclear complex showed stepwise oxidation of ruthenium centers, revealing the existence of the stable mixed-valence state. This is the first example of a mixed-valence dinuclear ruthenium complex bridged by a dithiolate ligand. Upon protonation at the nitrogen sites in the aromatic ring of $DMcT^{2-}$, the complex shows one-step two-electron oxidation from Ru_2(II,II) to Ru_2(III,III); thus, the single protonation on the bridging $DMcT^{2-}$ efficiently perturbs the π system to switch off the redox communication. The high affinity of the thiolate group is a key to forming a completely reversible conversion system of redox−protonation coupled reactions. The present bridging ligand forms stable M−S bonds; therefore, further utilization of the family of $DMcT^{2-}$ as bridging ligands may comprise a new chemistry of mixed-valence complexes.

Supporting Information Available: Absorption spectra of **1**·$(PF_6)_2$ upon addition of TsOH in CH_3CN, a cyclic voltammogram of **1**·$(PF_6)_2$, spectroelectrochemistry measurement of **1**·$(PF_6)_2$ upon addition of 1 equiv of TsOH, and crystallographic details in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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