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Chapter 4

COMPARISON OF Sm(III) AND Cr(VI) IONS FOR VISIBLE LIGHT INDUCED REDUCTION IN METHANOL BY HYBRID SYSTEMS OF CHIRAL SCHIFF BASE Cu(II) COMPLEXES AND TiO₂

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ABSTRACT

This paper reports on effective visible light induced reduction of Cr(VI) ion chiral Schiff base Cu(II) complex and TiO₂ in non-aqueous organic solvent (methanol) as a model system for environmental clean-up. By using several new and known chiral Schiff base Cu(II) complexes, hybrid systems of the Cu(II) complexes and anatase TiO₂ were prepared and reduction of Cr(VI) ion after visible light irradiation.

The Cu(II) complexes were synthesized in a common procedure and characterized by means of elemental analysis, IR, UV-vis, CD, and ESR spectra. Hybrid systems of the Cu(II) complex and TiO₂ were prepared as methanol suspension. After visible light irradiation, Cr(VI) ion was

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reduced successfully, which was confirmed by diphenylthiocarbazide analysis method. To our knowledge, this visible light reaction in non-aqueous organic solvents can be observed for the first time. However, reduction of Cr(VI) ion could not be observed for only a part of components selected of the hybrid systems. Although similar reaction was tested for Sm(III) ion instead of Cr(VI) ion for comparison, no change could be detected in emission as well as absorption spectra in the case of Sm(III) ion due to inappropriate redox potential.

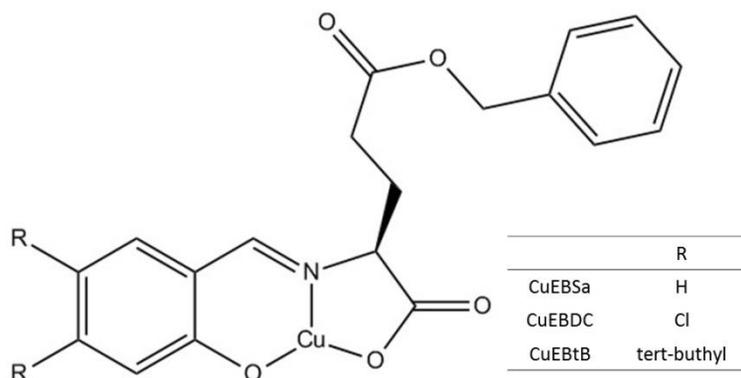
INTRODUCTION

Recently, we have reported photo-induced reduction of copper(II) complexes with TiO₂ by UV light irradiation [1-9]. Especially, some Schiff base copper(II) complexes having L-amino acid derivatives have been investigated by means of spectroelectrochemical or electrochemical measurements for photo-induced electron transfer reactions of some complexes by TiO₂ to give rise to copper(I) species after UV light irradiation. Beside them, in this course work, we have found that reaction conditions may depend on chemical structure of copper(II) complexes [1], complicate reaction mechanism was proposed based on experimental results [2], redox potential may be controlled by ligands [3-6], and azo-dyes can act as fluorescence probe for reduced copper(I) species [7-9].

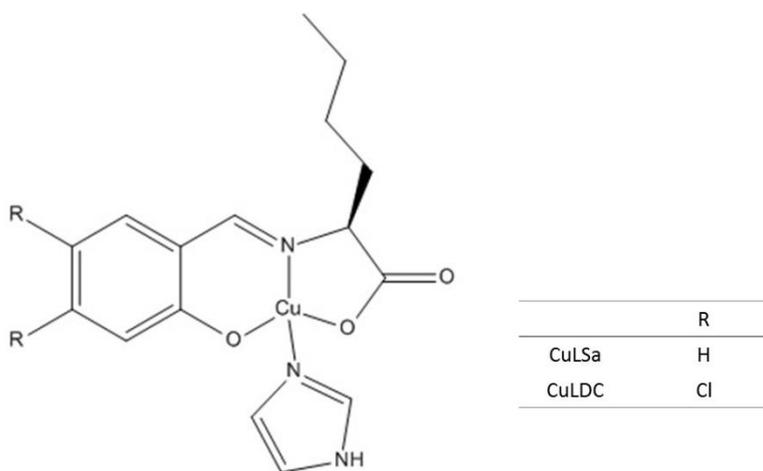
By the way, UV light-induced reduction of metal ions by TiO₂ has also been reported [10, 11]. The environmental standard and the effluent standard are established by government for Cr(VI) ion in Japan because it is poisonous due to a strong oxidizing agent. Though most of studies on reduction of Cr(VI) ion are carried out in aqueous solutions, few studies in organic solvents have been reported to date. It should be noted that Sm(III) ion is also tested for comparison because reduced Sm(II) ion is known to be relatively stable among lanthanide ions.

Herein, we have attempted *visible light*-induced reduction of Cr(VI) to Cr(III) in *organic solvent* (methanol) effectively by using hybrid system composed of TiO₂ and chiral Schiff base copper(II) complexes, known ones abbreviated as *CuEBSa*, *CuEBDC*, and *CuEBtB* (Scheme 1) [1] and new ones abbreviated as *CuLSa*, and *CuLDC* (Scheme 2). Interestingly, as for two components systems of TiO₂ and copper(II) complexes, the former cannot be reduced by TiO₂, while the latter can be reduced by TiO₂. Concentration of residual Cr(VI) ions is measured with a diphenylcarbazine method, which can

indicate that bottom sediment of Tama river (Tokyo, Japan) did contain Cr(VI) ions (less than 0.005 mg/L confirmed with an ICP method).



Scheme 1. Molecular structures of *CuEBSa*, *CuEBDC*, and *CuEBtB* [1].



Scheme 2. Molecular structures of *CuLSa* and *CuLDC*.

EXPERIMENTAL SECTION

Materials

All reagents and solvents were commercially available and were used as purchased without further purification. Amine ligands were prepared by

treatment of L-glutamic acid (10 mmol) and benzylalcohol (12 mmol) in 60 % H_2SO_4 at 343 K for 4h, and after vacuum concentration the product was neutralized to give rise to L-glutamic acid ester. *CuEBSa*, *CuEBDC*, and *CuEBtB* were prepared according to the literature procedure [1]. 1 mM Cr(VI) aqueous solution was prepared from $\text{K}_2\text{Cr}_2\text{O}_7$.

Preparations of CuLSa and CuLDC

To a methanol solution of L-leucine (2 mmol) and the corresponding salicylaldehyde (*CuLSa*) or 3,5-dichloro salicylaldehyde (CuLDC) (2 mmol) at 318 K, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (1 mmol) were added and stirred for 2 h. Then imidazol (1 mmol) was added and stirred for 1 h.

CuLSa. Yield 54.8 %. Anal. Found: C, 53.05; H, 5.08; N, 11.52 %. Calc. for $\text{C}_{16}\text{H}_{18}\text{CuN}_3\text{O}_3$: C, 52.81; H, 4.99; N, 11.55 %. IR (KBr) 1635 cm^{-1} (C=N). UV-vis (diffuse reflectance) 389 nm (π - π^*), 610 nm (d-d). CD (KBr) 347 nm, 415 nm. (absorption, methanol) 370 nm (π - π^*), 640 nm (d-d). CD (methanol) 370 nm (π - π^*). ESR(methanol, 77K) $g = 2.044$.

CuLDC. Yield 52.8 %. Anal. Found: C, 44.60; H, 3.70; N, 9.69 %. Calc. for $\text{C}_{16}\text{H}_{16}\text{CuCl}_2\text{N}_3\text{O}_3$: C, 44.41; H, 3.73; N, 9.71 %. IR (KBr) 1636 cm^{-1} (C=N). UV-vis (diffuse reflectance) 420 nm (π - π^*), 606 nm (d-d). CD (KBr) 289 nm, 416 nm. (absorption, methanol) 385 nm (π - π^*), 640 nm (d-d). CD (methanol) 390 nm (π - π^*). ESR(methanol, 77K) $g = 2.041$.

Physical Measurements

Elemental analyses (C, H, N) were carried out with a Perkin-Elmer 2400II CHNS/O analyzer at Tokyo University of Science. Infrared spectra were recorded a JASCO FT-IR 4200 spectrophotometer equipped with a polarizer in the range of $4000\text{-}400\text{ cm}^{-1}$ at 298 K.

Absorption electronic spectra were measured on a JASCO V-570 spectrophotometer in the range of 900-200 nm at 298 K. Circular dichroism (CD) spectra were measured on a JASCO J-725 spectropolarimeter in the range of 800-200 nm at 298 K. X-band ESR spectra of solutions were measured with a JEOL JES-FA200 spectrometer at 77K. Spectroelectrochemical measurements were carried out on a BAS SEC2000-UV/CVIS and ALS2323 system with Ag/AgCl electrodes in aqueous

solutions. UV and visible light source used was Hayashi LA-310UV and LA-251Xe, respectively with visible ($\lambda > 350$ nm) or UV ($\lambda < 350$ nm) cut filters.

RESULTS AND DISCUSSION

Characterization of copper(II) complexes. As mentioned in the experimental sections, the CD and UV-vis spectra in methanol solutions for *CuEBSa*, *CuEBDC*, *CuEBtB*, *CuLSa*, and *CuLSa*, have been recorded (d-d band at about 650 nm and π - π^* band at around 250-400 nm), X-band EPR spectra ($g = 2.03 - 2.05$ and their hyperfine splitting) which are normal values for the analogous (mononuclear) copper(II) complexes except for slight shift due to different ligands (in the region of about 500-800 nm).

In contrast to our related copper(II) complexes of four-coordinated ones, the results of elemental analysis for *CuEBSa*, *CuEBDC*, and *CuEBtB* in the solid states suggested to be three-coordinated ones or four-coordinated one with additional oxygen coordination by ligands of neighboring molecules. Because ESR spectra for *CuEBSa*, *CuEBDC*, and *CuEBtB* in the solutions exhibited similar features to analogous four-coordinated copper(II) complexes having solvent molecules as a ligand, *CuEBSa*, *CuEBDC*, and *CuEBtB* could be existed to be four-coordinated ones in the solutions.

Although appropriate single crystals of *CuLSa* and *CuLSa* suitable for X-ray crystallography could not be obtained unfortunately, their structures could be estimated as Scheme 2 because of their composition. Crystal structure of analogous salicylaldehyde copper(II) complexes having L-alanine instead of L-leucine moiety was determined to afford a four-coordinated [CuN₂O₂] environment (tridentate NO₂ ligand and one of the two coordination N atom is from imidazol ligand).

Therefore, identical four-coordinated [CuN₂O₂] environment was also estimated for *CuLSa* and *CuLSa* due to similar composition to the known complex.

Hybrid system of Cu(II) complex and TiO₂. Our previous studies elucidated that possibility of UV light-induced reduction of Cu(II) complex to Cu(I) complex by TiO₂ depends on chemical structures of copper(II) complexes.

Some copper(II) complexes such as *CuEBSa*, *CuEBDC*, and *CuEBtB* could not exhibit the photo-reduction reaction. On the other hand, *CuLSa* and *CuLSa* could exhibit the photo-reduction like many other analogous copper(II)

complexes. It should be noted that copper(II) complexes incorporating imidazol ligands result in other reaction mechanism against copper(II) complexes having solvent ligands. Reduction to Cu(I) ion to form three-coordinated complex accompanying with elimination of an imidazol ligand.

Although oxidation to Cu(II) ion is reversible, coordination of an imidazol ligand is irreversible even after recovering a four-coordinated $[\text{Cu}^{\text{II}}\text{N}_2\text{O}_2]$ environment (tridentate NO_2 ligand and one of the two coordination N atom is from *solvent* ligand).

Visible light could not excite electrons and could not employ for the photo-reduction reaction mentioned above and it must be low-efficient reaction. However, besides metal ions to be reduced, mixing visible-light absorbing metal complex into the hybrid system may be useful strategy for employing visible light for the photo-reduction reaction.

Photoreduction of Cr(VI) by hybrid systems. Figures 1-5 exhibit spectral changes of of hybrid systems of copper(II) complexes (*CuEBSa*, *CuEBDC*, *CuEBtB*, *CuLSa*, and *CuLDC*, respectively), TiO_2 , and Cr(VI) after visible light irradiation for 0, 20, 40, and 60 min.

The hybrid systems were prepared by adding 1 mL of 1 mM Cr(VI) ($\text{K}_2\text{Cr}_2\text{O}_7$) aqueous solution to 25 mL of methanol solution (by mixing 1 mM methanol solution of copper(II) complexes and 0.3 mM methanol suspension of TiO_2).

Soon after preparation of the hybrid systems of three components, visible light was irradiated. For all the hybrid systems, characteristic features of UV-vis spectra associated with copper(II) complexes were maintained, which indicated copper(II) complexes did not decompose even after light irradiation and were stable against except for photo-induced reaction (in other words merely mixing solutions).

After reaction for 0, 20, 40, and min, concentration of Cr(VI) ion was measured with a diphenylcarbazide method using UV-vis spectra. Although all five hybrid systems could be observed decreasing concentration of Cr(VI) ion after the photo-induced reactions, the system containing *CuLDC* exhibited the smallest decreasing reaction of Cr(VI) ions among them. In order to qualitative comparison of the degree of Cr(VI) concentration (namely residual Cr(VI) concentration), equation (1) is employed:

$$\Delta\alpha \text{ rate} = (\text{Abs}(540 \text{ nm}) - \text{BG}) / (\text{Abs}(540 \text{ nm at } 0 \text{ min}) - \text{BG}) \quad (1)$$

where BG means background values.

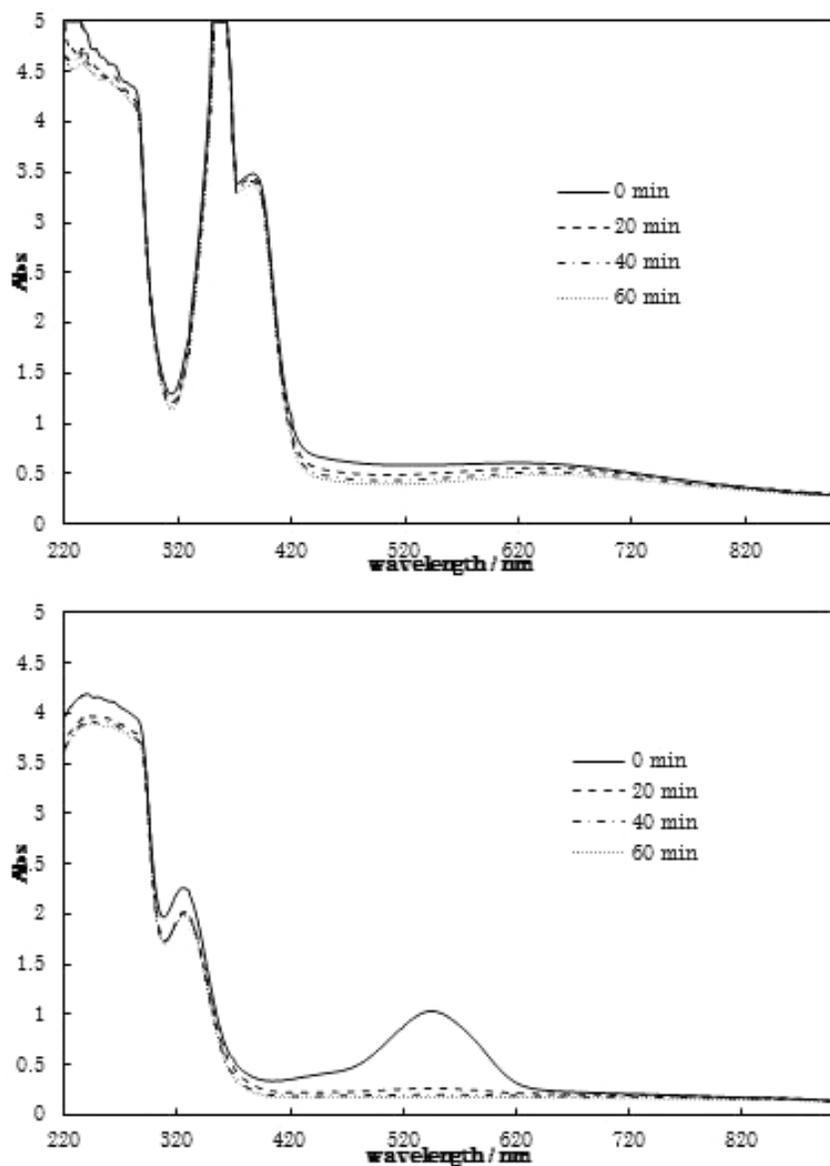


Figure 1. [Up] Changes of UV-vis spectra of a hybrid system of *CuEBSa*, TiO_2 , and Cr(VI) after reaction by irradiation of visible light for 0, 20, 40, and 60 min. [Down] UV-vis spectra with a diphenylcarbazide method.

Table 1 summarized the $\Delta\alpha$ rate values. The hybrid systems containing *CuEBSa*, *CuEBDC*, and *CuEBtB*, which could not be reduced by TiO_2 and UV

light irradiation, can reduce Cr(VI) species up to low concentration in the smaller time than the hybrid system without copper(II) complexes (only TiO₂).

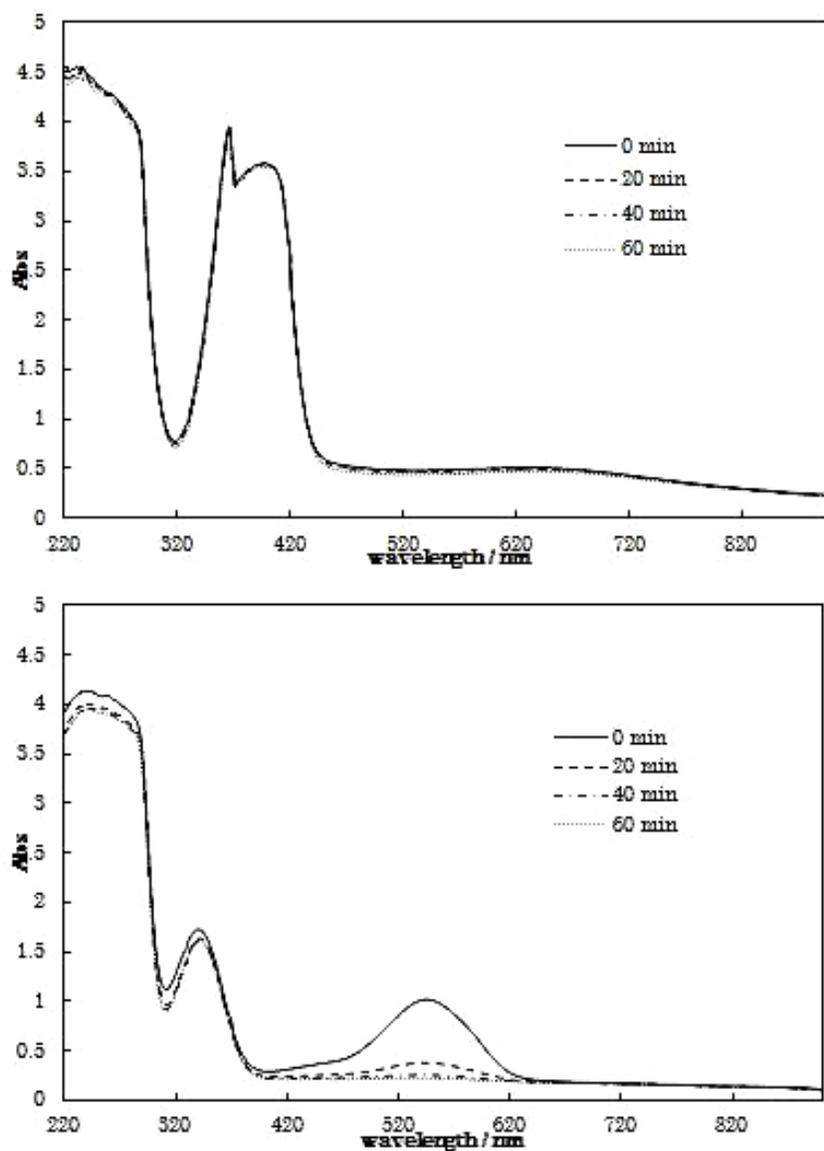


Figure 2. [Up] Changes of UV-vis spectra of a hybrid system of *CuEBDC*, TiO₂, and Cr(VI) after reaction by irradiation of visible light for 0, 20, 40, and 60 min. [Down] UV-vis spectra with a diphenylcarbazide method.

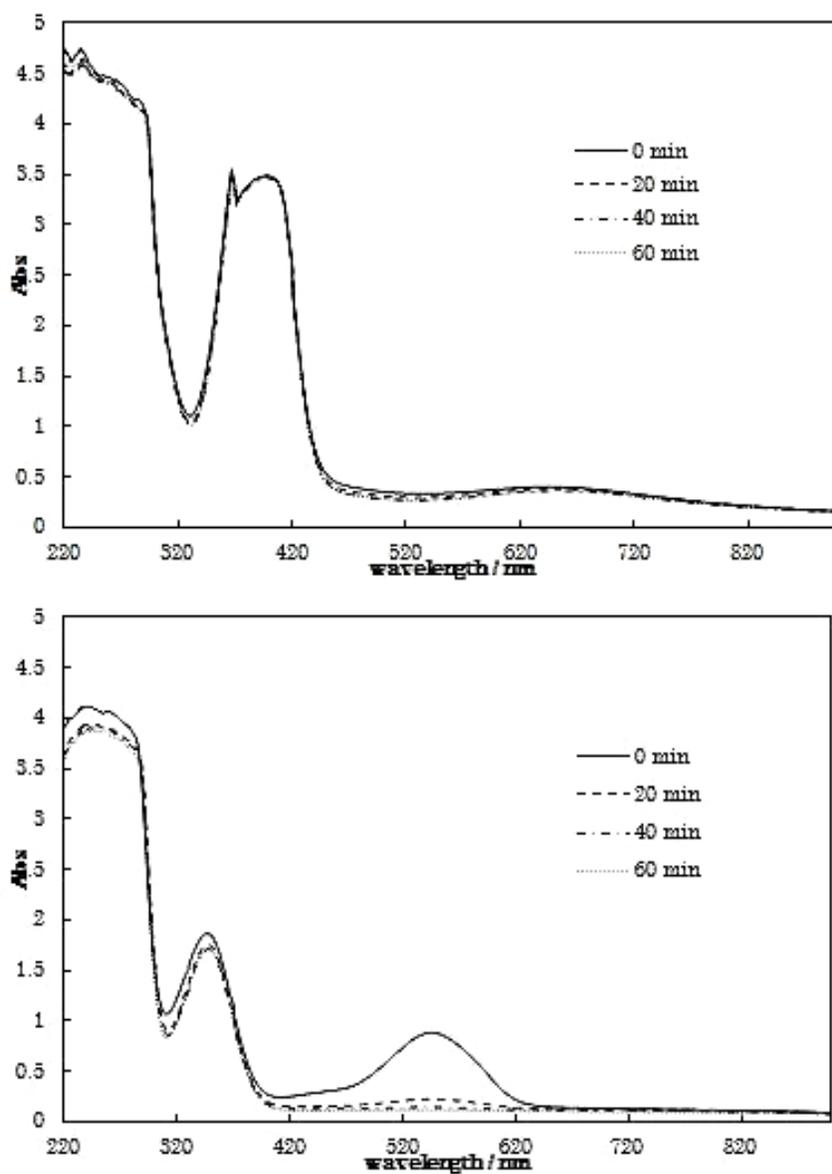


Figure 3. [Up] Changes of UV-vis spectra of a hybrid system of *CuEBtB*, TiO_2 , and Cr(VI) after reaction by irradiation of visible light for 0, 20, 40, and 60 min. [Down] UV-vis spectra with a diphenylcarbazide method.

On the other hand, *CuLSa* and *CuLDC*, which *could* be reduced by TiO_2 and *UV light* irradiation, could exhibited similar tendency to *CuEBSa*,

CuEBDC, and *CuEBtB*. However, *CuLDC* was not effective, the result of it was close to that of only TiO_2 .

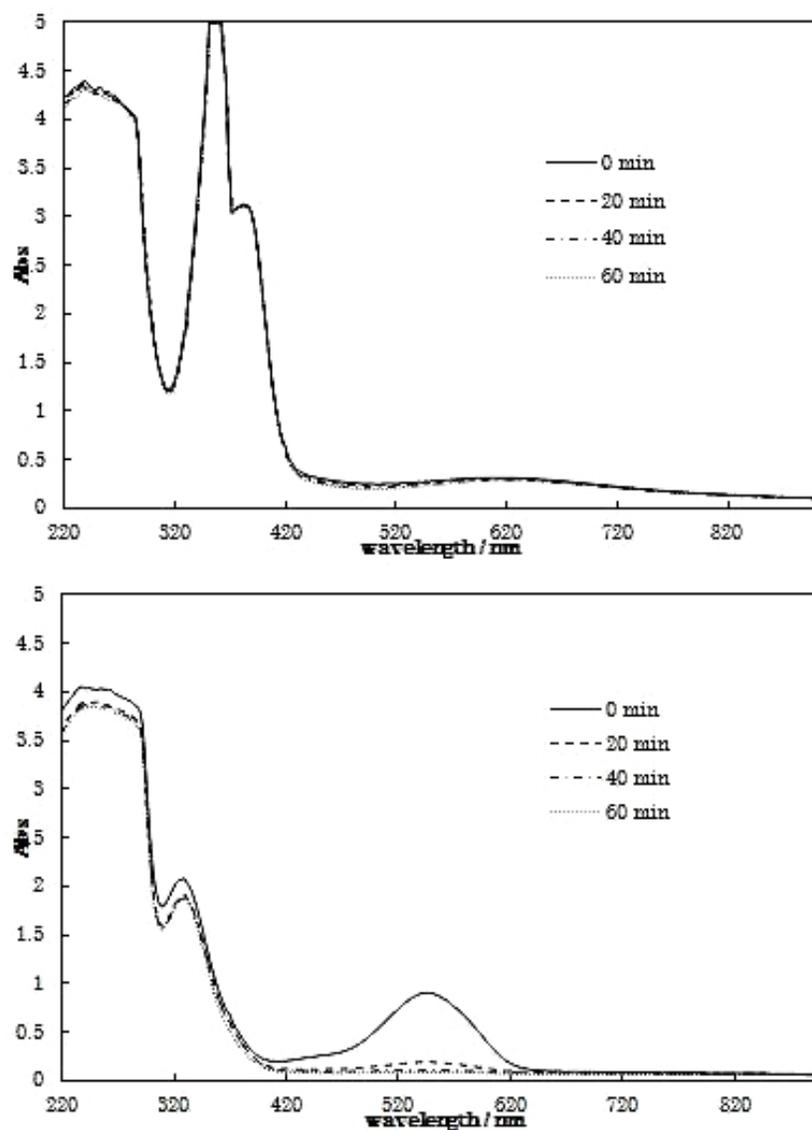


Figure 4. [Up] Changes of UV-vis spectra of a hybrid system of *CuLSa*, TiO_2 , and Cr(VI) after reaction by irradiation of visible light for 0, 20, 40, and 60 min. [Down] UV-vis spectra with a diphenylcarbazide method.

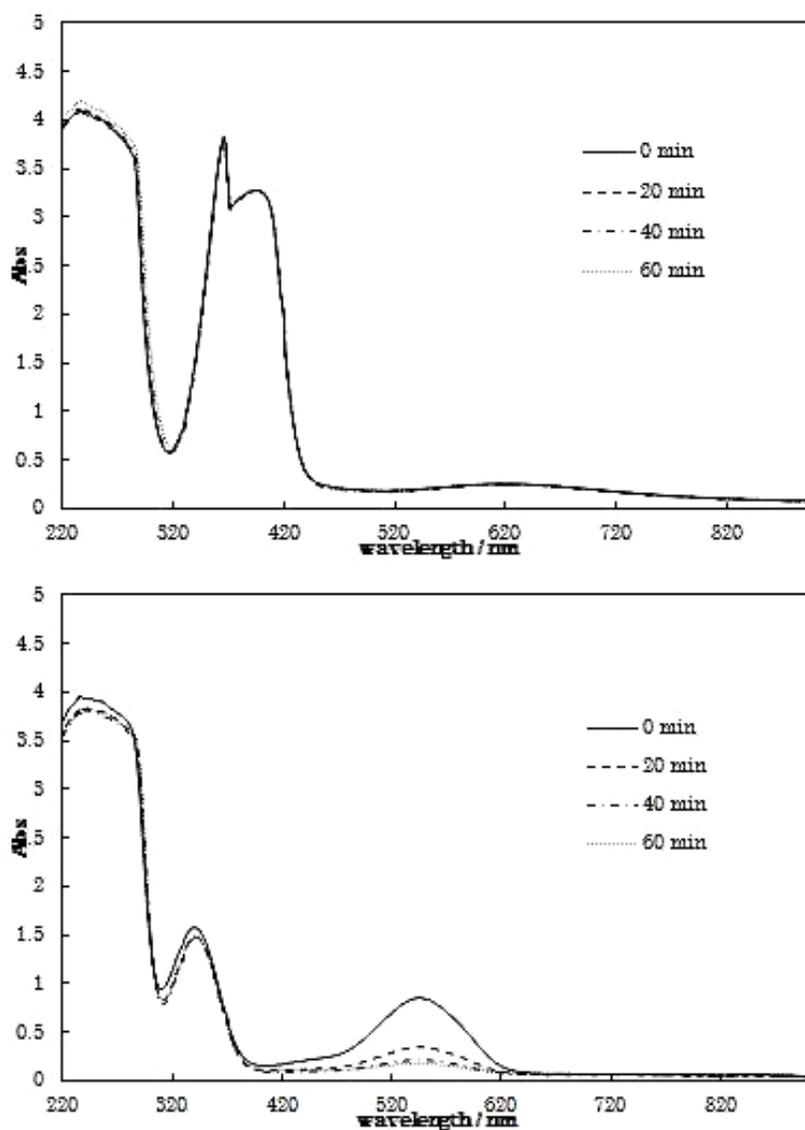


Figure 5. [Up] Changes of UV-vis spectra of a hybrid system of *CuLDC*, TiO_2 , and Cr(VI) after reaction by irradiation of visible light for 0, 20, 40, and 60 min. [Down] UV-vis spectra with a diphenylcarbazide method.

In this way, electrochemical tuning by substituent groups of aldehyde moiety significantly depends on some chemical structures of ligand, *e.g.*, L-amino acid precursors.

Table 1. Change of absorbance at 540 nm (Cr(VI) ions)

	Complexes	UV light irradiation time			
		0 min	20min	40 min	60 min
$\Delta\alpha$ rate	<i>CuEBSa</i>	1	0.109	0.037	0.010
	<i>CuEBDC</i>	1	0.210	0.057	0.021
	<i>CuEBtB</i>	1	0.155	0.052	0.019
	<i>CuLSa</i>	1	0.150	0.053	0.025
	<i>CuLDC</i>	1	0.350	0.181	0.136
	Non	1	0.370	0.230	0.184

Non means a control system without copper(II) complex.

In addition, irradiation of *UV light* instead of visible light could occur effective reduction of Cr(VI) species without copper(II) complexes (only TiO₂). Visible light could not occur photo-induced reduction of Cr(VI) species without copper(II) complexes (only TiO₂). Therefore, the following mechanism can be proposed. Since electron excitation of conductive band of TiO₂ can occur by not visible light but UV light, electron transfer from TiO₂ to Cr(VI) could not occur the system without copper(II) complexes (only TiO₂). In contrast to them, the hybrid systems added copper(II) complexes, visible light-excited electron transfer from copper(II) complexes to conductive band of TiO₂ could be suggested and further electron transfer to Cr(VI) species to be reduced as the experimental results exhibited.

Photoreduction of Sm(III) instead of Cr(VI) by hybrid systems. On the other hand, Figure 6 shows UV-vis and fluorescence spectra of a hybrid system containing Sm(III) instead of Cr(VI), *CuLSa*, and TiO₂ before and after visible light irradiation for 40 min.

The reason for selection of *CuLSa* is that it is the most effective reagent for reduction of Cr(VI) ion. Both UV-vis and fluorescence spectra did not exhibit spectral changes before and after visible light irradiation. The result suggested that Sm(III) ion could not be reduced and maintain trivalent species in the present hybrid system.

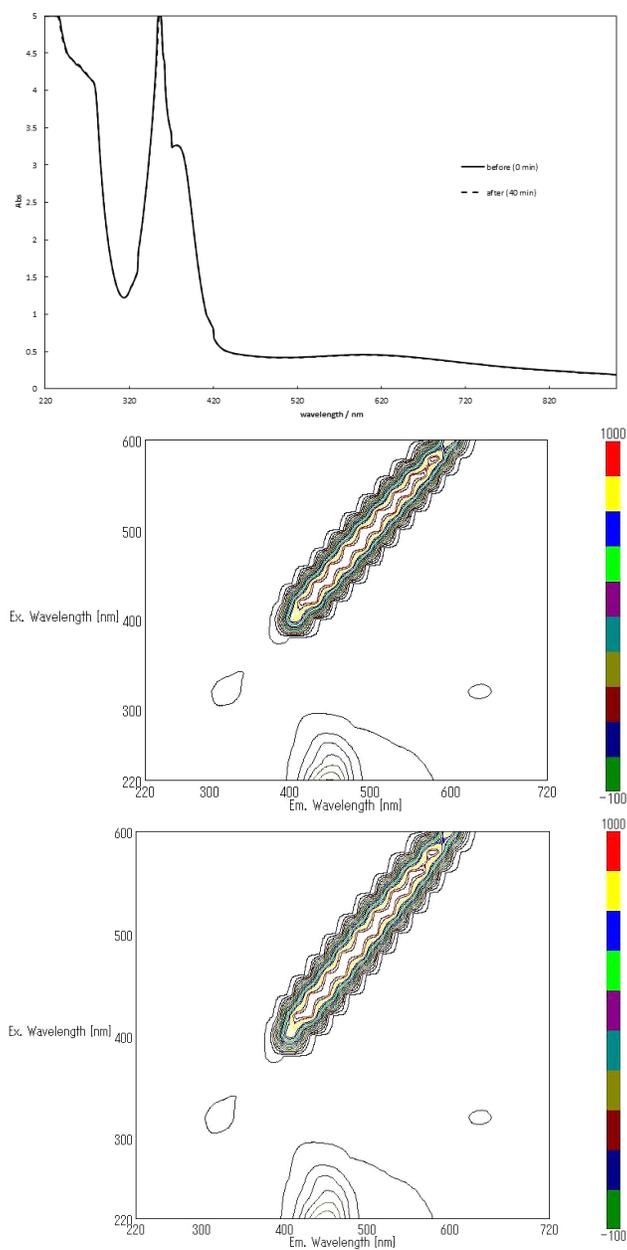


Figure 6. [Up] UV-vis and [down] fluorescence spectra of the hybrid system containing Sm(III) instead of Cr(VI) before and after visible light irradiation for 40 min.

Which attributed that Sm(III) is more difficult to be reduced than Cr(VI) and could not occur electron transfer between TiO₂ under the same experimental condition even if the most effective *CuLSa*.

Examination of working hypothesis of a concept. In the previous work [1], we have proposed “*working hypothesis of a concept*” for the course work. Model hybrid systems composed of TiO₂ microcrystals and chiral copper(II) complexes have been designed and tested for light absorbing effects from the following viewpoints. The results of the present work is added each items. Some new aspects could be found by this work.

1. Chemical reactions just after mixing to obtain hybrid systems.
No reaction without light irradiation could be observed.
2. Characteristic photo-absorption bands indicating intermolecular interactions (confirming by induced CD bands of chiral transfer or other phenomenon).
Some copper(II) complexes having well-tuned ligands can react photo-induced electron transfer even by *visible light* irradiation in the hybrid systems.
3. Chemical reactions after irradiation of UV light.
Of course UV light is more effective for photo-induced electron transfer of TiO₂ directly, visible light can also occur (probably different) chemical reaction for some copper(II) complexes.
4. Matrix environments besides solutions (dispersed into polymers or biomolecules), if it is possible.
Although environment besides solutions could not be examined even in the present work, the present work became the rare example of reduction of Cr(VI) species in organic solvents (methanol).

CONCLUSION

In summary, we have successfully reduced Cr(VI) ion to Cr(III) up to low concentration after relatively short time *visible light* irradiation by means of hybrid systems of Cr(IV) ion, TiO₂ and copper(II) complexes (*CuEBSa*, *CuEBDC*, *CuEBtB*, and *CuLSa*) in *methanol solutions* for the first time. On the other hand, Sm(III) ion could not be reduced and maintain trivalent species in the present hybrid system. Therefore, the present hybrid systems, which have reaction path including visible light excitation and electron transfer concerning

appropriate copper(II) complexes, may be effective only for specific metal ions being easy to be reduced.

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