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Carbon Monoxide Ligand-Exchange Reaction of Triruthenium Cluster Complexes Induced by Photosensitized Electron Transfer: A New Type of Photoactive CO Color Sensor

Mitsunari Itou,[†] Yasuyuki Araki,[†] Osamu Ito,*[,†] and Hiroaki Kido[‡]

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira, Sendai 980-8577, Japan, and Department of Materials Chemistry, College of Engineering, Nihon University, Tokusada, Tamura-machi, Kouriyama 963-8642, Japan

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Oxo-acetato-bridged triruthenium cluster complexes ($[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(L_1)(L_2)_2]^{+/0}$) show various color changes with variations of the total charge of the cluster complexes and terminal ligands. After photosensitized electron transfer via the triplet excited state of zinc tetraphenylporphyrin, the change of the formal oxidation state of the ruthenium ion allowed coordination with the carbon monoxide ligand accompanying the color changes.

The role of carbon monoxide gases is receiving great attention in various fields including neurotransmitters in vivo.[1] One of the important roles of CO is the intoxication caused by interruption of O_2 binding to the heme moiety with excess CO gases. Recently, many CO sensors have been developed; however, most of the CO detectors are sensitized with amperometric electrochemical methods.[2] Herein, we report a new type of CO-sensitive color sensor using oxo-acetato-bridged triruthenium cluster complexes ($[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(L_1)(L_2)_2]^{+/0}$), which show various color changes with variations of monodentate ligands (L_2) such as pyridine derivatives and weakly coordinating solvent molecules (L_1) such as CH_3CN, as shown in Figure 1a,[3] in addition to the change of the redox state, as shown in Figure 1b. An original idea in the present study is to control the redox state of triruthenium cluster complexes by photoinduced electron transfer using a photosensitizing electron donor such as zinc tetraphenylporphyrin (ZnTPP). With a change of the redox state, it would be anticipated that a CO exchange reaction with L_1 can be initiated.

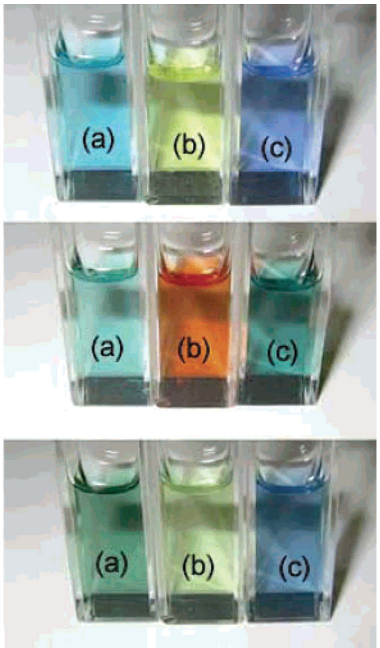

Figure 1. Color changes of ruthenium complexes (0.1 mM): (a) $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2]_6(CH_3CN)(L_2)_2]^{+}$; (b) one-electron-reduced species $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CH_3CN)(L_2)_2]^0$ with light excitation (>390 nm) of ZnTPP in the presence of BNAH in Ar-saturated CH_3CN; (c) CO-exchanged species $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CO)(L_2)_2]^0$ after light excitation in CO-saturated CH_3CN. L_2 = py (upper), cpy (middle), and dmap (lower).

By excitation of ZnTPP in the presence of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CH_3CN)(cpy)_2]^+$ (cpy = 4-cyanopyridine) and 1-benzyl-1,4-dihydronicotinamide (BNAH) in Ar-saturated CH_3CN, the absorption spectra in the visible and near-IR regions were observed, as shown in Figure 2. The bold line in Figure 2 shows the absorption spectrum of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CH_3CN)(cpy)_2]^+$; upon excitation with the Xe lamp (>390 nm), the intensities of the absorption bands at

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* To whom correspondence should be addressed. E-mail: ito@tagen.tohoku.ac.jp.

[†] Tohoku University.

[‡] Nihon University.

(1) (a) Barañano, D. E.; Ferris, C. D.; Snyder, S. H. *Trends Neurosci.* **2001**, *24*, 99−106. (b) Gilles-Gonzalez, M. A.; Gonzalez, G. *J. Inorg. Biochem.* **2005**, *99*, 1−22.

(2) (a) *Chemical and Biochemical Sensor*; Göpel, W., Jones, T. A., Kleitz, M., Lundstöm, J., Seiyama, T., Eds.; VCH: Weinheim, Germany, 1991; Part I. (b) Cao, Z.; Buttner, W. J.; Setter, J. R. *Electroanalysis* **1992**, *4*, 253−266. (c) Ihokura, K.; Watson, J. *The Stannic Oxide Gas Sensor*, 1st ed.; CRC Press: Boca Raton, FL, 1994.

(3) (a) Baumann, J. A.; Salmon, D. J.; Wilson, S. T.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3342−3350. (b) Baumann, J. A.; Wilson, S. T.; Salmon, D. J.; Hood, P. L.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2916−2920. (c) Toma, H. E.; Araki, K.; Alexiou, A. D. P.; Nikolaou, S.; Dovidauskas, S. *Coord. Chem. Rev.* **2001**, *219−221*, 187−234.

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Table 1. Spectroscopic and Kinetic Data of Triruthenium Complexes at Room Temperature

	λ_{max}/nm (log ϵ/M^{-1} cm^{-1})			k_{first}^{obs}/s^{-1}	
L	$[Ru_3(CH_3CN)(L_2)_2]^+$	$[Ru_3(CH_3CN)(L_2)_2]^0$	$[Ru_3(CO)(L_2)_2]^0$	photoinduced electron transfer[a]	CO
cpy	696 (3.64)/362 (3.80)	920 (3.96)/474 (3.94)	592 (3.69)/415 (3.20)	6.5×10^{-3}	1.5×10^{-4}
py	697 (3.65)/328 (3.76)	896 (3.90)/378 (3.92)	585 (3.60)/337 (3.73)	2.3×10^{-3}	3.4×10^{-4}
dmap	676 (5200)/429 (3.68)	890 (3.87)/326 (3.32)	583 (3.81)/403 (3.85)	1.1×10^{-3}	8.3×10^{-4}

[a] Rate constant during light illumination.

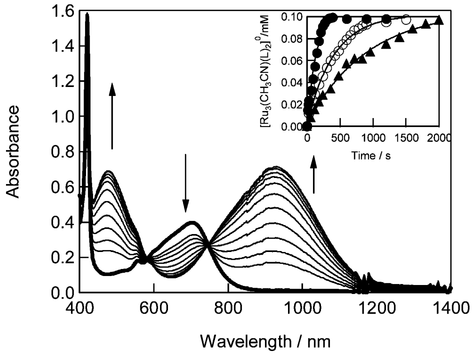
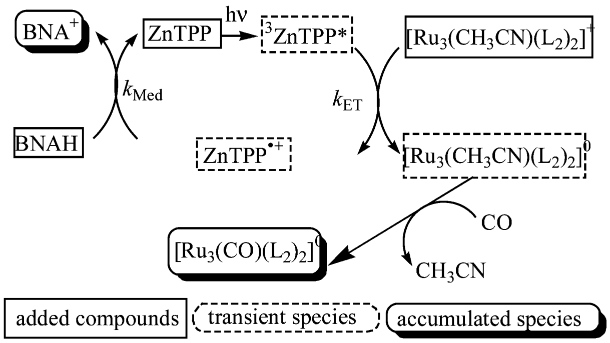


Figure 2. Absorption spectral changes under photoirradiation (>390 nm) of ZnTPP (0.002 mM) in the presence of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CH_3CN)(cpy)_2]^+$ (0.1 mM) and BNAH (0.15 mM) in Ar-saturated CH_3CN. Inset: Absorption time profiles at λ_{max} (around 900 nm) of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CH_3CN)(L_2)_2]^0$ (●, cpy; ○, py; ▲, dmap).

Scheme 1. Illustration of the Reaction Processes



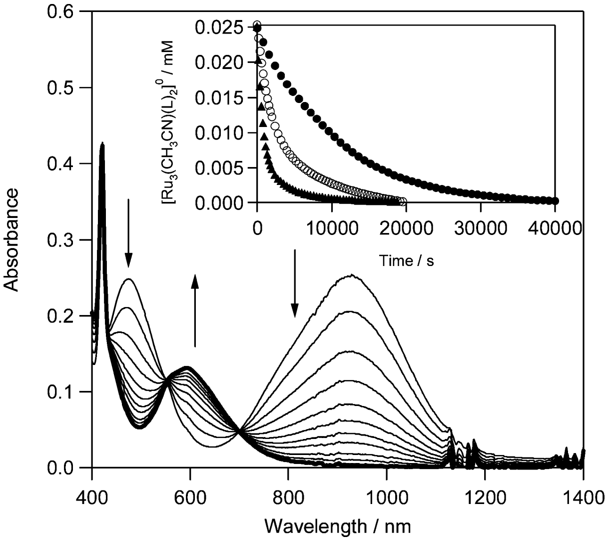


Figure 3. Absorption spectral changes observed after mixing of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CH_3CN)(cpy)_2]^0$ (0.05 mM) in Ar-saturated CH_3CN with CO-saturated CH_3CN (1:1) in the dark. Inset: Absorption time profiles at λ_{max} (around 900 nm) for $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CH_3CN)(L_2)_2]^0$ (●, cpy; ○, py; ▲, dmap).

480 and 943 nm due to $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CH_3CN)(cpy)_2]^0$ were increased with a concomitant decrease of the absorption intensity at 705 nm of $[Ru_3(\mu_3\text{-}O](\mu\text{-}CH_3CO_2)_6(CH_3CN)(cpy)_2]^+$. On the other hand, the absorption of the radical cation of ZnTPP (ZnTPP$^{•+}$), which is expected to appear at 600−650 nm,[4] was not observed in Figure 2, suggesting that ZnTPP$^{•+}$ was consumed by BNAH, yielding ZnTPP and 1-benzyl-nicotinamidinium ion (BNA$^+$), as shown in Scheme 1.[5] Then, the color of the solution changed from green (Figure 1a, middle) to orange (Figure 1b, middle). The absorption maxima inducing color changes in Figure 1 are summarized in Table 1. The time profiles (inset of Figure 2) show the increase of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CH_3CN)(L_2)_2]^0$ with consumption of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CH_3CN)(L_2)_2]^+$. When L_2 is changed from cpy to 4-(dimethylamino)pyridine (dmap), the rise rate of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CH_3CN)(L_2)_2]^0$ decreased drastically. The rise time profiles can be fitted with a single-exponential function, giving the first-order rate constant (k_{first}) as listed in Table 1. With the electron-acceptor ability of L_2 measured by pK_a,[4] the k_{first} values increase, suggesting that the electron-accepting process is the rate-determining step via the triplet state of ZnTPP (^{3}ZnTPP*).

Figure 3 shows the spectral changes when CO-saturated CH_3CN was added to the maximal concentration of the $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CH_3CN)(cpy)_2]^0$ solution generated by photoinduced electron transfer. The absorption band around 600 nm due to $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CO)(cpy)_2]^0$ was gradually increased, corresponding to the decreases of the absorptions around 480 and 920 nm of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CH_3CN)(cpy)_2]^0$. The formal oxidation state of the starting triruthenium complex is trivalent for each ruthenium ion (Ru^{III}cpy, Ru^{III}cpy, and Ru^{III}solvent), to which CO cannot coordinate, because of its strong back-donating ability. However, after the photosensitized electron-accepting process, the formal oxidation state of a one-electron-reduced complex changes to divalent (Ru^{III}cpy, Ru^{III}cpy, and Ru^{II}-solvent), in which the solvent at Ru^{II} is allowed to exchange with the CO ligand. The color change from Figure 1b to Figure 1c can be reasonably interpreted from the absorption spectral changes in Figure 3 (see also Table 1). As shown

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(4) (a) Itou, M.; Otake, M.; Araki, Y.; Ito, O.; Kido, H. *Inorg. Chem.* **2005**, *44*, 1580−1587. (b) Otake, M.; Itou, M.; Araki, Y.; Ito, O.; Kido, H. *Inorg. Chem.* **2005**, *44*, 8581−8586.

(5) (a) Mauserall, D.; Westheimer, F. H. *J. Am. Chem. Soc.* **1955**, *77*, 2261−2264. (b) Fukuzumi, S.; Koumitsu, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, *109*, 305−316. (c) Marcinek, A.; Adamus, J.; Huben, K.; Gebicki, J.; Bartczak, T. J.; Bednarek, P.; Bally, T. *J. Am. Chem. Soc.* **2000**, *122*, 437−443.

in the inset of Figure 3, the CO exchange reaction with CH_3CN is finally completed, yielding $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CO)(L_2)_2]^0$ with different rates. Interestingly, the rates of the CO replacement reaction with CH_3CN are in the order of dmap > py > cpy, whereas the electron-transfer rates show an opposite tendency (cpy > py > dmap). The rate for the photosensitized electron transfer was increased with a decrease in the electron density of the triruthenium cluster core by an electron-withdrawing cpy ligand. On the other hand, the rate of the CO replacement reaction with CH_3CN was accelerated by an electron-donating dmap ligand, as shown in Table 1, because dmap can stabilize the low oxidation state of the triruthenium cluster with its rich electron density.

These observed processes are illustrated in Scheme 1; photosensitized electron transfer via ^{3}ZnTPPP* occurs, generating $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CH_3CN)(L_2)_2]^0$, to which a CO molecule coordinates, producing $[Ru_3(\mu_3\text{-}O](\mu\text{-}CH_3CO_2)_6(CO)(L_2)_2]^0$ with the color change as shown in Figure 1. Here, BNAH acts as a sacrificial hole trap to prohibit back electron transfer.

In conclusion, we have demonstrated a new type of photoactive CO color sensor using triruthenium cluster complexes initiated by light illumination. Although the ligand-exchange reaction is allowed by electron transfer with the visible light, the UV light irradiation can dissociate the CO ligand,[6] affording the reversible devices with selective light irradiations.

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(6) (a) Akashi, D.; Kido, H.; Abe, M.; Sasaki, Y.; Ito, T. *Dalton Trans.* **2004**, 2883−2889. (b) Abe, M.; Masuda, T.; Kondo, T.; Uosaki, K.; Sasaki, Y. *Angew. Chem., Int. Ed*. **2005**, *44*, 416−419. (c) Zhou, W.; Ye, S.; Abe, M.; Nishida, T.; Uosaki, K.; Osawa, M.; Sasaki, Y. *Chem.*—*Eur. J.* **2005**, *11*, 5040−5054.