# Organic Films Containing Trinuclear Ruthenium Clusters that Exhibit Redox-state-dependent Heat-shielding Characteristics

Yuki Tomiyasu,[1] Masaaki Abe,*[1] Yasushi Morihara,[2] Hiroyuki Ohgi,[2] Tomiaki Otake,[3] and Yoshio Hisaeda*[1]
[1]*Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, Nishi-ku, Fukuoka 819-0395*
[2]*Kurashiki Research Laboratories, Kuraray Co., Ltd., Kurashiki 710-0801*
[3]*Tsukuba Research Laboratories, Kuraray Co., Ltd., Tsukuba 305-0841*

(Received March 9, 2009; CL-090238; E-mail: mabe@mail.cstm.kyushu-u.ac.jp)

We report here an unprecedented utility of redox-active transition-metal complexes as heat-shielding materials. A poly(vinyl alcohol) film containing mixed-valent cluster $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(mbpy^+)_3](PF_6)_3$ (**1**) (mbpy$^+$ = 1-methyl-4,4′-bipyridinium cation), which strongly absorbs light in the near-infrared region, shows heat-shielding characteristics whose efficiency is found to highly depend on the redox state of the cluster dye.

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Compounds that absorb light in the near-infrared (NIR) region[1,2] have attracted much attention due to their potential applications as optoelectronic devices,[3] Q-switching lasers,[4] and to telecommunication.[5] Another but less explored advancement for NIR dyes is their application as heat shield materials. The NIR light (800–2500 nm) from the sunlight is a principal origin of warming. Known and commercially available heat shield materials that absorb or reflect the sunlight include nanoparticles of transparent oxide conductors like indium tin oxide (ITO)[6] and are provided for sunlight protection purpose, for example, in the form of thin film placed inside window glass. Since most of such heat shield materials cover the wavelength range longer than ca. 1100 nm, the preparation of NIR dyes that cover the shorter wavelength range, i.e., 800–1100 nm, is a next step synthetic challenge for more advanced heat shield materials.

Multinuclear transition-metal compounds in mixed-valent states[7] provide potential for NIR molecular dyes with special emphasis on the redox-switchable ability in their changes of absorption spectra as a function of the oxidation state.[8] Herein we report preparation of polymer films containing transition-metal cluster-based NIR dyes that show redox-state-dependent heat shield characteristics. This is the first example reporting that mixed-valent transition-metal compounds are effectively used as heat shield materials.

We have employed oxo-centered carboxylate-bridged triruthenium clusters of the type $[Ru_3(\mu_3\text{-}O)(\mu\text{-}RCO_2)_6L_3]^{n+}$ (R = H, CH$_3$, C$_6$H$_5$, etc.; L = H$_2$O, pyridine derivatives, etc.)[9] as redox-dependent NIR dyes. They are highly $\pi$-conjugated metal complexes which show reversible redox processes in solution,[10–13] in an organic film,[14] and at a solution/electrode interface.[15] The redox interconversion between two oxidation states, (II,III,III) and (III,III,III), which are both isolated as solid materials, results in significant change in the photoabsorption pattern. Notably, the (II,III,III) clusters exhibit a highly intense absorption band (typically $\varepsilon > 10^4$ mol$^{-1}$ dm$^3$ cm$^{-1}$) in the NIR region (800–1000 nm) while one-electron-oxidized (III,III,III) clusters do not show photoabsorption in this region. Owing to these characteristics, we consider that this specific cluster can be applied to redox-switchable NIR dyes for the heat-shielding purposes, which is an unprecedented utility of mixed-valent transition-metal complexes.

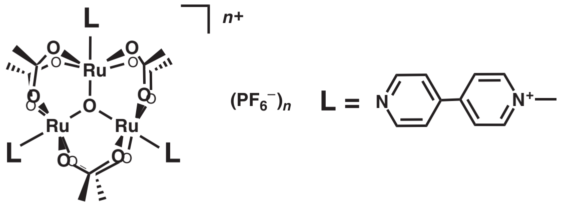

**Figure 1.** Molecular structures of Ru$_3$$^{II,III,III}$ cluster **1** ($n = 3$) and Ru$_3$$^{III,III,III}$ cluster **2** ($n = 4$).

We chose mixed-valent (II,III,III) cluster **1**[11] as a NIR dye (Figure 1). Cluster **1** exhibits absorption at $\lambda_{max} = 950$ nm ($\varepsilon = 2.5 \times 10^4$ mol$^{-1}$ dm$^3$ cm$^{-1}$)[11] which is more intense and red-shifted compared to the derivatives so far reported and shows an electrochromic response (Figure S1).[16] A remarkable solubility of **1** in water, due to the presence of three 1-methyl-4,4′-bipyridinium (mbpy$^+$) cations as terminal ligands, greatly facilitates homogeneous dispersion into the PVA matrix.

For film preparation, commercially available PVA produced by Kuraray Co., Ltd. was used in this study. The degrees of polymerization and saponification were 1700 and greater than 99 mol %, respectively. A **1**-dispersed PVA film containing 1.0 wt % **1** with approximately 100-μm thickness was prepared as described in the Supporting Information.[16] For comparison in the heat shield study, a PVA film containing a one-electron oxidized (III,III,III) cluster $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(mbpy^+)_3](PF_6)_4$[11] (**2**), **2**/PVA, which is fully transparent in the NIR region, was also prepared in a similar manner. The clusters appear to be dispersed homogeneously within the film. In fact, TEM measurements (Hitachi, H-800NA) did not show any sign of aggregation of the clusters at a 5-nm resolution. We have found that once air-sensitive **1** was embedded into the solid PVA film the complex showed remarkable long-term stability toward air owing to a significant impermeability of PVA to dioxygen.[17,18]

Transmission spectra (200–1800 nm) show a redox-state-dependent feature in the photoabsorption (Figure 2). The **1**/PVA film shows peaks at 950 nm (transmittance, 28%) and 600 nm (41%), while the **2**/PVA film shows no photoabsorption in the NIR region. On the basis of amounts of dispersed clusters and the film thickness, **1**/PVA and **2**/PVA contain $7.7 \times 10^{-3}$ mol cm$^{-3}$ of **1** and **2**, respectively.

The heat shield characteristics of the cluster-dispersed PVA films were examined using a home-made apparatus (Figure S2).[16] In short, the cluster-dispersed PVA film (ca. $5.0 \times 5.0$ cm$^2$) was placed on a glass plate, and an infrared light (185 W) was irradiated at the attached film at a distance of 10 cm. Temperature

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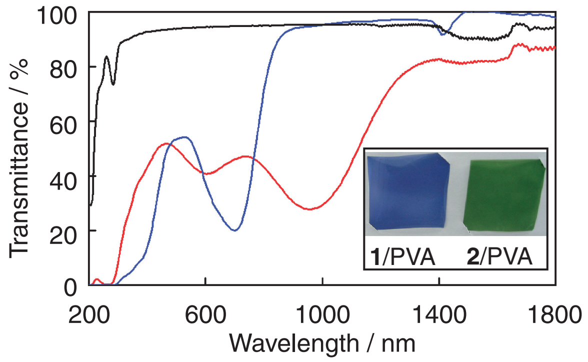

**Figure 2.** Cluster-dispersed PVA films prepared in this study. UV–vis–NIR transmittance spectra: A red line, **1**/PVA; blue line, **2**/PVA; black line, PVA only (blank). The inset shows photographs of the films.

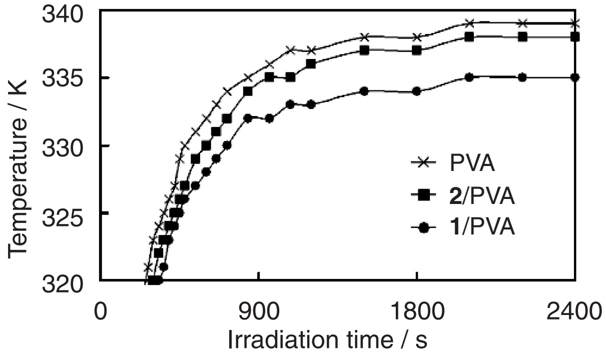

**Figure 3.** Heat shield effects of the cluster-dispersed PVA films.

profiles were measured to assess the heat shield ability of the films with a thermometer that was placed in the bottom of the film-attached closed box ($5.0 \times 4.0 \times 3.0\,\mathrm{cm}^3$).

We found a distinct redox-state-dependent feature in the heat shield performance, and the results are shown in Figure 3. For **1**/PVA, the temperature was increased up to 335 K (after 2100-s irradiation) which is lower than the temperature for the **2**/PVA film (338 K) and also for the blank film (PVA only, 339 K). The **2**/PVA film reached the temperature of 338 K. This indicates that the NIR absorber **1** provides the most effective heat barrier performance. The heat shield temperature observed here (4 K for **1**/PVA and 1 K for **2**/PVA relative to PVA blank film, Figure 3) is small, but it is significant in that the distinct absorption pattern of transition-metal complexes does influence the barrier effect. It is noted that the thermal barrier effect was considerably depressed when the amount of **1** incorporated within the film was decreased.

In summary, we have shown here an unprecedented utility of transition-metal complexes as heat-shielding materials by preparing polymer films containing redox-active triruthenium clusters. Most importantly, the heat shield performance is dependent on the redox state of the dispersed cluster chromophores, where the maximum barrier effect is obtained when the NIR-absorbing mixed-valent $\mathrm{Ru_3}^{\mathrm{II,III,III}}$ cluster is incorporated.

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16 Supporting Information describes preparative details for the cluster-dispersed films, electrochromic response of **1** in water (Figure S1), and schematic illustration of the apparatus used for heat shield study (Figure S2). This material is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
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18 The impermeable nature of PVA was also evident from an observation that **1**/PVA film developed on an ITO electrode surface does not show any cyclic voltammetric response, which is in contrast with the case of poly(4-vinylpridine)-coordinated triruthenium clusters reported in ref 14, where a reversible one-electron redox wave due to $\mathrm{Ru_3}^{\mathrm{II,III,III}}/\mathrm{Ru_3}^{\mathrm{III,III,III}}$ was observed.

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