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# Optical Molecular Thermometer Based on the Fluorescence of Fullerene Dispersed in Poly(methyl methacrylate) Film

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A new optical molecular thermometer based on the fluorescence intensities of the fullerene $C_{60}$ dispersed in poly(methyl methacrylate) (PMMA) film was developed. The fluorescence intensity of the $C_{60}$ film decreased with increasing the temperature in the range from 260 to 373 K. The Arrhenius plot of $\ln[(I(T)/I(T_{ref}))]$ versus $1/T$ for the $C_{60}$ film exhibits considerable linearity supported by the correlation factor, $r^2$, estimated to be 0.989 by the least squares method ($T_{ref}$ = 260 K). The $E/R$ value of the $C_{60}$ film is estimated to be 22.3 K. These results indicate that the $C_{60}$ film provides a linear temperature response in the range 260 to 373 K.

Recent years have seen a growing interest in optical sensors based on oxygen-induced or temperature-induced changes in the luminescence intensity of organic dyes.[1–4] Probes available for optical molecular thermometer are fluorescent, thermal-quenchable and non oxygen-quenchable organic and inorganic dyes, such as coumarin, perylene, pyronin, and rare earth metal compounds.[5–7] In general, the fluorescent dyes dispersed in organic polymer film are widely used for optical molecular thermometers. As dye molecules can interact with polymer molecules directly, the properties of sensing films strongly depend on the properties of the polymer. If one uses an oxygen permeable polymer such as polystyrene, the oxygen-induced fluorescence change of dye in polymer film can be observed. For the optical molecular thermometer, thus, the oxygen-impermeable polymers such as poly(methyl methacrylate) (PMMA) are widely used. One of the candidate probes available for the optical molecular thermometer is fullerene. Fullerenes possess useful electronic and photochemical properties.[8–11] We have previously reported on the development of the optical sensor based on the lifetime of the photoexcited triplet state of fullerene $C_{60}$ and $C_{70}$ in polystyrene film using laser flash photolysis system.[12–15] The photoexcited triplet state of fullerene is quenched by oxygen molecules effectively. As the fluorescence lifetime of fullerene $C_{60}$ is estimated to be 1.1 ns, on the other hand, the fluorescence of $C_{60}$ is not quenched by oxygen.[16] Thus, the fluorescence intensity of $C_{60}$ is changed by temperature changes. Thus, fullerene is an attractive compound for an optical molecular thermometer based on the thermal fluorescence intensity change.

In this paper, we describe a new optical molecular thermometer material, fullerene $C_{60}$ dispersed in poly(methyl methacrylate) (PMMA) film, and its molecular thermometer properties.

## Experimental

$C_{60}$ was obtained from Tokyo Kasei Inc and was purified by recrystallization with toluene-benzene solution. PMMA (average MW 280 000, GPC grade) was purchased from Aldrich.

The $C_{60}$ dispersed in PMMA film was formed by casting a mixture of 20 wt% PMMA and $C_{60}$ in toluene onto 1.4 × 5.0 cm non-luminescent glass slides. The $C_{60}$ concentration in the film was approximately $1.0 \times 10^{-3}$ mol dm$^{-3}$. The films were dried at room temperature and stored in the dark prior to use. The thickness of the films was determined by the use of a micron-sensitive calliper. The thickness of the prepared film was c.a. 50 µm.

The UV-vis absorption spectra of $C_{60}$ in PMMA film and in toluene solution were recorded using a Shimadzu UV-2400PC spectrometer.

The fluorescence spectrum of the $C_{60}$ film was measured using a Shimadzu RF-5300PC spectrofluorophotometer with a 150 W xenon lamp as the excitation light source. The excitation and emission bandpasses were 10 and 5.0 nm, respectively. The sample film was mounted at a 45° angle to minimize light scattering from the sample and substrate.

The temperature was controlled using an Oxford Instrument Optistat-DN cryostat system. The temperature range was controlled between 260 and 373 K. All the experiments were carried out under ambient conditions.

The theory of an optical molecular thermometer based on the fluorescence intensity change of $C_{60}$ film is as follows. The quantum yield ($\Phi$) in the absence of quencher is given by

$$\Phi = I / I_a = k_L/(k_L + k_D) \tag{1}$$

where $I_a$ is the absorption intensity. $k_L$ and $k_D$ are the rate constants for the fluorescence and the radiationless deactivation, respectively. The deactivation term, $k_D$ is decomposed into a temperature-independent part $k_0$ and a temperature-dependent part $k_1$ that is related to thermally activated intersystem crossing.[5] The $k_1$ can be assumed to have an Arrhenius form as follows.

$$k_1 = A \exp(-E / RT) \tag{2}$$

where $A$, $E$, and $R$ are a constant, the Arrhenius activation energy and the universal gas constant, respectively. Eq. 1 can be re-written as Eq. 2 of the radiationless deactivation rate

$$I_a / I(T) - I_a / I(0) = Bk_L^{-1}\exp(-E/RT) \quad (3)$$

where $B$ and $I(0)$ are a constant and the fluorescence intensity at absolute zero, respectively. If one divides Eq. 3 by a reference intensity $I_{ref}$ at a constant temperature $T_{ref}$, the absorption intensity $I_a$ is eliminated. Thus, Eq. 3 can be re-written as follows:

$$\ln [I(T)\,(I(0)-I(T_{ref}))/I(T_{ref})(I(0)-I(T))] = E/R(1/T - 1/T_{ref}) \quad (4)$$

In a normal working temperature range in which $T$ is close to $T_{ref}$, the factor $I(0)-I(T_{ref})/I(0)-I(T)$ is nearly 1.0. Thus, Eq. 4 can be re-written as an Arrhenius equation as follows:

$$\ln [I(T)/I(T_{ref})] = E/R(1/T - 1/T_{ref}) \quad (5)$$

The temperature sensing properties of $C_{60}$ film were characterized by the $E/R$ value and the linearity of the plot of ln $[I(T) / I(T_{ref})]$ versus $1/T$.

## Results and Discussion

The absorption spectra of $C_{60}$ in the PMMA film and in the toluene solution are shown in Fig. 1. The shape of the spectrum of $C_{60}$ film was almost the same as in the toluene solution (absorption peak position = 335 nm for film and 335 nm in toluene solution) and no peak shift was observed. Thus, $C_{60}$ is homogeneously dispersed in PMMA film.

$C_{60}$ film showed fluorescence at 694.8 and 730.4 nm as shown in Fig. 2. The excitation wavelength was 335.0 nm. The reference temperature is 260 K. The spectra (a), (b), (c) and (d) were measured at 260, 293, 323, and 373 K, respectively. The fluorescence intensity of the film depended on the temperature in the range between 260 and 373 K.

Figure 3 shows the plot of $I(T)/I(T_{ref})$ versus $T$ for the $C_{60}$ film. The $I(T)/I(T_{ref})$ value decreased with increasing the temperature. The plot exhibits considerable linearity supported by the correlation factor, $r^2$, estimated to be 0.990 by the least squares method. Thus, the $C_{60}$ film provides a linear temperature response in the range between 260 and 373 K. This result indicates that the fluorescence of $C_{60}$ in PMMA film is quenched thermally. Thus, $C_{60}$ in PMMA film can be used as an optical molecular thermometer device by employing its thermal fluorescence quenching ability as an indicator of temperature change.

Figure 4 shows the Arrhenius plot of ln $[(I(T)/I(T_{ref}))]$ versus $1/T$ for the $C_{60}$ film. The plot exhibits considerable linearity supported by the correlation factor, $r^2$, estimated to be 0.989 by the least squares method. In previous reports, the errors in the optical molecular thermometer using tris(thenoyltrifluoroacetonato)europium(III) dihydrate ($[Eu(tta)_3]\cdot 2H_2O$), perylene, and pyronin in the PMMA film were within 4.0, 3.6, and 3.5%, respectively.[5] For $C_{60}$ film, an error in plot was c.a. 3.3%.

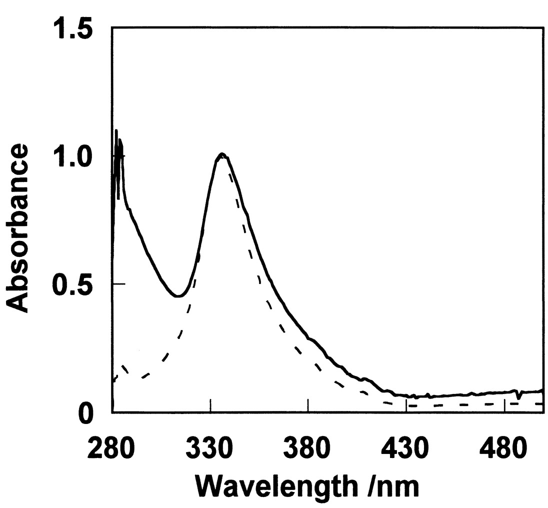


Fig. 1. UV-vis absorption spectra of the $C_{60}$ dispersed in PMMA film (solid line) and in toluene solution (dash line).

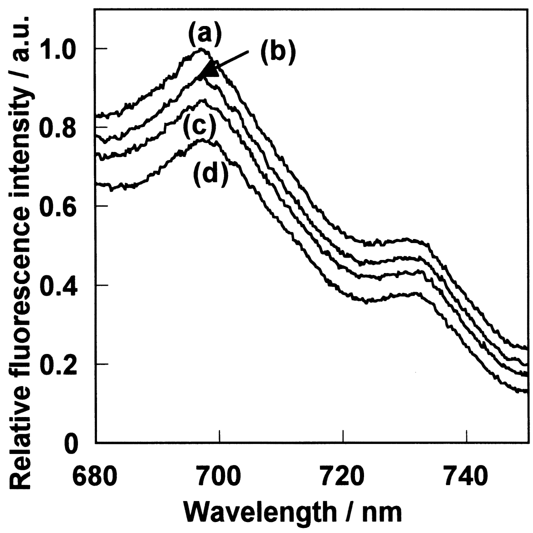


Fig. 2. Fluorescence spectrum of the $C_{60}$ dispersed in PMMA film at (a) 260, (b) 293, (c) 323, and (d) 373 K. Excitation wavelength was 335.0 nm.

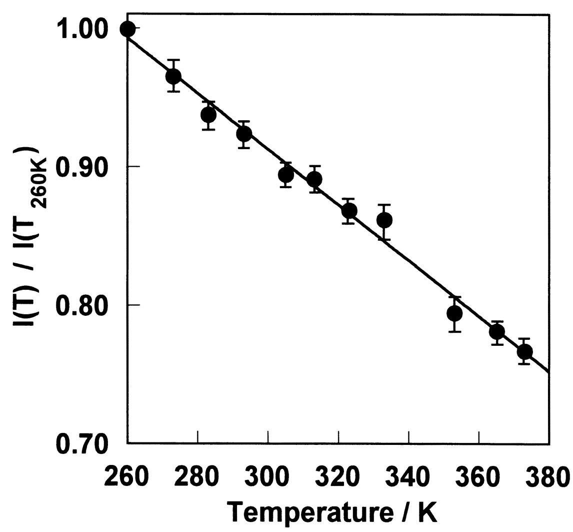


Fig. 3. Temperature-induced fluorescence intensity changes of the $C_{60}$ dispersed in PMMA film. Excitation and emission wavelengths were 335.0 and 694.8 nm, respectively. The reference temperature was 260 K.

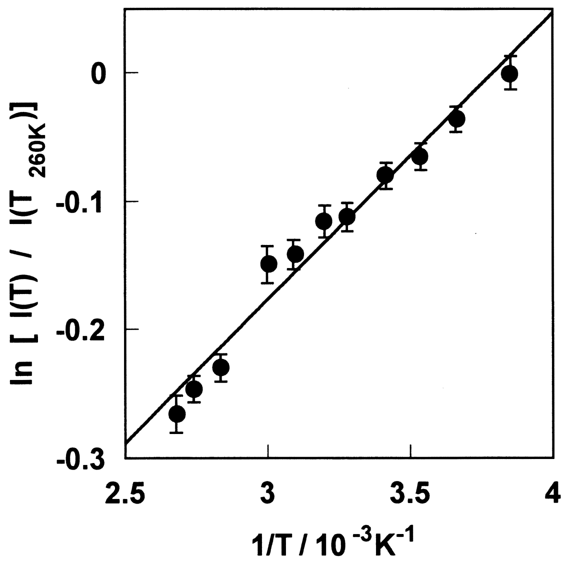


Fig. 4. Arrhenius plot of ln [(*I*(*T*) / *I*($T_{ref}$)) versus 1/*T* for the $C_{60}$ dispersed in PMMA film for temperatures in the range between 260 and 373 K. The reference temperature was 260 K. Excitation and emission wavelengths were 335.0 and 694.8 nm, respectively.

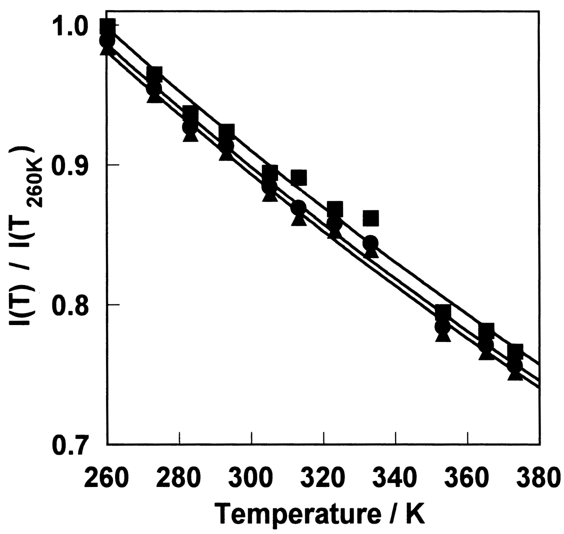


Fig. 5. Thermal stability test of $C_{60}$ film. The fluorescence intensity changes of $C_{60}$ film measured in the temperature range between 260 and 373 K for three times repeated. (●): 1st, (■): 2nd, and (▲): 3rd experiments. Excitation and emission wavelengths were 335.0 and 694.8 nm, respectively.

Thus, the molecular thermometer using $C_{60}$ film has a good accuracy for temperature measurement. The *E*/*R* value of the $C_{60}$ film is estimated to be 22.3 K. These results indicate that the $C_{60}$ film provides a linear temperature response in the range between 260 and 373 K.

The photostability and thermal stability of the $C_{60}$ film are important factors for desirable optical sensors. To characterize the photostability of $C_{60}$ film, the absorption spectrum of $C_{60}$ film was measured after irradiation with 150 W tungsten lamp. As no spectrum change was observed, it is concluded that the $C_{60}$ film has a good photostability under the irradiation. Next let us focus on the thermal stability of $C_{60}$ film. The fluorescence intensity changes of $C_{60}$ film were measured in the temperature range between 260 and 373 K. This procedure was repeated for three times to check the thermal stability. Figure 5 shows a thermal stability test of $C_{60}$ film. The fluorescence intensity and thermometer property (slope of *E*/*R*) did not change. Thus, the $C_{60}$ film has a good thermal stability.

## Conclusions

In this study, an optical molecular thermometer based on the fluorescence intensity change of the fullerene $C_{60}$ dispersed in PMMA film was developed. The fluorescence intensity of the $C_{60}$ film decreased with increasing the temperature and the $C_{60}$ film provides a linear temperature response in the range between 260 and 373 K. This system is a novel molecular thermometer and could open a new application in research fields of optical sensing techniques and fullerene chemistry.

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