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Fullerene C_{60} immobilized in polymethylmethacrylate film as an optical temperature sensing material

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Abstract. A new optical temperature sensor based on the fluorescence intensities of the fullerene C_{60} immobilized in polymethylmethacrylate (PMMA) film was developed. The fluorescence intensity of the C_{60} film decreased with increasing the temperature in the range 260-373 K. 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 260-373 K.

Keyword. Optical temperature sensing – fullerene – fluorescence quenching – Arrhenius activation energy – polymer film.

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 temperature sensor are fluorescent, thermal-quenchable and non oxygen-quenchable organic and inorganic dyes, such as coumarin, perylene, pyronin and rare earth metal compounds [5-7]. One of the candidate probes available for the optical temperature sensor is fullerene. Fullerenes possess useful electronic and photochemical properties [8-10]. As the fluorescence lifetime of fullerene C_{60} is estimated to be 1.1 ns, the fluorescence of C_{60} is not quenched by oxygen [11]. Thus, the fluorescence intensity of C_{60} is changed by temperature changes. Thus, fullerene is attractive compound for optical temperature sensing based on the fluorescence intensity change thermally.

In this letter we describe a new optical temperature sensing material, fullerene C_{60} immobilized in polymethylmethacrylate (PMMA) film, and its temperature sensing properties.

Experimental

C_{60} was obtained from Tokyo Kasei Inc. and was purified by recrystalization with toluene-benzene. PMMA (average M.W. 280 000, GPC grade) was purchased from Aldrich. The C_{60} immobilized 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 1.0×10^{-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 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 45º angle to minimize light scattering from the sample and substrate. The temperature (260-373 K) was controlled using an Oxford Instrument Optistat-DN cryostat system. All the experiments were carried out under ambient condition.

Theory of optical temperature sensing based on the fluorescence intensity change of C_{60} film is as follows. The quantum yield (Φ) 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. 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. The eq. (1) is re-written by the eq. (2) of the radiationless deactivation rate:

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

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where B and $I(0)$ are a constant and the fluorescence intensity at absolute zero, respectively. By divided eq. (3) by 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 in the 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 was characterized by the E/R value and linearity of plot of $\ln [I(T)/I(T_{ref})]$ *versus* $1/T$.

Results and discussion

C_{60} film showed fluorescence at 694.8 and 730.4 nm as shown in figure 1. The excitation wavelength was 330.0 nm. The fluorescence intensity of the film depended on the temperatures in the range 260-373 K. This result indicates that the fluorescence of C_{60} in PMMA film is quenched thermally, and that this film can thus be used as an optical temperature sensing device.

Figure 2 shows the Arrhenius plot of $\ln[(I(T)/I(T_{ref}))]$ *versus* $1/T$ for the C_{60} film. The excitation and emission wavelengths were 330.0 and 694.8 nm, respectively. The plot exhibits considerable linearity supported by the correlation factor, r^2, estimated to be 0.989 by the least squares method.

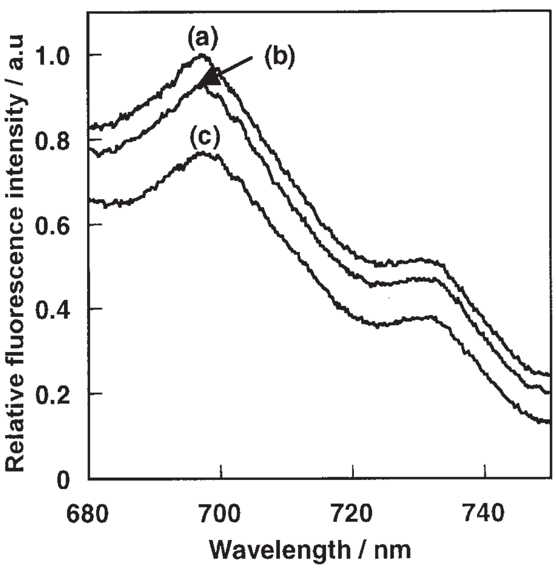

Figure 1. Fluorescence spectrum of the C_{60} immobilized in PMMA film at (a) 260, (b) 293 and (c) 373 K. Excitation wavelength was 330 nm.

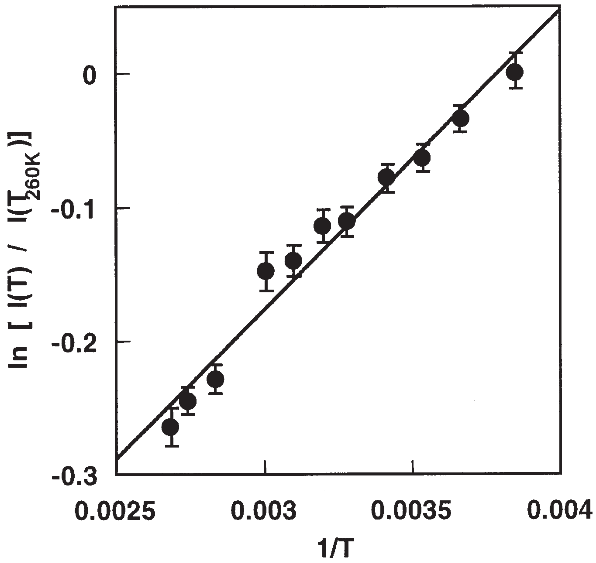

Figure 2. Arrhenius plot of $\ln[(I(T)/I(T_{ref}))$ versus $1/T$ for the C_{60} immobilized in PMMA film for temperatures for 260 to 373 K. The reference temperature was 260 K. Excitation and emission wavelengths were 330.0 and 694.8 nm, respectively.

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 260-373 K. The measurement error of the C_{60} film was within 5 % in five repeated experiments as shown in figure 2.

The photostability of the C_{60} film is important factor to apply for optical sensor. To study the photostability of C_{60} film, the absorption spectrum change of C_{60} film was measured before and after irradiation with 330 nm using a 150 W Xenon lamp and optical filter on the film for 24 h. As little spectrum change was observed, the C_{60} film has a good photostability under irradiation.

Conclusion

In this study, an optical temperature sensor based on the fluorescence intensity change of the fullerene C_{60} immobilized 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 260-373 K. This system is novel temperature sensor and could open a new application in research fields of optical sensing techniques and fullerene chemistry.

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