

A Molecular Thermometer Based on the Delayed Fluorescence of C₇₀ Dispersed in a Polystyrene Film

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A new optical molecular thermometer, based on the thermally activated delayed fluorescence of C₇₀ dispersed in a polystyrene film, was developed. In the presence of oxygen, the fluorescence intensity of the C₇₀ film is essentially temperature independent in a wide range. In the absence of oxygen, however, the fluorescence intensity markedly increases with temperature. At room temperature (25°C), and after degassing the sample, the fluorescence intensity of C₇₀ increases 22 times, while at 100°C the fluorescence intensity is increased by 70 times. With our system, the very weak fluorescence of C₇₀ ($\Phi_F \cong 5 \times 10^{-4}$, in toluene) can be increased up to 91 times (up to an estimated maximum value $\Phi_F = 0.046$). The estimate value of the singlet-triplet gap (29 kJ mol⁻¹) and the fluorescence lifetime (0.63 ns) of the C₇₀ in film are in agreement with the values reported in the literature for C₇₀ in solution. The values of the phosphorescence lifetime at room temperature (23 ms) and the quantum yield of triplet formation (0.989) were also determined. The system is completely reversible with respect to heating-cooling cycles.

KEY WORDS: Molecular fluorescence thermometry; C₇₀; thermally activated delayed fluorescence; polystyrene film.

INTRODUCTION

Temperature is a fundamental property of matter, and its measurement is often required for both scientific research and industrial applications. Real-time temperature monitoring is of paramount importance in industrial testing and manufacturing and also in many biomedical diagnostic and treatment processes.

Given that the fluorescence can be both excited and measured optically, fluorescence-based temperature sensors are advantageous compared to contact temperature sensors in applications where electromagnetic noise is strong or it is physically difficult to connect a wire, as there is no contact with the medium in the measurement process. Further advantages of the molecular fluorescence

thermometer are the very fast response and the space resolution that can go from the macroscale (fluorescent paints) down to the nanoscale (fluorescence microscopy).

There are several thermal sensors based on molecular optical properties, namely luminescence. The use of fiber optics in conjugation with phosphors, whose luminescence lifetime changes with temperature, is a well-established method [1]. More recently, several studies have been devoted to fluorescence molecular thermometry [2–5], including one molecular thermometer based on the fluorescence quenching of fullerene C₆₀ dispersed in a polymer (PMMA) film [6].

The common mechanism of molecular fluorescence is *prompt fluorescence* (PF), where emission occurs after $S_n \leftarrow S_0$ absorption and excited state relaxation to S₁. A second unimolecular mechanism is *thermally activated delayed fluorescence* (TDF), where after excitation and once attained S₁ (first excited singlet), intersystem crossing to the triplet manifold (triplet state T₁) occurs, followed by a second intersystem crossing back to S₁, and

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by fluorescence emission proper. TDF is significant only when the energy difference between S_1 and T_1 (ΔE_{ST}) is small and when the lifetime of T_1 is long enough. In spite of being known for a long time, TDF continues to be a rare and usually weak phenomenon, with few observations in some dyes [7], aromatic ketones [8,9], thiones [10], and aromatic hydrocarbons [11–13].

The unique photophysical properties of C_{70} , namely the quantum yield of triplet formation close to one [14], the small S_1 – T_1 gap [15] and the long intrinsic phosphorescence lifetime [16], lead to the discovery of a strong TDF in fullerene C_{70} [17]. Its dependence with temperature, in conjugation with a high thermal stability of C_{70} , opens new perspectives in molecular thermometry. The initial studies [17] were made in paraffin solution and for temperatures below 70°C. Also a C_{70} derivative [18], fullerene C_{60} [19] and some C_{60} derivatives [20,21] exhibit TDF, but weaker than that of C_{70} .

Herein, we describe a new optical molecular thermometer material, based on the strong TDF exhibited by fullerene C_{70} dispersed in a polystyrene (PS) film. The molecular thermometer properties are presented, along with the estimated values for ΔE_{ST} and Φ_T . As far as we know, this is the first molecular thermometer based on thermally activated delayed fluorescence.

EXPERIMENTAL

Materials

C_{70} (>99.9%) and PS (average $M_w \sim 280000$ by GPC, pellets) were purchased from Aldrich and used as received. Toluene (Fluka) was of spectroscopic grade. To prepare the film sample, C_{70} (2 mg) and PS pellets (200 mg) were mixed into a toluene solution (2 mL), and the film was coated onto a quartz plate at room temperature. The thickness of the film after complete solvent evaporation was 20 μm . The plate was introduced in a quartz cell and degassed at room temperature with a turbomolecular pump (final pressure: ca. 3×10^{-8} atm), and the respective cell sealed afterwards.

Methods

Absorption spectra of C_{70} in the PS film and in toluene were recorded on a Shimadzu UV-3101PC UV-vis-NIR spectrophotometer. Luminescence spectra were obtained in a Spex Fluorolog F112A fluorimeter in a front face configuration. Excitation wavelength was 470 nm, and the excitation and emission slits were 18 and 9 nm, respectively. The sample film was mounted slightly away

from a 45° angle in order to minimize specular reflection of excitation light. Emission spectra were not corrected for the spectral response of the optics and photomultiplier. Temperature was controlled to within $\pm 0.5^\circ\text{C}$. Time-resolved picosecond fluorescence intensity decays were obtained by the single-photon timing method with laser excitation. The set-up consisted of a mode-locked Coherent Innova 400-10 argon-ion laser that synchronously pumped a cavity dumped Coherent 701-2 dye laser, delivering 3–4 ps pulses (with ca. 40 nJ/pulse) at a frequency of 3.4 MHz. Intensity decay measurements were made by alternated collection of impulse and decays with the emission polarizer set at the magic angle position. Impulse was recorded slightly away from excitation wavelength with a scattering suspension. For the decays, a cut-off filter was used, effectively removing all excitation light. Detection was always done by passing the emission through a depolarizer and then through a Jobin-Yvon HR320 monochromator with a grating of 100 lines/mm. Usually no less than 5000 counts were accumulated at the maximum channel. The detector employed was a Hamamatsu 2809U-01 microchannel plate photomultiplier. The instrument response function had an effective FWHM of 35 ps. Decay data analysis was performed with the Globals Unlimited software package (Laboratory for Fluorescence Dynamics, University of Illinois, USA).

RESULTS AND DISCUSSION

The absorption spectrum of C_{70} -PS is close to that of C_{70} in toluene and no peak shifts are observed. These results agree with a homogeneous dispersion of C_{70} in the PS film.

The fluorescence of C_{70} -PS film at different temperatures is shown in Fig. 1. The fluorescence was measured between 25 and 100°C. Almost all measurements were recorded with the sample degassed, except one measurement at 25°C. From Fig. 1 it is possible to observe the strong temperature dependence of C_{70} fluorescence, the delayed fluorescence (DF) being much stronger than the PF. After degassing the sample at room temperature, the DF is 22 times stronger than the PF (20 times in C_{70} in paraffin [17]). Table I summarizes the I_{DF}/I_{PF} values for C_{70} -PS and compares them with the C_{70} in paraffin [17] data. The I_{DF}/I_{PF} ratio for C_{70} -PS is always higher when compared with the values for C_{70} in paraffin, it being possible to go to higher temperatures, and at 100°C the DF is 70 times stronger than the PF. The C_{70} -PS system is completely reversible (cooling the sample from 100°C to room temperature allows to recover the values measured

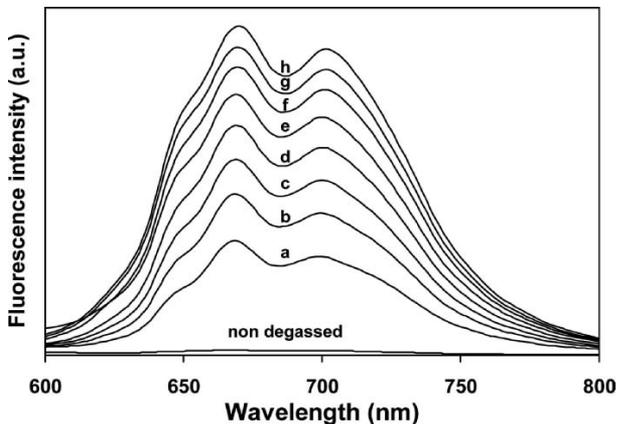


Fig. 1. Fluorescence spectra of C₇₀-PS film at different temperatures: (a) 25, (b) 40, (c) 50, (d) 60, (e) 70, (f) 80, (g) 90 and (h) 100°C. The sample in a–h was previously degassed

upon heating). The experiments were repeated three times, exhibiting a high reproducibility.

The standard method of analysis of the delayed fluorescence, due to Parker [7], is to measure the steady-state DF and the steady-state phosphorescence (P) intensities, as a function of temperature, and then to determine the S₁–T₁ energy gap (ΔE_{ST}) from a plot of $\ln(I_{DF}/I_P)$ vs. $1/T$. However, in our case, we use an alternative approach already applied to the C₇₀-paraffin system [17], where the steady-state intensities ratio of DF to PF, given by

$$\frac{I_{DF}}{I_{PF}} = \frac{\Phi_{DF}}{\Phi_{PF}} = \frac{1}{\Phi_S \Phi_T - 1} \quad (1)$$

where Φ_T is the quantum yield of triplet formation and Φ_S is the corresponding yield of singlet formation by back intersystem crossing [17]. Equation (1) can be rewritten

as

$$\ln \left[\frac{I_{DF}}{I_{PF}} - \left(\frac{1}{\Phi_T} - 1 \right) \right] = \ln \left[\left(\frac{1}{\Phi_S^\infty} - 1 \right) \frac{1}{\Phi_T} \right] + \frac{\Delta E_{ST}}{RT} \quad (2)$$

where Φ_S^∞ is the quantum yield of singlet formation at very high temperatures. It is therefore possible to obtain ΔE_{ST} from the temperature dependence of the ratio I_{DF}/I_{PF} . However, the correct value of Φ_T (assumed temperature independent) is required for a linear least-squares fit. The shape of the plot is a very sensitive function of Φ_T , not being, in general, a straight line. Variation of this parameter in the search for maximum linearity yields its best value and, simultaneously, ΔE_{ST} , and clearly demonstrates the extreme sensitivity to Φ_T in the high temperature domain. As can be seen from Fig. 2, the Φ_T recovered in this way may be of high precision and the effect on the linearity is clear.

Using this method, it was possible to obtain a value for Φ_T of 0.989 (best fit) and a singlet-triplet energy gap of 29 kJ mol⁻¹, both in good agreement with the values determined for C₇₀ in paraffin (0.994 and 25 kJ mol⁻¹, respectively).

To estimate a maximum value for Φ_T , Eq. (1) has to be rewritten as

$$\Phi_T = \frac{1}{1 + \frac{I_{PF}}{I_{DF}} \Phi_S} \quad (3)$$

and because Φ_S is smaller than or equal to unity, a lower bound for Φ_T is

$$\Phi_T^{\min} = \frac{1}{1 + \frac{I_{PF}}{I_{DF}}} \quad (4)$$

Φ_T^{\min} is the closest to Φ_T , the closest Φ_S is to one, that is, the highest is the temperature. At 100°C, $I_{DF}/I_{PF} = 70$,

Table I. Values of the Photophysical Parameters for C₇₀-PS and C₇₀ in Paraffin

Parameters	C ₇₀ -PS	C ₇₀ in paraffin [17]
I_{DF}/I_{PF} (25°C)	22	20
I_{DF}/I_{PF} (50°C)	39	35
I_{DF}/I_{PF} (70°C)	53	50
I_{DF}/I_{PF} (100°C)	70	—
ΔE_{ST} (kJ mol ⁻¹)	29	25
Φ_T	0.989	0.994
Φ_F^{\max}	0.046	0.080
τ_P (ms) (25°C)	23	36
τ_F (ns)	0.63	0.65

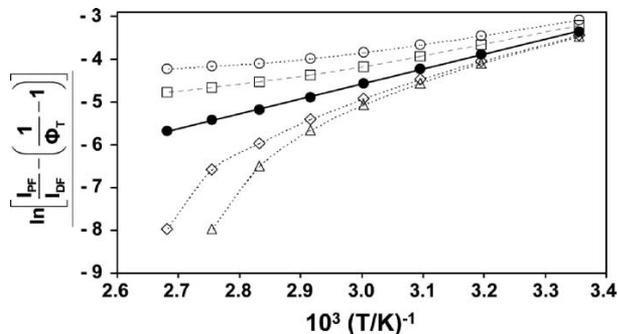


Fig. 2. Fit of I_{DF}/I_{PF} (700 nm) vs. $1/T$, according to Eq. (2), for temperatures from 25 to 100°C. The effect of Φ_T on the linearity is clear: $\Phi_T = 1.000$ (○), 0.994 (□), 0.989 (●—best value), 0.986 (◇) and 0.985 (△).

and therefore, from Eq. (4), $\Phi_T^{\min} = 0.986$. This simple calculation already puts Φ_T within narrow limits. On the other hand, from the experimental value $\Phi_T = 0.989$ and from Eq. (1), one obtains for the high-temperature limit ($\Phi_S \cong 1$), that $(I_{DF}/I_{PF})_{\max} = 90$. In this way, the global fluorescence quantum yield ($\Phi_T = \Phi_{PF} + \Phi_{DF}$) of C_{70} in PS film can in principle be 91 times higher than that of prompt fluorescence, and thus attain the impressive value of $91 \times (5 \times 10^{-4}) = 0.046$.

For C_{70} -PS, a lifetime of phosphorescence (τ_P) of 23 ms at room temperature (36 ms in the case of C_{70} in paraffin) and a fluorescence lifetime (τ_F) of 0.63 ns (0.65 ns in the case of C_{70} in paraffin) were measured.

The experimental values of I_{DF}/I_{PF} at the different temperatures were compared with the theoretical values, which were calculated by

$$\frac{I_{DF}}{I_{PF}} = (a + be^{c/T})^{-1} \quad (5)$$

where

$$a = \frac{1}{\Phi_T} - 1, \quad b = \frac{1}{\Phi_T} \left(\frac{1}{\Phi_S^\infty} - 1 \right), \quad c = \frac{\Delta E_{ST}}{R} \quad (6)$$

The predicted and experimental values of I_{DF}/I_{PF} as a function of the temperature are presented in Fig. 3. Although the maximum experimental temperature was 100°C, it is in principle possible to go to higher temperatures and further increase the I_{DF}/I_{PF} ratio.

For the practical application of the system as a molecular thermometer further studies are necessary, namely on its sensitivity, precision and long term stability. These aspects will be addressed in a forthcoming publication.

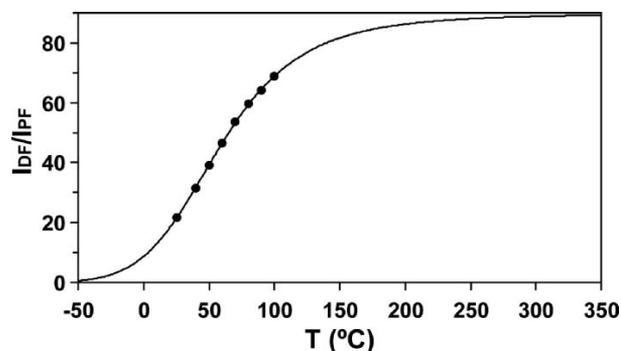


Fig. 3. Plot of experimental (●) and theoretical (solid line) I_{DF}/I_{PF} (700 nm) vs. temperature, according to Eq. (5), for C_{70} -PS.

CONCLUSIONS

The temperature dependence of the fluorescence intensity of C_{70} , in conjugation with its immobilization in a solid matrix (polystyrene film), lead to the development of a new optical molecular thermometer. Under appropriate conditions (100°C and absence of oxygen) the C_{70} fluorescence increase 70 times, compared to aerated room temperature conditions. Extrapolation of the results to higher temperatures predicts a maximum increase of the fluorescence of C_{70} by two orders of magnitude (estimated maximum value $\Phi_F = 0.046$), through the mechanism of thermally activated delayed fluorescence. The value of the singlet-triplet gap, $\Delta E_{ST} = 29 \text{ kJ mol}^{-1}$, was calculated from the temperature dependence of the delayed thermal fluorescence. The values of quantum yield of triplet formation (0.989), fluorescence decay (0.63 ns) and phosphorescence lifetime at room temperature (23 ms) of the film were also determined.

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