An Optical Thermometer Based on the Delayed Fluorescence of C\textsubscript{70}

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Abstract: A sensitive and broad-ranged optical thermometer, based on the thermally activated delayed fluorescence of fullerene C\textsubscript{70}, is presented. It consists of C\textsubscript{70} molecularly dispersed in a polymer film. Several polymer matrices were investigated. In the absence of oxygen the fluorescence intensity increases markedly with temperature. At 25°C the fluorescence intensity of C\textsubscript{70} increases maximally by a factor of between 17 and 22, depending on the polymer, whereas at 100°C the fluorescence intensity can be 79 times higher. In the absence of oxygen and for temperatures above 20°C, the red fluorescence of C\textsubscript{70} in the films is so intense that it is easily perceived by the naked eye. For the systems studied, the fluorescence intensity is very sensitive to temperature. This results in a working range from -80 to at least 140°C in the case of C\textsubscript{70} in poly(3,4-dihydro-2H-pyran)-based (PtBMA). Perylene was incorporated into the film as an internal reference in order to enable ratiometric measurements. The sensitivity of the lifetime of the delayed fluorescence to temperature is also high and results in an even wider working range. The performance of the C\textsubscript{70}/PtBMA film was measured against a well-known optical temperature probe, [Ru(phen)$_3$]$_2^+$ (phen = phenanthroline). The results show that the C\textsubscript{70}/PtBMA film is a very good system for optical temperature-sensing over a wide range of temperatures, outperforming known standards.

Introduction

Temperature is a basic physical parameter, and its measurement is often required both in scientific research and in industrial applications. Real-time temperature monitoring is of paramount importance in industrial testing and manufacturing and also in many biomedical diagnostic and treatment processes. Among the many optical methods which are employed for sensing, luminescence has attracted special attention because it is sensitive, versatile, and can be used even in very strong electromagnetic fields which are employed, for example, in hyperthermal cancer therapy.\textsuperscript{[1]} Given that luminescence can be both excited and measured optically, luminescence-based remote temperature sensors have advantages over 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 sensing process.\textsuperscript{[2–4]} Furthermore, temperature imaging using planar sensors is easily achieved in this way. Additional advantages of a luminescence-based thermometer are the usually fast response and the spatial resolution that can extend from the macroscale (in the case of luminescent paints) down to the nanoscale (such as in fluorescence microscopy).

Whereas virtually any intra- or intermolecular temperature-dependent process that affects the photophysical properties of a luminophore (spectrum, intensity, lifetime, polarization) can in principle be used for the design of a molecular thermometer, all available working luminescence thermometers are based on inorganic solids or organic molecules incorporated into solid-state matrices, including polymer particles and films. In these systems, the decay times and intensities almost invariably decrease with an increase in temperature owing to thermally activated quenching processes.\textsuperscript{[4–9]}

The common mechanism of molecular fluorescence\textsuperscript{[10]} is prompt fluorescence (PF) in which emission occurs after $S_1 \rightarrow S_0$ absorption and excited-state relaxation to $S_1$.
second, much less common, unimolecular mechanism is thermally activated delayed fluorescence (TADF)\[^{[20]}\] in which, after excitation to the first excited singlet state (S\(_1\)), intersystem crossing to the triplet manifold (triplet state T\(_1\)) occurs followed by a second intersystem crossing back to S\(_1\). The cycle may be repeated a number of times before fluorescence finally takes place. TADF is significant only if the S\(_1\)–T\(_1\) energy gap (\(\Delta E_{ST}\)) is small and if the lifetime of T\(_1\) is long enough. Despite being known for a long time, TADF continues to be a rare and usually weak phenomenon; there have been just a few observations in xanthene dyes\[^{[18]}\] aromatic ketones\[^{[11,12]}\] thiones\[^{[13]}\] and aromatic hydrocarbons\[^{[14-16]}\] Probably for this reason TADF has not been used before for temperature measurement, with one single, but interesting exception. Harris and co-workers\[^{[17]}\] proposed the use of the known delayed fluorescence of Acridine Yellow for the development of a molecular thermometer in the −50 to +50°C range. However, the TADF of this compound is very weak, which precludes fluorescence intensity measurements without the use of a time delay. Furthermore, the observed triplet decay is complex, preventing a clear interpretation of the results.

Fullerene C\(_{70}\) has unique photophysical properties: its quantum yield for triplet formation is close to one, its \(\Delta E_{ST}\) is quite small, and its intrinsic triplet lifetime is in the order of several milliseconds\[^{[16-20]}\] This led to the discovery\[^{[21]}\] that C\(_{70}\) has an exceptionally intense TADF. There is presently a need for sensors covering a wide temperature range, and we perceived that C\(_{70}\) is well-suited for this purpose given that the fluorescence intensity of C\(_{70}\) increases markedly with temperature between −80 and at least 140°C and that the TADF lifetime decreases markedly with temperature between −50°C and an estimated upper limit of at least 450°C (as described in this work). Apart from a strong TADF, C\(_{70}\) exhibits good photostability and has high molar absorption (e.g., 2 × 10^4 m\(^{-1}\)cm\(^{-1}\) at 470 nm). Note that other fullerenes, for example, a C\(_{70}\) derivative\[^{[22]}\] fullerene C\(_{60}\)\[^{[23]}\] and some C\(_{60}\) derivatives\[^{[24,25]}\] also exhibit TADF, but in all these cases it is much weaker than that of C\(_{70}\).

We describe herein a new type of polymer thermometer whose function is based on the delayed fluorescence of C\(_{70}\)\[^{[26]}\] These thermometers cover a broad range of temperature, encompassing the important physiological interval. Several polymers have been used as matrices for C\(_{70}\). Temperature-dependent imaging of the C\(_{70}\) films was carried out using both steady-state and lifetime methods. In the presence of oxygen, the fluorescence intensity of the C\(_{70}\) film is essentially temperature-independent. However, in its absence, the fluorescence intensity increases markedly with temperature. At room temperature (25°C), and after degassing the sample, the fluorescence intensity of C\(_{70}\) increases with temperature maximally by a factor of 22, depending on the polymer, while at 100°C, the fluorescence intensity can be 79 times higher. The systems studied cover a working range from −80 to at least 140°C.

### Results and Discussion

**Thermally activated delayed fluorescence kinetics:** The kinetics of thermally activated delayed fluorescence can be represented by Scheme 1, where \(I_{exc}\) is the excitation intensity, \(k_F\) and \(k_P\) are the radiative rate constants for fluorescence and phosphorescence, respectively, \(k_{ISC}^T\) and \(k_{ISC}^G\) are the nonradiative rate constants for deactivation to the ground state (internal conversion from S\(_1\), and intersystem crossing from T\(_1\), respectively), and \(k_{ISC}^S\) and \(k_{ISC}^T\) are the intersystem crossing rate constants for singlet-to-triplet and triplet-to-singlet conversion, respectively. The rate constant \(k_{ISC}^T\) corresponds to an activated process and is strongly temperature-dependent [Eq. (1), where \(\Delta E_{ST}\) is the S\(_1\)–T\(_1\) energy gap]\[^{[21,27,28]}\]

\[
k_{ISC}^T = A \exp \left( -\frac{\Delta E_{ST}}{RT} \right)
\]

For strong TADF to occur, the following inequalities need to be met: \(k_{ISC}^G \gg k_G^T\) and \(k_{ISC}^G \gg k_G^S\) and \(k_{ISC}^T \gg k_T^G\). In most cases \(k_{ISC}^G \gg k_{ISC}^T\) and \(k_{ISC}^G \gg k_T^G\) are also observed. Intercollision of the singlet and triplet emissive states occurs many times before photon emission or nonradiative decay can take place. In this way, a fast pre-equilibrium between S\(_1\) and T\(_1\) exists, and for a sufficiently long time both S\(_1\) and T\(_1\) decay with a common rate constant, given by Equation (2)\[^{[29]}\]

\[
k = \frac{k_{ISC}^G}{k_{ISC}^G + k_{ISC}^T} k_T^G + \frac{k_{ISC}^T}{k_{ISC}^S + k_{ISC}^T} k_T^S
\]

Given the inequalities mentioned above, Equation (2) simplifies to Equation (3), where \(\Phi_T\) is the quantum yield for triplet formation, \(\Phi_T = F^T/(k_T^G + k_T^S + k_{ISC}^T)\), and \(\tau_{DF}\) is the delayed fluorescence (and phosphorescence) lifetime. From Equation (1) and Equation (3), Equation (4) can be obtained, where \(B = (1 - \Phi_T)/A\). From a fit to the temperature dependence of the delayed fluorescence lifetime using Equation (4) and by assuming that \(k_T^G\) is temperature-independent, it is possible to determine \(\Delta E_{ST}\), \(B\), and \(k_T^G\).

\[
k = \frac{1}{\tau_{DF}} = k_T^G + (1 - \Phi_T)k_{ISC}^T
\]

\[
\frac{1}{\tau_{DF}} = k_T^G + B \exp \left( -\frac{\Delta E_{ST}}{RT} \right)
\]

The fluorescence quantum yield is given by Equation (5), where the quantum yields for prompt \(\Phi_{PF}\) and delayed \(\Phi_{DF}\) fluorescence obey the relation given by Equation (6)\[^{[29]}\] and the quantum yield for singlet formation is defined by Equation (7).
C$_{70}$ delayed fluorescence: general aspects and polymer matrix effects: To evaluate the influence of the polymer matrix structure on the photophysics and TADF of C$_{70}$, three polymers were selected: Polystyrene (PS), poly(tert-butyl methacrylate) (PtBMA), and poly(1-vinylnaphthalene) (P1VN). The films were prepared by evaporating a toluene solution of C$_{70}$ and the polymer deposited on a quartz plate. After film formation and drying, the plates were placed in a quartz cell that was degassed at room temperature and afterwards sealed. All the films exhibited absorption spectra similar to that of C$_{70}$ in toluene (for PS and P1VN) or methyloclohexane (for PtBMA). These results are in agreement with a molecular dispersion of C$_{70}$ in the polymeric films.

The fluorescence of the C$_{70}$/PS film at different temperatures and over a full heating–cooling cycle is shown in Figure 1. The first spectrum was recorded at room temperature (25°C) before degassing and corresponds to prompt fluorescence (PF). Without degassing, the fluorescence intensity is temperature-independent. After degassing, a 22-fold enhancement of the room-temperature fluorescence was observed. This enhancement is a consequence of the additional contribution of delayed fluorescence (DF) to the overall emission. Heating of the sample to 100°C (Figure 1a) (a temperature at which the DF is 70 times higher than the PF) shows that the fluorescence of C$_{70}$ has a strong temperature dependence. The C$_{70}$/PS film exhibits full reversibility and fluorescence intensity cycles without hysterisis. The experiment was repeated three times and exhibited a high degree of reproducibility.

The values of $I_{DF}/I_{PF}$ for the C$_{70}$/PS film at different temperatures are collected in Table 1, and compared with the values previously measured for a solution of C$_{70}$ in liquid paraffin.\[31\] The $I_{DF}/I_{PF}$ ratios for the C$_{70}$/PS film are always higher than the values reported for C$_{70}$ in paraffin. The values of $I_{DF}/I_{PF}$ for the films were also measured over a wider temperature range than for C$_{70}$ in paraffin. The stability of the C$_{70}$/PS after long-term storage is also high, with comparable ratios (less than 2% variation) of $I_{DF}/I_{PF}$ being measured after several weeks of storage.

Identical temperature cycles were carried out for the C$_{70}$/P1VN and C$_{70}$/PtBMA films. Responses similar to that of the C$_{70}$/PS film were observed. The films exhibit very good reversibility in the thermal cycles and high reproducibility. The $I_{DF}/I_{PF}$ values for these films at several temperatures are also reported in Table 1. The maximum $I_{DF}/I_{PF}$ value was obtained at 100°C with the C$_{70}$/PtBMA system.

From an analysis of the delayed fluorescence data using the method previously developed\[31\] it is possible to obtain $\Delta E_{\text{ST}}$ from the temperature dependence of the $I_{DF}/I_{PF}$ ratio. However, the correct value of $\Phi_T$ (assumed to be temperature-independent) is required for a linear least-squares fit. The shape of the plot is very sensitive to $\Phi_T$ and is in gener-

\[31\] See reference [21].

Table 1. Experimental $I_{DF}/I_{PF}$ values (700 nm) for the C$_{70}$/polymer systems at various temperatures.

<table>
<thead>
<tr>
<th>System</th>
<th>25°C</th>
<th>50°C</th>
<th>70°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{70}$/paraffin</td>
<td>20</td>
<td>35</td>
<td>50</td>
<td>–</td>
</tr>
<tr>
<td>C$_{70}$/PS</td>
<td>22</td>
<td>39</td>
<td>53</td>
<td>70</td>
</tr>
<tr>
<td>C$_{70}$/P1VN</td>
<td>17</td>
<td>30</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>C$_{70}$/PtBMA</td>
<td>18</td>
<td>35</td>
<td>51</td>
<td>79</td>
</tr>
</tbody>
</table>
al nonlinear (Figure 2). Variation of this parameter in the search for maximum linearity yields its best value and, simultaneously, $\Delta E_{ST}$, and clearly demonstrates the extreme sensitivity to $\Phi_T$ in the high temperature domain. Figure 2 shows that the value of $\Phi_T$ determined in this way is quite precise.

![Figure 2](image.png)

Figure 2. Fit of $\ln[I_{PF}/I_{PF}-(1/\Phi_T-1)]$ versus $1/T$ according to Equation (9) for the C$_{70}$/PtBMA film in the temperature range of 25–100°C. The best straight line ($r^2=0.999$) is obtained for $\Phi_T=0.993$.

By using this method, it was possible to obtain for C$_{70}$/PtBMA a value for $\Phi_T$ of 0.993 and an effective singlet–triplet energy gap of 26 kJ mol$^{-1}$, both in good agreement with the values determined for C$_{70}$ in paraffin (0.994 and 26 kJ mol$^{-1}$, respectively). From the experimental value, $\Phi_T=0.993$, and from Equation (7), one finds for the high-temperature limit that $(I_{DF}/I_{PF})_{\text{max}}=142$. In this way, the global fluorescence quantum yield ($\Phi_T=\Phi_{PF}+\Phi_{DF}$) of C$_{70}$ in PtBMA film can be maximally 143 times higher than that of prompt fluorescence and thus attain the significant value of 143 $\times$ $(5 \times 10^{-4})=0.071$. These calculations were also carried out for the other two polymer systems and the results are given in Table 2, along with those for the C$_{70}$/paraffin system. The prompt fluorescence lifetime $\tau_{PF}$ at room temperature was also measured for all the systems (0.60–0.63 ns) and the values are very similar to the value for C$_{70}$/paraffin (0.65 ns).

The experimental and fitted values of $I_{DF}/I_{PF}$ as a function of temperature are presented in Figure 3, with the fitting being made to Equation (10) and also Equation (11), Equation (12), and Equation (13).

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

(10)

$$a = \frac{1}{\Phi_T} - 1$$

(11)

$$b = \frac{1}{\Phi_T} \left( \frac{1}{\Phi_T} - 1 \right)^{-1}$$

(12)

$$c = \frac{\Delta E_{ST}}{R}$$

(13)

As can be seen from Figure 3, the fit is quite good. 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.

The three systems have an identical $I_{DF}/I_{PF}$ response for temperatures less than 40°C. Above this temperature, the curves start to diverge, as can be seen in Figure 3. The C$_{70}$/P1VN system attains an extrapolated $(I_{DF}/I_{PF})_{\text{max}}$ of 70, whereas C$_{70}$/PS reaches an extrapolated $(I_{DF}/I_{PF})_{\text{max}}$ value of 90. With the C$_{70}$/PtBMA system it is possible in principle to obtain a value for $(I_{DF}/I_{PF})_{\text{max}}$ of 142. Clearly, this is the system that displays the best photophysical properties for temperature-sensing at higher temperatures. An explanation for the superior photophysical properties of the C$_{70}$/PtBMA system (see Table 2) lies in the inertness of the backbone of PtBMA to possible quenching interactions with C$_{70}$. Weak $\pi-\pi$ interactions between the fullerene and the phenyl rings$^{[30]}$ of the backbone of P1VN and PS are the likely reason for the lower efficiency of these systems.

Temperature sensitivity of fluorescence intensity: The temperature sensitivity of fluorescence intensity can be defined either as the variation of the fluorescence quantum yield with temperature, which is the absolute sensitivity $S_A$ [Eq. (14)], or as the relative variation of the fluorescence

![Figure 3](image.png)

Figure 3. Plot of experimental and calculated (solid lines) $I_{DF}/I_{PF}$ values (700 nm) versus temperature, according to Equation (10) for C$_{70}$/PtBMA (squares), C$_{70}$/PS (triangles), and C$_{70}$/P1VN (circles).

Table 2. Photophysical parameters for C$_{70}$ in the three polymers and in liquid paraffin.

<table>
<thead>
<tr>
<th>System</th>
<th>$\Phi_T$</th>
<th>$\Delta E_{ST}$ [kJ mol$^{-1}$]</th>
<th>$\Phi_{PF}^{\text{max}}$</th>
<th>$-\log \Phi_{S}^{\text{max}}$ [10$^{-n}$]</th>
<th>$\tau_{PF}^{[a]}$ [ns]</th>
<th>$\tau_{DF}^{[a]}$ [ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{70}$/paraffin$^{[a]}$</td>
<td>0.994</td>
<td>26</td>
<td>0.080</td>
<td>–</td>
<td>0.65</td>
<td>36</td>
</tr>
<tr>
<td>C$_{70}$/PS</td>
<td>0.989</td>
<td>29</td>
<td>0.046</td>
<td>1.285</td>
<td>0.63</td>
<td>21</td>
</tr>
<tr>
<td>C$_{70}$/P1VN</td>
<td>0.986</td>
<td>27</td>
<td>0.036</td>
<td>2.688</td>
<td>0.60</td>
<td>20</td>
</tr>
<tr>
<td>C$_{70}$/PtBMA</td>
<td>0.993</td>
<td>26</td>
<td>0.071</td>
<td>5.663</td>
<td>0.62</td>
<td>27</td>
</tr>
</tbody>
</table>


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quantum yield with temperature, which is the relative sensitivity \( S_R \) [Eq. (15)].

\[
S_A = \frac{d\Phi_F}{dT} \\
S_R = \frac{1}{\Phi_F} \frac{d\Phi_F}{dT} = -\frac{d\ln\Phi_F}{dT}
\]  \( \text{(14)} \)

\[
S_R = \frac{d\Phi_F}{dT} \text{ Relative sensitivity}
\]  \( \text{(15)} \)

We will use the relative sensitivity as it directly reflects the relative variation of the fluorescence intensity. The temperature dependence of \( S_R \) for the C\(_{70}\)/polymer systems is displayed in Figure 4. It can be seen that the C\(_{70}\)/polymer systems have some of the highest temperature sensitivities known over a broad temperature range.\(^2\)

In order to be useful in practice, a minimum value of 0.5% K\(^{-1}\) for \( S_R \) is assumed. With this value, the lower temperature limit is \(-80^\circ\text{C}\) for all polymers. At the other end of the scale, the C\(_{70}\)/PtBMA system displays the highest high-temperature limit (140°C), whereas for the other two polymers the upper limit is 110°C. Note that the lower and upper temperature values found may not be the real ones because, whilst a condition such as \( S_R > 0.5\% \text{K}^{-1} \) is necessary, it is not necessarily a satisfactory one. In fact, an arbitrarily small value for the absolute intensity cannot be set owing to background noise, and this aspect is best evaluated from the temperature dependence of the fluorescence quantum yield (Figure 5). It can be seen that this dependence may somewhat increase the lower temperature limits found, \(-80^\circ\text{C}\), but will not change the estimated upper temperature limits.

**Delayed fluorescence lifetime:** The delayed fluorescence lifetimes \( t_{DF} \) of all the systems were determined for the temperature range under study and the room-temperature data are collected in Table 2. As expected, the fluorescence lifetimes decrease with increasing temperature owing to the increase in the rate constant of the reverse intersystem crossing from T\(_1\) back to S\(_1\) [see Eq. (4)]. The experimental data were fitted to Equation (4) (with \( \Delta E_{ST} \) fixed at the value determined from the steady-state fit, Table 2). The \( t_{DF} \) values for the C\(_{70}\)/PtBMA film as a function of temperature are shown in Figure 6. From the fit one obtains \( A = 4.3 \times 10^7 \text{s}^{-1} \) and \( k_{T\rightarrow G}^T = 29 \text{s}^{-1} \), both parameters being in good agreement with previous determinations in liquid paraffin.\(^{21}\)

**Temperature sensitivity of delayed fluorescence lifetime:** The relative sensitivity of the lifetime of the C\(_{70}\)/PtBMA system towards temperature is shown in Figure 7. The response covers a wide range, and the slope is quite steep. The temperature dependence of the lifetime of the [Ru(phen)]/PAN system\(^{31,32}\) is included for comparison. Again, in order to estimate a working temperature range, a minimum value of 0.5% K\(^{-1}\) for \( S_R \) was assumed. The results show a working temperature range of between 7°C (lifetime: 30 ms) and an estimated upper limit of 515°C (estimated lifetime: 175 ms). The estimated upper limit nevertheless only applies if the matrix remains solid as well as chemically and photophysically inert.

**Temperature sensing using steady-state fluorescence:** In measurements based on steady-state fluorescence intensities
it is advantageous to use an internal standard. This is referred to as the ratiometric method. In our case, the standard to be incorporated into the C70/PtBMA film must fulfil the following requirements: 1) A temperature-independent fluorescence quantum yield; 2) a fluorescence spectrum with no overlap with that of C70; 3) a common excitation wavelength with C70. Perylene was chosen as a standard as its fluorescence intensity is temperature-independent in the film and temperature range used, its fluorescence spectrum does not overlap the C70 spectrum, and excitation can be made at 420 nm for both fluorophores. Perylene is also known for its high thermal stability.\[33\] After addition of a very small amount of perylene (which suffices owing to its high $F$) to the film-forming mixture, fluorescence was excited at 420 nm and the emission spectra were recorded under the same conditions. Also, the ratios of $I_F$ of perylene (recorded at 470 nm) and $I_F$ of C70 at (700 nm) were also computed. By using the same excitation wavelength (420 nm) it was possible to measure two independent fluorescence intensities (470 and 700 nm) derived from two different species, fullerene and the standard, and to relate their ratio to the temperature by means of a calibration curve. The temperature dependence of this data is shown in Figure 8. The line obtained is almost linear for temperatures between 25 and 70°C.

C70/PtBMA versus [Ru(phen)]3/PAN: Fluorescence intensity and lifetime imaging: The fluorescence intensity of C70/PtBMA was also determined by steady-state fluorescence imaging. A similar system has been described previously\[34\] and is based on a fast gateable monochrome charged-coupled device (CCD) camera and a number of pulsed light-emitting diodes (LEDs) as the light source. The light-encoded information is stored, pixel by pixel, in a grayscale format with background subtraction. Fluorescence intensity images of a C70/PtBMA film in the absence of oxygen at different temperatures are shown in Figure 9.

In addition to intensity-based imaging methods in which the quantification of a data matrix may be disturbed not only by a heterogeneous light field but also by a non-uniform distribution of the indicator within the planar sensing film, the intensity ratio $G_1/G_2$ is not affected in the RLD method. Figure 10 shows the results in pseudo-color code. The lifetimes are similar to those presented in Figure 6. A strong temperature dependence is again observed with the lifetime decreasing with increasing temperature.
The luminescence properties of ruthenium(II) polypyridyl complexes exhibit a strong temperature dependence. In particular, [Ru(phen)₃]³⁺ (tris(1,10-phenanthroline)ruthenium) is a common optical temperature probe that displays efficient temperature quenching and high sensitivity. It is used because 1) it can be incorporated into solid matrices such as sol-gels or polymers; 2) it is commercially available; 3) it is photostable; 4) it has a large Stokes shift; 5) it can be excited in the visible region. However, the luminescence of RuII polypyridyl complexes is quenched by oxygen, and to avoid this interference in temperature sensing, poly(acrylonitrile) (PAN) was used as a matrix as a result of its very low gas permeability.

The temperature dependence of the luminescence quantum yields of C₇₀/PtBMA and [Ru(phen)₃]³⁺/PAN systems are always much shorter and its intensity is expected to remain high above 130°C. Work is in progress on the incorporation of C₇₀ into polymers with low oxygen permeability.

Figure 11. Temperature dependence of the luminescence quantum yields (Φₜ) of C₇₀/PtBMA (solid line) and [Ru(phen)₃]³⁺/PAN (dashed line). Experimental points are shown as circles.

The luminescence lifetimes of these two systems decrease with temperature. However, the lifetimes of the [Ru(phen)₃]³⁺/PAN system are always much shorter and its intensity continuously decreases with temperature. Above 110°C the [Ru(phen)₃]³⁺/PAN system has a lifetime below 1 μs. Above 130°C the intensities are too low for routine measurement. The temperature sensitivity of the lifetime of the [Ru(phen)₃]³⁺/PAN system is also shown in Figure 7.

The lifetime of C₇₀, on the other hand, is expected to remain in the hundreds of microseconds range at temperatures up to 500°C (see Figure 7), and its intensity is expected to remain high above 130°C (see Figure 5).

Conclusion

A study of the temperature dependence of the fluorescence intensity of C₇₀ in a solid polymer film has led to the development of a new type of optical molecular thermometer. Several polymers (PtBMA, P1VN, and PS) were tested. With one of these (PtBMA), and under appropriate conditions (100°C and the absence of oxygen), the fluorescence of C₇₀ increases by a factor of 79 relative to the fluorescence under aerated room-temperature conditions. Extrapolation of the results to higher temperatures allows the prediction of a maximum increase in the fluorescence of C₇₀ of two orders of magnitude (estimated maximum value of Φₜ = 0.071) through thermally activated delayed fluorescence. We have determined the values of the effective singlet–triplet energy gap (ΔEₛₜ), the quantum yield of triplet formation (Φₜₜ), the fluorescence decay times (τᵣₑₜ) at room temperature, and the delayed fluorescence lifetimes (τₑₜ) of the different systems. The C₇₀/PtBMA system exhibits the highest range of temperatures over which the relative variation exceeds 0.5% K⁻¹ (~80 to 140°C). The smaller range of sensitivity and the less favorable photophysical properties obtained with PS and P1VN are very likely due to π–π interactions between the fullerene and the phenyl rings of the backbone of the polymers, which are absent in PtBMA. The polymer films exhibit a high reversibility in heating/cooling temperatures cycles, and the results are reproducible. The C₇₀/PtBMA system was calibrated (and self-referenced) through the incorporation of perylene as an internal standard (perylene).

Note that visual perception of the usually very weak fluorescence of C₇₀ (and of all other pristine fullerenes) has not been reported previously. In the absence of oxygen and at temperatures above 20°C, the red fluorescence of C₇₀ in the films is so intense that it is easily perceived by the naked eye. We present in this work (Figure 12) the first color pictures of the fluorescence of a fullerene.

The temperature dependence of the C₇₀/PtBMA system was compared with a film of [Ru(phen)₃]³⁺ in PAN which is a common and well-documented optical temperature probe showing high sensitivity. Above 80°C, the C₇₀/PtBMA system displays fluorescence quantum yields higher than those of [Ru(phen)₃]³⁺/PAN and has much longer fluorescence lifetimes, estimated to remain in the hundreds of microseconds range at temperatures up to 500°C. Work is in progress on the incorporation of C₇₀ into polymers with low oxygen permeability. Use of such media would obviate the need to degas the C₇₀ film. On the other hand, the extreme sensitivity of C₇₀ fluorescence intensity to molecular oxygen also makes its use advantageous in ultratrace oxygen sensing.

The C₇₀-based luminescence thermometer is a new development in the molecular thermometry field owing to the possibility of using a highly sensitive probe that covers not only both the low temperature and the physiological temperature ranges, but that can also be used for temperatures well above 100°C.
Experimental Section

Materials: C70 (> 99.9%), polystyrene (PS, average Mw = 280000, pellets), poly(1-vinyl-naphthalene) (PVYN, average Mw = 100000, powder), poly(3-tert-butyl methacrylate) (PtBMA, average Mw = 170000, crystals), tris(1,10-phenanthroline)ruthenium chloride hydrate and perylene were purchased from Aldrich (www.sigmaaldrich.com) and used as received. Toluene (Fluka, www.sigmaaldrich.com) and methyl cyclohexane (Alrich, www.sigmaaldrich.com) were of spectroscopic grade. [Ru(phen)3](PF6)2 was synthesized according to the literature.[30] Poly(acrylonitrile) (PAN, powder, average Mw = 170000) was purchased from Polyscience (www.polyscience.de). A 2809U-01 microchannel plate photomultiplier tube served as the detector. Its response was characterized by using a spectrum of light focused by a 750/100 nm filter (AHF Analysentechnik, www.ahf.de) into the entrance slit of the monochromator. A 633 nm He-Ne laser, 10 mW, was used to define the excitation line. The filter was used to approximate the spectral response of the optics and photomultiplier. The temperature was controlled to within ±0.5°C.

Spectral characterization: Absorption spectra of C70 in the polymer films in methycyclohexane and in toluene were recorded with a UV-3101PC UV-Vis-NIR spectrophotometer (Shimadzu, www.shimadzu.com). Luminescence spectra were obtained with a Fluorolog F112A fluorimeter (Spex, www.jobinynon.com) in a front-face configuration. The 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 to minimize specular reflection of the excitation light. Emission spectra were not corrected for the spectral response of the optics and photomultiplier. The temperature was controlled to within ±0.5°C. Time-resolved picosecond fluorescence intensity decays were obtained by the single-photon timing method with laser excitation, with excitation at 355 nm and emission at 700 nm. The setup consisted of a mode-locked Ti:sapphire laser (pulse width 60 fs, repetition rate 1 kHz, 1 kHz) with a scattering suspension. For the decays, a cut-off filter (Schott, FF 01-700) was inserted into the beam path before the sample. Steady-state and fluorescence lifetime images were acquired using a mode-locked Ti:sapphire laser (pulse width 60 fs, repetition rate 1 kHz, 1 kHz) with a scattering suspension. For the decays, a cut-off filter (Schott, FF 01-700) was inserted into the beam path before the sample.

Preparation of the films: To prepare the fullerene-containing films, C70 (2.37 mmol) and the polymer (200 mg) were dissolved in toluene (1 mL) and perylene in toluene (1 mL, 1 x 10−4 mol) was added. The plate was introduced into a quartz cell and degassed at room temperature with a turbomolecular pump (final pressure: ca. 3 x 10−5 atm) and then the cell was sealed.

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References

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Globals Unlimited, Laboratory for Fluorescence Dynamics, University of Illinois (USA).

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