

A Dual Fluorescence Temperature Sensor Based on Perylene/Exciplex Interconversion

Nirmala Chandrasekharan* and Lisa A. Kelly*

Department of Chemistry and Biochemistry
University of Maryland, Baltimore County
Baltimore, Maryland 21250

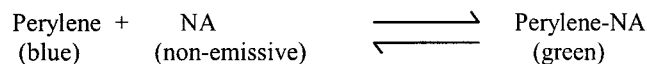
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Molecular sensors have received an enormous amount of attention in the current literature. Chemical sensors for peptides and proteins,¹ sugars,² and neutral or charged species³ have been recently reviewed. However, the development of molecular sensors to detect changes in “environmental” properties, such as temperature and pressure, has received very little attention in the chemical literature. In the literature, we found just one example of a two-component fluorescent temperature sensor.⁴ In this report, the naphthalene fluorescence intensity is modified by the temperature-dependent nickel(II) high-spin/low-spin interconversion in a covalently attached macrocycle. The studies were performed in solution phase, and the response is at a single wavelength region of the UV ($\lambda_{\text{max}} = 340 \text{ nm}$).

The incorporation of a molecular thermometer into a solid coating has utility in mapping temperature changes on two-dimensional surfaces. In the aerodynamic community, these materials are referred to as temperature-sensitive paints, or TSPs.⁵ In comparison with conventional techniques, such as thermocouple taps, the TSP provides a way to obtain simple, inexpensive, and full-field measurements of temperature, with much higher spatial resolution.⁶ An optimal TSP will be incorporated in a clear, coatable material, to provide a luminescent temperature response in the visible spectral region, and produce a ratiometric response to temperature changes, to eliminate the need to normalize for intensity fluctuations at the excitation source.

Our work is directed toward developing a material that shows a temperature dependent ratiometric change in luminescence in the visible region of the spectrum. Significantly, it is inherently a “two-color” material. The response is ratiometric, and normalization for excitation source fluctuations is thus unnecessary. The sensor is also independent of concentration changes of the luminophors. The luminescent “reporter” molecules are incorporated into a transparent polymer matrix, and the temperature response of the system is characterized. In this work, we report the temperature-dependent change of a perylene monomer/exciplex fluorescence spectrum. The ratiometric variation of the emission intensities is analyzed using a two-state equilibrium model (Scheme 1).

Scheme 1



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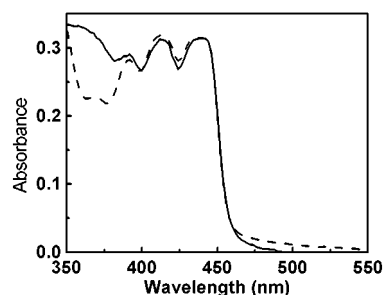


Figure 1. Absorption spectrum of 0.017 wt % of perylene and 18.96 wt % of *N*-allyl-*N*-methylaniline in a polystyrene matrix shown as a solid line. The dotted line is the absorption spectrum of the film composed of perylene alone.

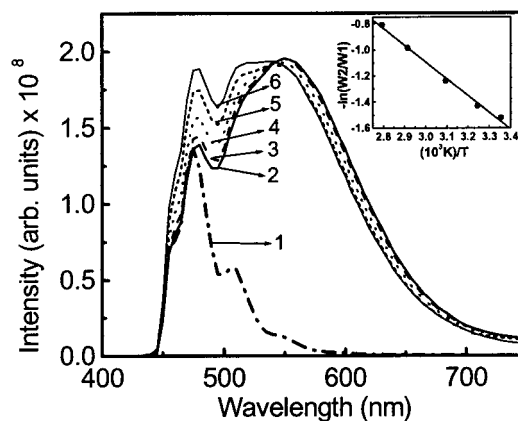


Figure 2. Effect of temperature on the changes in the emission spectra of a polystyrene film composed of 0.017 wt % of perylene and 18.96 wt % of *N*-allyl-*N*-methylaniline for (2) 298 K; (3) 304 K; (4) 323 K; (5) 343 K; (6) 358 K. The emission spectrum of a film of perylene alone is shown in (1) at 298 K. The excitation wavelength was 386 nm in all cases. The inset is a plot of the modified van't Hoff equation. The dashed line in the inset is the linear fit to the calculated values of the natural logarithm of the ratio of the weights obtained for the areas of the exciplex to the monomer, as a function of reciprocal temperature.

Perylene and *N*-allyl-*N*-methylaniline (NA) were encapsulated and anchored, respectively, in a soft elastic polystyrene matrix. The polymer containing styrene, *N*-allyl-*N*-methylaniline, and divinylbenzene was prepared using the free radical initiator, 2,2'-azobisisobutyronitrile (AIBN) in the presence of dissolved perylene.⁷

The absorption spectrum of the film is shown in Figure 1 as a solid line. At wavelengths longer than 375 nm, it matches very well with the absorption spectrum of a film composed of the perylene luminophor alone (dashed line), with bands at 440, 414, 392, and 366 nm. From the result it is concluded that the excitation light (386 nm) is absorbed exclusively by the perylene. The corrected emission spectra of the films are shown in Figure 2. The bold solid line (2) is the emission spectrum of a film composed of perylene and NA, recorded at room temperature. The spectrum exhibits a shoulder at 463 nm, a sharp peak at 475 nm, and a prominent broad band centered at 551 nm. An emission spectrum of a polystyrene film with encapsulated perylene is shown for comparison, as a dashed-dotted line. Thus, the bands at 463 and 475 nm can be assigned to the perylene monomer,

(7) A polymer solution (0.4875 g) containing 18.96 wt % of the aniline derivative, 55.94 wt % styrene, and 0.017 wt % perylene dissolved in toluene was copolymerized with 5.63 wt % divinylbenzene (cross-linker), 19.27 wt % methylsalicylate (plasticizer), and 0.19 wt % AIBN as the initiator. The mixture was deaerated and heated in an oil bath at 80° C for 1 h.

and the broad band centered at 551 nm is due to exciplex formation⁸ between perylene and NA.

On controlled heating of the film, the intensity of the bands at 463 and 475 nm increases. An isoemissive point at 543 nm is observed. A concomitant intensity decrease in the long-wavelength region of the spectrum is observed. We ascribe these temperature-dependent changes to the interconversion between the exciplex and the perylene monomer. With increasing temperature, the equilibrium depicted in Scheme 1 is shifted toward the monomer. The isoemissive point is evidence for the simple two-state model shown in Scheme 1. The fluorescence spectrum of a polystyrene film in which perylene only is encapsulated, shows no temperature dependence.

To test this proposed two-state model and calculate the enthalpy of the monomer to exciplex interconversion equilibrium, the emission spectra were fitted to a sum of Gaussians. The perylene monomer emission spectrum fit well using a sum of four Gaussians ($A1 + A2 + A3 + A4$). The exciplex was adequately modeled using two Gaussians ($A5 + A6$), centered at 543 and 600 nm. The spectral contributions from the perylene $W1*(A1 + A2 + A3 + A4)$ and exciplex $W2*(A6)$ were used to model the spectra at each temperature by changing only the weighting factors, $W1$ and $W2$.⁹ The ratio of the exciplex to monomer was taken as the ratio of $W2/W1$. The inset in Figure 2 shows the negative logarithmic dependence of the ratio of the weighting factors as a function of reciprocal temperature. A reasonably good linear fit was obtained. Standard deviations for each of the data points are given as error bars for three sets of experiments conducted on three different pellets. The enthalpy of the reaction was calculated from the slope of the plot to be 2.6 ± 0.2 kcal/mol. The dissociation energy for the exciplex formed between perylene and *N,N*-dimethylaniline in benzene has been calculated to be 8.1 kcal/mol by Ware et al.¹⁰ Hence, the value obtained by us is quite reasonable for this type of complex formation. The percentage variation of the ratiometric intensity per degree centigrade was found to be $\sim 1\%/^{\circ}\text{C}$. A striking feature of the monomer-to-exciplex interconversion with temperature is the appearance of strong blue emission under hot conditions and green emission when the sample is cooled, upon illumination with UV light. Figure 3 is a photograph giving a visual demonstration of the response of the film at two different temperatures. To investigate the reversibility of this phenomenon, we performed a temperature cycle, recording the spectra over a heat run and then recording the same during a cooling run. Shown in Figure 4 are the corrected emission spectra recorded at three different temperatures. The solid lines are those obtained during the heat run, and the dashed lines denote the spectra obtained during the cooling run. The ratiometric response shows reversibility within 2% for all the samples studied.

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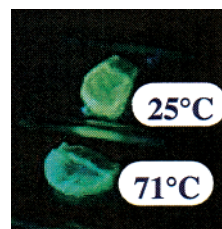


Figure 3. A snapshot of polystyrene films, composed of 0.017 wt % of perylene and 18.96 wt % of *N*-allyl-*N*-methylaniline, at two different temperatures. The samples were subjected to UV irradiation. It can be clearly seen that the monomer emission dominates at the higher temperature and that the exciplex emission is dominant at the lower temperature.

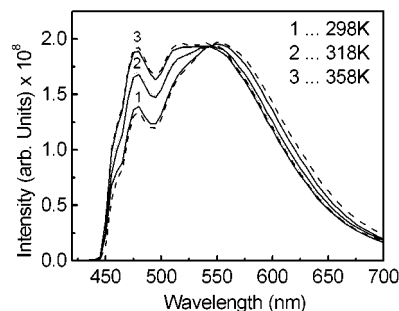


Figure 4. Plot of the emission spectra over a temperature cycle. The spectra recorded while heating are indicated by solid lines and those recorded while cooling are given by broken lines for (1) 298 K; (2) 318 K; (3) 358 K.

In conclusion, we have successfully synthesized a luminophoric film that shows a ratiometric change in luminescence in the temperature range 25–85 °C. We believe the temperature range can be extended by tuning the plasticity of the polystyrene matrix. With the spectrometer and scan rate employed, the smallest temperature change that can be measured is 2 °C. The accuracy was determined by the fluctuations in the measured temperature (± 1 °C). The results indicate that these luminophoric polymer films can give rise to a new class of molecular temperature sensors or molecular thermometers. To the best of our knowledge, this is the first report of a luminescent film that exhibits a ratiometric response with temperature. Since temperature-dependent equilibria on the excited state surface are ubiquitous, the phenomenon is certain to be a universal one. This strategy can be easily extended to other aromatic hydrocarbon acceptor/aniline donor systems, for example, benzene/aniline or anthracene/aniline, that show two-color emission as a function of temperature. Studies involving tunability over the entire visible wavelength range, as well as a wider range of temperatures, are in progress.

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