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Optical thermometer based on the stability of a phosphorescent 6-bromo-2-naphthol/α-cyclodextrin$_2$ ternary complex

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The phosphorescence lifetime of a water-soluble ternary complex of 6-bromo-2-naphthol and α-cyclodextrin has been found to decrease by more than two orders of magnitude over a 58 °C temperature range, which makes this molecular system well suited for use as the first optical thermometer based solely on phosphorescence lifetimes.

A ternary molecular complex consisting of two molecules of α-cyclodextrin (CD) and one molecule of 6-bromo-2-naphthol (BN) emits readily detectable BN phosphorescence in aqueous solutions containing molecular oxygen, an efficient triplet-state quencher.[1] It is believed that the triplet-state BN molecule is protected from quenching by being encapsulated in the hydrophobic core of the CD molecules, which are assumed to make contact with each other concentrically along the rim of the larger opening of the toroidal CD molecule. The phosphorescence lifetime of the BN/CD$_2$ complex is reported herein to have a very high temperature sensitivity and to be useful as the first reported aqueous optical molecular thermometer based only on phosphorescence lifetimes.

There has been increasing interest in the use of molecular luminescence to make remote temperature measurements by passing the luminescence signal from the sensor material through an optical fiber[2] or by incorporating the luminescent probe molecule directly into the site at which the temperature is to be measured.[3] Most of these optical thermometers make use of fluorescence and have been designed around temperature-dependent excited state lifetimes,[2–10] shifts in fluorescence or absorption spectra,[11–14] changes in fluorescence intensity,[3,10,15] or black-body radiation spectra.[16]

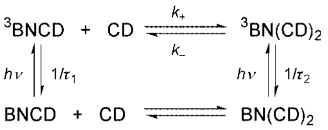
One of the highest sensitivities for an optical thermometer was reported for the delayed fluorescence of acridine yellow dissolved in a rigid saccharide glass.[10] In this sensor material the sensitivity is ultimately determined by the triplet-state lifetime. Over the reported temperature range, the lifetime of delayed fluorescence and the ratio (intensity of delayed fluorescence)/(intensity of phosphorescence), $I_{\mathrm{df}}/I_{\mathrm{p}}$, changed only about four-fold, and the average percentage relative sensitivities to temperature of the delayed fluorescence lifetime and the $I_{\mathrm{df}}/I_{\mathrm{p}}$ ratio were reported to be 2.0% and 4.5%, respectively.[10]

The following is a brief description of our instrumentation and experimental procedure. Excitation pulses (FWHM of 6–7 ns and typical energy of 1–10 mJ) at 280 nm or 345 nm were produced as the frequency-doubled output of a Quanta Ray Nd/YAG-pumped dye laser. Phosphorescence was focused into a 0.25 m Jarrell Ash spectrometer and detected at 525 nm, the wavelength for maximum phosphorescence intensity. The spectrometer was operated with a spectral resolution of approximately 40 nm. The photomultiplier was gated off electronically for 2 μs to coincide with the occurrence of the large scattered light signal. For each lifetime measurement, 500–1000 oscilloscope traces were averaged so that a drop of phosphorescence intensity of up to three orders of magnitude could be analyzed. Sample temperature was maintained within ±0.1 °C by using a circulating constant-temperature bath. All solutions contained CD and BN concentrations of 0.01 M and 9.4×10^{-5} M, respectively.

Phosphorescence signals were fitted by non-linear least squares regression and generally were found to be single exponential for at least the first two to three orders of magnitude decay in signal. The only exception was at the highest temperature, 59.7 °C, where the phosphorescence intensity was reduced sufficiently to prevent reliable curve-fitting beyond the initial drop of 1.5 orders of magnitude. The residuals for single-exponential fits were random, and correlation coefficients were usually greater than 0.998. The standard deviation for all measured phosphorescence lifetimes, τ, was less than 0.5%. Within experimental uncertainty, τ values were the same when either 280 nm or 345 nm was used as the excitation wavelength.

The value of $1/\tau$ increases dramatically from 800 s^{-1} to 133 000 s^{-1} over the temperature range 1.6–59.7 °C, and the good fit of the Arrhenius equation to the data is seen in Fig. 1. The slight leveling of the plot at the lowest temperature is not unexpected in view of the approach of the reciprocal phosphorescence lifetime to a limiting value, which for 1-bromonaphthalene in glass is 71 s^{-1} at 77 K.[17] Nevertheless, if all data are included, the Arrhenius activation energy, $E_{\mathrm{a},}$ of 69 ± 2 kJ mol^{-1} for Fig. 1 is 2.4 times larger than the activation energy of 28.3 kJ mol^{-1} for the delayed fluorescence lifetime of acridine yellow.[10] For a plot of $1/\tau$ *vs.* temperature (K) the relative sensitivity is defined as the slope divided by the value of $1/\tau$ and is expressed as E_{a}/RT^2. The percentage relative sensitivity ranges from 11% at 1.6 °C to 7.5% at 59.7 °C. The large sensitivity reported herein is, to our knowledge, the largest value reported for an optical thermometer, and the small standard deviations associated with the values of τ reveal that temperature differences smaller than 0.1 °C can be measured.

Since BN phosphorescence is detectable only from the ternary complex in aerated solutions, the following mechanism, which has been used for similar phosphorescent complexes,[18,19] is reasonable.



Use of the steady state approximation in solving the associated rate equations shows that the phosphorescence should decay with a single exponential lifetime, τ, expressed in eqn. (1).

$$(1/\tau - 1/\tau_2)^{-1} = \frac{k_+[\mathrm{CD}]}{k_-/\tau_1} + \frac{1}{k_-} \qquad (1)$$

Values of τ were measured for [CD] in the range 0.008–010 M at 24 °C and 50 °C. The value of τ_2 is independent of [^{3}BN(CD)$_2$] and was varied until a plot of the left-hand side of eqn. (1) *vs.* [CD] was linear and had the largest correlation coefficient. The value of k_- was determined from the intercept. The percentage increase was found to be larger for k_- than for $1/\tau_2$ as the temperature was increased from 24 °C to 50 °C and showed the cause for the large value of E_{a} to be dissociation of the ternary complex.[20] Excellent support for this conclusion

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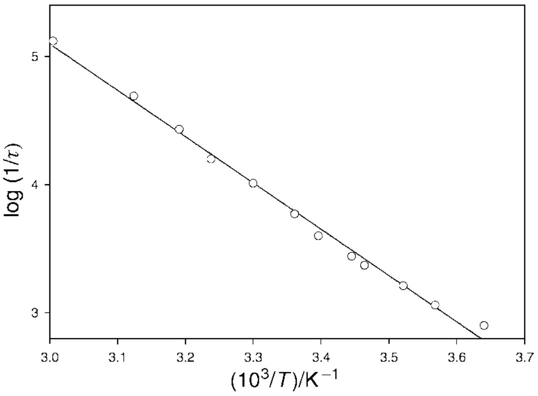

Fig. 1 Arrhenius plot of the reciprocal phosphorescence lifetime, 1/τ for the $BN(CD)_2$ complex.

comes from recent theoretical and experimental studies of the ternary complex of triplet state naphthalene with two α-cyclodextrin molecules.[21] The optimized, low-energy theoretical structure of the complex shows that naphthalene is longitudinally encapsulated between the CD molecules, the secondary cyclodextrin hydroxylic rims face each other, and hydrogen bonds between the hydroxylic groups stabilize the complex. Triplet–triplet absorption was used experimentally to measure an activation energy of 66.5 kJ mol^{-1} associated with oxygen quenching of encapsulated triplet state naphthalene. The similarity of the activation energies reported herein and in reference 21 shows that the shortening of τ with increasing temperature depends little on the structural difference between BN and naphthalene. Since quenching by oxygen occurs upon complete or partial dissociation of the complex, the activation energy arises primarily from the breaking of several hydrogen bonds between the cyclodextrin rings.

BN does not have good long-term stability by itself in aqueous solution, and a sample kept in the dark for seven months developed a light brownish tint. However, CD acts as a good stabilizer, and a sample of the $BN(CD)_2$ complex stored for seven months in the dark developed no tint, and no change in the UV/visible spectrum was detected. Although prolonged use of a solution containing BN and CD at room temperature produced no change in phosphorescence signal, prolonged use at 60 °C caused the phosphorescence intensity to decrease by a few percent.

In summary, the first optical thermometer based only on phosphorescence lifetimes is reported, which has the following important advantages. 1) It has perhaps the highest sensitivity reported for an optical thermometer. 2) Adequate phosphorescence can be produced by using a range of excitation wavelengths, notably between 280–345 nm. The laser-induced phosphorescence intensities of the $BN(CD)_2$ complex and 6-bromo-2-naphthyl sulfate (BNS) in deaerated solution are similar.[22] Since similar phosphorescence intensity of BNS is produced by both laser and broad bandpass-filtered, 7 J flashlamp excitation, it should also be possible to produce adequate phosphorescence from the $BN(CD)_2$ complex using a simple, relatively inexpensive flashlamp excitation source. 3) The instrumentation required to produce and detect long-lived phosphorescence is relatively low in cost. 4) The water solubility of the molecular complex should make it useful as a direct probe of temperature in physiological samples and solutions. 5) Over most of the operational temperature range, the phosphorescence lifetime changes in accordance with the Arrhenius equation which permits a direct correlation to be drawn between τ and temperature without additional calibration. The limitations of the $BN(CD)_2$ optical thermometer are its relatively limited operational temperature range and its slow degradation at prolonged high temperatures. However, the small amounts of BN and CD required as samples in a functional thermometer are inexpensive and can be replaced as necessary.

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