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Room temperature phosphorescence of the 1-bromonaphthalene/β-cyclodextrin inclusion complex: comparison between right-angle and front-face illumination geometry

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The importance of correction for inner filter effects has been demonstrated in the case of the widely studied 1-bromonaphthalene/β-cyclodextrin inclusion complex by means of right-angle and front-face illumination geometry.

Cyclodextrin induced room temperature phosphorescence is widely applied in many fields. 1-Bromonaphthalene (1-BrN) forms an inclusion complex with β-cyclodextrin (β-CD) that exhibits weak room temperature phosphorescence (RTP) in the liquid state. The inclusion of a third component enhances RTP without the need for deoxygenation and the use of many different molecules has been reported.[1] Dissolutions of 1-BrN, at a concentration of 1.00×10^{-5} M, have a considerable absorption at the excitation wavelength of 281 nm (ε = 6466 cm^{-1} M^{-1}). The high value of absorbance ($A = 0.065$) makes the correction for inner filter effects necessary.

It is well known that fluorescence intensities are proportional to the concentration of the analyte over only a limited range of absorbances. In fluorescence instruments that use right-angle geometry, the intensity of the exciting light at the centre of the cuvette is diminished due to the absorption of the sample. This effect may decrease the intensity of the excitation at the point of observation or decrease the observed fluorescence by absorption of the emitted fluorescence. The relative importance of each process depends upon the absorbance of the sample at the excitation and emission wavelengths.[2] These effects define the so called "inner filter effect" (IFE). Phosphorescence intensities are also influenced by the absorption of the sample and thus IFE may be present. Since usually the sample has no absorption at long emission wavelengths, the classical equation used to correct inner filter effects[2] is not efficient in phosphorescence studies as it cannot take account of the entire effects.

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The apparent luminescence intensity and spectral distribution can be dependent upon the absorbance of the sample and the precise geometry of sample illumination. In a previous paper[3] we have demonstrated the influence of IFE on fluorescence intensities and the importance of its correction. Front-face illumination, when the illuminated surface is orientated about 30° from the incident beam, has two advantages: (a) less reflected light enters into the emission monochromator and (b) the incident light is distributed over a larger surface area, decreasing the sensitivity of the measurement to the precise placement of the cuvette within its holder. One disadvantage of this orientation is a decreased sensitivity because a larger fraction of the incident light is reflected off the surface of the cuvette.[2a] Phosphorescence intensities measured at front-face illumination geometry do not suffer for IFE and this instrumental configuration assures reliable results.

Articles that have studied the 1-bromonaphthalene/β-cyclodextrin (1-BrN/β-CD) inclusion complex[1] with different third components have not taken into consideration the influence of IFE in their results. In this work, five third components were studied and the optimization of β-CD and methanol is also shown.

RTP spectra were recorded on a Perkin-Elmer LS-50B luminescence spectrometer equipped with a pulsed xenon lamp (10 μs half-width, 60 Hz), an R928 photomultiplier tube and a computer working with FL Winlab software. All right-angle phosphorescence measurements were performed in a standard 1.0 cm path length quartz cuvette and complementary front-face phosphorescence measurements were performed using the front-face accessory and 1.0 cm path length cylindrical quartz cuvette of the same diameter of the powder holder. Excitation and emission bandwidths were set at 5 and 2.5 nm, respectively. A gate time of 5.00 ms and a delay time of 0.10 ms were used for the measurements. 1-BrN excitation wavelength was set at 281 nm and phosphorescence intensities were measured at 518 nm.

Fig. 1 and 2 show the effect of the third component on the RTP intensities of 1-BrN/β-CD in the presence of 20% v/v of

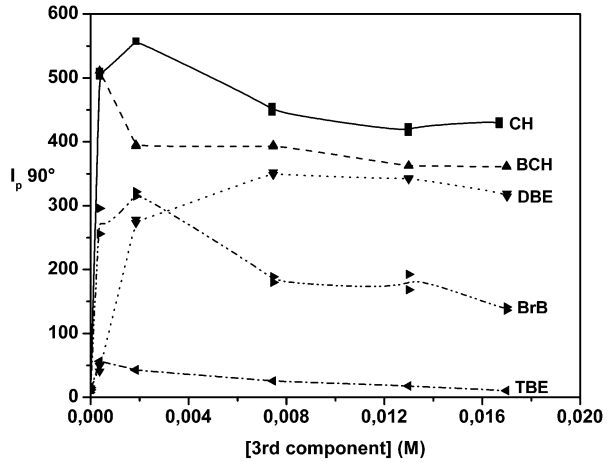

Fig. 1 Room temperature phosphorescence of 1-BrN at different concentrations of the third component measured at right-angle illumination geometry. [β-CD] = 5.00×10^{-3} M; [1-BrN] = 1.00×10^{-5} M; 20% v/v methanol.

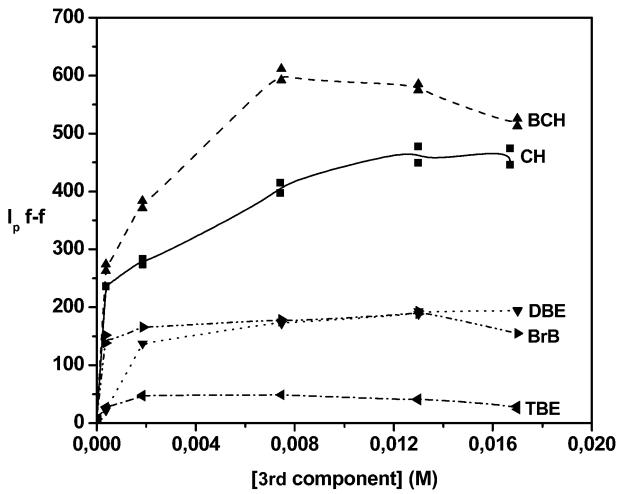

Fig. 2 Room temperature phosphorescence of 1-BrN at different concentrations of the third component measured at front-face illumination geometry. [β-CD] = 5.00×10^{-3} M; [1-BrN] = 1.00×10^{-5} M; 20% v/v methanol.

methanol (1-BrN is solubilized in it). The concentration of 1-BrN chosen was that used in the papers cited.[1] The curves in Fig. 1 belong to right-angle illumination geometry, while those in Fig. 2 belong to front-face illumination geometry. Cyclohexane (CH), bromocyclohexane (BCH), 1,2-dibromoethane (DBE), 1,1,2,2-tetrabromoethane (TBE) and 1-bromobutane (BrB) were studied as third components.

It can be seen that the behaviour of the third component is different when phosphorescence is measured with right-angle or front-face illumination geometry. The major enhancement of RTP intensities is caused by CH and BCH. The presence of microcrystals suspended in solution is seen in the five third components, because of the decrease in β-CD solubility. The microcrystals consist of β-CD and its inclusion complexes, which makes the microenvironment more rigid and induces stronger phosphorescence.[4] Thus, the inclusion of CH or BCH in the 1-BrN/β-CD system produces a more protected complex,

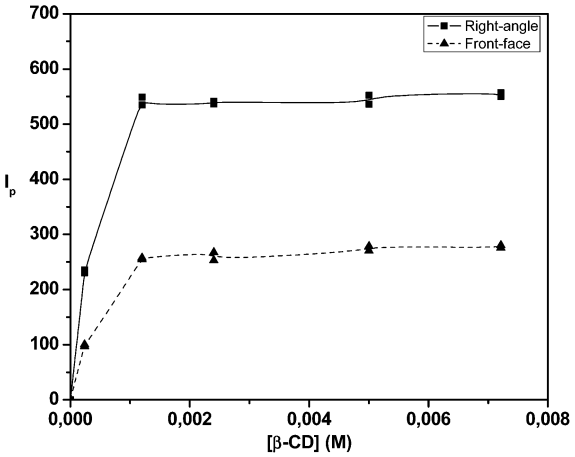

Fig. 3 Room temperature phosphorescence of 1-BrN at different concentrations of β-CD measured at right-angle and front-face illumination geometry. [1-BrN] = 1.00×10^{-5} M; [CH] = 1.85×10^{-3} M; 20% v/v methanol.

compared to those formed by the others, that favors the RTP. Even low concentrations of BCH lead to a considerable amount of precipitate that introduces a great variability in the measured RTP intensities. The same occurs with concentrations of CH higher than 1.85×10^{-3} M.

Fig. 3 and 4 show the effect of β-CD and methanol on the RTP intensities, respectively. It is clearly seen that the behaviour of methanol is different when phosphorescence is measured with right-angle or front-face illumination geometry, but this is not the case for β-CD. Low concentrations of methanol produce more precipitate and hence there is a relationship of commitment between reproducibility and intensity, as in the case of CH and BCH. The optimum conditions chosen are: [β-CD] = 5.00×10^{-3} M; [1-BrN] = 1.00×10^{-5} M; [CH] = 1.85×10^{-3} M; 20% v/v methanol. Although these conditions are the same as those expected with right-angle illumination geometry, it is important to remark that IFE plays an important role when analyzing a particular system.

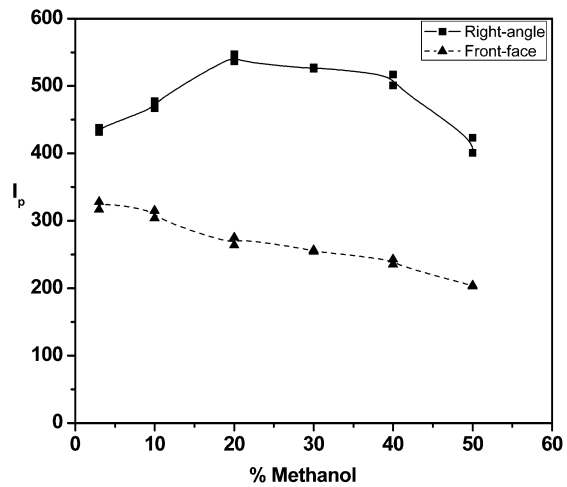

Fig. 4 Room temperature phosphorescence of 1-BrN at different concentrations of methanol measured at right-angle and front-face illumination geometry. [β-CD] = 5.00×10^{-3} M; [1-BrN] = 1.00×10^{-5} M; [CH] = 1.85×10^{-3} M.

In conclusion, the study of the 1-bromonaphthalene/β-cyclodextrin inclusion complex at concentrations of 1-BrN of 1.00×10^{-5} M requires the use of front-face illumination geometry in order to eliminate the inner filter effects. The optimization of the components can lead to the same result, but the evaluation of association constants or determination of a third or fourth component would be influenced by inner filter effects and a consequently erroneous conclusion. The knowledge of the absorption spectra of a particular system guarantees the correct interpretation of the obtained results, making it the first step to be performed in any analysis. If the absorbance values at the excitation wavelength are greater than 0.02 (as generally there is no absorption at the emission wavelength), front-face illumination geometry must be used if a reliable result is to be obtained.

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