



Solvatochromic fluorescence characteristics of cinnamoyl pyrone derivatives



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ABSTRACT

The solvatochromic fluorescence behavior of cinnamoyl pyrone derivatives has been studied in several polar and non-polar solvents. The fluorescence spectra of these compounds exhibit red shift from its absorption spectra and present an excellent correlation with solvent polarity. Cinnamoyl pyrones show a significant spectral shift in fluorescence emission as a function of water composition in binary aqueous solutions mixture. This change is due to the specific intermolecular hydrogen bonding of cinnamoyl pyrones with a molecules of water, due to the deactivation of the lowest excited singlet state of these compounds. The relative quantum yields are calculated. It is found that the quantum yields of the cinnamoyl pyrones vary with the change in the solvent polarity indicating the dependency of fluorescence properties on the solvent nature. It has been observed that the addition of water and pH medium can affect the fluorescence properties of cinnamoyl pyrones in ethanol. This study exhibited that due to the solvent sensitive emission, cinnamoyl pyrone derivatives are a good compound to be used as fluorescence probes.

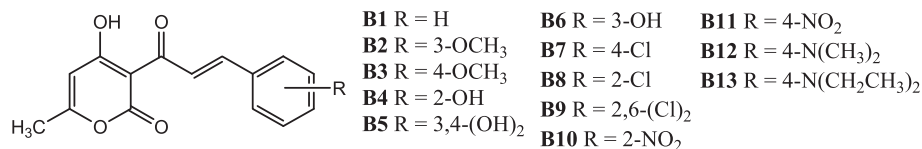
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1. Introduction

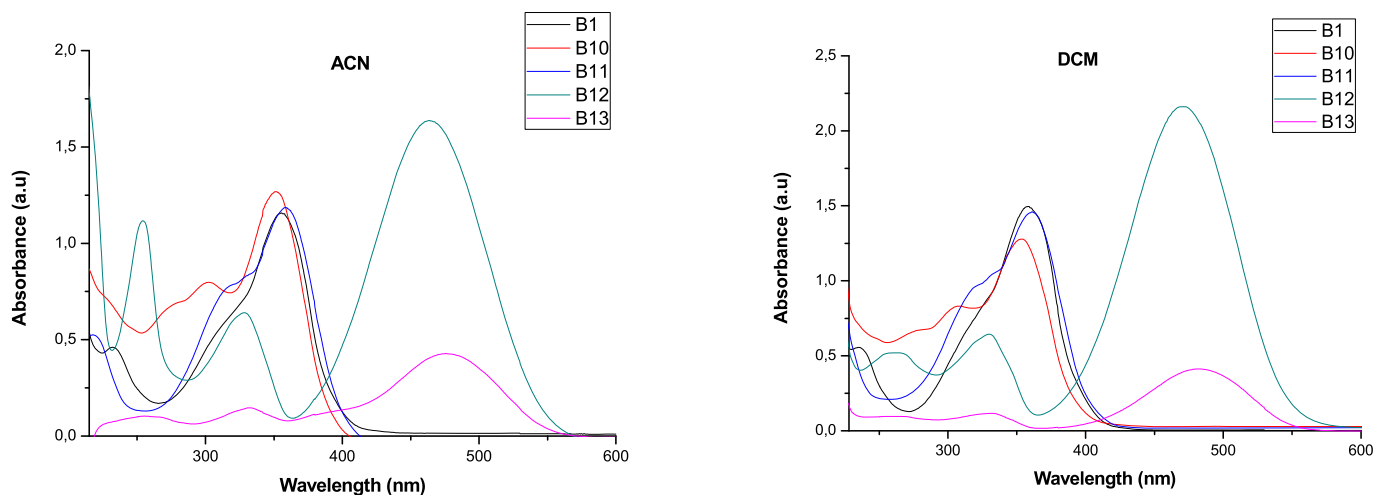
Fluorescence sensors have been receiving a considerable attention due to their potential applications in biochemical and medical analyses and optoelectronic devices [1–3]. It is known that the spectral behavior of an organic molecule is strongly related to its structure in both ground and excited states. The knowledge of the solvent effect on the absorption and fluorescence spectra is of particular importance. A change in the nature of solvent is accompanied by a change in polarity, dielectric constant and polarizability of the surrounding medium. Thus, the change of solvents from apolar to polar aprotic, or to polar protic affects the ground state and the excited state differently. The excited state dipole moment of a molecule control the tenability range of their emission energy as a function of solvent

polarity and can be useful to optimize the performance of a laser dye [4]. Solvatochromism, which describes the spectral change of solute induced by changes in solvent polarity, provides a convenient way for the monitoring of interactions between solute and solvent, including specific (such as hydrogen bonding and electron donor-acceptor interactions) and non-specific (polarity-polarizability effects) interactions [5]. Cinnamoyl pyrone derivatives were intensively investigated as photostable emitting dyes for fluorescent polymer compositions which permit to create new emitting functional materials based on polymer compositions [6]. Such molecules were proposed as sensors for the examination of medium polarity in biological and medical investigations [7]. The goal of the present work is to report the influence of chemical and physical environments, such as the effect of the substituent (nature and position), solvent, and pH medium, on the absorption and fluorescence spectra and fluorescence quantum yield (ϕ) of some cinnamoyl pyrone derivatives. The study has been performed in various non-polar, polar aprotic and polar protic solvents to monitor general as well as specific solvent effects.

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Scheme 1.

Fig. 1. UV-visible absorption spectra of some cinnamoyl pyrone derivatives **B1**, **B10**–**B13** in acetonitrile (ACN) and dichloromethane (DCM) ($c = 6.72 \times 10^{-6}$ M).

2. Experimental

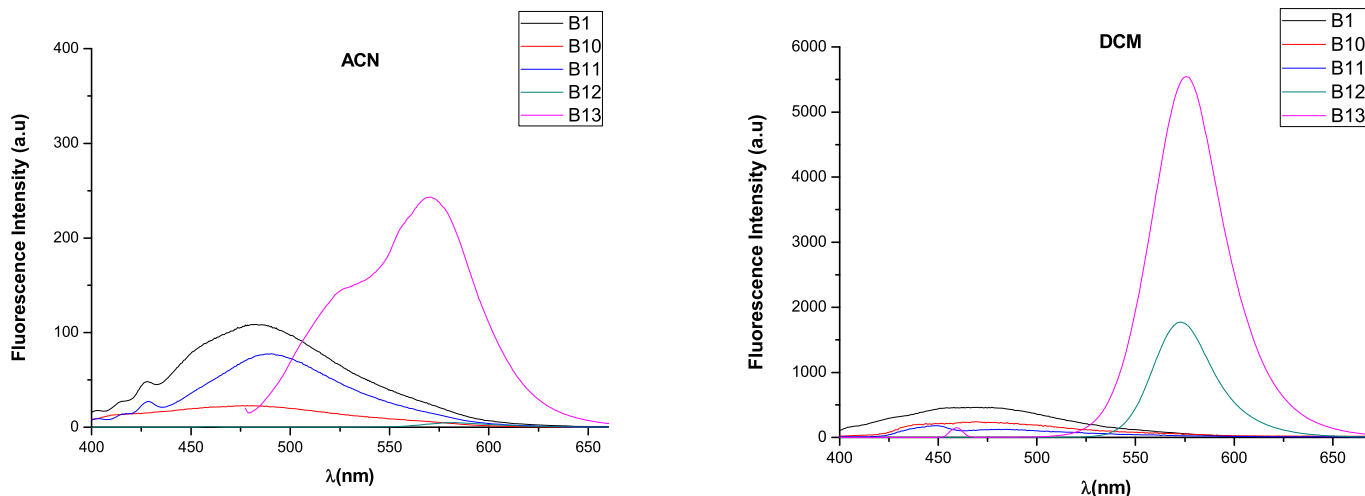
2.1. Materials and methods

A selection of cinnamoyl pyrone derivatives were synthesized according to literature [8] and their structure depicted in Scheme 1. All chemicals and solvents used for synthesis and spectroscopic measurements were of analytical reagent grade and obtained from Fluka and used without further purification. The absorption and fluorescence spectra were recorded at room temperature and using a 1 cm quartz cuvette on, respectively, a JENWAY-6800 UV-visible Spectrophotometer and a Jasco-FP 8200 Fluorometer. Excitation and emission slit width was fixed to 10 nm. The excitation source was a long-life xenon flash lamp and excitation

wavelengths were set on that of maximum absorption of each cinnamoyl pyrone derivatives. The method of pH measurements in non-aqueous media was based on the work of Rondinini [9]. All pH values were recorded on a multifunctional pH-meter (HANNA HI 2550). The fluorescence quantum yield (ϕ) was measured relative to rhodamine B as standard ($\phi = 0.65$) [10], according to the following Eq. (1)

$$\phi = \frac{\phi_{std} F A_{std} \eta^2}{F_{std} A \eta_{std}^2} \quad (1)$$

where F and F_{std} are the peak areas of sample and standard solutions, respectively; A and A_{std} are the absorption at excitation wavelength of sample and standard, respectively; η and η_{std} are the

Fig. 2. Fluorescence emission spectra of cinnamoyl pyrone derivatives in acetonitrile (ACN) and dichloromethane (DCM) ($c = 6.72 \times 10^{-6}$ M).

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