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Temperature effects on excitation and deactivation processes of coumarin 102. A comparison with coumarin 153

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ABSTRACT

The temperature effects on coumarin 102 steady-state absorption and fluorescence, and on the decay of its excited state are presented. Our results have shown that similar to coumarin 153, hydrogen bonding between coumarin 102 and protic solvents has an important impact on the deactivation process of the excited state of this dye. But the nature of this hydrogen bonding and especially its temperature dependence is clearly different for these coumarins. This difference leads in consequence to totally different temperature dependencies of the fluorescence lifetime and fluorescence quantum yield of both solutes. Direct experimental evidence is presented that different hydrogen bonding abilities of structurally similar coumarins may lead to distinct photophysical properties both in the ground, excited Franck–Condon and relaxed states, as well as at various temperatures. To obtain a better understanding of the differences between hydrogen bonds formed by coumarin 102 and by coumarin 153 in the excited state, fluorescence anisotropy kinetic measurements as a function of temperature were performed for both dyes as well in one highly protic solvent. Fluorescence anisotropy decays provided experimental evidence that rotation of coumarin 102 is slower than that of coumarin 153 due to stronger hydrogen bonds formed by the former dye, and that for the same reason in coumarin 102 rotation slows down more quickly than in coumarin 153 with decreasing temperature.

1. Introduction

Studies of the temperature (T) effects on spectral (thermochromism) and photophysical properties of different molecules have been gaining increasing interest for two main reasons. First, rising fundamental knowledge on the spectroscopic properties for large number of molecules at room temperature stimulates studies on the thermal dependence of these properties. This is natural, as temperature changes are common occurrence of our daily life. Second, an important application of thermochromism has been found in the development of adaptive solar energy control materials [1]. On the other hand, decreasing temperature is an important tool to decrease the time constants of different processes that take place as a result of electronic excitation, e.g. charge transfer reaction [2] or solvation dynamics [3]. Much longer time constants of these processes make them easier to study by the means of time-resolved experimental techniques even using setups of picosecond temporal resolution. Taking into account all the experimental work done until now in the field of temperature effects on photophysical and photochemical properties, it is surprising that only a few works have so far been devoted to the study of temperature dependence of the fluorescence quantum yield, ϕ_F. A few examples can be found [4]. Meanwhile, such measurements are indispensable for experimental determination of the temperature dependence of rates of different deactivation paths of the excited molecule. If any compound is intended to be applied in practice, this dependence has to be known and well understood. Recently, we responded to this demand by undertaking studies of the influence of temperature on coumarin 153 (C153) excitation and deactivation processes, when dissolved in several different solvents [5–7]. C153 is a well-known dye molecule, used widely in different studies. Our results have shown that even this relatively simple dye has a complicated thermal dependence of the absorption and emission spectrum position and shape, different in non-specifically interacting solvents, in hydrogen donating and in hydrogen accepting solvents. Additionally, we have shown that the fluorescence lifetime, τ_F, and ϕ_F, change with temperature in a way dependent on the nature of the solvent. In non-specifically interacting and hydrogen accepting solvents similar dependencies of these quantities have been

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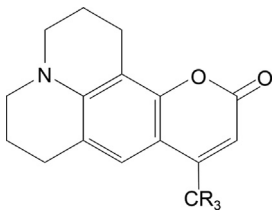
observed, distinct from the one observed in hydrogen donating solvents. Interestingly, formation of hydrogen bond between C153 and propionitrile, a hydrogen accepting solvent [8], has been found to affect absorption and emission spectrum position. But in the same solvent τ_F, ϕ_F and the fluorescence transition dipole moment, $M_{e\rightarrow g}$, have been found to follow temperature dependencies similar to the one found for C153 in 1-chloropropane – a solvent interacting exclusively non-specifically [8]. Additionally, slight modulations of $M_{e\rightarrow g}$ of C153 with changing temperature have been observed and interpreted together with steady-state absorption and emission spectra position and shape temperature dependencies as a consequence of the influence of temperature on the equilibrium distance along normal coordinates between the minima of the S_0 and S_1 states potential energy curves.

This work focuses on the temperature effects on the photophysical properties of coumarin 102 (C102, Scheme 1). C102 was selected as it has very similar structure to that of C153. A methyl group present in C102 is replaced by the trifluoromethyl group in C153 (Scheme 1). Thus, the study reported herein was undertaken to provide information on modification of the temperature effects on photophysical properties caused by replacement of fluoride with hydrogen on the methyl group.

This slight difference in structure is known to modify C102 hydrogen bonding ability when compared to C153, e.g. in 1-propanol [9]. Strongly electronegative fluoride atoms are responsible for a decrease in electron density on the lone pair of the carbonyl C=O group in C153, when compared to C102. As the carbonyl group is widely accepted as the primary hydrogen bonding site in both coumarins, this decrease results in a weaker hydrogen bond formed by C153 than C102 with protic solvents [10,11]. The same effects lead to slight differences in the ground, μ_g, and excited state, μ_e, dipole moments, 6.55 D [5], and 9.7 D [12] or 11.4 D [13], respectively, for C153 (for other values of μ_e reported in literature see Ref. [13]). For C102 the values of 6.98 D [12], and 10.09 D (AM1) [14] or 10.0 D [13] have been reported. Small differences in structure, dipole moments, hydrogen bonding ability and size lead to differences in solvatochromic shifts of absorption and emission spectra.

Both absorption and emission bands, corresponding to the $S_0 \leftrightarrow S_1$ transitions, are shifted to the blue for C102 in many solvents, when compared to C153 [15], in agreement with the theoretically predicted values of the $S_0 \rightarrow S_1$ transition energies [16] for both dyes. In 20 different solvents the solvatochromic plots made on the basis of the positions of absorption spectra (ν_{abs}^{max}) and emission spectra (ν_{em}^{max}) for both dyes [15] follow a very similar pattern (including protic solvents). At first glance, one could see only an offset between absorption solvatochromic plots for C102 and C153, the same occurs for emission. In consequence this similarity in solvatochromic plots causes that Stokes shift ($\Delta\nu_S = \nu_{abs}^{max} - \nu_{em}^{max}$) determined for both dyes follow a very similar pattern as well, as it can be determined from the work of Moog et al. [15]. The Stokes shift being very similar for both dyes in non-polar solvents, rises slightly with solvent polarity and especially with proticity, somewhat more quickly for C153 than C102. This indicates that a small additional stabilization of the emitting relaxed state (S_1^{rel}) relative to the absorbing Franck–Condon state (S_1^{FC}) is present in C153, while absent in C102. However, the results in 1-propanol [9] suggest that while at least in alcohols hydrogen bonding lead to a greater stabilization of S_1^{FC} in C153, S_1^{rel} is more stabilized through hydrogen bond in C102. A similar conclusion follows from a solvatochromic study of C102 [17]. Thus, the slightly quicker rise of $\Delta\nu_S$ for C153 with solvent proticity must result from a more significant change in the non-specific solvation energy when the dye relaxes from S_1^{FC} to S_1^{rel} than in C102. Indeed, this is the case as has been shown by analysis of two solvatochromic plots ($\nu_{abs}^{max}(\pi^*)$ and $\nu_{em}^{max}(\pi^*)$, where π^* is the Kamlet–Taft scale non-specific polarity parameter [18]), reported in Ref. [9] for both dyes in polar aprotic solvents. Thus, on the basis of the steady-state solvatochromic plots, the energy of hydrogen bond formed by C102 rises in energy in S_1^{rel} more than hydrogen bond formed by C153. However, the behavior of hydrogen bond formed through the C=O group of C102 after the solute excitation is far from being well understood. Femtosecond infrared transient absorption, grating scattering and two-pulse photon echo measurements led to the supposition that the cleavage of this hydrogen bond takes place in the 170 – 200 fs time range after excitation [19]. This result is not consistent with the additional red shift of the emission observed in protic environment and it has been assumed in Ref. [19b] that C102 in S_1^{rel} is strongly stabilized by the protic surrounding persisting in the pre-hydrogen bond -cleavage configuration. A slightly different image has been proposed in Ref. [20]. Here, the cleavage of hydrogen bond occurring in a similar time range (250 fs), has been postulated to be followed by reformation of the hydrogen bond in 30 ps. The opposite picture has been proposed in Refs. [21,22], in which a rise in energy of the same hydrogen bond, right after C102 excitation, was assumed to take place – a conclusion in agreement with the rise in the electron density found theoretically at the C=O group in the LUMO state of C102 when compared to the HOMO state [21b,23]. Finally, a hydrogen bond formation between C102 amino nitrogen atom and solvent hydrogen atom has been analyzed as well [24]. It was concluded that excitation of C102 leads to a decrease in the stabilization of the dye S_1 state through this hydrogen bond, in opposition to the hydrogen bond formed through the carbonyl group.

As no such deep discussion of hydrogen bonding characteristics of C153 can be found in the literature one can conclude that besides a small difference following from the analysis of Stokes shift $\Delta\nu_S$ calculated from Moog et al. results [15], the similarities in steady-state spectra positions of both coumarins, are indicators of similar photophysical properties of both dyes. We will show that it is not the case and that both dyes reveal significantly different photophysical properties, both at room temperature, at higher and lower temperatures. Our results clearly show that the commonly accepted assumption of similarities in photophysical properties of very structurally similar C102 and C153 may lead to erroneous interpretations, as these properties might be significantly different.



Scheme 1. Coumarin 102 (R≡H) and 153 (R≡F) structure.

2. Materials and methods

The emission spectra were measured using an upgraded Aminco SPF-500 spectrofluorimeter with single photon counting detection. Absorption spectra were measured using a Jasco V-550 spectrometer. Temperature control was performed using an Oxford Instruments Optistat DN cryostat. Room temperature emission spectra used in fluorescence quantum yield measurements were collected using a JobinYvon-Spex Fluorolog 3-22 spectrofluorometer. Time-resolved fluorescence measurements were performed using a Time Correlated Single Photon Counting (TCSPC) system with an instrument response function (IRF) of 30 ps full-width at half of the maximum (FWHM). The time per channel was set to