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Red-edge and inhomogeneous broadening effects of the electronic spectra of ethyl 5-(4-aminophenyl)-3-amino-2,4-dicyanobenzoate

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Abstract

Fluorescence excitation, fluorescence and phosphorescence spectra of ethyl 5-(4-aminophenyl)-3-amino-2,4-dicyanobenzoate (EAADCy) were recorded in tetrahydrofuran (THF) at room (293 K) and low-temperature (77 K). In our previous publication [M. Józefowicz, M. Aleksiejew, J.R. Heldt, A. Bajorek, J. Pączkowski, J. Heldt, Chem. Phys. 338 (2007) 53], it was shown that at room temperature, the fluorescence spectrum of EAADCy in THF consists of two bands. The short-wavelength emission corresponds to the molecular conformation in which the donor and acceptor moieties are orthogonal to each other, on the other hand, the long-wavelength emission is assumed to originate from a singlet excited state of molecule in which two moieties are coplanar. In present communication, the fluorescence and phosphorescence behavior of the EAADCy has been studied as a function of the excitation wavelength. The luminescence spectra of the molecule under study in THF glass at 77 K show considerable dependence on the excitation wavelengths. Such dependence of the wavelength of maximum intensity of luminescence (fluorescence and phosphorescence) spectrum and the full width at half maximum of phosphorescence spectrum ($\Delta\tilde{\nu}^{\mathrm{ph}}_{1/2}$) on the excitation wavelength is a characteristic demonstration of the red-edge effect. These results along our previous studies [M. Józefowicz, M. Aleksiejew, J.R. Heldt, A. Bajorek, J. Pączkowski, J. Heldt, Chem. Phys. 338 (2007) 53] indicate that EAADCy forms a typically spectrally inhomogeneous system.

Keywords: Ethyl 5-(4-aminophenyl)-3-amino-2,4-dicyanobenzoate; Red-edge effect; Inhomogeneous broadening

1. Introduction

Molecules with polarity-sensitive spectroscopic properties are very useful in photochemical and photobiological studies for the understanding of microscopic solvent environments [1–5]. Such fluorophores are obviously most useful as optical probes when small perturbations cause large changes in spectroscopic properties. Ethyl 5-(4-aminophenyl)-3-amino-2,4-dicyanobenzoate (EAADCy, see Scheme 1), organic molecule containing separate electron donor and electron acceptor groups, is very sensitive to the microenvironment (absorption, excitation and fluorescence spectra, and fluorescence decay times of EAADCy strongly depend on the solvent polarity) [6], thus qualifying the use of the tested compound as molecular probe to study the microenvironment in different systems. In previous publication [6], we reported on the spectroscopic and photochemical properties of EAADCy in various neat solvents of different polarity. The most interesting feature of this molecule is its structure. On the basis of the experimental results and quantum chemical calculations, it was shown that at room temperature, EAADCy exists as an equilibrium mixture of all possible twisted and coplanar conformations. These conformers interchange rapidly in a fluid medium whereas in a rigid medium the probe molecules are trapped in various geometric configurations. The inhomogeneous distribution of species, each possessing different absorption and relaxation properties should be manifested by red-edge excitation effects and inhomogeneous broadening of the absorption and emission spectra.

In general, for molecules in nonviscous solvent at room temperature, the dipolar relaxation of the solvent molecules around the fluorophore in the excited state is much faster than the fluorescence lifetime [7,8]. It is obvious from this condition that emission maximum should be independent on the excitation wavelength. On the other hand, in rigid media, where the solvent reorientation relaxation is inhibited and the dipolar relaxation time for the solvent shell around a fluorophore is comparable

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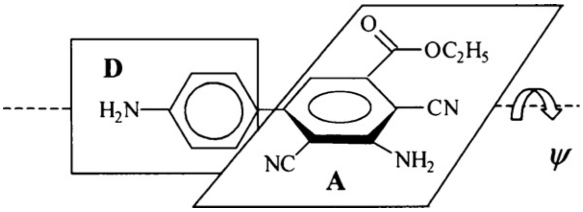


Scheme 1. Chemical structure of ethyl 5-(4-aminophenyl)-3-amino-2,4-dicyanobenzoate (EAADCy).

to or longer than its fluorescence lifetime, the probe molecule can exhibit red-edge effect [9–15]. In this case, the fluorescence spectra can depend on the excitation wavelength, fluorescence excitation spectra can depend on the detection wavelength of the fluorescence band, and the excited-state energy transfer, if present, fails at the red-edge excitation [9]. The origin of the red-edge excitation shift lies in the change solute-solvent interaction in the ground and excited states (change in the dipole moment upon excitation) and presence of various conformers, having different geometries and absorbing at different wavelengths. Since the dipole moment of the fluorophore changes upon excitation, the solvent dipoles have to reorient around this new excited state dipole moment of the fluorophore so as to attain an energetically favorable orientation. The reorientation of the solvent dipoles strongly depends on the restriction offered by the surrounding matrix to their mobility. In rigid and viscous media, excitation at the long-wavelength slope of the absorption spectrum (red edge) selectively excites those fluorophores (conformers) which interact more strongly with the solvent molecules in the excited state.

In the present paper, attention is focused on spectral inhomogeneity of emitting EAADCy molecules. The steady-state fluorescence excitation, fluorescence and phosphorescence spectra of molecules under study in THF glass at 77 K show considerable dependence on the excitation/emission wavelengths. We present results of systematic studies concerning the effect of the red-edge excitation on fluorescence, excitation and phosphorescence spectra of EAADCy at 77 K.

2. Theoretical background of inhomogeneous broadening

Before discussing the origin of the observed excitation wavelength dependence on the low-temperature excitation, fluorescence and phosphorescence spectra, the concept of inhomogeneous broadening of electronic spectra of polar molecules in motionally restricted media, such as very viscous and rigid solutions, should be recalled. It is well known [9–15] that for a polar fluorophore, there exists a statistical distribution of solvation states based on their dipolar interactions with the solvent molecules in both the ground and excited states. When the interaction is strong, and many configurations are possible, the spectra may become broad and completely blurred. The large width of the absorption and emission bands of polar fluorophore is largely due to existence of an almost continuous manifold of vibrational sublevels and presence of various conformers in each electronic state. Each sub-state can possess a sharp maximum, but when added their contributions give a broad-band emission spectrum of a Gaussian shape. It has been shown that the solvate sub-state distribution function at thermal equilibrium is Boltzman's [14]. These conformational broadening factors cause fluorescence band broadening at its short-wavelength slope.

Phenomenological description of inhomogeneous broadening of electronic spectra of organic molecules in solutions has been given by Nemkovich et al. [14]. They have shown that in each elementary cell (solvation shell) of the dipolar solute molecule the near surrounding is polarised due to the dipole moment, μ_g, of the solute, thus giving rise to a reaction field, R, in the cell:

$$R = f\mu_g, \tag{1}$$

where f is a factor of reaction field.

Inhomogeneous broadening occurs because a set of cell has different solvation shells and different reaction field R. The electronic transition frequency, $\tilde{\nu}_i$, of the solute as a function of the reaction field can be written as [14]:

$$\tilde{\nu}_i = \tilde{\nu}_{0i} - \frac{\Delta\mu_i R}{hc}, \tag{2}$$

where $\Delta\mu_i = \mu_{ei} - \mu_{gi}$, and μ_{gi}, μ_{ei} are the dipole moments of a fluorophore in the ground and excited states, respectively. ν_{0i} is the 0–0 transition frequency of a free molecule of "i-th" conformer.

As it was mentioned earlier, the range of the inhomogeneous broadening, which dictates photoselection of the energetically different species, depends on the values of dipole moments of the dye molecule in the ground and excited states, and on the dielectric properties and structure of a solvent. For its estimation one can use an expression obtained in the Onsager sphere approximation [9,14]:

$$\Delta\tilde{\nu}_{\mathrm{inh}} = A\,\Delta\mu\, a^{-3/2}(kT)^{1/2}, \tag{3}$$

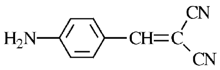
where

$$A = \left(\frac{2}{h}\right)\left[\frac{\varepsilon - 1}{2\varepsilon + 1}\right]^{1/2}. \tag{4}$$

ε is the dielectric constant of the medium, and a is the Onsager sphere radius.

3. Experimental details

The dye under the study was prepared using methodology described by Milart and Sepioł [16]. The main substrate for its synthesis (see structure below) fluoresces very weakly. Other substrates are: $H_3C–CO–C(O)OC_2H_5$ and $CH_2(CN)_2$ do absorb well below 300 nm.



The obtained product of condensation was purified by crystallization and by column chromatography. Its ^1H NMR spectra does not show traces of impurities. The crude product of synthesis was crystallized from a mixture of nitromethane:etanol (3:2) yielding yellow amorphous solid, which was additionally puri-